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RETARDING DAMAGE TO HAIR ON THE HEAD WITH POLYMERIZABLE VINYL MONOMERS IN BLEACHING OR DYEING PROCESSES

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8 Claims 10

ABSTRACT OF THE DISCLOSURE

A process for preventing or retarding the damage to hair during coloring operations (e.g., bleaching or dyeing with oxidation dyes) by simultaneously polymerizing in said hair a polymerizable monomer; the polymerization being brought about by the oxidizing agent used in the bleaching or dyeing operation and the further insolubilization of the polymer formed being caused by a bridging agent, which bridges the polymeric chains.

This invention relates to processes for preventing or retarding the damage to hair during the coloring of the same and to compositions useful in effecting this purpose. It has application to those processes wherein the hair is merely lightened by the action of a bleaching agent, as well as those processes which utilize a dye that requires an oxidizing agent to develop the color of the dye. It also has application to those combined hair coloring procedures which employ a bleaching agent to lighten the hair, followed by dyes or toners that do or do not require an oxidizing agent for their development.

Hair coloring, as defined above and as now practiced, takes several forms which utilize an oxidizing agent that has a tendency to damage hair and make it more porous. In the simplest and the least sophisticated procedure, hair is bleached by simply subjecting it to the action of a bleaching agent. Common agents used for this purpose are ammoniacal peroxide, alkali peroxide, or one of the above mixed with ammonium or potassium persulfate, etc.

In another procedure wherein the condition of the hair is such as not to require a pre-bleaching treatment, the hair may be colored by the application of an oxidation dye composition. This dye composition usually contains one or more dyes whose colors are developed by an oxidizing agent. This oxidizing agent usually takes the form of hydrogen peroxide.

In more sophisticated hair coloring procedures and particularly in the high fashion "blonding" procedure, the coloring operation usually takes place in two steps. In the first step, the hair is lightened through the use of an oxidizing agent, most usually a composition containing hydrogen peroxide and a persulfate compound. The hair is then toned by the application of the so-called toners which are oxidation dye compositions that require an oxidizing agent for their development. In some instances the dyeing is effected through the use of non-oxidation dyes.

The process known in the art as retouching (i.e., making the regrowth area the same color as the rest of the hair) involves applying as a lightening mixture, an alkaline, peroxide-persulfate mixture to the root ends of

the hair while attempting to minimize contact of the previously lightened hair with the fresh lightening mixture. Also in many cases at the end of the root lightening step (45 min. to 1½ hours after application of bleach to the roots), the lightening mixture is pulled down over the remainder of the hair shaft by means of a comb or the like. This latter treatment generally lasts for about 5 minutes and is used to remove faded toner left in the hair by a previous coloring treatment.

All of the hair coloring procedures described above exemplify those processes in the hair coloring art which require the use of an oxidizing agent and which tend to damage hair and make it more porous. In some instances the hair is subjected to multiple treatments with compositions containing oxidizing agents and the damage may be compounded. This is illustrated by the so-called "retouching" procedure.

There are two ways in which the hair is attacked by alkaline peroxide with each retouch application: (1) There is always, even in the most skillful application of the lightener to the root area, a small area of "overlap" of fresh lightener from the virgin roots over onto the hair which has been previously lightened. (2) The final five minutes of lightening when the last traces of previously applied toner are removed from the entire hair shaft gives an additional opportunity for the hair to lose some of its natural body and strength. Both of these effects are additive each time the hair is retouched.

It may be seen that by the time a band of hair grows out from the roots to the ends of the hair, the ordinary practices of the art produce hair ends which have been subjected to alkaline peroxide solutions many times. These ends are much more porous and brittle than the hair area adjacent to the scalp. The degree of porosity and brittleness of the hair increases as one progresses from root to end. In addition to being objectionable from the standpoint of possible breakage of the hair during cosmetic manipulations, there is a problem of uneven color distribution along the hair shaft when toners are applied.

A measure of remedy suggested for these problems involves applying pastes of oils, waxes, and protein hydrolyzates to retard the action of the lightener on the porous areas of the hair. Also the problem of very weak toner-take on excessively porous hair may be partially overcome by application of additional coloring materials to the porous areas. Essentially, however, these measures are of a nonpermanent nature as the increased body imparted to the hair by the conditioning agents currently in use is lost when the hair is shampooed.

It has now been found, in accordance with the present invention, that the damage to hair attending the coloring thereof as defined above, may be prevented or retarded by treating said hair during the coloring thereof with a water soluble polymerizable vinyl monomer containing an acid forming group or a salt thereof and polymerizing said monomer in situ with the aid of an oxidizing agent. The oxidizing agent used in the coloring operation may serve this purpose. The polymeric chains of vinyl monomer formed in the procedure of this invention are preferably bridged by bridging agents which reduce the water solubility of said polymer.

It is accordingly an object of the present invention to provide processes for preventing or retarding the damage of hair during the coloring of the same.

It is also an object of the present invention to provide

compositions of matter capable of effecting the above object.

Other and more detailed objects of this invention will be apparent from the following description and claims.

As noted above, the processes of the present invention involve the treatment of hair with a polymerizable vinylic monomer during the coloring thereof. It is contemplated by this invention that the polymerization and coloring of the hair may be effected at the same time or may be accomplished sequentially. In some aspects of this invention when they are carried on sequentially, it is also within the purview of this invention that these steps can be carried out in any order, i.e., the polymerization can be brought about before or after the lightening operation.

The processes of the present invention lend themselves to a good deal of variation. In one procedure wherein the coloring operation comprises a simple "lightening" action due to the action of a bleaching agent, the hair is pre-treated with an aqueous solution containing the polymerizable vinylic monomer and bridging agent. After the hair is well wetted with this solution, a second solution containing the bleaching agent (which is an oxidizing agent) is then applied. This procedure may be applied to hair which is unbleached or hair that has been given a previous bleaching treatment.

A simple extension of the procedure described above involves the application of a toner to the hair after the final treatment with the bleaching agent. This usually comprises mixing an oxidation dye composition with an oxidizing agent which will develop the color of the oxidation dyes and then applying this mixture to the hair. It is also possible in this case to substitute a non-oxidation dye system for the oxidative dye system.

In still another procedure, hair, which may or may not have been previously bleached, is first treated with an oxidation dye composition to which has been added oxidizing agent and polymerizable vinylic monomer. After a period of time the hair is then treated with an aqueous solution of the bridging agent.

In again another procedure, hair (which may or may not have been bleached) is wetted with an aqueous solution containing the polymerizable monomer and the bridging agent. After the elapse of a period of time, the hair is dyed out with an oxidation dye composition to which has been added the oxidizing agent.

An alternative procedure for coloring the hair by bleaching in accordance with this invention involves wetting the hair with an aqueous solution containing the polymerizable vinylic monomer and the oxidizing agent. This solution is permitted to act on the hair for a period of time and then the bridging agent, preferably in the form of an aqueous solution, is applied to the hair.

The present invention also has utility in retouching previously bleached hair and particularly pre-bleached hair which has been made overporous or has been otherwise damaged. In this procedure, the entire head is first saturated with an alkaline aqueous solution of a water-soluble monomeric vinylic compound, as described above. In addition, the solution contains a bridging agent, such as water soluble polyvalent cations or long-chain, water-soluble monovalent organic cations.

After the application of this solution, it is combed through the hair. The oxidizing agent mixture is then applied in the usual retouch fashion to the virgin roots of the hair (regrowth area). After the roots have been in contact with the oxidizing agent mixture for the desired period of time, this mixture on the roots is smoothed over the entire head of hair. Five minutes or less after this last step, the hair is shampooed and towel dried, ready for the toner application if desired.

Although applicants do not want to be bound by any theory, it is believed that the vinylic monomer used in this invention, because of the relatively small size of its molecules, enters into the interior of the hair structure. Inside the hair structure, it polymerizes to relatively

long chain molecules under the influence of the oxidizing agent. These molecules, because of their size cannot readily leave the interior of the hair structure. Furthermore, the action of the bridging agent in bridging adjacent polymeric chains further insolubilizes the polymers and locks them within hair structure. This action serves to strengthen the hair treated and minimize any damage caused by the oxidizing agent.

The agent most commonly used in lightening hair is essentially hydrogen peroxide in an alkaline solution with varying amounts of compounds, such as persulfate salts, to accelerate the action of the agent. The strongest of the agents which are currently used for lightening are sold as powders which are mixed with commercially available (20 volume) hydrogen peroxide. These are the so-called "powder bleaches." Although these agents are very fast acting compared to the liquid lighteners, they are not generally used for retouch applications because their potent action tends to damage the hair excessively when applied a second time to previously lightened hair. From the standpoint of both beauty operators and patrons, however, a faster acting lightener is a desirable feature, but the overlap problem created by the "powder bleaches" precludes their use in retouch application as it is currently practiced. By using the protective action afforded by the present invention, use can now be made of said faster acting "powder bleaches."

It is also advantageous, in accordance with the present invention, to use in conjunction with the polymerizable vinylic compound and bridging agent a material which will facilitate the entry of these materials into the hair. For this purpose it is useful to use alkaline solutions of the treating agents which promote the swelling of the hair, and the entry of the active ingredients.

The materials employed in practicing the present invention may be used in any convenient form. Thus, they may be applied as aqueous solutions or suspensions, gels, pastes, creams, etc. in a manner well-known to those skilled in this art.

As mentioned above, it is a feature of the present invention to utilize a polymerizable vinylic monomer having acid forming groups or salts thereof. These acid forming groups are important for the purposes of the present invention in that they provide sites at which neighboring polymer chains may be bridged by means of bridging agent utilized in this invention to render the polymer less water soluble. As used herein, the term acid forming groups is intended to encompass the acid groups per se, as well as groups which will be converted into acid groups under the conditions of use of the present invention.

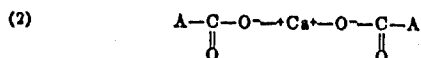
In general, however, the polymerizable vinylic compounds that may be used in accordance with the present invention are water-soluble compounds described by the general formula:



wherein R_1 , R_2 and R_3 are selected from the group consisting of hydrogen, alkyl, aryl and halide, and X is selected from the group consisting of acid groups and salts thereof (e.g., $-\text{COOH}$, $-\text{SO}_3\text{H}$). By way of illustration the following polymerizable vinylic compounds may be mentioned: acrylic acids, sodium acrylate, potassium acrylate, monoethanolamine acrylate, potassium acrylate, calcium acrylate, methacrylic acid, sodium methacrylate, monoethanolamine methacrylate, potassium methacrylate, calcium methacrylate, itaconic acid and salts of itaconic acid.

The bridging agents used in accordance with the present invention to further insolubilize the polymerized vinylic compound formed can be of a variety of types. One class of bridging agent comprises water-soluble compounds (e.g., salts, oxides, hydroxides) of elements of

Group II or III of the Periodic Table capable of yielding multivalent cations (divalent, trivalent, etc.). These are believed to function as bridging agents through the formation of a salt-like structure involving the acid groups of neighboring polymeric chains and the cations of the bridging agent. These bridges can be visualized in the case wherein the polymerizable vinylic compound is a carboxy acid and the bridging agent is a calcium salt or compound as follows:



wherein A is a polymeric chain. Although only one bridge is illustrated in the Formula 2 between the polymeric chains, it should be understood that there can be many such bridges. By way of illustration the following compounds can serve as bridging agents which will supply the cationic type bridge: CaCl_2 , ZnCl_2 , BaCl_2 , $\text{Al}_2(\text{SO}_4)_3$, and difunctional quaternary ammonium compounds, such as N-Tallow, N-N-dimethyl-N'-N'-trimethyl-1,3-propylene-diammonium chloride (Aliquat 726); N-Tallow-1,3-propylene-diaminedioleate (Diam 26 Dioleate).

Another class of bridging agent that may be used in accordance with the present invention may be described as agents capable of providing long-chain organic monovalent cations. The mechanism by which these long chain cations work to provide a bridge between neighboring polymer chains is not quite clear. However, it is believed that this probably involves chain entanglement. By way of illustration this class of bridging agent may be exemplified by the following: cetyl pyridinium chloride; cetyl trimethylammonium chloride; stearyl amine.

As mentioned above, an oxidizing agent capable of polymerizing the vinylic monomer is used in accordance with the present invention. In the usual practice of this invention, this oxidizing agent will also be instrumental in coloring the hair. As used herein, the term "oxidizing agent" is used in its broad sense and is intended to encompass a single oxidizing agent, as well as a combination of oxidizing agents. Moreover, it is also intended to cover complex compositions which include other components which may or may not be active ingredients. Thus, the term "oxidizing agent" is intended to apply to compositions which contain, in addition to the active oxidizing agent, such things as thickeners, carriers, surface active agents, basic materials, etc. The term "oxidizing agent" is also intended to extend to oxidation dye compositions which contain sufficient oxidizing agent to function in polymerizing the vinylic monomer.

The oxidizing agent used in this invention can vary considerably. By way of illustration the following may be mentioned: H_2O_2 , ammonium persulfate, sodium persulfate, potassium persulfate, pastes made from a combination of aqueous H_2O_2 and said persulfates, etc.

The oxidation dye compositions that can be employed in accordance with the present invention are also quite varied. Any of the compositions of this character which are well known to those skilled in this art are utilizable. Thus, for example, the oxidation dye formulas shown on page 508 of "Cosmetics, Science and Technology" by Edward Sagarin (1957) Interscience Publishers, Inc., New York, are suitable for the present purposes.

In accordance with the present invention, as mentioned above, to facilitate the penetration of the active materials into the hair, it is useful to incorporate a swelling agent in the treating compositions. These materials are generally basic in nature and give the treating solutions a relatively high pH. A pH between 8 and 9 or 10 is particularly suitable for this purpose. However, a pH between about 7 to 11 can be used.

Any of a number of bases both organic and inorganic may be used to obtain the suitable pH. By way of example, the following may be mentioned: monoethanolamine, NaOH , KOH , NH_3 , $\text{Ca}(\text{OH})_2$, etc.

The concentration of vinylic monomer, bridging agent

and oxidizing agent and time of treatment that is utilized in accordance with the present invention is interrelated and may be varied considerably. Any combination of these parameters which result in the incorporation into the hair structure of a polymer of high enough molecular weight to reinforce the hair strength will serve the purposes of this invention. This will be made clearer by a discussion of the mechanism of the polymerization reaction believed to be operating in the present invention.

The rate of conversion of monomer to polymer is made up of three steps: initiation, propagation, and termination. The initiation step consist of forming monomer free radicals, either by direct activation, or by forming other free radicals which then add to monomer. The rate of formation of monomer radicals (initiation) will be proportional to the monomer concentration and also the concentration of initiating radicals (which will in turn be proportional to initiator concentrations, i.e., the concentration of oxidizing agent).

The propagation step will be primarily dependent on monomer concentration. This is the step which, relative to the initiation and termination steps, determines the molecular weight of the polymer formed (i.e., if propagation is fast compared to the termination and initiation steps, the molecular weight of the polymer formed will be high).

The rate of the termination step is proportional to the total concentration of all radicals; initiator, monomer, and growing chain species. (See, for example, P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, 1953, chapter 4.)

From the above considerations, it is seen that a high rate of conversion of monomer to polymer may be obtained with high monomer and initiator concentrations, but this must be balanced off against the lower molecular weight of polymer obtained at high rates of conversion (when the initiation and termination steps are fast compared to the propagation step). If much of the polymer is of low molecular weight, then the reinforcing action of the polymer will be reduced.

Moreover, for practical purposes, the time of treatment cannot be unduly long. This must be taken into consideration in determining the concentration of the components of the compositions utilized in this invention, since the time interval during which a proper degree of polymerization takes place is dependent on the concentration of the various components of the composition. The concentration of vinylic monomer and oxidizing agent is therefore so arranged so that a sufficient degree of polymerization will take place so as to reinforce the hair within a time period generally used in the beauty trade for treating hair on the human head.

In general, however, the concentration of vinylic monomer present in the solution used either serially with the bridging agent and/or simultaneously with the bridging agent will be in the range of a .05 M. to 2.5 M.

The bridging agent is generally used in the concentration range of .05 M. to 2.5 M., the divalent bridging agent usually being employed in the range of .05 M. to 1.25 M. and the monovalent agent in the range of .1 M. to 2.5 M.

The concentration of oxidizing agent in the compositions applied to the hair will vary with the particular type of application involved, as well as other factors. Where the oxidizing agent serves as a bleach, its concentration will be very high and may approach saturated solutions. In the case where the oxidizing agent serves as the agent by developing the color for an oxidation dye, the values will be much lower. In this case it may vary from about .5% to about 15% by weight.

The time during which the vinylic polymerization is allowed to proceed will also vary. In general, however, this will be between 5 to 60 minutes. When the bridging agent is used simultaneously with the vinylic monomer, it, obviously, will be allowed to act over the same period of time as the vinylic monomer. However, where the

bridging agent is applied after the application of the vinylic monomer, it is permitted to remain in contact with the hair over a period of 1 to 10 minutes and ideally for 5 minutes.

The following examples are further illustrative of the present invention. It should be understood, however, that this invention is not limited thereto.

The oxidation dye composition mentioned in some of the examples set out below has the following formula:

Composition A

	Percent
Ammonium hydroxide (26° Bé.)	10.00
Isopropanol	2.5
Perfume	0.5
Oleic acid	35.00
Polyoxyethylene sorbitan monooleate	10.00
Water soluble lanolin (polyoxyethylene (4) lanolin)	1.75
Lecithin	1.25
Trisodium phosphate	0.25
1,5-dihydroxynaphthalene	0.4
Polyoxyethylene (4) lauryl ether	3.5
p-Methylaminophenolsulfate	0.25
p-Phenylenediamine	0.6
2,4-diaminoanisole sulfate	0.55
Pyrogallol	2.5
Sodium sulfite	0.6
Water, qs to 100.0%.	

EXAMPLE 1

A sample of normal brown hair was treated with a bleach mixture containing 15 grams of ammonium persulfate and 40 ml. of 6% H_2O_2 for 1½ hours at 30° C. This sample was then divided into three parts: (a) control, not treated further, (b) control treated again as above, and (c) treated as (b), *except* before the second bleach the sample was wet with a pretreating solution of 2.2 grams potassium acrylate, 1.5 grams $CaCl_2$ (anhydrous), 20 ml. H_2O (solution pH 7.5). The relative tensile modulus values (measured in water) of the samples were found to be 5.3, 3.9, and 7.4 for (a), (b), and (c), respectively.

EXAMPLE 2

Starting hair was treated for two successive 2-hour treatments with the bleach mixture described in Example 1. The hair was then separated into two samples: (a) control, given 5 cycles of a two-step blonding, representing the treatment given to all but the hair roots during successive retouches. The cycle was: 5-minute treatment with the said bleach mixture, shampoo, 30-minute treatment with Composition A + 20 volume H_2O_2 , light shampoo, then dried, (b) 5 cycles as in (a), *except* each cycle was preceded by a wetting with the pretreating solution as described in Example 1 (c). After the wetting, the hair was allowed to sit for 45 minutes (representing the root bleach-out time) before applying the bleach mixture.

The evaluation of samples (a) and (b) were made on the basis of dye-take, swelling on immersion in water (as measured microscopically), and relative tensile modulus values (as measured in water). The dye-takes were equivalent in shade but the control sample (a) was somewhat deeper in intensity. The transverse swelling for (a) was twice as much (on an area basis and also on a volume basis because the longitudinal swellings were essentially equal) as for (b). The tensile modulus values were 0.9 and 3.2 for (a) and (b), respectively.

EXAMPLE 3

The following mixture was applied to some bleached hair (modulus Index 4.5) for 45 minutes:

Composition A	oz.	2
20 Vol. H_2O_2	oz.	2
Sodium acrylate	g.	10

After 45 minutes, the hair was shampooed and rinsed with a solution of:

$CaCl_2$	g.	2
H_2O	ml.	20

The hair so treated had a color of the same intensity as a control (no acrylate), but the shade was different. The modulus index of the treated hair was 5.3, whereas modulus index of the control went to 3.6.

EXAMPLE 4

Some bleached hair (modulus Index 4.7) was wet with a solution containing:

Sodium acrylate	g.	
$CaCl_2$	g.	1.4
H_2O	ml.	20

After the above solution had been on the hair for 45 minutes, the hair was dyed out with Composition A + 20 vol. H_2O_2 for 45 minutes. The modulus index of the pretreated hair was 4.8, while the untreated toned hair had a modulus index of 4.3.

EXAMPLE 5

Na Acrylate	g.	10
20 vol. H_2O_2	oz.	2
4% aqueous NH_3	oz.	2

were mixed and placed on some bleached hair (modulus Index 4.8) for 45 minutes. The hair treated in this fashion had a modulus index of 5.3 after it was rinsed first with water and then with a solution containing 2.0 g. $CaCl_2$ and 20 ml. H_2O . A control sample of hair from the same batch of starting hair treated as above but with no sodium acrylate, had a modulus index of 4.1 after treating.

What is claimed is:

1. A process for dyeing hair in an aqueous medium with an oxidation dye composition which comprises subjecting said hair to a preliminary bleaching treatment, subsequently wetting said hair with a mixture of a water-soluble polymerizable monomeric vinyl compound in the concentration range of .05 M to 2.5 M selected from the group consisting of vinyl compounds having acid forming groups and salts thereof and a bridging agent in the concentration range of .05 M to 2.5 M and subsequently dyeing said hair with an oxidation dye composition containing an oxidizing agent in the concentration range of .5% to 15% by weight; said monomeric vinyl compound being selected from the group consisting of acrylic acid, sodium acrylate, potassium acrylate, monoethanolamine acrylate, calcium acrylate, methacrylic acid, sodium methacrylate, monoethanolamine methacrylate, potassium methacrylate, calcium methacrylate and itaconic acid; and said bridging agent being selected from the group consisting of $CaCl_2$, $ZnCl_2$, $BaCl_2$, $Al_2(SO_4)_3$; N-Tallow, N-N-dimethyl-N'-N'-N'-trimethyl-1, 3-propylene-diammonium chloride; N-Tallow-1, 3-propylene-diaminedioleate, cetyl pyridinium chloride, cetyl trimethyl-ammonium chloride and stearyl amine.

2. A process for dyeing hair in an aqueous medium with an oxidation dye composition which comprises treating said hair with a composition containing an oxidation dye, an oxidizing agent in the concentration range of .5% to 15% by weight and a water-soluble polymerizable monomeric vinyl compound in the concentration range of .05 M to 2.5 M having an acid forming group or salts thereof and subsequently treating said hair with a composition containing a bridging agent in the concentration range of .05 M to 2.5 M; said monomeric vinyl compound being selected from the group consisting of acrylic acid, sodium acrylate, potassium acrylate, monoethanolamine acrylate, calcium acrylate, methacrylic acid, sodium methacrylate, monoethanolamine methacrylate, potassium methacrylate, calcium methacrylate and itaconic acid; and said bridging agent being selected from the group consisting of $CaCl_2$, $ZnCl_2$,

BaCl₂, Al₂(SO₄)₃; N-Tallow, N-N-dimethyl-N'-N'-N'-trimethyl-1, 3-propylene-diammonium chloride; N-Tallow-1, 3-propylenediaminedioleate, cetyl pyridinium chloride, cetyl trimethylammonium chloride and stearyl amine.

3. A process according to claim 2 wherein the process is carried out on previously bleached hair.

4. A process for dyeing hair in an aqueous medium with an oxidation dye composition which comprises treating said hair with a composition containing a water-soluble monomeric vinyl compound in the concentration range of .05 M to 2.5 M having an acid forming group or salts thereof and a bridging agent in the concentration range of .05 M to 2.5 M, and subsequently treating said hair with an oxidation dye composition containing an oxidizing agent in the concentration range of .5% to 15% by weight; said monomeric vinyl compound being selected from the group consisting of acrylic acid, sodium acrylate, potassium acrylate, monoethanolamine acrylate, calcium acrylate, methacrylic acid, sodium methacrylate, monoethanolamine methacrylate, potassium methacrylate, calcium methacrylate and itaconic acid; and said bridging agent being selected from the group consisting of CaCl₂, ZnCl₂, BaCl₂, Al₂(SO₄)₃; N-Tallow, N-N-dimethyl-N'-N'-N'-trimethyl-1, 3-propylenediammonium chloride; N-Tallow-1, 3-propylenediaminedioleate, cetyl pyridinium chloride, cetyl trimethylammonium chloride and stearyl amine.

5. A process according to claim 4 wherein the process is carried out on previously bleached hair.

6. A process for simultaneously lightening and protecting hair in an aqueous medium which comprises subjecting said hair to the action of a composition comprising a bleaching agent in the concentration range of .5% to 15% by weight and a water-soluble monomeric vinyl compound in the concentration range of .05 M to 2.5 M having acid forming groups or salts thereof and subsequently treating said hair with a bridging agent in the concentration range of .05 M to 2.5 M; said monomeric vinyl compound being selected from the group consisting of acrylic acid, sodium acrylate, potassium acrylate, monoethanolamine acrylate, calcium acrylate, methacrylic acid, sodium methacrylate, monoethanolamine methacrylate, potassium methacrylate, calcium methacrylate and itaconic acid; and said bridging agent being selected from the group consisting of CaCl₂, ZnCl₂, BaCl₂, Al₂(SO₄)₃; N-Tallow, N-N-dimethyl-N'-N'-N'-trimethyl-1, 3-propylene-diammonium chloride; N-Tallow-1, 3-propylenediaminedioleate, cetyl pyridinium chloride, cetyl trimethylammonium chloride and stearyl amine.

7. A process according to claim 6 wherein the process is carried out on pre-bleached hair.

8. A process for retouching, previously bleached hair

having new hair growth, in an aqueous medium which comprises applying to said new growth an aqueous composition containing a water-soluble polymerizable monomeric vinyl compound in the concentration range of .05 M to 2.5 M containing acid groups or salts thereof and a bridging agent in the concentration range of .05 M to 2.5 M capable of rendering polymeric chains of said vinyl compounds less soluble in water and then applying to said new growth an aqueous composition containing an oxidizing agent in the concentration range of .5% to 15% by weight capable of promoting the polymerization of said monomeric compound and lightening said hair; said monomeric vinyl compound being selected from the group consisting of acrylic acid, sodium acrylate, potassium acrylate, monoethanolamine acrylate, calcium acrylate, methacrylic acid, sodium methacrylate, monoethanolamine methacrylate, potassium methacrylate, calcium methacrylate and itaconic acid; and said bridging agent being selected from the group consisting of CaCl₂, ZnCl₂, BaCl₂, Al₂(SO₄)₃; N-Tallow, N-N-dimethyl-N'-N'-N'-trimethyl-1, 3-propylene-diammonium chloride; N-Tallow-1, 3-propylenediaminedioleate, cetyl pyridinium chloride, cetyl trimethylammonium chloride and stearyl amine.

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