(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 173 356 A1

# (12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
**31.05.2017 Bulletin 2017/22**

(51) Int Cl.:
***B65D 81/32*** $^{(2006.01)}$ ***A45D 19/02*** $^{(2006.01)}$

(21) Application number: **15195943.4**

(22) Date of filing: **24.11.2015**

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**
Designated Extension States:
**BA ME**
Designated Validation States:
**MA MD**

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## (54) PACKAGE KIT FOR A DYE SYSTEM AND METHOD FOR DYEING A SUBSTRATE

(57) The invention relates to a package kit for a tint, the kit comprising at least a first, a second and a third container, and a method for dyeing a substrate using the package kit of the invention.

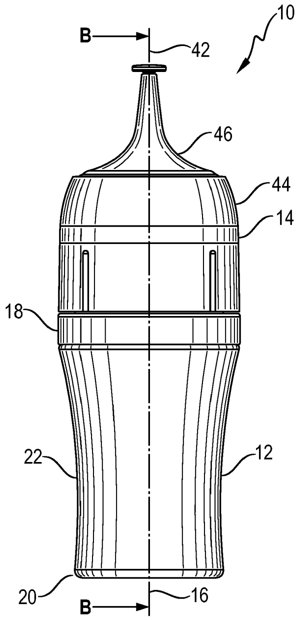

Fig. 1

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## Description

**[0001]** The invention relates to a package kit for a tint, the kit comprising at least a first, a second and a third container, and a method for dyeing a substrate using the package kit of the invention.

## BACKGROUND OF THE INVENTION

**[0002]** Consumers desiring to colour their hair typically have two options available namely to use a commercially available retail product or kit or use the services of a professional salon. The latter whilst providing a highly desirable colour outcome, is considerably more expensive than the retail option and thus not available to many consumers particularly those who colour regularly.

**[0003]** For consumers who have previously coloured their hair, the color and condition of the hair is not homogenous along the entire length. The hair strands will comprise root virgin hair or new growth hair which has not been previously coloured and conversely at the tips hair which has experienced one or multiple hair colouring treatments. The tips of the hair typically are the most damaged portion of the hair and the colour will have changed over time dependant on the wash fade profile and number of types of hair colorant applied, amongst many relevant factors. The intermediate hair length is typically a medium between these two extreme conditions. As a consequence in the salon, for consumers who have previously coloured their hair, the salon stylists typically will colour the root virgin hair first with a specific composition to most effectively colour the hair to the desired end result. However, the remaining length of the hair and tips which has been previously coloured and may have undergone multiple colouring cycles is coloured with a separate and different composition to that applied at the roots. In this manner the salon stylist aims to provide a homogenous end colour result along the entire length of hair from root to tip independent of the variations of starting hair colour and condition along the hair length.

**[0004]** However, such a proposition is currently not available to consumers as a retail product, as it would add further to the complexity and cost and is thus not consumer desirable. Nevertheless, experienced home colour users continually strive to improve the overall colour outcome and indeed as outlined in the instruction packs of many retail products will often direct the consumer to apply the product to the virgin roots first prior to the application of the product along the entire length of hair. However these instructions are imprecise, often not followed, and the results achieved using this method are not comparable with those from a salon stylist. Not only is the overall colour result not as homogenous as that provided by a salon stylist, and may result in over deposition of colour and over bleaching or brassiness, but the rheology of the product also does not necessarily easily allow specific application at the root line as well as easy pull through the remaining length of hair, whilst ensuring no dripping, and good adhesion to the roots during root application. Alternative products on the retail market have been designed to be used only on the roots to address root growth. However these are not entirely satisfactory and a root touch up line may be clearly identifiable. Moreover these products do not remove the need for a separate colouring step for the remaining hair length.

**[0005]** Thus, there still exists a need to provide a retail colour system for use on roots and the entire hair length, without the need for providing and preparing two separate compositions to provide similar results as those associated with professional salon stylists and improved results versus current retail executions.

**[0006]** In many cases the tint used in a hair dye is susceptible to oxidative influences, especially to molecular oxygen found in the air. Many successful attempts have been made to shield the tint from such influences, e.g., by using metal tubes or specific laminates or plastic packs which can essentially eliminate the contact between the tint and the oxidative environment. Most of these attempts, however, result in a serious disadvantage for the user insofar, as they require a transfer of the tint into a developer solution by the end user. Additionally, the solutions involving plastics for producing a tint container involve blow molding techniques, which severely restricts the options for the design of the container.

**[0007]** It has thus been an object of the invention to provide a package kit that overcomes the above described disadvantages of the packages known from the prior art.

## SUMMARY OF THE INVENTION

**[0008]** The present invention relates to a package kit for a hair dye comprising

- a first container with a first opening containing a first composition
- a second container with a first opening and a second opening containing a second composition,
- the first and second container having means to be coupled with each other and forming a connection with fluid communication through the first openings of the first and second container, characterized in that
- one of the first composition and the second composition comprises an a tint and one of the first composition and the second composition comprises a developer so that the first and second composition form a dye upon mixing,
- the container comprising the tint has an oxygen transmission rate of 30 $cm^3$*mm/($m^2$*d*MPa) or lower or a water

vapor transmission rate of 7 g/mm/($m^2$*d) or lower, or both,

- the first and the second container comprise means to reversibly couple the first and the second containers such that the first openings are in fluid connection
- the opening or the openings of the container enclosing the tint are sealed with a first seal only in case of the first container enclosing the tint or with a first and a second seal in case of the second container enclosing the tint.

**[0009]** The invention further relates to a method for dyeing a substrate having at least a first zone and a second zone with the first zone and the second zone having different properties, wherein a package kit as described above is provided, the first composition comprising a developer, the second composition comprising a tint and a third composition comprising a modifier, the method comprising the steps of

- mixing the first and second composition to give a fluid dye
- applying a part of the fluid dye to the first zone,
- mixing the remaining fluid dye with the third composition to give a modified dye and
- applying the modified dye at least to the second zone.

## Definitions

**[0010]** As used herein the term "hair" to be treated may be "living" i.e. on a living body or may be "non-living" i.e. in a wig, hairpiece or other aggregation of non-living keratinous fibers. Mammalian, preferably human hair is preferred. However wool, fur and other keratin containing fibers are suitable substrates for the compositions according to the present invention.

**[0011]** By "dyeing" composition it is meant a composition suitable for changing the color of hair. The dyeing composition is referred hereinafter as "the composition", unless otherwise specified. The dyeing composition can comprise oxidative dye precursors, direct dyes or even no, or substantially no, dyes in case of bleaching only compositions where the change of color is mainly caused by the degradation of the natural melanin contained in the hair shaft by the oxidizing agent. The term "dyeing" composition as used herein covers hair bleaching and hair oxidative dyeing products.

**[0012]** In a preferred embodiment according to the present invention, the dyeing compositions are applied to hair which has already been previously dyed with dyeing compositions. In such a case, the terms "root", "hair roots", "root hair line" and "virgin hair" all refer to the portion of hair having grown, since the last dye, said portion of hair being virgin, i.e. naturally-coloured and the terms "hair lengths and tips" refer to the remaining portion of hair having been already previously dyed.

**[0013]** All percentages are by weight of the respective compositions, i.e. of the dyeing composition or the first, second and third composition, unless otherwise specified. The total weight to be considered is the total weight of the mixture of the necessary compositions applied on the hair simultaneously (i.e. the weight found "on head"), typically resulting from mixing a developer composition (also oxidizing composition/component) with a tint composition (also called dye composition/component), unless otherwise specified. All ratios or percentages are weight ratios or weight percentages unless specifically stated otherwise.

**[0014]** The term "container" relates to a vessel for containing a composition useful for the treatment of a keratinous substrate according to the invention. A "container" according to the invention generally has a volume in a range of from about 1 to about 1000 ml. the term "volume" when used with regard to a "container" according to the invention relates to the volume of the container fit for the storage of a composition, which can, but must not coincide with the overall volume of the container.

## Short description of the Figures

**[0015]** Further optional details and features of the present invention will be disclosed in more detail in the subsequent description of specific embodiments, preferably in conjunction with the dependent embodiments. Therein, the respective optional features may be realized in an isolated fashion as well as in any arbitrary feasible combination, as the skilled person will realize. The scope of the invention is not restricted by the specific embodiments. The embodiments are schematically depicted in the Figures. Therein, identical reference numbers in these Figures refer to identical or functionally comparable elements.

**[0016]** In the Figures:

| | |
|---|---|
| Figure 1 | shows a perspective view of package kit according to an embodiment of the present invention; |
| Figure 2 | shows a cross-sectional view of the package kit taken along line B-B of Figure 1; |

Figure 3 shows a top view of the second container of the package kit;

Figure 4 shows a perspective view of the second container;

Figure 5 shows a cross-sectional view of the second container taken along line A-A of Figure 4; and

Figure 6 shows a perspective view of a third container of the package kit.

## Detailed description of the invention

**[0017]** The invention relates to a package kit as described above. A package kit according to the invention is a combination of items which, by being used together in a prescribed way, allow for a more facile and even application of a dye for the consumer. A package kit for a composition according to the invention comprises

- a first container with a first opening,
- a second container with a first opening and a second opening,
- the first and second container having means to be coupled with each other and forming a connection with fluid communication through the first openings of the first and second container.

**[0018]** The containers which form part of the kit according to the invention hold different compositions which can be of limited stability when subjected to light or oxygen or both. Since the dyeing of hair often involves the use of a developer and a tint, one of the containers contains a composition comprising a developer and one of the containers contains a composition comprising a tint. The container comprising the tint preferably is made of a material that has a low oxygen transmission rate in order to prevent the tint from contact with oxygen at storage. Preferably the material of the container comprising the tint has an oxygen transmission rate of 30 $cm^3*mm/(m^2*d*MPa)$ or lower, e.g., 25 $cm^3*mm/(m^2*d*MPa)$ or lower, or 20 $cm^3*mm/(m^2*d*MPa)$ or lower, or 10 $cm^3*mm/(m^2*d*MPa)$ or lower.

**[0019]** As an alternative or in addition, it can be useful to control the vapor transmission rate of the material of the container comprising the tint in order to limit the contact of the tint with water-vapor upon storage. Preferably the material has a water vapor transmission rate of 7 $g/mm/(m^2*d)$ or lower, or 5 $g/mm/(m^2*d)$ or lower, or 2 $g/mm/(m^2*d)$ or lower or 1 $g/mm/(m^2*d)$ or lower.

**[0020]** The first container can generally have any shape and volume which is useful in the art of hair dyeing. Generally the volume is such that the composition is useful in a retail environment addressing the end-user. A typical volume for the first container can be about 10 to about 800 ml, e.g., about 20 to about 500 or about 30 to about 300 ml.

**[0021]** Generally, the first container can have an essentially cylindrical form with an essentially circular circumference along a longitudinal axis of the container. The container does not necessarily have a symmetrical circumference along its longitudinal axis, it can also be possible that the circumference of the container varies along the longitudinal axis of the container, e.g., changes its shape, or symmetry or both. Generally it has proven to be advantageous, if the first container has a form which can be easily gripped by the end-user, e.g., a circular or elliptical form. It is also possible that the container is shaped such that handling is facilitated by giving the container a shape which coincides with ergonomic features of the human hand.

**[0022]** Generally the first container can be made of any material. It is, however advantageous if the first container is made at least in part from a material which is elastically deformable under pressure, such that the end-user can build up pressure in a closed first container by squeezing the container walls. The squeezability can be limited to specific parts of the container, e.g., by using a different material in the area to be made squeezable, or by using different material strengths in different areas.

**[0023]** The first container can, as will be described below in more detail, comprise a tint. In such a case the first container is made of a material which prevents the contact of the tint with an oxidative environment. It is, however, preferred if the first container comprises a composition which contains a developer. In this case the material properties can be better tuned with regard to shape and squeezability.

**[0024]** The first container is in those cases where it does not contain a tint generally made of a material which is transparent or translucent. In both cases the transparency or translucency of the material should be such that it is possible to recognize the amount of a composition present inthe first container.

**[0025]** The first container has a first opening. While it can be possible to have more than one opening in the first container, it is advantageous to have a first container with just one opening. It has proven to be advantageous if the first container has a comparatively large opening in order to facilitate mixing of ingredients transferred to the first container. The opening of the first container can generally have any circumferential shape, e.g., angular, partially angular, elliptic or circular. In a preferred embodiment the opening has a circular or at least essentially circular circumference. The size of the first opening of the first container is preferably chosen such that the diameter of the opening is large enough to facilitate the passage of flowable material with a high viscosity, as described below.

**[0026]** Thus, it has been found to be advantageous if the ratio of the length of the largest spatial extension of the first container measured rectangular to the longitudinal axis and the diameter of the first opening of the first container is less than 2. In other words, the largest spatial extension of the first container measured rectangular to the longitudinal axis should be twice as wide or less as compared to the largest width of the first opening of the first container. It can be preferred, if the above mentioned ratio is between 1.9 and 0.5, e.g., between 1.5 and 0.7 or between 1.9 and 0.8, especially between about 1.1 and 0.9.

**[0027]** The kit according to the invention further comprises a second container with a first opening and a second opening.

**[0028]** The second container can generally have any shape and volume which is useful in the art of hair dyeing. Generally the volume is such that the composition is useful in a retail or professsional salon environment addressing the end-user or a salon professional. While in its absolute size generally dependent on the content, the second container has a size which is smaller than, equal to or is larger than the size of the first container, the term "size relating to exterior dimensions. The second container has a volume which is smaller than, equal to or is larger than the volume of the first container, the term "volume" relating to the volume available for storage and handling of the composition contained in the container, the actual volume can be larger. It can be preferred, if the volume of the second container is smaller than the volume of the first container.

**[0029]** A typical preferred volume for the second container can be about 3 to about 300 ml, e.g., about 5 to about 100 or about 10 to about 80 ml.

**[0030]** Generally, the second container can have any shape which provides for an efficient use of the kit according to the invention. Thus, the shape of the second container should be chosen such that it provides for a facile application of a hair dye formed within a bottle consisting of connected first and second containers, as will be described in more detail below. It has proven to be useful if the second container has an essentially hemispherical or otherwise domelike shape with an essentially circular circumference along a longitudinal axis of the second container.

**[0031]** While it is possible that the second container holds a composition comprising a developer, it is generally preferred that the second container contains a composition comprising a tint. It is advantageous if the second container is made at least in part from a rigid material which is only deformable under higher pressure, such that the end-user will not be able to build up pressure in a closed second container by squeezing the container walls.

**[0032]** The second container can, as will be described below in more detail, comprise a developer. It is, however, preferred if the second container comprises a composition which contains a tint.

**[0033]** The second container is preferably made of a material which is neither transparent nor translucent. The material should be such that the composition comprised in the second container is not subjected to light, unless the container is opened.

**[0034]** In a further embodiment of the invention, especially in cases where the second container comprises the tint, the second container can comprise more than one material, e.g., a first and a second material. In such a case the container has a compartment containing a composition comprising the tint, as described further below, and can have further parts which do not come in contact with the tint and are made from a different material. Such further parts can, e.g., be part of a connection means for connecting the first and the second container. It is especially possible to choose first and second material such that both materials allow for a specific aesthetic appearance, or chose a second material with regard to specific advantages with regard to its function as a substrate to receive print or with regard to specific advantages with embossing.

**[0035]** In those cases the part of the second container which comes into contact with the tint is made of a first material having an oxygen transmission rate of 30 $cm^3*mm/(m^2*d*MPa)$ or lower, as described above, or a water vapor transmission rate of 7 $g/mm/(m^2*d)$ or lower, as described above, or both, the first material being in contact with the composition comprising the tint, and a second material with an oxygen transmission rate which is higher than the oxygen transmission rate of the first material or with a water vapor transmission rate which is equal to or different from the water vapor transmission rate of the first material, or both.

**[0036]** It is also preferred if the material which comes into contact with the tint during storage is capable of being injection molded. Possible and preferred materials for manufacturing the container containing the composition comprising the tint are polyamides. Thus, especially in case the second container contains the composition comprising the tint, the first material of the second container is a polyamide. An example for a polyamide fulfilling the requirements according to the invention is EMSGrivory Grivory® HB 5299 HV PA, a polyamide available from EMS-CHEMIE AG, Unternehmensbereich EMS-GRIVORY Europa, Via Innovativa 1, 7013 Domat/Ems, Switzerland.

**[0037]** The second container has a first opening. It has proven to be advantageous if the first opening of the second container has a comparatively large opening in order to facilitate mixing of ingredients transferred to the first container. The first opening of the second container can generally have any circumferential shape, e.g., angular, partially angular, elliptic or circular, as long as it is compatible with the first opening of the first container such that both container can be fastened to one another. In a preferred embodiment the first opening of the second container has a circular or at least essentially circular circumference. The size of the first opening of the second container is preferably chosen such that the diameter of the opening is large enough to facilitate the passage of flowable material with a high viscosity as described below.

**[0038]** The second container also has a second opening. The second opening is generally designed to form an exit for the dye obtained by mixing of the contents of the first and second container. The dye can exit through the second opening by gravitational action only, but it is also possible and in fact can be a preferred choice, if the dye exits through the second opening of the second container at least in part due to pressure generated by the end user. The second opening can be a simple hole in the second container. It is, however, preferred if the second opening is part of a structure which can assist in reaching specific areas of the substrate, especially specific areas of the human hair, e.g., the root portion of the hair near the scalp. It has thus proven to be advantageous if the second opening is located not directly at a surface of the second container but at an elevated position, e.g., at the end of a dispensing tip or nozzle which is in fluid communication with the second container. The dispensing nozzle is preferably an elongate, generally conical member forming part of the structure of the second container having a through passage extending axially along the member, and a tip portion which, has an opening through which a dye can be released. The second opening of the second container does not necessarily have to be restricted to just one single opening. It has proven to be advantageous in some cases if the second opening is formed by a two or more of similar nozzle openings, which can be arranged in a row or any other geometric pattern which is useful in allowing to reach a specific area of the hair, especially the root section.

**[0039]** In a most preferred embodiment of the invention, the second container has a generally cylindrical main body with a dome like upper portion which extends into a tip comprising the second opening. A corresponding second container is depicted in Fig. 3 as described above.

**[0040]** In order to facilitate storage and transport of the containers, the first opening of the first container and the first and second opening of the second container have a removable closure which prevents the content from accidentally leaving the container as well as protecting the contents from environmental influences. In case of the container comprising the tint, specific measures should be taken in order to prevent water vapor or oxygen to enter the container. The opening or the openings of the container enclosing the tint are thus sealed with a first seal only in case of the first container enclosing the tint or with a first and a second seal in case of the second container enclosing the tint. The term "seal" relates to a closure which fulfills at least the same standards with regard to oxygen transmission and vapor transmission as the material enclosing the composition comprising the tint. In case of the seal covering the first opening, which is generally a larger opening than the second opening, it is preferred if the seal is a foil, especially a laminated diaphragm, preferably with values for oxygen transmission and water vapor transmission which are equal to or lower than the corresponding values of the container.

**[0041]** Generally it can be preferred if the seal comprises a foil which effectively reduces oxygen transfer, e.g., a thin metal foil such as an aluminum foil. It can be advantageous if such a metal foil is laminated with a polymer film on the product side as well as on the side facing away from the product to be enclosed. Effective laminates for the product side can be polyolefins such as polyethylene, effective laminates for the side facing away from the product can be polyesters such a poly(ethylene terephthalate) and the like. The polymer films can be adhered to the metal foil surface by the aid of an adhesive. It can be especially preferred to us a polymer film on the product side which can be easily sealed against a respective surface surrounding the opening of the container to be sealed.

**[0042]** The first opening of the container comprising the developer can generally be closed by any type of closure, most conveniently it is closed by a simple transport cap which can, e.g., be snapped on or screwed on, as long as it prevents the contents of the container from spilling out during transport or storage.

**[0043]** The second opening of the first container is generally small, compared to the first opening, and can be sealed by any means available for the closure of a small opening, such as a cap or the like. It has, however proven to be successful if the closure of the second opening is achieved by forming the closure as an integral part of the second container, especially as an integral part of the tip being a part of the second container, which has a predetermined breaking point for removing the closure.

**[0044]** The first and the second container comprise means to reversibly couple the first and the second containers such that the first openings of the first and second container are in fluid connection.

**[0045]** The first and second container are separate parts of the kit, but are coupled in order to provide their beneficial function with regard to the formation of a dye. Both containers have means to be reversibly coupled, e.g., by a snap on feature or, in a preferred embodiment, by a screw thread. As preferably at least one of the first openings is sealed by a laminated seal, in order to provide a fluid connection between the containers one of the containers, must provide a means to rupture the seal in order to establish a fluid communication. While this is possible for snapon connections by providing respective pins in one of the containers which puncture or rupture the seal of the first opening of the container comprising the tint, it may be preferably to connect the containers by a screwing motion with a screw thread.

**[0046]** In a preferred embodiment of the invention, when the second container contains a composition comprising a tint, the first container comprises means to open the first seal of the second container when the first and second container are coupled, such that the first and second container are in fluid connection through the first opening of the first container and the first opening of the second container.

**[0047]** In a preferred embodiment the means to open the first seal of the second container when the first and second container are coupled, remove at least a part of the seal such that the removed part is disconnected from a remaining part.

**[0048]** The package kit according to the invention provides the advantage that the container containing the tint, preferably the second container, can be manufactured by an injection molding step.

**[0049]** In case the second container comprises two or more materials, the preferably method of manufacture is by subjecting the first material to a first injection molding step and applying the second material in a second injection molding step, preferably in an overmolding step.

**[0050]** The first and second material can provide for a second container which comprises a first cavity formed by the first material and containing the composition comprising the tint and a second cavity formed by the second material, wherein the second cavity essentially surrounds the first cavity as a recess. Advantageously, the recess formed by the second material has the coupling means for coupling the second container to the first container.

**[0051]** It is also within the scope of the invention that the package kit comprises a third container, which contains a modifier. The third container has a first opening and a second opening, the first opening being larger than the second opening. The first opening of the third container has means to be coupled with the first container after the second container has been removed. The coupling means can be equipped for a reversible coupling, but is also within the scope of the invention that the coupling means for coupling the first and the third container result in an essentially permanent coupling.

**[0052]** The material of which the third container is made can generally be any material which is compatible with the intended use, preferably a polymeric material. The third container can be transparent, translucent or opaque or a mixture of any of two or three of these features. The first opening of the third container is closed by an appropriate closing means. For ease of use it can be preferred that the first opening of the third container is closed by a foil or diaphragm. Upon coupling of the first and the third container means for rupturing a seal, which can, e.g., be present in the first container, can rupture the closure of the third container and enable a fluid communication between the first and the third container.

**[0053]** The second opening of the third container is equipped to facilitate the application of a modified dye, resulting from mixing a remainder of the dye in the first container and the modifier of the third container to the substrate, especially to human hair. While the second hole of the first substrate was preferably equipped to apply a dye to parts of the hair in the root region, the second opening of the third container can be equipped to apply the modified dye to a different portion of the hair, e.g., a zone adjacent to the root region or the hair tips or the like. Thus the second opening of the third container is preferably also part of a structure which is adapted to deliver the modified dye to different part of the hair. It can be preferred if the second opening of the third container is also part of a nozzle like structure, as already explained for the second container. The second openig can be a single opening or a group of openings, adapted to fit specific treatment needs.

## Detailed description of the embodiments

**[0054]** Figure 1 shows a perspective view of a package kit 10 for a dye. Basically, the package kit 10 comprises a first container 12 and a second container 14. The first container 12 and the second container 14 are adapted to be coupled with each other as will be described below in further detail. Figure 1 shows the first container and the second container coupled with each other. In such a coupled state, the package kit is substantially bottle-shaped. The first container 12 can comprise a transit cap (not shown) sitting on top of the first container 12 during transit to a consumer. However, also other means for closing the first container, such as a diaphragm or a membrane or the like, are possible within the scope of the invention.

**[0055]** Figure 2 shows a cross-sectional view of the package kit 10 taken along line B-B of Figure 1. As can be taken from Figure 2, the first container 12 comprises a longitudinal axis 16. Preferably, the first container 12 is formed symmetrically around the longitudinal axis 16. For example, the first container 12 is essentially cylindrically formed around the longitudinal axis 16, which may be a rotational axis. The first container 12 comprises a top 18, a bottom 20 and a side wall 22 extending in a circumferential direction around the longitudinal axis 16 and connecting the top 18 and the bottom 20. The first container 12 comprises a first opening 24. The first opening 24 is located at the top 18. The first opening 24 extends perpendicularly to the longitudinal axis 16. The first opening 24 comprises a diameter 26. The first container 12 is formed such that a ratio of a length of the largest spatial extension 28 of the first container 12 measured perpendicular or rectangular to the longitudinal axis 16 and the diameter 26 of the first opening 24 is less than 2 such as 1.5. Thus, the first opening 24 of the first container 12 is comparably large. In case the first container 12 comprises a circular cross-section perpendicular to the longitudinal axis, the largest spatial extension 28 of the first container 12 measured perpendicular or rectangular to the longitudinal axis 16 is identical to a diameter of the first container 12 perpendicular or rectangular to the longitudinal axis 16. With other words, the diameter 26 of the first opening 24 is not smaller than a half of the largest width of the first container 12.

**[0056]** As mentioned above, the first container 12 and the second container 14 are adapted to be coupled with each other. For this purpose, the first container 12 comprises a means 30 to be coupled with the second container 14. Particularly, the means 30 is formed as a screw thread 32 arranged at the top 18 such that the first container 12 and the second container 14 may be reversibly coupled with each other. More particularly, the first container 12 comprises an outer thread 34. The first container 12 further comprises a means 36 adapted to rupture a first seal 38 of the second container 14 as will described below in further detail. The means 36 is at least one cutting edge 40 arranged adjacent the first opening 24 of the first container 12 and protruding in a direction parallel to the longitudinal axis 16 from the first container 12.

**[0057]** The second container 14 comprises a longitudinal axis 42. In a state, in which the first container 12 and the second container 14 are coupled with each other, the longitudinal axis 16 of the first container 12 and the longitudinal axis 42 overlap with each other. Preferably, the second container 14 is formed symmetrically around the longitudinal axis 42. For example, the second container 14 is cylindrically formed around the longitudinal axis 42, which may be a rotational axis. The second container 14 comprises a lower portion 44 and top portion 46. The lower portion 44 is formed substantially as a circular cylinder. The top portion 46 is formed as a nozzle 48. With other words, a diameter of the top portion gradually decreases in a direction away from the lower portion 44. The second container 14 comprises a first opening 50 and a second opening 52. The first opening 50 is located at an end of the lower portion 44 facing away from the top portion 46. The second opening 52 is located at an end of the top portion 46 facing away from the lower portion 44. The first opening 50 of the second container 14 has a larger opening area than the second opening 52. The first opening 50 is sealed with the first seal 38 which is comparably large. The first seal 38 is a laminated diaphragm. The second opening 52 is sealed with a second seal 54 which is comparably small. The second seal 54 is an integral part of the second container 14. Particularly, the top portion 46 comprises a predetermined breaking point 56 adjacent the second seal 54. The predetermined breaking point 56 may be shaped as a notch in a material of the second container 14. Thus, the second seal 54 may be broken away by a user so as to expose the second opening 52.

**[0058]** Figure 3 shows a top view of the second container 14. As can be taken from Figure 3, the second seal 54 may be oval shaped. Such a design of the second seal 54 facilitates the removal of the second seal 54 as it is easier for a user to grip the second seal 54.

**[0059]** With reference to Figure 2 again, the first opening 50 extends perpendicularly to the longitudinal axis 42. The first opening 50 comprises a diameter 58. The second container 14 is formed such that a ratio of a length of the largest spatial extension 28 of the first container 12 measured perpendicular or rectangular to the longitudinal axis 16 and the diameter 58 of the first opening 50 of the second container 14 is less than 2 such as 1.5. In case the second container 12 comprises a circular cross-section perpendicular to the longitudinal axis 16, the largest spatial extension 28 of the first container 12 measured perpendicular or rectangular to the longitudinal axis 16 is identical to a diameter of the first container 12 perpendicular or rectangular to the longitudinal axis 16. With other words, the diameter 58 of the first opening 50 of the second container 14 is not smaller than a half of the largest width of the first container 12. Thus, the first opening 50 of the second container 14 is comparably large, whereas the second opening 52 of the second container 14 is comparably small.

**[0060]** The second container 14 is preferably made of two different materials. Particularly, the second container 14 is made of a first material 60 having an oxygen transmission rate of 30 $cm^3*mm/(m^2*d*MPa)$ or lower or a water vapor transmission rate of 7 $g/mm/(m^2*d)$ or lower, or both, and a second material 62 with an oxygen transmission rate which is higher than the oxygen transmission rate of the first material 60 or with a water vapor transmission rate which is equal to or different from 60, preferably lower than the water vapor transmission rate of the first material, or both.

**[0061]** The oxygen transmission rate is measured according to ISO 15105-1 at 23°C and 85% relative humidity. It should be noted that the oxygen transmission rate for the material used does not have to be constant under different climatic circumstances. It is within the scope of the invention to use a material that change its oxygen transmission rate depending on parameters such as temperature or humidity. For example, it can be advantageous to use a first material that shows an increase in oxygen barrier properties, i.e., a decrease in oxygen transmission rate, with increasing humidity.

**[0062]** The water vapor transmission rate (WVTR) is measured according to ISO 15105-1.

**[0063]** In order to manufacture the first container 14, the first material 60 is subjected to a first injection molding step and the second material 62 is applied in a subsequent second injection molding step. The second injection molding step is preferably an overmolding step. Thus, the second material 62 encloses the first material 62. More particularly, the second material 62 encloses the first material 62 at the lower portion 44 of the second container 14. Thereby, the second container 14 comprises a first cavity 64 formed by the first material 60 and a second cavity 66 formed by the second material 62. The second cavity 66 essentially surrounds the first cavity as a recess 68.

**[0064]** As mentioned above, the first container 12 and the second container 14 are adapted to be coupled with each other. For this purpose, the recess 68 formed by the second material 62 comprises a means 70 to be coupled with the first container 12. Particularly, the means 70 is formed as a screw thread 72 arranged at the end of the lower portion 44 facing away from the top portion 46 such that the first container 12 and the second container 14 may be reversibly coupled with each other. More particularly, the recess 68 of second container 14 comprises an inner thread 74. The inner thread 74 is adapted to engage with the outer thread 34 of the first container 12

**[0065]** Figure 4 shows a perspective view of the second container 14. As mentioned above, the first material 60 and the second material 62 are different from each other. Therefore, it might be the case that the second material 62 does not reliably adhere to the first material 60. For this purpose, the second container 14 may comprise means for preventing a release of the second material 62 from the first material 60. The first material 60 and the second material 62 may be connected to one another by means of a form-locking joint. A form-locking joint in the sense of the present invention is a joint of two parts, wherein one of the two parts obstructs a movement of the other one relative to one another. For example, the first material 60 may comprise slots 76 and the second material 62 may comprise ribs 78 which are shaped complementary to the slots 76. The slots 76 may be formed in the first material 60 at the transition of the lower portion 44 and the top portion 46 and/or adjacent the first opening 50 of the second container 14. The slots 76 preferably partially extend in an axial direction with respect to the longitudinal axis 42. With other words, the slots 76 do not have to extend over a complete length of the first material 60 in the axial direction with respect to the longitudinal axis 42. It is also to be noted that the slots 76 do not penetrate the first material 60 completely in a radial direction with respect to the longitudinal axis 42. The slots 76 are thus not formed as elongated through holes but as depressions. The ribs 78 can be formed at the transition of the lower portion 44 and the top portion 46 and/or adjacent the first opening 50 of the second container 14. The ribs 78 also extend in an axial direction with respect to the longitudinal axis 42 towards the top portion 46. Analogously to the slots 76, the ribs 78 do not extend across the complete length of the lower portion 44 in the axial direction with respect to the longitudinal axis 42. The ribs 78 are shaped complementary to the slots 76. The slots 76 engage with the ribs 78. Thus, a rotational movement of the second material 62 relative to the first material 60 around the longitudinal axis 42 is prevented.

**[0066]** Figure 5 shows a cross-sectional view of the second container 14 taken along line A-A of Figure 4. The first material 60 may comprise a first recess 80 or cut-out extending in a circumferential direction adjacent the first opening 50 of the second container 14 and a second recess 82 or cut-out extending in a circumferential direction at the transition of the lower portion 44 and the top portion 46. The second material 62 may comprises a first protrusion 84 extending in a circumferential direction at a lower end of the second material 62 and a second protrusion 86 extending in a circumferential direction at a top end of the second material 62. The first protrusion 84 and the second protrusion 86 protrude towards the first material 60. The first protrusion 84 engages with the first recess 80 and the second protrusion 86 engages with the second recess 82. Thus, an axial movement of the second material 62 along the longitudinal axis 42 relative to the first material 60 is prevented.

**[0067]** The first container 12 contains a first composition. The second container 14 contains a second composition. The first composition comprises a developer and the second composition comprises a tint so that the first composition and the second composition form a dye upon mixing. The first material 60 is in contact with the first composition comprising the tint. Further, as the second material 62 encloses the first material 60, the second material 62 is not in contact with the first composition comprising the tint.

**[0068]** In order to couple the first container 12 and the second container 14 with each other, the second container 14 is disposed on the first container 12. More particularly, the second container 14 is disposed with its lower portion 44 onto the top 18 of the first container 12. Thus, the first opening 24 of the first container 12 and the first opening 50 of the second container face each other. The first container 12 and the second container 14 are coupled with each other by means of the coupling means 30, 70. Particularly, the second container 14 is rotated around the longitudinal axis 42. Thereby, the inner thread 74 of the second container 14 engages with the outer thread 34 of the first container 12. The rotational movement of the second container 14 relative to the first container 12 also causes an axial movement with respect to the longitudinal axis 16 towards the second container 14. When the first container 12 and the second container 14 are coupled with each other, the means 36 ruptures the first seal 38 of the second container 14. More particularly, the cutting edge 40 cuts the first seal 38 of the second container 14 such that the first container 12 and the second container 14 are in fluid connection through the first opening 24 of the first container 12 and the first opening 50 of the second container 14. With other words, when the first container 12 and the second container 14 are coupled with each other, a connection with fluid communication through the first opening 24 of the first container 12 and the first opening 50 of the second container 14 is formed. Particularly, the means 36 is adapted to open at least a part of the first seal 38 such that a fluid communication is established through the opening. The opening of the seal can be done such that all of the seal material is still connected to the second container. It is, however, also possible to perform the opening of the seal such that at least a part of the seal is removed from a remaining part of the first seal 38 when the first container 12 and the second container 14 are coupled. Preferably, the first seal 38 can be opened or is at least in part removable by the means 36. Thereby, the first composition and the second composition may be mixed so as to form a flowable dye. The so formed flowable dye may be removed from the package kit 10 after the second seal 54 of the second container 14 is opened or removed.

**[0069]** The package kit 10 described above may be modified in several ways. The first composition may comprise the tint and the second composition may comprise the developer. The opening or the openings of that container enclosing the oxidation dye are sealed with a first seal only in case of the first container 12 enclosing the tint or with a first seal and a second seal in case of the second container 14 enclosing the tint. The first container 12, or the second container

14, or both may comprise means to open the seal of the first container 12, or the second container 14, or both when the first and second container 12, 14 are coupled, such that the first and second container 12, 14 are in fluid connection through the first opening 24 of the first container 12 and the first opening 50 of the second container 14.

**[0070]** Figure 6 shows a perspective view of a third container 88. The third container 88 comprises a third composition. The third composition comprises a modifier. The third container 88 comprises a comparably large first opening 90 and a comparably small second opening 92. The first opening 90 and the second opening are arranged at opposing ends of the third container 88. The first opening 90 is sealed with a comparably large first seal 94 and the second opening is sealed with a comparably small second seal 96. The basic construction of the third container 88 is similar to the second container 14. Particularly, the third container 88 is adapted to be reversibly coupled with the first container 12 similar to the second container 14, thereupon rupturing the large first seal 94 on the large first opening 90 of the third container 88 and forming a connection in fluid communication through the large first openings 24, 90 of the first and third container 12, 88.

**[0071]** The package kit 10 may be used with a method for colouring hair making it is possible to preserve a more natural root-to-tip transition. Whilst not being bound by theory it is believed that mixing the developer component with the tint component to obtain a non-diluted dyeing composition and applying a first portion of the non-diluted dyeing composition directly onto the root virgin hair as a first zone, delivers an effective composition to both lighten and colour previously uncoloured hair to the desired level. However, retaining a portion of this nondiluted dyeing composition and mixing it with a modifier component thereto provides a resultant modified dyeing composition which reduces the overall effective lightening and colouring capacity of the dyeing composition which can then be applied to the remaining pre-coloured hair length as a second zone, which requires less lightening and dye deposition in order to deliver a colour result similar to that resulting from the application of the first portion of the nondiluted composition applied to the roots. Whilst not being bound by theory it is believed that the use of a modifier with the second portion of the non-diluted composition reduces the concentration of actives species such as dye precursors, oxidizing agent such as hydrogen peroxide and alkalising agents if present before the dye formation process has completed thereby still enabling penetration of the dyes species into the hair shaft to provide permanent hair colour.

**[0072]** Basically, the method comprises the following steps. The first and second compositions are mixed to give a flowable dyeing composition (flowable dye), preferably a liquid dye. A part of the flowable dye is then applied to the first zone. The remaining dye is mixed with the third composition to give a modified flowable, preferably liquid dye. The modified dye is then applied to the second zone.

**[0073]** The third composition, i.e., the modifier, can influence the properties of the remaining dye in different ways, it can, e.g., simply provide for a difference in physical properties of the product, such as rheology, or it can provide for a different chemical behavior towards the substrate, e.g., by influencing the dye color or intensity, or introducing additional beneficial features such as repair functions for the hair and the like.

**[0074]** In order to describe the method in more detail, the first container 12 is coupled to the second container 14 in the above described manner. Thereby, the first seal 38 of the second container 14 is ruptured by the cutting edge 40 which allows the first and second compositions to mix to give a flowable, preferably a liquid tint. After removal of the second seal 54 of the second container 14, a predetermined amount of the thus formed tint is applied to a first zone of the substrate. The predetermined amount is less than the total amount of the thus formed dye. The term "predetermined" relates to any amount which is less than the total amount of the dye formed after adding the third composition. The term "predetermined" can mean that the amount can be chosen by the person using the kit, but it can also mean that the amount is prescribed.

**[0075]** It can be preferred if the container holding the dye is translucent or even transparent and has one or more marks on it providing guidance as to how much of the dye should be retained as a "predetermined" amount.

**[0076]** Subsequently, the second container 14 is removed from the first container 12, e.g., by being unscrewed.

**[0077]** Afterwards, the first container 12 is coupled to the third container 88 similar to the second container 14. Thereby, the first seal 94 of the third container 88 is ruptured by the cutting edge 40 which allows the remaining dye and the third composition to mix to give a modified dye. After removal of the second seal 96, the thus formed modified dye is applied to a second zone of the substrate, e.g., to a second zone of the hair. It is to be noted that the application of the dye to the first zone may be performed with a first applicator and the application of the modified oxidation dye to the second zone may be performed with a second applicator and the first and second applicator are different.

**[0078]** The volume of the first component, preferably being the developer component in the kit, may be 10 mL to 120 mL, preferably 40 mL to 70 mL, more preferably 55 mL to 65 ml. The volume of the second component, preferably being the tint component in the kit, may be 10 mL to 120 mL, preferably 40 mL to 70 mL, more preferably 55 mL to 65 ml. The volume of the third component, being the modifier component, may be 10 mL to 120 mL, preferably 15 mL to 30 mL, more preferably 20 mL to 25 ml.

**[0079]** In a package kit according to the invention, one of the first composition and the second composition comprises a tint and one of the first composition and the second composition comprises a developer so that the first and second composition form a dye upon mixing.

**[0080]** Retail dye compositions are often sold in kits comprising, in individually packaged components such as separate containers, a component comprising a tint, e.g., comprising oxidative dye precursors and alkalizing agent which is typically ammonia in a suitable carrier and; and a component comprising a developer, e.g., comprising an oxidizing agent (usually hydrogen peroxide). The consumer mixes the dye component and oxidizing component together immediately before use and applies it onto the hair. For, the professional hair salon market, the component with the tint and the component with the developer are often supplied independently to allow the professional to select a preferred combination.

**[0081]** As will be appreciated by the person skilled in the art the package kit according to the invention can be used for a plethora of different applications in the area of dyeing substrates, especially of dyeing hair. As a result, the different contents as contained in the different container can have varying compositions, depending on the aim of the combination of compositions in the parts of the kit.

**[0082]** It will further be appreciated by the skilled person that the kit according to the invention can comprise more than the three containers described herein. Any additional container being part of the kit can be equipped to be coupled with another container of the kit, or can be a discrete entity. Such additional containers can, e.g., comprise compositions for after-treatment of the substrate, e.g., a shampoo composition or the like.

**[0083]** A typical use of the kit according to the invention will be the dyeing of a substrate, especially the dyeing of human hair. As described above, he kit comprises a first, a second and a third composition, mixing the first and the second composition preferably resulting in the formation of a hair colorant or dye.

## Oxidizing Agent

**[0084]** One of the first and second compositions, preferably the first composition, is a developer composition, comprising an oxidizing agent. The oxidizing agent is present in an amount sufficient to bleach the melanin pigment in the hair and/or oxidize dye precursors. Typically, such an amount ranges from 1% to 20%, or from 3% to 15%, or from 6% to 12% by weight of the developer component. Inorganic peroxygen materials capable of yielding hydrogen peroxide in an aqueous medium are suitable and include, but are not limited to: hydrogen peroxide; inorganic alkali metal peroxides (e.g. sodium periodate and sodium peroxide); organic peroxides (e.g. urea peroxide, melamine peroxide); inorganic perhydrate salt bleaching compounds (e.g. alkali metal salts of perborates, percarbonates, perphosphates, persilicates, and persulphates, in some embodiments, sodium salts thereof), which may be incorporated as monohydrates, tetrahydrates, etc.; alkali metal bromates; enzymes; and mixtures thereof. Mixtures of two or more oxidizing agents may be used, for example hydrogen peroxide and sodium persulphate. The oxidizing agents may be provided in solution or as a powder which is dissolved prior to use.This is a preferred embodiment for persulphate based oxidizing agents. The oxidizing agent may be hydrogen peroxide. The first or second composition of the invention may comprise air oxidation or auto oxidation hair colorants.

**[0085]** One of the first and second compositions, preferably the second composition, comprises a tint.

**[0086]** The tint can be a dye component comprising at least one oxidative dye precursor and/or an alkalizing agent. Oxidative dye precursors are usually classified either as primary intermediates (also known as developers) or couplers (also known as secondary intermediates). Various couplers may be used with primary intermediates in order to obtain different shades. Oxidative dye precursors may be free bases or the cosmetically acceptable salts thereof.

**[0087]** Typically, the tint composition may comprise a total amount of oxidative dye precursors ranging up to 12%, alternatively from 0.1% to 10%, alternatively from 0.3% to about 8%, alternatively from 0.5% to about 6%, by weight of the total composition.

**[0088]** Suitable primary intermediates include, but are not limited to: toluene-2,5-diamine, pphenylenediamine, *N*-phenyl-p-phenylenediamine, *N,N*-bis(2-hydroxyethyl)-pphenylenediamine, 2-hydroxyethyl-p-phenylenediamine, hydroxypropyl-bis-(N-hydroxyethylp-phenylenediamine), 2-methoxymethyl-p-phenylenediamine, 2-(1,2-dihydroxyethyl)-p- phenylenediamine, 2,2'-(2-(4-aminophenylamino)ethylazanediyl)diethanol, 2-(2,5-diamino-4- methoxyphenyl)propane-1,3-diol, 2-(7-amino-2H-benzo[b][1,4]oxazin-4(3H)-yl)ethanol, 2- chloro-p-phenylenediamine, p-aminophenol, p-(methylamino)phenol, 4-amino-m-cresol, 6- amino-m-cresol, 5-ethyl-*o*-aminophenol, 2-methoxy-p-phenylenediamine, 2,2'-methylenebis-4-aminophenol, 2,4,5,6-tetraminopyrimidine, 2,5,6-triamino-4-pyrimidinol, 1-hydroxyethyl-4,5-diaminopyrazole sulfate, 4,5-diamino-1-methylpyrazole, 4,5-diamino-1-ethylpyrazole, 4,5- diamino-1-isopropylpyrazole, 4,5-diamino-1-butylpyrazole, 4,5-diamino-1-pentylpyrazole, 4,5-diamino-1-benzylpyrazole, 2,3-diamino-6,7-dihydropyrazolo[1,2-a]pyrazol-1(5H)-one dimethosulfonate, 4,5-diamino-1-hexylpyrazole, 4,5-diamino-1-heptylpyrazole, methoxymethyl-1,4-diaminobenzene, N,N-bis(2-hydroxyethyl)-N-(4-aminophenyl)-1,2-diaminothane, salts thereof and mixtures thereof.

**[0089]** Suitable couplers include, but are not limited to: resorcinol, 4-chlororesorcinol, 2-chlororesorcinol, 2-methylresorcinol, 4,6-dichlorobenzene-1,3-diol, 2,4-dimethylbenzene-1,3 diol, m-aminophenol, 4-amino-2-hydroxytoluene, 2-methyl-5-hydroxyethylaminophenol, 3-amino-2,6-dimethylphenol, 3-amino-2,4-dichlorophenol, 5-amino-6-chloro-o-cresol, 5-amino-4-chloro-o-cresol, 6-hydroxybenzomorpholine, 2-amino-5-ethylphenol, 2-amino-5-phenylphenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol, 2-amino-5-ethoxyphenol, 5-methyl-2-(methylamino)phenol, 2,4-diaminophenoxyethanol, 2-amino-4-hydroxyethylaminoanisole, 1,3-bis-(2,4-diaminophenoxy)-propane, 2,2'-(2-methyl-1,3-phenylene)bis(azanediyl)diethanol, benzene-1,3-diamine, 2,2'-(4,6-diamino-1,3-phenylene)bis(oxy)diethanol, 3-(pyrrolidin-1-yl)aniline, 1-(3-(dimethylamino)phenyl)urea, 1-(3-aminophenyl)urea, 1-naphthol, 2-methyl-1-naphthol, 1,5-naphthalenediol, 2,7-naphthalenediol or 1-acetoxy-2-methylnaphthalene, 4-chloro-2-methylnaphthalen-1-ol, 4-methoxy-2-methylnaphthalen-1-ol, 2,6-dihydroxy-3,4-dimethylpyridine, 2,6-dimethoxy-3,5-pyridinediamine, 3-amino-2-methylamino-6-methoxypyridine, 2-amino-3-hydroxypyridine, 2,6-diaminopyridine, pyridine-2,6-diol, 5,6-dihydroxyindole, 6-hydroxyindole, 5,6-dihydroxyindoline, 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one, 1,2,4-trihydroxybenzene, 2-(benzo[d][1,3]dioxol-5-ylamino)ethanol (also known as hydroxyethyl-3,4-methylenedioxyaniline), and mixtures thereof.

**[0090]** The primary intermediates and couplers are usually incorporated into the tint component.

## Alkalizing agent

**[0091]** The tint component may optionally comprise an alkalizing agent, preferably a source of ammonium ions and/or ammonia. Alkalizing agent may include alkanolamines, for example monoethanolamine, diethanolamine, triethanolamine, monopropanolamine, dipropanolamine, tripropanolamine, 2-amino-2-methyl-1,3-propanediol, 2-amino-2-methyl-1-propanol, and 2-amino-2-hydroxymethyl-1,3-propanediol; guanidium salts; and alkali-metal and ammonium hydroxides and carbonates, such as sodium hydroxide and ammonium carbonate; and mixtures thereof. A preferred alkalizing agent is monoethanolamine. Particularly, preferred alkalizing agents are those which provide a source of ammonium ions. Any source of ammonium ions is suitable for use herein. Preferred sources include ammonium chloride, ammonium sulphate, ammonium nitrate, ammonium phosphate, ammonium acetate, ammonium carbonate, ammonium hydrogen carbonate, ammonium carbamate, ammonium hydroxide, ammonium percarbonate salts, ammonia and mixtures thereof. Particularly preferred are ammonium carbonate, ammonium carbamate, ammonia, ammonium hydroxide and mixtures thereof.

## Diluent component

**[0092]** The first or second composition according to the present invention, or both, can comprise a diluent component. The diluent component comprises water and optionally at least one active component. The active component(s) may be selected from, surfactants, polymers, conditioning actives, solvents, C6 to C30 fatty alcohols, thickeners and mixtures thereof, preferably surfactants, polymers, conditioning agents and mixtures thereof as described hereinafter. Preferably, the diluent component may comprise up to 99%, or up to 90%, or up to 85% by weight of water. Preferably, the diluent component may comprise up to 25%, or from 1% to 20%, or from 5% to 20% by weight of the active component(s). Whilst not being bound by theory it is believed that the diluent component acts to dilute the concentration of the second portion of the non-diluted hair coloring composition in particular the concentration of oxidizing agent and oxidative dye precursors and alkalizing agent if present, to thereby reduce the overall effectiveness of the provision of lightening and color to the substrate.

**[0093]** When the first and second component are mixed, the resulting dye generally may comprise from 0.1% to 20%, or from 0.5% to 5%, or from 1% to 3% by weight of an alkalizing agent, preferably ammonium ions. Preferably, if present, the ammonium ions and carbonate ions are present in the hair coloring composition at a weight ratio of from 3:1 to 1:10, preferably 2:1 to 1:5.

## Further constituents

**[0094]** As has been explained above, mixing the first and second composition results in a hair colorant. The first and second composition must be different insofar, as one of the compositions must be a developer composition, preferably the first composition, and one of the compositions must be a tint composition, preferably the second composition. Apart from these constraints, further constituents of the compositions can be chosen according to the targeted features of the composition based on general constituents of hair dyes. In the following further constituents are described, which can form part of the first, second or third composition, or can be part of the first and second composition, or first and third composition, or second and third composition, or first second and third composition. Thus, when the term "the compositions" is used in the following text, it refers to any combination as described above, if not indicated otherwise.

## Composition Components

**[0095]** One or more of the compositions may further comprise additional components, effective for use in oxidative dye compositions, including but not limited to: solvents; direct dyes; radical scavengers; thickeners and or rheology modifiers; chelants; pH modifiers and buffering agents; carbonate ion sources; peroxymonocarbonate ion sources; surfactants; polymers; fragrances; enzymes; dispersing agents; peroxide stabilizing agents; antioxidants; natural ingredients, e.g. proteins and protein derivatives, and plant extracts; conditioning agents; ceramides, preserving agents; and opacifiers and pearling agents (such as titanium dioxide and mica). These components may be comprised in the developer component, the tint component, the modifier component or any combination thereof. Some adjuvants referred to above, but not specifically described below, which are suitable are listed in the International Cosmetics Ingredient Dictionary and Handbook, (8th ed.; The Cosmetics, Toiletry, and Fragrance Association). Particularly, vol. 2, sections 3 (Chemical Classes) and 4 (Functions) are useful in identifying specific adjuvants to achieve a particular purpose or multipurpose.

## Direct Dyes

**[0096]** The compositions, especially the tint composition or the modifier composition or both may comprise compatible direct dyes in an amount sufficient to provide colouring, particularly with regard to intensity. Typically, such an amount will range from 0.05% to 4%, by weight of the non-diluted or diluted hair colouring composition. Suitable direct dyes include but are not limited to: Acid Yellow 1; Acid Orange 3; Disperse Red 17; Basic Brown 17; Acid Black 52; Acid Black 1; Disperse Violet 4; 4-nitro-o-phenylenediamine; 2-nitro-p-phenylenediamine; Picramic Acid; HC Red No. 13; 1,4-bis-(2'-hydroxyethyl)-amino-2-nitrobenzene; HC Yellow No. 5; HC Red No. 7; HC Blue No. 2; HC Yellow No. 4; HC Yellow No. 2; HC Orange No. 1; HC Red No. 1; 2-chloro-5-nitro-N-hydroxyethyl-p-phenylenediamine; HC Red No. 3; 4-amino-3-nitrophenol; 2-hydroxyethylamino-5-nitroanisole; 3-nitro-p-hydroxyethylaminophenol; 2-amino-3-nitrophenol; 6-nitro-o-toluidine; 3-methylamino-4-nitrophenoxyethanol; 2-nitro-5-glycerylmethylaniline; HC Yellow No. 11; HC Violet No. 1; HC Orange No. 2; HC Orange No. 3; HC Yellow No. 9; 4-nitrophenyl aminoethylurea; HC Red No. 10; HC Red No. 11; 2-hydroxyethyl picramic acid; HC Blue No. 12; HC Yellow No. 6; hydroxyethyl-2-nitro-p-toluidine; HC Yellow No. 12; HC Blue No. 10; HC Yellow No. 7; HC Yellow No. 10; HC Blue No. 9; N-ethyl-3-nitro PABA; 4-amino-2-nitrophenyl-amine-2'-carboxylic acid; 2-chloro-6-ethylamino-4-nitrophenol; 6-nitro-2,5-pyridinediamine; HC Violet No. 2; 2-amino-6-chloro-4-nitrophenol; 4-hydroxypropylamino-3-nitrophenol; HC Yellow No. 13; 1,2,3,4-tetrahydro-6-nitrochinoxalin; HC Red No. 14; HC Yellow No. 15; HC Yellow No. 14; 3-amino-6-methylamino-2-nitropyridine; 2,6-diamino-3-((pyridine-3-yl)azo)pyridine; Basic Red No. 118; Basic Orange No. 69; N-(2-nitro-4-aminophenyl)-allylamine; 4-[(4-amino-3-methylphenyl)(4-imino-3-methyl-2,5-cyclohexadien-1-ylidene) methyl]-2-methyl-benzeneamine-hydrochloride; 2-[[4-(dimethyl-amino)phenyl]azo]-1,3-dimethyl-1H-imidazolium chloride; 1-methyl-4-[(methylphenyl-hydrazono)methyl]-pyridinium, methyl sulfate; 2-[(4-aminophenyl)azo]-1,3-dimethyl-1H-imidazolium chloride; Basic Red 22; Basic Red 76; Basic Brown 16; Basic Yellow 57; 7-(2',4'-dimethyl-5'-sulfophenylazo)-5-sulfo-8-hydroxynaphthalene; Acid Orange 7; Acid Red 33; 1-(3'-nitro-5'-sulfo-6'-oxophenylazo)-oxonaphthalene chromium complex; Acid Yellow 23; Acid Blue 9; Basic Violet 14; Basic Blue 7; Basic Blue 26; sodium salt of mixture of mono- & disulfonic acids (mainly the latter) of quinophthlanone or 2-quinolylindandione; Basic Red 2; Basic Blue 99; Disperse Red 15; Acid Violet 43; Disperse Violet 1; Acid Blue 62; Pigment Blue 15; Acid Black 132; Basic Yellow 29; Disperse Black 9; 1-(N-methylmorpholinium-propylamino)-4-hydroxy-anthraquinone methylsulfate; HC Blue No. 8; HC Red No. 8; HC Green No. 1; HC Red No. 9; 2-hydroxy-1,4-naphthoquinone; Acid Blue 199; Acid Blue 25; Acid Red 4; Henna Red; Indigo; Cochenille; HC Blue No. 14; Disperse Blue 23; Disperse Blue 3; Disperse Blue 377; Basic Red 51; Basic Orange 31; Basic Yellow 87; and mixtures thereof. Preferred direct dyes include but are not limited to: Disperse Black 9; HC Yellow 2; HC Yellow 4; HC Yellow 15; 4-nitro-o-phenylenediamine; 2-amino-6-chloro-4-nitrophenol; HC Red 3; Disperse Violet 1; HC Blue 2; Disperse Blue 3; Disperse Blue 377; Basic Red 51; Basic Orange 31; Basic Yellow 87; and mixtures thereof.

## pH Modifiers and Buffering Agents

**[0097]** The compositions of the present invention may have a pH of from 12 to 7.5, or from 11 to 8.4, or from 10 to 8.5. They may further comprise a pH modifier and/or buffering agent in an amount that is sufficiently effective to adjust the pH of the composition to fall within a range from 3 to 13, or from 7.5 to 12, or from 8.5 to 9.5 in some embodiments particularly those comprising a source of carbonate ions. Preferably the pH modifier or buffering agent is comprised in the tint component.

**[0098]** Suitable pH modifiers and/or buffering agents for use herein include, but are not limited to: ammonia, alkanolamides such as monoethanolamine, diethanolamine, triethanolamine, monopropanolamine, dipropanolamine, tripropanolamine, tripropanolamine, 2-amino-2-methyl-1-propanol, and 2-amino-2-hydroxymethyl-1,3,-propandiol and guanidium salts, alkali metal and ammonium hydroxides and carbonates; in some embodiments, sodium hydroxide and ammonium carbonate, and acidulents such as inorganic and inorganic acids, e.g., phosphoric acid, acetic acid, ascorbic acid, citric acid or tartaric acid, hydrochloric acid, and mixtures thereof.

## Chelants

**[0099]** The compositions of the present invention may contain a chelant (or "chelating agent" or "sequestering agent" or "sequestrant") or salt thereof. The presence of redox metals such as copper, iron, and calcium in tap water used by consumers, though only present at low levels of 5 to 100 ppm and, for calcium, 4000 to 10000 ppm, may effect the color chemistry of oxidative hair dyes. The presence of chelants may limit this effect. The term "salts thereof" means all salts comprising the same functional structure as the chelant they are referring to and includes alkali metal, alkaline earth, ammonium, substituted ammonium salts (e.g., monoethanolammonium, diethanolammonium, triethanolammonium), in particular all sodium, potassium or ammonium salts. The non-diluted and/or diluted hair colouring compositions may comprise from 0.01% to 5%, or from 0.25% to 3%, or from 0.5% to 1% by weight of chelant, salts thereof, derivatives thereof, or mixtures thereof. The chelant may be present in the developer component, the tint component, the modifier component or any combination thereof. Chelants are well known in the art and a non-exhaustive list thereof can be found in AE Martell & RM Smith, Critical Stability Constants, Vol. 1, Plenum Press, New York & London (1974) and AE Martell & RD Hancock, Metal Complexes in Aqueous Solution, Plenum Press, New York & London (1996), both incorporated herein by reference. Suitable chelants for use herein are carboxylic acids (in particular aminocarboxylic acids), phosphonic acids (in particular aminophosphonic acids) and polyphosphoric acids (e.g., linear polyphosphoric acids), and the salts thereof.

**[0100]** Aminocarboxylic acid chelants for use herein have at least one carboxylic acid moiety (-COOH) and at least one nitrogen atom. Examples of aminocarboxylic acid chelants suitable for use herein include diethylenetriamine pentaacetic acid (DTPA), ethylenediamine disuccinic acid (EDDS), ethylenediamine diglutaric acid (EDGA), 2-hydroxypropylenediamine disuccinic acid (HPDS), glycinamide-N,N'-disuccinic acid (GADS), ethylenediamine-N-N'-diglutaric acid (EDDG), 2-hydroxypropylenediamine-N-N'-disuccinic acid (HPDDS), ethylenediaminetetraacetic acid (EDTA), ethylenedicysteic acid (EDC), EDDHA (ethylenediamine-N-N'- bis(ortho-hydroxyphenyl acetic acid)), diaminoalkyldi(sulfosuccinic acids) (DDS), N,N'-bis(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid (HBED) and salts thereof and mixtures thereof. Other suitable aminocarboxylic type chelants for use herein are iminodiacetic acid derivatives such as N-2-hydroxyethyl N,N diacetic acid or glyceryl imino diacetic acid, iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2- hydroxypropyl-3-sulfonic acid, β-alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid chelants, ethanoldiglycine acid, and salts thereof and mixtures thereof. Dipicolinic acid and 2-phosphonobutane-1,2,4- tricarboxylic acid are also suitable. Preferred for use herein is ethylenediamine-N,N'-disuccinic acid (EDDS), and salts thereof.

**[0101]** Amino-phosphonic acid type chelants suitable for use herein are defined as chelants comprising an amino-phosphonic acid moiety (- $PO_3H_2$) or its derivative - $PO_3R_2$ wherein R2 is a $C_1$ to $C_6$ alkyl or aryl radical and salts thereof. Suitable amino-phosphonic acid type chelants for use herein are aminotri-(1-ethylphosphonic acid), ethylenediamine-tetra-(1-ethylphosphonic acid), aminotri-(1- propylphosphonic acid), and aminotri-(isopropylphosphonic acid). Preferred chelants for use herein are aminotri-(methylenephosphonic acid), ethylene-diamine-tetra- (methylenephosphonic acid) (EDTMP) and diethylene-triamine-penta-(methylenephosphonic acid) (DTPMP) and mixtures thereof. Examples of other chelants suitable for use herein include but are not limited to polyethyleneimines, polyphosphoric acid chelants, etidronic acid, Methylglycine diacetic acid, N- (2-hydroxyethyl)iminodiacetic acid, Iminodisuccinnic acid, N,N-Dicarboxymethyl-L-glutamic acid and N-lauroyl-N,N',N"-ethylenediamine diacetic acid.

**[0102]** In some embodiments, the non-diluted and diluted hair colouring compositions of the invention comprise a carboxylic acid chelant, a phosphonic acid chelant, a polyphosphoric acid chelant, salts thereof, or mixtures thereof. In certain embodiments, the compositions of the invention comprise diethylenetriamine pentaacetic acid (DTPA), ethylenediamine-N,N'-disuccinic acid (EDDS), ethylenediamine-N,N'-diglutaric acid (EDDG), 2-hydroxypropylenediamine-N,N'-disuccinic acid (HPDDS), glycinamide-N,N'-disuccinic acid (GADS), ethylenediamine-N-N'-bis(ortho-hydroxyphenyl acetic acid) (EDDHA), diethylenetriamine-penta-(methylenephosphonic acid) (DTPMP), salts thereof, or mixtures thereof. In further embodiments, the compositions of the invention comprise from 0.1% to 5% of diethylene-triamine-penta-(methylenephosphonic acid) and from 0.1% to 5% of ethylenediamine-N,N'-disuccinic acid.

## Radical scavenger

**[0103]** The compositions according to the present invention may comprise a radical scavenger. As used herein the term radical scavenger refers to a species that can react with a radical, preferably a carbonate radical to convert the radical species by a series of fast reactions to a less reactive species. The radical scavenger is also preferably selected such that it is not an identical species as the alkalising agent and is present in an amount sufficient to reduce the damage to the hair during the colouring /bleaching process. The compositions of the present invention may comprise from 0.1 % to 10% by weight, preferably from 1% by weight to 7% by weight of a radical scavenger.

**[0104]** Suitable radical scavengers for use herein may be selected from the classes of alkanolamines, amino sugars, amino acids, esters of amino acids and mixtures thereof. Suitable compounds include 3-amino-1-propanol, 4-amino-1-butanol,5-amino-1-pentanol, 1-amino-2- propanol, 1-amino-2-butanol, 1-amino-2-pentanol, 1-amino-3-pentanol, 1-amino-4-pentanol, 3-amino-2-methylpropan-1-ol, 1-amino-2-methylpropan-2-ol, 3-aminopropane-1,2-diol, glucosamine, N-acetylglucosamine, glycine, arginine, lysine, proline, glutamine, histidine, sarcosine, serine, glutamic acid, tryptophan, or mixtures thereof, or the salts, such as the potassium, sodium, or ammonium salts thereof, or mixtures thereof. The compositions may comprise glycine, sarcosine, lysine, serine, 2 methoxyethylamine, glucosamine, glutamic acid, morpholine, piperdine, ethylamine, 3 amino-1-propanol, or mixtures thereof.

## Solvent

**[0105]** The compositions of the present invention may comprise a solvent. The solvent may be selected from water or a mixture of water and at least one organic solvent to dissolve the compounds that would not typically be sufficiently soluble in water. Suitable organic solvents for use herein include, but are not limited to: C1 to C4 lower alkanols (e.g., ethanol, propanol, isopropanol), aromatic alcohols (e.g. benzyl alcohol and phenoxyethanol); polyols and polyol ethers (e.g., carbitols, 2-butoxyethanol, propylene glycol, propylene glycol monomethyl ether, diethylene glycol monoethyl ether, monomethyl ether, hexylene glycol, glycerol, ethoxy glycol, butoxydiglycol, ethoxydiglycerol, dipropyleneglycol, polygylcerol), and propylene carbonate. When present, organic solvents are typically present in an amount ranging from 1% to 30%, by weight of the non-diluted and/or diluted hair colouring compositions. The solvent may comprise water, ethanol, propanol, isopropanol, glycerol, 1,2-propylene glycol, hexylene glycol, ethoxy diglycol, or mixtures thereof.

## Thickeners

**[0106]** The compositions may comprise a thickener in an amount sufficient to provide the composition with a viscosity so that it can be readily applied to the hair without unduly dripping off the hair and causing mess. Typically, such an amount will be at least 0.1%, in some embodiments, at least 0.5%, in other embodiments, at least 1%, by weight of the non-diluted or diluted hair colouring composition. Preferred polymeric thickeners include a polymer thickener, comprising at least one polymer selected from associative polymers, polysaccharides, non-associative polycarboxylic polymers, and mixtures thereof. As used herein, the expression "associative polymers" means amphiphilic polymers comprising both hydrophilic units and hydrophobic units, for example, at least one C8 to C30 fatty chain and at least one hydrophilic unit. Associative polymers are capable of reversibly combining with each other or with other molecules. Representative associative thickeners that may be used are associative polymers chosen from:

(i) nonionic amphiphilic polymers comprising at least one hydrophilic unit and at least one fatty-chain unit;
(ii) anionic amphiphilic polymers comprising at least one hydrophilic unit and at least one fatty-chain unit;
(iii) cationic amphiphilic polymers comprising at least one hydrophilic unit and at least one fatty-chain unit; and
(iv) amphoteric amphiphilic polymers comprising at least one hydrophilic unit and at least one fatty-chain unit.

**[0107]** The nonionic amphiphilic polymers comprising at least one fatty chain and at least one hydrophilic unit may, for example, be chosen from:

(1) celluloses modified with groups comprising at least one fatty chain; for example: hydroxyl-ethylcelluloses modified with groups comprising at least one fatty chain chosen from alkyl, alkenyl and alkylaryl groups;
(2) hydroxypropyl guars modified with groups comprising at least one fatty chain;
(3) polyether urethanes comprising at least one fatty chain, such as C8-C30 alkyl or alkenyl groups;
(4) copolymers of vinylpyrrolidone and of fatty-chain hydrophobic monomers;
(5) copolymers of C1-C6 alkyl acrylates or methacrylates and of amphiphilic monomers comprising at least one fatty chain;
(6) copolymers of hydrophilic acrylates or methacrylates and of hydrophobic monomers comprising at least one fatty chain.

**[0108]** The anionic amphiphilic polymers comprising at least one hydrophilic unit and at least one fatty-chain unit, may, for example, be chosen from those comprising at least one fattychain allyl ether unit and at least one hydrophilic unit comprising an ethylenic unsaturated anionic monomeric unit, for example, a vinylcarboxylic acid unit and further, for example, chosen from units derived from acrylic acids, methacrylic acids and mixtures thereof, wherein the fatty-chain allyl ether unit corresponds to the monomer of formula below:

$$CH2=C(R1)CH2OBnR \qquad (I)$$

in which R1 is chosen from H and CH3, B is an ethyleneoxy radical, n is chosen from zero and integers ranging from 1 to 100, R is chosen from hydrocarbon-based radicals chosen from alkyl, alkenyl, arylalkyl, aryl, alkylaryl and cycloalkyl radicals, comprising from 8 to 30 carbon atoms, and, further, for example, from 10 to 24 carbon atoms and even further, for example, from 12 to 18 carbon atoms. The anionic amphiphilic polymers may further be chosen, for example, from those comprising at least one hydrophilic unit of unsaturated olefinic carboxylic acid type, and at least one hydrophobic unit of the type such as a (C8-C30) alkyl ester or (C8-C30) oxyethylenated alkyl ester of an unsaturated carboxylic acid. The hydrophilic unit of unsaturated olefinic carboxylic acid type corresponds to, for example, the monomer of formula (II) below:

CH2=C(R1)COOH (II)

in which R1 is chosen from H, CH3, C2H5 and CH2COOH, i.e. acrylic acid, methacrylic, ethacrylic and itaconic acid units. And the hydrophobic unit of the type such as a (C8-C30) alkyl ester or (C8-C30) oxyethylenated alkyl ester of an unsaturated carboxylic acid corresponds to, for example, the monomer of formula (III) below:

CH2=C(R1)COOBnR2 (III)

in which R1 is chosen from H, CH3, C2H5 and CH2COOH (i.e. acrylate, methacrylate, ethicrylate and itaconate units), B is an ethyleneoxy radical, n is chosen from zero and integers ranging from 1 to 100, R2 is chosen from C8-C30 alkyl radicals, for example, C12-C22 alkyl radical.

**[0109]** Representative anionic amphiphilic polymers that can be used may further be cross-linked. The crosslinking agent can be a monomer comprising a group (IV)

CH2=C< (IV)

with at least one other polymerizable group whose unsaturated bonds are not conjugated with respect to one another. Mention may be made, for example, of polyallyl ethers such as polyallylsucrose and polyallyl pentaerythritol.

**[0110]** The cationic amphiphilic polymers used are, for example, chosen from quaternized cellulose derivatives and polyacrylates comprising amino side groups. The quaternized cellulose derivatives are, for example, chosen from quaternized celluloses modified with groups comprising at least one fatty chain, such as alkyl, arylalkyl and alkylaryl groups comprising at least 8 carbon atoms, and mixtures thereof, quaternized hydroxyethylcelluloses modified with groups comprising at least one fatty chain, such as alkyl, arylalkyl and alkylaryl groups comprising at least 8 carbon atoms, and mixtures thereof. The alkyl radicals borne by the above quaternized celluloses and hydroxyethylcelluloses, for example, contain from 8 to 30 carbon atoms. The aryl radicals, for example, are chosen from phenyl, benzyl, naphthyl and anthryl groups.

**[0111]** Among amphoteric amphiphilic polymers comprising at least one hydrophilic unit and at least one fatty-chain unit, mention may be made, for example, of methacrylamidopropyltrime-thylammonium chloride/acrylic acid/C8-C30 alkyl methacrylate copolymers, wherein the alkyl radical is, for example, a stearyl radical. Preferable associative polymeric thickeners for use herein comprise at least one hydrophilic unit which is unsaturated carboxylic acid or its derivative, and at least one hydrophobic unit which is a C8 to C30 alkyl ester or oxyethylenated C8-C30 alkyl ester of unsaturated carboxylic acid. The unsaturated carboxylic acid is preferably acrylic acid, methacrylic acid or itaconic acid. Examples can be made of materials sold under trade name Aculyn-22, Permulen TR1, Carbopol 2020, Carbopol Ultrez-21, Structure 2001, Structure 3001. Another preferable associative polymer for use in the polymer thickening systems of the present invention include polyether polyurethane, for example materials Aculyn-44, Aculyn-46. Another preferable associative polymer for use herein is cellulose modified with groups comprising at least one C8 - C30 fatty chain, such as Natrosol Plus Grade 330 CS. Non-associative cross-linked polycarboxylic polymers for use herein can be chosen, for example, from: (i) cross-linked acrylic acid homopolymers; (ii) copolymers of acrylic or (meth)acrylic acid and of C1-C6 alkyl acrylate or (meth)acrylate. Preferable polymers are Carbopol 980, 981, 954, 2984, 5984, Synthalen M/ L/ K, Aculyn-33.

**[0112]** The polysaccharides for use herein are, for example, chosen from glucans, modified and unmodified starches (such as those derived, for example, from cereals, for instance wheat, corn or rice, from vegetables, for instance yellow pea, and tubers, for instance potato or cassaya), amylose, amylopectin, glycogen, dextrans, celluloses and derivatives thereof (methylcelluloses, hydroxyalkylcelluloses, ethyl hydroxyethylcelluloses, and carboxymethylcelluloses), mannans, xylans, lignins, arabans, galactans, galacturonans, chitin, chitosans, glucuronoxylans, arabinoxylans, xyloglucans, glucomannans, pectic acids and pectins, alginic acid and alginates, arabinogalactans, carrageenans, agars, glycosaminoglucans, gum arabics, gum tragacanths, ghatti gums, karaya gums, carob gums, galactomannans, such as guar gums, and nonionic derivatives thereof (hydroxypropyl guar) and bio-polysaccharides, such as xanthan gums, gellan gums, welan gums, scleroglucans, succinoglycans and mixtures thereof.

**[0113]** For example, suitable polysaccharides are described in "Encyclopedia of Chemical Technology", Kirk-Othmer, Third Edition, 1982, volume 3, pp. 896-900, and volume 15, pp. 439-458, in "Polymers in Nature" by E. A. MacGregor and C. T. Greenwood, published by John Wiley & Sons, Chapter 6, pp. 240-328,1980, and in "Industrial Gums-Polysaccharides and their Derivatives", edited by Roy L. Whistler, Second Edition, published by Academic Press Inc., the content of these three publications being entirely incorporated by reference. The polysaccharide is preferably a bio-polysaccharide, particularly preferable are biopolysaccharides selected from xanthan gum, gellan gum, welan gum, scleroglucan or succinoglycan, for example materials such as Keltrol T, Rheozan. Another preferable polysaccharide is hydroxypropyl starch derivative, particularly preferable hydroxypropyl starch phosphate, for example Structure XL®. Suitable for use herein are salt tolerant thickeners, including but not limited to: xanthan, guar, hydroxypropyl guar, scleroglucan, methyl cellulose, ethyl cellulose (as AQUACOTE), hydroxyethyl cellulose (NATROSOL), carboxymethyl cellulose, hydroxypropylmethyl cellulose, microcrystalline cellulose, hydroxybutylmethyl cellulose, hydroxypropyl cellulose (as KLUCEL), hydroxyethyl ethyl cellulose, cetyl hydroxyethyl cellulose (as NATROSOL Plus 330), N-vinylpyrollidone (as POVIDONE), Acrylates/Ceteth-20 Itaconate Copolymer (as STRUCTURE 3001), hydroxypropyl starch phosphate (as STRUCTURE ZEA), polyethoxylated urethanes or polycarbamyl polyglycol ester (e.g. PEG-150/Decyl/SMDI copolymer (as ACULYN 44), PEG-150/Stearyl/SMDI copolymer (as ACULYN 46), trihydroxystearin (available as THIXCIN), acrylates copolymer (e.g. as ACULYN 33) or hydrophobically modified acrylate copolymers (e.g. Acrylates / Steareth-20 Methacrylate Copolymer (as ACULYN 22), acrylates/steareth-20 methacrylate crosspolymer (as ACULYN 88), acrylates/vinyl neodecanoate crosspolymer (available as ACULYN 38), acrylates/beheneth-25 methacrylate copolymer (as ACULYN 28), acrylates/C10-30 alkyl acrylate crosspolymer (as Carbopol® ETD 2020), non-ionic amphophilic polymers comprising at least one fatty chain and at least one hydrophilic unit selected from polyether urethanes comprising at least one fatty chain, and blends of Ceteth - 10 phosphate, Di-cetyl phosphate and Cetearyl alcohol (as CRODAFOS CES).

**[0114]** Preferred thickeners for use in the first developer component include acrylates copolymer, hydrophobically modified acrylate copolymers (e.g. Acrylates / Steareth-20 Methacrylate Copolymer) and mixtures thereof. Preferred thickeners polymers for use in the dye component include, blends of Ceteth - 10 phosphate, Di-cetyl phosphate and Cetearyl alcohol (as CRODAFOS CES).

## Gel network thickener system

**[0115]** The non-diluted and diluted hair colouring compositions of the present invention may comprise at at least one gel network thickener system. Said system may comprise at least one low HLB surfactant and/or amphophile having a high melting point, and at least one additional second surfactant as specified hereinafter. Suitable gel network thickener systems are disclosed in PCT application WO2006/060598A1.

**[0116]** Said low HLB surfactant and/or amphophile may have preferably an HLB of 6 or less and melting point of at least 30°C. It may be selected from the group consisting of cetyl, stearyl, cetostearyl or behenyl alcohols, steareth-2, glycerol monostearate and mixtures thereof. Said second surfactant may be anionic, non-ionic or cationic. Anionic surfactants may be selected from the group consisting of alkyl ether phosphates having in average 1-3 ethylene oxide units and comprising an alkyl radical comprising from 8 to 30 carbon atoms. Said non-ionic surfactants may be selected from the group consisting of those comprising one or more polyethyleneoxide chain including polyoxyethylene alkyl ethers having from 100 to 200 ethylene oxide units (e.g. steareth-100, steareth-150). Said cationic surfactant may be selected from the group consisting of behentrimonium chloride, behenamidopropyltrimonium methosulfate, stearamidopropyltrimonium chloride, arachidtrimonium chloride and mixtures thereof. A preferred gel network thickening system comprises fatty alcohols having 14 to 30 carbon atoms (cetyl and/or stearyl alcohol) and alkyl ether phosphates (e.g. from 1 to 3 ethylene oxide units).

**[0117]** The non-diluted and/or the diluted compositions of the present invention may comprise a total amount of gel network thickening system of from 2% to 10% by weight of the non-diluted or diluted hair colouring composition. The weight ratio of the low HLB surfactants to the second specified surfactants is preferably from 10:1 to 1:1.

## Carbonate Ion Source

**[0118]** The compositions of the present invention may comprise a source of carbonate ions, carbamate ions, or hydrogen carbonate ions, in a sufficient amount to reduce damage to the hair during the colouring process. Such an amount may range from 0.1% to 15%, or from 0.1% to 10%, or from 1% to 7%, by weight of the non-diluted or diluted hair colouring composition.

**[0119]** Suitable sources for the ions include but are not limited to: sodium carbonate, sodium hydrogen carbonate, potassium carbonate, potassium hydrogen carbonate, guanidine carbonate, guanidine hydrogen carbonate, lithium carbonate, calcium carbonate, magnesium carbonate, barium carbonate, ammonium carbonate, ammonium hydrogen carbonate and mixtures thereof. In some embodiments, the source of carbonate ions is sodium hydrogen carbonate, potassium hydrogen carbonate, or mixtures thereof. The source of carbonate ions may be ammonium carbonate, ammonium hydrogen carbonate, or mixtures thereof.

## Conditioning agent

**[0120]** The compositions may comprise a conditioning agent. The conditioning agent may be present in the developer component, the tint component, the modifier component, a separate conditioner component or any combination thereof.

Conditioning agents suitable for use herein are selected from silicone materials, amino silicones, C6 to C30 fatty alcohols, polymeric resins, polyol carboxylic acid esters, cationic polymers, cationic surfactants, insoluble oils and oil derived materials and mixtures thereof. Additional materials include mineral oils and other oils such as glycerin and sorbitol. Particularly useful conditioning materials are cationic polymers. Conditioners of cationic polymer type can be chosen from those comprising units of at least one amine group chosen from primary, secondary, tertiary and quaternary amine groups that may either form part of the main polymer chain, or be borne by a side substituent that is directly attached to the main polymer chain, described hereinafter. The conditioning agent will generally be used at levels of from 0.05% to 20%, preferably of from 0.1% to 15%, more preferably of from 0.2% to 10%, even more preferably of from 0.2% to 2% by weight of the nondiluted or diluted hair colouring composition. The conditioning agent may be included in a separate pre- or post-treatment composition.

**[0121]** Silicones can be selected from polyalkylsiloxane oils, linear polydimethylsiloxane oils containing trimethylsilyl or hydroxydimethylsiloxane endgroups, polymethylphenylsiloxane, polydimethylphenylsiloxane or polydimethyldiphenylsiloxane oils, silicone resins, organofunctional siloxanes having in their general structure one or a number of organofunctional group(s), the same or different, attached directly to the siloxane chain or mixtures thereof.

**[0122]** Said organofunctional group(s) are selected from: polyethyleneoxy and / or polypropyleneoxy groups, (per)fluorinated groups, thiol groups, substituted or unsubstituted amino groups, carboxylate groups, hydroxylated groups, alkoxylated groups, quaternium ammonium groups, amphoteric and betaine groups. The silicone can either be used as a neat fluid or in the form of a pre-formed emulsion.

**[0123]** Suitable silicones include silicones containing groups that may be ionized into cationic groups, for example aminosilicones containing at least 10 repeating siloxane (Si(CH3)2-O) units within the polymer chain, with either terminal, graft, or a mixture of terminal and graft amino functional groups. Example functional groups are not limited to aminoethylaminopropyl, aminoethylaminoisobutly, aminopropyl. In the case of graft polymers, the terminal siloxane units can be $(CH_3)_3$Si-O, $R_{12}(CH_3)$2Si-O, where R12 can be either OH or OR13, where R13 is a C1-C8 alkyl group, or a mixture of both terminal groups. These silicones are also available as preformed emulsions. Commercially available aminosilicones include DC-2-8566, DC-7224, DC-2-8220, SF1708, SM2125, Wacker Belsil ADM 653/1100/1600/652/6057E/8020, DC929, DC939, DC949, SM2059. Aminosilicones may also contain additional functional groups. Additional functional groups can include polyoxyalkylene, the reaction product of amines and carbinols, and alky chains. For example products know as methoxy PEG/PPG-7/3 Aminopropyl Dimethicone, such as Abil Soft AF100, or products know as Bis (C13-15 Alkoxy) PG Amodimethicone, such as DC 8500.

**[0124]** Cationic polymers suitable for use herein can be chosen from those comprising units of at least one amine group chosen from primary, secondary, tertiary and quaternary amine groups that may either form part of the main polymer chain or be borne by a side substituent that is directly attached to the main polymer chain. Such cationic polymers generally have a number average molecular mass ranging from 500 to about 5 x $10^6$, or more preferably from 1000 to 3 x $10^6$. Preferably the cationic polymers are selected from polymers of the polyamine, polyamino amide and polyquaternary ammonium type. Polymers of the polyamine, polyamino amide and polyquaternary ammonium type that may be used include but are not limited to:

1) Homopolymers and copolymers derived from acrylic or methacrylic esters or amides. Copolymers of these polymers can also comprise at least one unit derived from comonomers which may be chosen from the family of acrylamides, methacrylamides, diacetone acylamides, acrylamides and methacrylicamides substituted on the nitrogen with at least one group chosen from lower (C1-C4) alkyls, acrylic and methacrylic acids and esters thereof, vinlylactams such as vinlypyrrolidone and vinylcaprolactam, and vinyl esters. Copolymers of acrylamide and of methacryloyloxyethyltrimethylammonium methosulfate, examples of which include polymers known as Polyquaternium-5 (herein referred as PQ"), such as Reten 210/220/230/240/1104/1105/1006, Merquat 5/5SF. Copolymers of vinylpyrrolidone and dimethylaminopropyl methacrylamide, examples of which include polymers known as PQ-28, such as Gafquat HS-100. Copolymers of vinyl pyrrolidone and dialkyaminoalkyl acrylates or methactylates, examples of which include polymers known as PQ-11, such as Gafquat 440/734/755/755N, Luviquat PQ11 PM, Polyquat-11 SL. Copolymers vinylpyrrolidone, dimethylaminopropyl methacrylamide and methacryloylaminopropyl lauryldimonium chloride, examples of which include polymers known as PQ-55, such as Styleze W-20. Copolymers of acrylic acid, acrylamide and methacrylamidopropyltrimonium chloride, examples of which include polymers known as PQ-53, such as Merquat 2003. Copolymers of dimethyaminopropylacrylate (DMAPA), acrylic acid and acrylonitrogens and diethyl sulfate, examples of which include polymers known as PQ-31, such as Hypan QT100. Copolymers of acrylamide, acrylamidopropyltrimonium chloride, 2-amidopropylacrylamide sulfonate, and dimethyaminopropylacrylate (DMAPA), examples of which include polymers known as PG-43, such as Bozequat 4000. Copolymers of acrylic acid, methylacrylate and methacrylamidopropyltrimonium chloride, examples of which include polymers known as PQ-47, such as Merquat 2001/2001N. Copolymes of methacryloyl ethyl betaine, 2-hydroxyethyl methacrylate and methacryloyl ethyl trimethyl ammonium chloride, examples of which include polymers known as PQ-48, such as Plascize L-450. Copolymers of acrylic acid diallyl dimethyl ammonium chloride and acrylamide, examples

of which include polymers known as PQ-39, such as Merquat 3330/3331. Further examples include copolymers of methacrylamide methacrylamido-propyltrimonium and methacryloylethyltrimethyl ammonium chloride and their derivatives, either homo or copolymerised with other monomers, examples of which include polymers known as: PQ-8, PQ-9, PQ-12, PQ-13; PQ-14, PQ-15, such as Rohagit KF720 F, PQ-30, such as Mexomere PX, PQ-33, PQ-35, PQ-36, such as Plex 3074 L, PQ-45, such as Plex 3073L, PQ-49, such as Plascize L-440, PQ50 such as Plascize L-441, PQ-52.

2) Cationic polysaccharides, such as cationic celluloses and cationic galactomannan gums. Among the cationic polysaccharides that maybe mentioned, for example, are cellulose ether derivatives comprising quaternary ammonium groups and cationic cellulose copolymers or cellulose derivatives grafted with a water-soluble quaternary ammonium monomer and cationic galactomannan gums. Examples include but are not limited to: Copolymers of hydroxyethylcelluloses and diallyldimethyl ammonium chlorides, examples of which include polymers known as PQ-4, such as Celquat L200/H100. Copolymers of hydroxyethylcelluloses and a trimethyl ammonium substituted epoxide, examples of which include polymers known PQ-10, such as AEC Polyquaternium-10, Catinal C-100/HC-35/HC-100/HC-200/LC-100/LC-200, Celquat SC-240C/SC-230M, Dekaquat 400/3000, Leogard GP, RITA Polyquta 400/3000, UCARE Polymer JR-125/JR-400/JR-30M/LK/LR400/LR30M. Copolymers of hydroxyethylcelluloses and lauryl dimethyl ammonium substituted epoxides, examples of which include polymers known as PQ-24, such as Quatrisoft polymer LM-200. Derivatives of Hydroxypropyl Guar, examples of which include polymers known as Guar Hydroxypropyltrimonium Chloride, such as Catinal CG-100/CG-200, Cosmedia Guar C-261N/C-261N/C-261N, DiaGum P 5070, N-Hance Cationic Guar, Hi-Care 1000, Jaguar C-17/C-2000/C-13S/C-14S/Excel, Kiprogum CW, Kiprogum NGK. Hydroxypropyl derivatives of Guar Hydroxypropyltrimonium Chloride, examples of which include polymers known as Hydroxypropyl Guar Hydroxypropyltrimonium Chloride, such as Jaguar C-162.

3) Polyamino amide derivatives resulting from the condensation of polyalkylene polyamines with polycarboxylic acids followed by alkylation with difunctional agents. Among the derivative, mention may be made for example to adipic acid / dimethylaminohydroxypropyl / diethylenetriamine.

4) Polymers obtained by reaction of a polyalkylene polyamine comprising two primary amines groups and at last one secondary amine group with a decarboxylic acid chosen from diglycolic acids and saturated aliphatic dicarboxylic acids comprising from 3 to 8 carbon atoms. Nonlimiting examples of such derivatives include the adipic acid / epxoypropyl / diethylenetriamine.

5) Cyclopolymers of dialkdiallylamine or of dialkyldiallyammonium, among which polymers mention may be made of: Dimethyldiallyammonium chloride polymers, examples of which include polymers known as PQ-6, such as Merquat 100, Mirapol 100, Rheocare CC6, AEC polyquaternium-6, Agequat 400, Conditioner P6, Flocare C106, Genamin PDAC, Mackernium 006. Copolymers of acrylamides and dimethyldiallylammonium chlorides monomers, examples of which include polymers known as PQ-7, such as AEC Polyquaternium-7, Agequat-5008/C-505, Conditioner P7, Flocare C107, Mackernium 007/007S, ME Polymer 09W, Merquat 550/2200/S, Mirapol 550, Rheocare CC7/CCP7, Salcare HSP-7/SC10/Super 7. Copolymers of dimethyldiallylammoniumchlorides and acrylic acids, examples of which include polymers known as polyquaternary-22, such as Merquat 280/Merquat 295.

6) Quaternary diammonium polymers comprising repeat units corresponding to [-N+(R1)(R2) - A1 - N+(R3)(R4) - B1 -] [2X-], in which R1, R2, R3 and R4, which may be identical or different, are chosen from aliphatic, alicyclic and arylaliphatic radicals comprising from 1 to carbon atoms and from lower hydroxyalkylaliphatic radicals, or R1, R2, R3 and R4, together or separately, constitute, with the nitrogen atoms to which they are attached, heterocycles optionally comprising a second heteroatom other then nitrogen, or R1, R2, R3 and R4, are choen from liner or branched C1-C6 alkyl radicals substituted with at least one group chosen from nitrile, ester, acyl and amide groups and groups of -CO-O-R5-D and-CO-NH-R5-D wherein R5 is chosen from alkylene groups and D is chosen from quaternary ammonium groups. A1 and B1, which may be identical or different, are chosen from linear and branched, saturated or unsaturated polymethylene groups comprising 2 to 20 carbon atoms. The polymethylene groups may comprise, linked to or intercalated in the main ring, at least one entity chosen from aromatic rings, oxygen and sulphur atoms and sulphoxide, sulphone, disulphide, amino, alkylamino, hydroxyl, quaternary, ammonium, ureido, amide and ester groups, and X- is an anion derived from inorganic and organic acids. D is chosen from a glycol residue, a bis-secondary diamine residue, a bis-primary diamine residue or a ureylene group. An examples of which include polymers known as Hexadimethrine chloride, where R1, R2, R3 and R4 are each methyl radicals, A1 is (CH2)3 and B1 is (CH2)6 and X = Cl. Further examples of which include polymers known as PQ-34 where R1 and R2 are ethyl radicals and R3 and R4 are methyl radicals and A1 is (CH2)3 and B1 is (CH2)3 and X = Br, such as Mexomere PAX.

7) Polyquaternary ammonium polymers comprising repeating units of formula [-N+(R6)(R7)-(CH2)r-NH-CO-(CH2)q-(CO)t-NH-(CH2)s-N+(R8)(R9)-A-][2X-], in which R6, R7, R8 and R9 which may be identical or different, are chosen from a hydrogen atom and a methyl, ethyl, propyl, hydroxyethyl, hydroxypropyl, and -CH2CH2(OCH2CH2)pOH radicals, wherein p is equal to 0 or an integer ranging from 1 to 6, wherein R6, R7, R8 and R9 do not all simultaneously represent a hydrogen atom. R and s which maybe identical or different are each an integer ranging from 1 to 6, q is equal to 0 or an integer ranging from 1 to 34 and X-is anion such as a halide. T is an integer chosen to be equal to 0 or 1. A is chosen from divalent radicals such as -CH2-CH2-O-CH2-CH2-. Examples of which include: Polymers known as PQ-2, where r=s=3, q=O,t=0, R6, R7, R8 and R9 are methyl groups, and A is-CH2-CH2-O-CH2- CH2, such as Ethpol PQ-2, Mirapol A-15. Polymers known as PQ-17 where r=s=3, q=4, t=1 R6, R7, R8 and R9 are methyl groups, and A is -CH2-CH2-O-CH2-CH2. Polymers known as PQ-18, where r=s=3, q=7, t=1 R6, R7, R8 and R9 are methyl groups, and A is -CH2-CH2- O-CH2-CH2. Polymers known as the block copolymer formed by the reaction of Polyquaternium-2 with Polyquaternium-17, known as PQ-27, such as Mirapol 175.

8) Copolymers of vinylpyrrolidones and of vinylimidazoles and optionally vinylcaprolactums, examples of which include polymers known as PQ-16 formed from methylvinylimidazolium chlorides and vinylpyrrolidones, such as Luviquat FC370/FC550/FC905/HM-552. Or copolymers of vinylcaprolactams and vinylpyrrolidones with methylvinylimidazolium methosulfates, examples of which include polymers known as PQ-46, such as Luviquat Hold. Or copolymers of vinylpyrrolidones and quaternized imidazolines, examples of which include polymers known PQ-44, such as Luviquat Care.

9) Polyamines such as the product Polyquart H sold by Cognis under the reference name polyethylene glycol (15) tallow polyamine in the CTFA dictionary.

10) Cross linked methacryloyloxy(C1-C4)alkyltri(C1-C4)alkylammonium salt polymers such as the polymers obtained by homopolymerisation of dimethylaminoethyl methacrylates quaternized with methyl chloride, or by copolymerisation of acrylamides with dimethylam noethyl methacrylates quaternized with methyl chloride, the homo or copolymerisation being followed by crosslinking with a compound comprising olefinic unsaturation, such as methylenebisacrylamides, examples of which include polymers known as PQ-37, such as Synthalen CN/CR/CU, or as a dispersion in another media such as Salcare SC95/SC96, Rheocare CTH(E). Or in another example of which include polymers known as PQ-32, or when sold as a dispersion in mineral oil such as Salcare SC92.

11) Further examples of cationic polymers include polymers known as PQ-51, such as Lipidure-PMB, as PQ-54, such as Qualty-Hy, as PQ-56 such as Hairrol UC-4, and as PQ-87 such as Luviquat sensation.

12) Silicone polymers comprising cationic groups and/or groups which may be ionised into cationic groups. For example: cationic silicones of the general formula (R10-N+(CH3)2)-R11-(Si(CH3)2-O)x-R11-(N+(CH3)2)-R10), where R10 is an alkyl derived from coconut oil, and R11 is (CH2CHOCH2O(CH2)3 and x is a number between 20 and 2000, examples of which include polymers known as Quaternium 80, such as Abil Quat 3272/3474. Silicones containing groups which may be ionised into cationic groups, for example aminosilicones containing at least 10 repeating siloxane -(Si(CH3)2-O) units within the polymer chain, with either terminal, graft or a mixture of terminal and graft amino functional groups. Example functional groups are not limited to aminoethylaminopropyl, aminoethylaminoisobutly, aminopropyl. In the case of graft polymers, the terminal siloxane units can either be (CH3)3Si-O or R12(CH3)2Si-O, where R12 can be either OH or OR13, where R13 is a C1-C8 alky group, or a mixture of both functional terminal groups. These silicones are also available as preformed emulsions. Polymer with terminal siloxane units of (CH3)3Si-O examples of which include polymers known as trimethylsilylamodimethicone, such as DC-2-8566, DC 7224, DC- 2-8220, SF1708, SM 2125, Wacker Belsil ADM 653. Further examples include polymers with terminal siloxane units of (R120)(CH3)2Si-O where R12 can be either OH or OR13, where R13 is a C1-C8 alky group, or a mixture of both functional terminal groups, known as amodimethicone, such as Wacker Belsil ADM 1100/ADM 1600/ADM 652/ADM 6057E/ADM 8020, DC929, DC939, DC949, SM2059.

**[0125]** Silicones containing groups which may be ionised into cationic groups - for example silicones containing at least 10 repeating siloxane -(Si(CH3)2-O) units within the polymer chain, with either terminal, graft or a mixture of terminal and graft aminofunctional groups, together with additional functional groups. Additional functional groups can include polyoxyalkylene, the reaction product of amines and carbinols, alky chains. For example products know as methoxy PEG/PPG-7/3 Aminopropyl Dimethicone, such as Abil Soft AF100. For example products know Bis (C13-15 Alkoxy) PG Amodimethicone, such as DC 8500.

**[0126]** The non-diluted and diluted hair colouring compositions and/or components of the present invention may comprise at least 0.2%, or from 0.5% to 2% by weight of the composition of a cationic polymer.

Surfactants

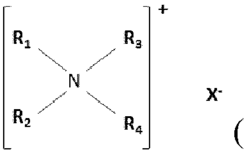
**[0127]** The compositions according to the present invention may comprise one or more surfactants. Surfactants suitable for use herein generally have a lipophilic chain length of from 8 to 30 carbon atoms and can be selected from anionic, nonionic, amphoteric and cationic surfactants and mixtures thereof. The total level of surfactant may be from 2% to 30%, or from 8% to 25%, or from 10% to 20% by weight of the composition.

**[0128]** The developer component may comprise from 0 to 5% by weight of surfactant. The tint component may comprise from 0 to 10% by weight of surfactant. The modifier component may comprise less than 10%, preferably less than 8%, more preferably less than 6% by weight of surfactant, even more preferably is substantially free of surfactant. The inventors have surprisingly found that if a modifier component comprising a too high level of surfactant is added to the remainder of the mixture of the first and second composition to obtain the diluted hair colouring composition, a substantial drop of viscosity may be observed to such an extent that the viscosity of the diluted hair colouring composition may be too low to be applied to the hair lengths and tips and without dripping from the hair. Anionic surfactants, where may be present in the range of from 0.1% to 20%, or from 0.1% to 15%, or from 5% to 15% by weight of the non-diluted or diluted hair colouring composition; amphoteric or nonionic surfactants, may independently be present is in the range of from 0.1% to 15%, or from 0.5% to 10%, or from 1% to 8% by weight of the non-diluted or diluted hair colouring composition.

**[0129]** Suitable anionic surfactants, which can be used, alone or as mixtures, include salts (such as alkaline salts, for example, sodium salts, ammonium salts, amine salts, amino alcohol salts and magnesium salts) of the following compounds: alkyl sulphates, alkyl ether sulphates, alkylamido ether sulphates, alkylarylpolyether sulphates, monoglyceride sulphates; alkyl sulphonates, alkyl phosphates, alkylamide sulphonates, alkylaryl sulphonates, a-olefin sulphonates, paraffin sulphonates; alkyl sulphosuccinates, alkyl ether sulphosuccinates, alkylamide sulphosuccinates; alkyl sulphosuccinamates; alkyl sulphoacetates; alkyl ether phosphates; acyl sarcosinates; acyl isethionates and N-acyltaurates. The alkyl or acyl radical of all of these various compounds, for example, comprises from 8 to 24 carbon atoms, and the aryl radical, for example, is chosen from phenyl and benzyl groups. Among the anionic surfactants, which can also be used, mention may also be made of fatty acid salts such as the salts of oleic, ricinoleic, palmitic and stearic acids, coconut oil acid or hydrogenated coconut oil acid; acyl lactylates in which the acyl radical comprises from 8 to 20 carbon atoms. Weakly anionic surfactants can also be used, such as alkyl-D-galactosiduronic acids and their salts, as well as polyoxyalkylenated ($C_6$-$C_{24}$) alkyl ether carboxylic acids, polyoxyalkylenated ($C_6$-$C_{24}$) alkylaryl ether carboxylic acids, polyoxyalkylenated ($C_6$-$C_{24}$) alkylamido ether carboxylic acids and their salts, for example, those comprising from 2 to 50 ethylene oxide groups, and mixtures thereof. Anionic derivatives of polysaccharides, for example carboxyalkyl ether of alkyl polyglucosides, can be also used. The nonionic surfactants are compounds that are well known (see, for example, in this respect "Handbook of Surfactants" by M. R. Porter, published by Blackie & Son (Glasgow and London), 1991, pp. 116-178). They can be chosen, for example, from polyethoxylated, polypropoxylated and polyglycerolated fatty acids, alkyl phenols, $\alpha$-diols and alcohols comprising a fatty chain comprising, for example, from 8 to 18 carbon atoms, it being possible for the number of ethylene oxide or propylene oxide groups to range, for example, from 2 to 200 and for the number of glycerol groups to range, for example, from 2 to 30. Mention may also be made of copolymers of ethylene oxide and of propylene oxide, condensates of ethylene oxide and of propylene oxide with fatty alcohols; polyethoxylated fatty amides preferably having from 2 to 30 mol of ethylene oxide and their momoethanolamine and diethanolamine derivatives, polyglycerolated fatty amides, for example, comprising on average from 1 to 5, and such as from 1.5 to 4, glycerol groups; polyethoxylated fatty amines such as those containing from 2 to 30 mol of ethylene oxide; oxyethylenated fatty acid esters of sorbitan having from 2 to 30 mol of ethylene oxide; fatty acid esters of sucrose, fatty acid esters of polyethylene glycol, alkylpolyglycosides, N-alkylglucamine derivatives, amine oxides such as ($C_{10}$-$C_{14}$)alkylamine oxides or N-acylaminopropylmorpholine oxides.

**[0130]** The amphoteric surfactants can be chosen, for example, from aliphatic secondary and tertiary amine derivatives in which the aliphatic radical is chosen from linear and branched chains comprising from 8 to 22 carbon atoms and comprising at least one water-soluble anionic group (for example carboxylate, sulphonate, sulphate, phosphate or phosphonate); mention may also be made of ($C_8$-$C_{20}$)alkylbetaines, sulphobetaines, ($C_8$-$C_{20}$)alkylamido($C_1$-$C_6$)alkylbetaines or ($C_8$-$C_{20}$)alkylamido($C_1$-$C_6$)alkylsulphobetaines. Among the amine derivatives, mention may be made of the products sold under the name Miranol, as described, for example, in U.S. Pat. Nos. 2,528,378 and 2,781,354 and having the structures of: R2-$CONHCH_2CH_2$-$N^+(R_3)(R_4)(CH_2COO^-)$, (VI) in which: $R_2$ is chosen from alkyl radicals derived from an acid $R_2$-COOH present in hydrolysed coconut oil, and heptyl, nonyl and undecyl radicals, $R_3$ is a $\beta$-hydroxyethyl group and $R_4$ is a carboxymethyl group;and of R5- $CONHCH_2CH_2$-N(B)(C) (VII) wherein B represents -$CH_2CH_2OX'$, C represents - $(CH_2)_z$-Y', with z=1 or 2, X' is chosen from the -$CH_2CH_2$-COOH group and a hydrogen atom, Y' is chosen from -COOH and -$CH_2$-CHOH-$SO_3H$ radicals, $R_5$ is chosen from alkyl radicals of an acid $R_5$-COOH present in coconut oil or in hydrolysed linseed oil, alkyl radicals, such as $C_7$, $C_9$, $C_{11}$ and $C_{13}$ alkyl radicals, a $C_{17}$ alkyl radical and its iso form, and unsaturated $C_{17}$ radical. These compounds are classified in the CTFA dictionary, 5th edition, 1993, under the names disodium cocoamphodiacetate, disodium lauroamphodiacetate, disodium caprylamphodiacetate, disodium capryloamphodiacetate, disodium cocoamphodipropionate, disodium lauroamphodipropionate, disodium caprylamphodipropionate, disodium capryloamphodipropionate, lauroamphodipropionic acid, and cocoamphodipropionic acid. Salts of diethyl aminopropyl cocoaspartamid can be also used.

**[0131]** The cationic surfactants may be chosen from: A) the quaternary ammonium salts of general formula (VIII) below:

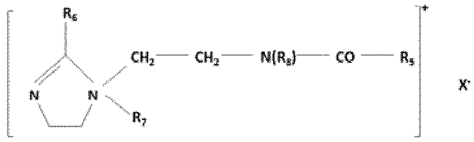


(VIII)

wherein $X^-$ is an anion chosen from halides (chloride, bromide and iodide), ($C_2$-$C_6$)alkyl sulphates, such as methyl sulphate, phosphates, alkyl and alkylaryl sulphonates, and anions derived from organic acids, such as acetate and lactate, and i) the radicals $R_1$ to $R_3$, which may be identical or different, are chosen from linear and branched aliphatic radicals comprising from 1 to 4 carbon atoms, and aromatic radicals such as aryl and alkylaryl. The aliphatic radicals can comprise at least one hetero atom such as oxygen, nitrogen, sulphur and halogens. The aliphatic radicals are chosen, for example, from alkyl, alkoxy and alkylamide radicals, $R_4$ is chosen from linear and branched alkyl radicals comprising from 16 to 30carbon atoms. The cationic surfactant is, for example, a behenyltrime-thylammonium salt (for example chloride).

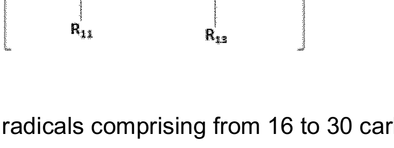
ii) the radicals $R_1$ and $R_2$, which may be identical or different, are chosen from linear and branched aliphatic radicals comprising from 1 to 4 carbon atoms, and aromatic radicals such as aryl and alkylaryl. The aliphatic radicals can comprise at least one hetero atom such as oxygen, nitrogen, sulphur and halogens. The aliphatic radicals are chosen, for example, from alkyl, alkoxy, alkylamide and hydroxyalkyl radicals comprising from 1 to 4 carbon atoms; $R_3$ and $R_4$, which may be identical or different, are chosen from linear and branched alkyl radicals comprising from 12 to 30 carbon atoms, the said alkyl radicals comprise at least one function chosen from ester and amide functions. $R_3$ and $R_4$ are chosen, for example, from ($C_{12}$-C22)alkylamido(C2-C6)alkyl and ($C_{12}$-$C_{22}$) alkylacetate radicals. The cationic surfactant is, for example, a dicetyldimethyl ammonium salt (for example chloride);

B) - the quaternary ammonium salts of imidazolinium, such as that of formula (IX) below:



(IX)

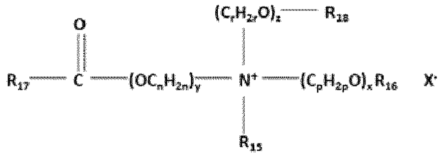
in which $R_5$ is chosen from alkenyl and alkyl radicals comprising from 8 to 30 carbon atoms, for example fatty acid derivatives of tallow, $R_6$ is chosen from a hydrogen atom, $C_1$-$C_4$ alkyl radicals and alkenyl and alkyl radicals comprising from 8 to 30 carbon atoms, $R_7$ is chosen from $C_1$-$C_4$ alkyl radicals, R8 is chosen from a hydrogen atom and $C_1$-$C_4$ alkyl radicals, and $X^-$ is an anion chosen from halides, phosphates, acetates, lactates, alkyl sulphates, alkyl sulphonates and alkylaryl sulphonates. $R_5$ and $R_6$ may be, for example, a mixture of radicals chosen from alkenyl and alkyl radicals comprising from 12 to 21 carbon atoms, such as fatty acid derivatives of tallow, $R_7$ is methyl and $R_8$ is hydrogen. Such a product is, for example, Quaternium-27 (CTFA 1997) or Quaternium-83 (CTFA 1997), which are sold under the names "Rewoquat®" W75, W90, W75PG and W75HPG by the company Witco, C)-the diquaternary ammonium salts of formula (X):



(X)

in which $R_9$ is chosen from aliphatic radicals comprising from 16 to 30 carbon atoms, $R_{10}$, $R_{11}$, R12, R13 and R14, which may be identical or different, are chosen from hydrogen and alkyl radicals comprising from 1 to 4 carbon atoms, and $X^-$ is an anion chosen from halides, acetates, phosphates, nitrates and methyl sulphates. Such diquaternary ammonium salts, for example, include propanetallowdiammonium dichloride; and

D)-the quaternary ammonium salts comprising at least one ester function, of formula (XI) below:



$$R_{17}-\overset{\overset{\displaystyle O}{\|}}{C}-(OC_nH_{2n})_y-\overset{\overset{\displaystyle (C_rH_{2r}O)_z-R_{18}}{|}}{\underset{\underset{\displaystyle R_{15}}{|}}{N^+}}-(C_pH_{2p}O)_xR_{16}\quad X^-$$

(XI)

in which: R15 is chosen from C1-C6 alkyl radicals and C1-C6 hydroxyalkyl and dihydroxyalkyl radicals; R16 is chosen from: a radical R19C(O)-, linear and branched, saturated and unsaturated C1-C22 hydrocarbon-based radicals R20, and a hydrogen atom, R18 is chosen from: a radical R21C(O)-, linear and branched, saturated and unsaturated C1-C6 hydrocarbon-based radicals R22, and a hydrogen atom, R17, R19 and R21, which may be identical or different, are chosen from linear and branched, saturated and unsaturated C7-C21 hydrocarbon-based radicals; n, p and r, which may be identical or different, are chosen from integers ranging from 2 to 6; y is chosen from integers ranging from 1 to 10; x and z, which may be identical or different, are chosen from integers ranging from 0 to 10; X- is an anion chosen from simple and complex, organic and inorganic anions; with the proviso that the sum x+y+z is from 1 to 15, that when x is 0, then R16 is R20 and that when z is 0, then R18 is R22. The ammonium salts of formula (XI) can be used, in which: R15 is chosen from methyl and ethyl radicals, x and y are equal to 1; z is equal to 0 or 1; n, p and r are equal to 2; R16 is chosen from: a radical R19C(O)-,methyl, ethyl and C14-C22 hydrocarbon-based radicals, and a hydrogen atom; R17, R19 and R21, which may be identical or different, are chosen from linear and branched, saturated and unsaturated C7-C21, hydrocarbon-based radicals; R18 is chosen from: a radical R21C(O)- and a hydrogen atom. Such compounds are sold, for example, under the names Dehyquart by the company Cognis, Stepanquat by the company Stepan, Noxamium by the company Ceca, and Rewoquat WE 18 by the company Rewo-Witco.

Viscosity

**[0132]** The developer component and the tint component may be, independently from one another, prepared as so called thin liquids or creams. Each of the first, second and third composition as well as a mixture of first and second and first, second and third composition may have a viscosity which induces a shear stress of from 20 to 200 Pa at 10 $s^{-1}$ as measured according to the viscosity test method. The mixture of first and second composition, the dye composition, may have a viscosity which induces a shear stress of from 60 to 200 Pa at 10 $s^{-1}$ as measured according to the viscosity test method and the modified dye composition may have a viscosity which induces a shear stress of from 20 to 180 Pa at 10 $s^{-1}$ as measured according to the viscosity test method. Each of the dye composition or modified dye composition may have a viscosity which induces a shear stress of from 20 to 60 Pa at 10 $s^{-1}$, when the composition is applied to the hair according to the invention. The dye composition may have a viscosity which induces a shear stress of from 30 to 200 Pa at 10 $s^{-1}$, more preferably from 100 to 200 Pa at 10 $s^{-1}$, even more preferably from 130 to 180 Pa at 10 $s^{-1}$ when the non-diluted hair colouring composition is applied to the hair with a brush and bowl applicator. The modified dye composition may have a viscosity which induces a shear stress of from 20 to 180 Pa at 10 $s^{-1}$, more preferably from 40 to 180 Pa at 10 $s^{-1}$, even more preferably from 70 to 170 Pa at 10 $s^{-1}$. Whilst not being bound by theory, it is believed that the provision of the dye compositions having viscosity values as described hereinabove enables the first portion of the non-diluted hair colouring composition to be applied directly to the roots without any dripping or running down the hair lengths and also enables the diluted hair colouring composition to be easily applied and distributed along the entire remaining hair length with minimal to no dripping from the hair. The kit may further comprise a set of instructions comprising instructing the user to colour its hair according to the method defined hereinbefore. The set of instruction may comprise:

i) mixing the first component with a second component to obtain a dye composition;
ii) applying a first portion of the dye composition obtained in step i) to the hair, preferably the hair roots and retaining a second portion of the dye composition obtained in step i);
iii) mixing the retained second portion with a third component, being a modifier component, at a mixing ratio of about 4:1 to about 1:2 to obtain a modified dye composition;
iv) applying the modified dye composition to the hair, preferably the hair lengths and tips
v) rinsing the hair.

**[0133]** The set of instructions may comprise any additional step which is disclosed hereinbefore in the method for colouring hair section of the application.

Viscosity test method:

**[0134]** The viscosity of a composition is measured using a TA Instruments AR 2000 Rheometer or equivalent device equipped with a Peltier plate and a 6cm flat acrylic plate with cross hatchings. The instrument is calibrated according to the manufacturer's instructions and the Peltier plate is set at 25.0°C. The cone is raised to a position approximately 4.5 cm above the plate.

Immediately after the mixing, approximately 10g of the mixture is transferred gently onto the centre of the Peltier plate using a spatula. The cone is lowered to obtain the specified gap between the tip of the cone and the upper surface of the Peltier plate. The gap setting is specified by the manufacturer of the cone and is typically approximately 1000 microns. The rheometer is programmed to operate in rotational mode with the shear stress ramped from 0.1 to 600 Pa over a period of 4 minutes, termination at 1000 reciprocal seconds. Rotation is initiated immediately after the specified gap is established. Viscosity data collected during the measurement period are shear stress (Pa) plotted as a function of shear rate ($s^{-1}$).

**[0135]** The following examples show typical compositions of first, second and third compositions according to the invention:

## Tint component formulations

**[0136]**

| Tint Component | 6/0 | 5/0 | 7/0 | 9/0 | 10/0 | 7/7 | 5/43 |
|---|---|---|---|---|---|---|---|
| Cetearyl alcohol and dicetyl phosphate and Ceteth-10 phosphate (Crodafos CES) | | | | | | | |
| Cetearyl alcohol | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| Steareth-200 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Propylenglycol | 7.5 | 7.5 | 7.5 | 7.5 | 7.5 | 7.5 | 7.5 |
| EDTA disodium salt | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Ascorbic acid | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 |
| Sodium sulfit | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 |
| Sodium sulfate | 1 | 1 | 1 | 0.5 | 0.5 | 1 | 1 |
| Ammonium sulfate | | | | 0.5 | 0.5 | | |
| Na3-ethlenediamine disuccinate | 3.35 | 3.35 | 3.35 | 3.35 | 3.35 | 3.35 | 3.35 |
| Toluene-2,5-diamine Sulfate | 0.935 | 1.309 | 0.69 | 0.182 | | 0.7 | 1.4 |
| 4-Amino phenol | 0.115 | 0.161 | 0.083 | 0.066 | | | 0.58 |
| Resorcinol | 0.455 | 0.637 | 0.337 | 0.11 | | 0.165 | 0.88 |
| 2-Methyl-recorcinol | | | | | | 0.165 | |
| 2.4-Diaminophenoxyethanol HCL | 0.018 | 0.025 | 0.01 | | | | |
| m-Amminophenol | 0.105 | 0.145 | 0.074 | 0.045 | | 0.013 | 0.185 |
| 2-Methyl-5-hydroxyethylaminophenol (Paox) | 0.025 | 0.035 | 0.02 | 0.003 | | 0.039 | 0.34 |
| 2-Amino-6-chloro-4-nitrophenol | | | | | | 0.008 | |
| Ammonium Hydroxide 25% | 0.7428 | 1.04 | 0.546 | 0.163 | | 0.51 | 1.28 |
| Ammonia 25% of buffer | | | | 0.48 | 0.48 | | |
| Ammonium Hydroxide 25% | 6.37 | 4 | 7.28 | 7.69 | 5.5 | 4.5 | 4.5 |
| Perfume | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 |

(continued)

| Tint Component | 6/0 | 5/0 | 7/0 | 9/0 | 10/0 | 7/7 | 5/43 |
|---|---|---|---|---|---|---|---|
| Water up to 100 % | | | | | | | |

**Developer component formulations**

**[0137]**

| Developer component | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Water Purified | Up to 100 | Up to 100 | Up to | Up to 100 |
| Disodium EDTA. | 0.04 | 0.04 | | |
| Etidronic Acid | 0.08 | 0.08 | 0.01 | 0.01 |
| Aculyn 33 | 9.00 | 9.00 | | |
| Acrylates Steeareth-20 methacry- | 0.10 | 0.10 | | |
| Hydrogen peroxide solution, 50% | 12.00 | 18.00 | 12.00 | 18.00 |
| Simethicone Emulsion | 0.01 | 0.01 | | |
| Cetearyl alcohol | | | 3.4 | 3.4 |
| Ceteareth-25 | | | 0.8 | 0.8 |
| Salicyclic acid | | | 0.1 | 0.1 |
| Disodium phosphate | | | 0.08 | 0.08 |

**Modifier component A formulation** (expressed in percentages by weight of the total composition):

**[0138]** The modifier component A comprises 1.8 % Propylene glycol, 1.5 % Hydroxycellulose, 2.0 % Quaternium-80 (in 50% glycol), 1.25 % Soytrimmonium chloride (60%), 0.5 % PEG-40 hydrogenated castor oil, 0.4 % Phenoxyethanol, 0.7 % Cocoamidopropyl betaine, 0.002 % Formic acid, 0.2 % Perfume, 0.3 % DMDM hydantoin, 0.1 % Hydrolised sweet almond protein, 0.1 % Disodium EDTA and up to 100% water.

**Modifier component B formulation** (expressed in percentages by weight of the total composition):

**[0139]** The modifier component B comprises 0.1 % Guar hydroxypropyltrimonium chloride, 4.0 % Cetrimonium chloride, 0.4 % Phenoxyethanol, 0.3 % Methyl paraben, 0.05 % Titanium dioxide, 4.0 % Cetearyl alcohol, 0.5 % Fragrance, 0.1 % Fruit extract and up to 100% water.

**Modifier component C formulation (After colouring conditioner component 1)** (expressed in percentages by weight of the total composition):

**[0140]** The modifier component C (after colouring conditioner component 1) comprises 2.0 % Stearamidopropyl dimethylamine, 2.5% Cetyl alcohol, 4.5 % Stearyl alcohol, 0.1 % Ethylene diamine tetra acetic acid EDTA, 0.4333 % Preservatives, 4.995 % Amodimethicone, 0.005 % Trimethylsiloxysilicate MQ resin, 0.64 % L_Glutamic acid, 0.2250 % Panthenyl ethyl ether, 0.045 % Panthenol, 0.05% Safflower, 0.05 % Coconut oil, 0.1 % Hydrolyzed sweet almond, 0.005 % Aloe Gel, 0.4 % perfume and up to 100 % water.

**[0141]** The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm."

## Claims

1. Package kit for a tint comprising

    - a first container with a first opening containing a first composition
    - a second container with a first opening and a second opening containing a second composition,
    - the first and second container having means to be coupled with each other and forming a connection with fluid communication through the first openings of the first and second container, **characterized in that**
    - one of the first composition and the second composition comprises an a tint and one of the first composition and the second composition comprises a developer so that the first and second composition form a dye upon mixing,
    - the container comprising the tint has an oxygen transmission rate of 30 $cm^3*mm/(m^2*d*MPa)$ or lower or a water vapor transmission rate of 7 $g/mm/(m^2*d)$ or lower, or both,
    - the first and the second container comprise means to reversibly couple the first and the second containers such that the first openings are in fluid connection
    - the opening or the openings of the container enclosing the tint are sealed with a first seal only in case of the first container enclosing the tint or with a first and a second seal in case of the second container enclosing the tint.

2. Package kit according to claim 1, **characterized in that** the first opening of the second container has a larger opening area than the second opening.

3. Package kit according to claim 1 or 2, **characterized in that** the second container comprises the tint.

4. Package kit according to any of the preceding claims, **characterized in that** at least one seal of the container enclosing the oxidation dye precursor is a laminated diaphragm.

5. Package kit according to any of the preceding claims, **characterized in that** the ratio of the length of the largest spatial extension of the first container measured rectangular to the longitudinal axis and the diameter of the first opening of the first container is less than 2.

6. Package kit according to any of the preceding claims, **characterized in that** the ratio of the diameter of the first opening of the second container and the length of the largest spatial extension of the first container rectangular to the longitudinal axis is less than 2.

7. Package kit according to any of the preceding claims, **characterized in that** the first container comprises means to open the first seal of the second container when the first and second container are coupled, such that the first and second container are in fluid connection through the first opening of the first container and the first opening of the second container.

8. Package kit according to claim 7, **characterized in that** the means to open the first seal of the second container when the first and second container are coupled, remove at least a part of the seal such that the removed part is disconnected from a remaining part.

9. Package kit according to any of the preceding claims, **characterized in that** the seal sealing the second opening of the second container is an integral part of the second container.

10. Package kit according to any of the preceding claims, **characterized in that** the second container comprises the tint and is made of a first material having an oxygen transmission rate of 30 $cm^3*mm/(m^2*d*MPa)$ or lower or a water vapor transmission rate of 7 $g/mm/(m^2*d)$ or lower, or both, the first material being in contact with the composition comprising the tint, and a second material with an oxygen transmission rate which is higher than the oxygen transmission rate of the first material or with a water vapor transmission rate which is equal to or different from the water vapor transmission rate of the first material, or both.

11. Package kit according to claim 10, **characterized in that** the second material is not in contact with the composition comprising the oxidation dye.

12. Package kit according to claim 10 or 11, **characterized in that** the first material is subjected to a first injection molding step and the second material is applied in a second injection molding step, preferably in an overmolding step.

**13.** Package kit according to any of claims 10 to 12, **characterized in that** the second container comprises a first cavity formed by the first material and containing the composition comprising an oxidation dye and a second cavity formed by the second material, wherein the second cavity essentially surrounds the first cavity as a recess.

**14.** Package kit according to any of claims 10 to 13, **characterized in that** the recess formed by the second material has the coupling means for coupling the second container to the first container.

**15.** Package kit according to claim 14, **characterized in that** the coupling means is a screw thread.

**16.** Method for dyeing a substrate having at least a first zone and a second zone with the first zone and the second zone having different properties, wherein a package kit according to any of the preceding claims is provided, the first composition comprising a developer, the second composition comprising a tint and a third composition comprising a modifier, the method comprising the steps of

- mixing the first and second composition to give a fluid dye
- applying a part of the fluid dye to the first zone,
- mixing the remaining fluid dye with the third composition to give a modified dye and
- applying the modified dye at least to the second zone.

**17.** Method according to claim 16, **characterized in that** the physical or chemical properties or both of the modified dye is different from the physical or chemical properties of the remaining fluid dye.

**18.** Method according to any of the claims 16 or 17, **characterized in that** the rheology of the modified oxidation dye is different from the rheology of the oxidation dye.

**19.** Method according to any of the claims 16 to 18, **characterized in that** the dyeing kit comprises

- a first container containing a first composition and having a large opening
- a second container containing a second composition and having a large opening sealed with a first seal and a small opening sealed with a second seal,
- a third container containing a third composition and having a large opening sealed with a first seal and a small opening sealed with a second seal,

wherein

- the second and third container are adapted to be coupled with the first container, thereupon opening the first seal on the large opening of the second or third container, respectively, and forming a connection in fluid communication through the large openings of the first and second or third container,
- and a dye formed by mixing of the first and second composition, or a modified dye formed by mixing of a part of the dye and the third composition, can be applied to a substrate through a small opening in the second and third container, respectively, after removal of the second seal.

**20.** Method according to any of the claims 16 to 19, **characterized in that** the application of the dye to the first zone is performed with a first applicator and the application of the modified dye to the second zone is performed with a second applicator and the first and second applicator are different.

**21.** Method according to claim 19, comprising the steps of

- coupling the first container to the second container, thereby opening the first seal of the second container and allowing the first and second compositions to mix to give a fluid dye,
- applying a predetermined amount of the thus formed fluid dye to the first zone, where the predetermined amount is less than the total amount,
- removing the second container from the first container,
- coupling the first container to the third container, thereby rupturing the first seal of the third container and allowing the remaining fluid dye and the third composition to mix to give a modified dye,
- applying the thus formed modified dye to the second zone.

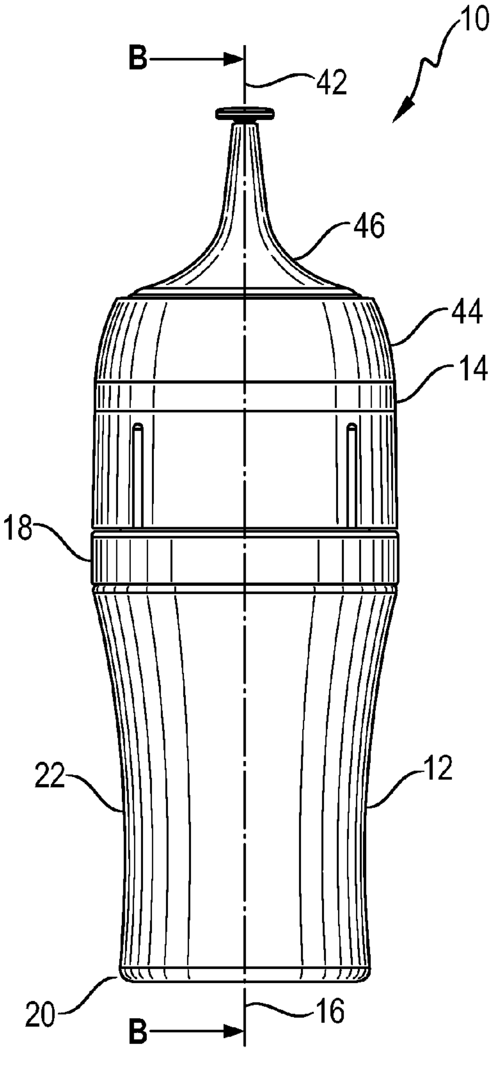

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Fig. 1

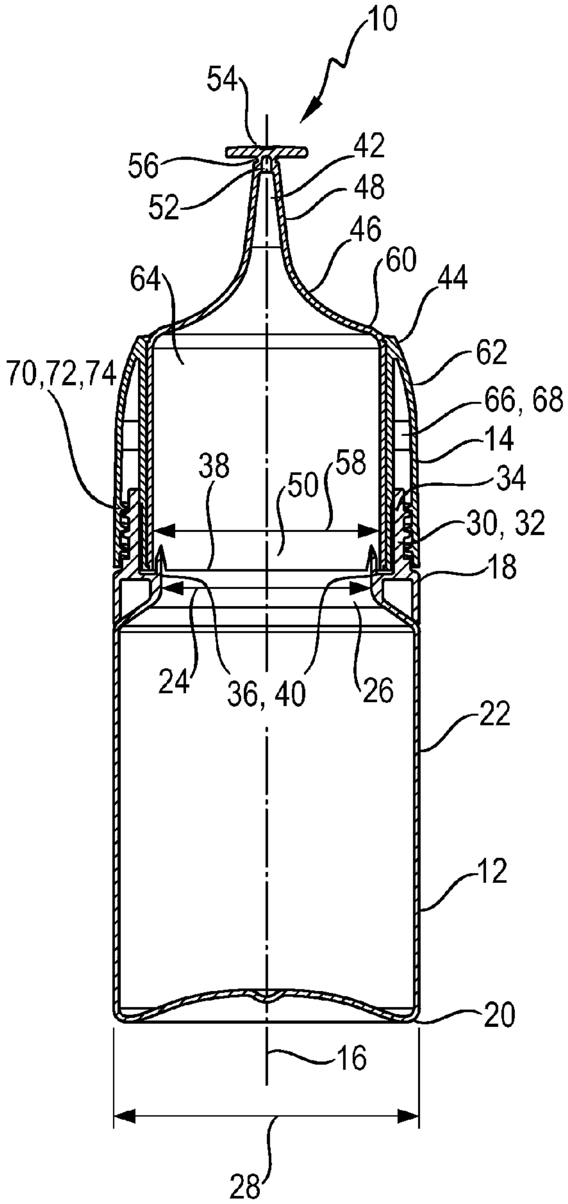
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Fig. 2

Fig. 3

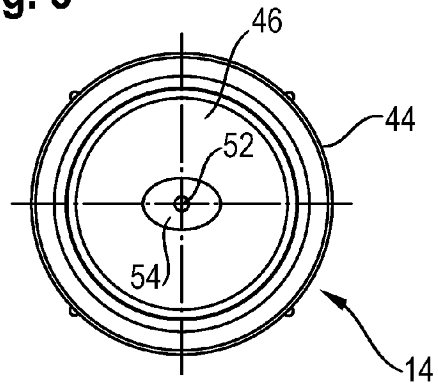


Fig. 4

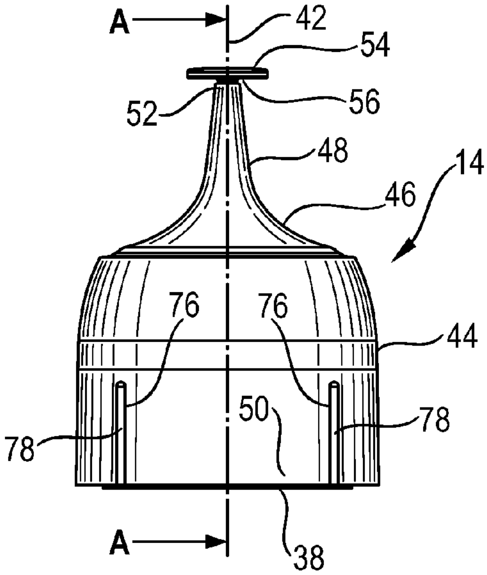


Fig. 5

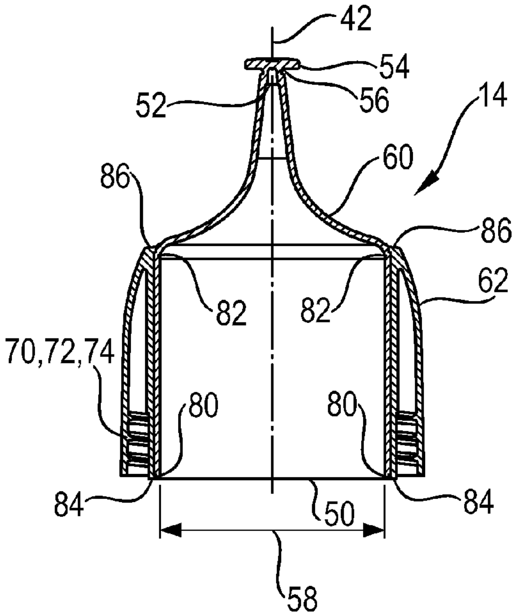
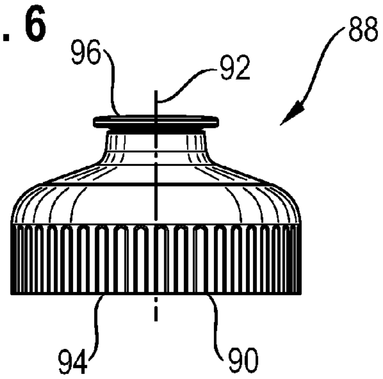


Fig. 6



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# EUROPEAN SEARCH REPORT

Application Number
EP 15 19 5943

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|---|---|---|---|
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