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ACTIVATOR SOLUTION FOR MACHINELESS
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1

This invention relates to the art of permanent waving and in particular to solutions suitable for activating heating pads normally used in producing machineless waves.

The object of this invention is to provide an activator solution that will cause the reaction to take place between the chemicals in a conventional water activated machineless heating pad in the same manner as though the pad were wet with water.

Another object of this invention is to provide a heating pad activating solution that contains ingredients capable of leaving the hair soft and glossy after the solution has ceased to serve as an activator, in effect producing results superior to those obtained by the so-called "oil machineless" type of wave.

A further object is to provide an improved activating solution for use with water activated machineless pads containing an oil-like substance that will be deposited on the hair after the water in the mixture has been driven off by the heat generated by the pad and will not be easily rinsed from the hair when it is washed after the wave has been set.

A conventional heating pad used in producing water activated machineless waves generally comprises a mixture of dry ingredients such as potassium chlorate, finely-divided aluminum, copper carbonate, and aluminum sulphate with or without an inert filler. These ingredients react with each other when they are moistened with water, producing the heat necessary to wave the hair. Since the waving solutions generally employed are alkaline in nature, while the active ingredients in the heating pad are acidic in nature, the alkaline waving solution must be prevented from soaking into the heating pad and neutralizing the acidic components making the heating pad useless. This is ordinarily prevented by placing an applicator pad between the wet surface of the hair and the permeable surface of the machineless heating pad. The ordinary applicator pad comprises a sheet of water resisting material laminated to a sheet of water-absorbent material. The water-absorbent sheet of the applicator is moistened and placed in contact with the heating pad envelope. The water diffuses through the permeable covering of the heating pad and initiates the reaction between the chemicals.

A particular feature of my invention is that my novel activator solution eliminates the necessity of using an applicator pad having an impermeable sheet to prevent the alkaline hair waving solution from entering the heating pad.

The pads in general use for giving so-called "oil machineless" waves differ in composition

2

from the type of heating pads activated with water. This type of pad usually consists of a porous envelope in which there is contained a mixture comprising 40% to 60% by weight of potassium permanganate and an inert filler. These pads are activated by so-called "oily solutions" which are generally no more than an aqueous solution of glycerol, sorbitol, or ethylene glycol. The alcoholic solution soaks into the pad and when the alcohols come in contact with the permanganate they become oxidized and generate heat.

A general objection to the use of this "oil machineless" type of heating pad is that permanganates in general have a rather high water solubility making the resulting solution highly colored. These solutions may cause injurious stains if brought in contact with the hair or fabrics.

Another disadvantage attending the use of permanganate heating pads and their activator solution is that the so-called oily portions of the solution, that is, the alcohols, such as glycerol, sorbitol and the ethylene glycols actually impart no lasting body to the hair because they are completely washed away when the hair is rinsed after the waving process is completed.

Another objection to the use of permanganate heating pads is that the amount of heat developed by the normal size pad is low compared to that developed by a water activated heating pad of equivalent size. Therefore, it would be necessary to use a much larger heating pad to produce a wave similar to that obtained with the water machineless pad. Since this is impractical due to limiting dimensions of the curlers, the result is that an "oil machineless" wave generally produces weaker curls than a water activated machineless wave.

The activator solutions normally used in giving "oil machineless" waves cannot be employed to activate a standard water machineless pad because they contain water soluble organic substances which when dissolved in the water in quantities, sufficient to give it an oily appearance, lower the dielectric properties of water and reduce its solvent power for any highly ionized inorganic salt and thereby prevents the steaming of the pad. As a result the operator must carry in stock two complete kits to be equipped to give a water machineless wave, or an oil machineless wave.

I overcome the above difficulties by provision of a novel activating aqueous solution that is colorless, contains desirable amounts of high molecular weight organic compounds and can be used to activate the ordinary water activated machineless heating pad generating approxi-

mately the same amount of heat as will be developed if the pad were wet with water.

My novel aqueous solution imparts a lasting gloss and body to the hair even though the high molecular weight organic compound is present in smaller amounts than in the conventional oil activator solution used with permanganate pads. These substances do not easily rinse away when the permanent waving solution is washed out of the hair. Since the heating pads employed are the water-activated type and contain no permanganate or other highly colored oxidizing salt, there is no danger of staining and this particularly objectionable feature encountered in the ordinary oil machineless wave is therefore entirely eliminated.

My novel pad activating solution comprises water and an organic water-soluble, high molecular weight, aliphatic compound capable of imparting oily properties to the water when dissolved in it. A suitable accelerator or accelerators mixture is added to the aqueous solution.

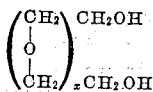
My accelerator or combination of accelerators performs two independent functions; first it compensates for any inhibiting effect of the dissolved organic substances, and secondly it protects the heating pad from the injurious effect of the alkaline waving solution.

The organic substances that I employ in the preparation of this pad activating solution comprise long, straight chain aliphatic compounds of C, H, and O having at least one oxygen-containing polar group for every three carbon atoms.

A preferred arrangement is one in which the polar groups are fairly evenly distributed among from 65%-100% of the carbon atoms in the chain, that is, one polar group is present between 1-3 carbon atoms. This would allow a maximum of 35% of the total carbon atoms in the chain to be arranged side by side without having any polar groups between them if necessary. However even distribution of the polar groups tends to insure greater water solubility and therefore compounds having such a distribution are more desirable. The substances selected should be of such a nature that they are not too readily soluble, thus preventing them from being rinsed away when the hair is subsequently washed. Furthermore, the substance should not become sticky or tacky at any stage of the evaporation but should in 5% to 20% concentrations impart sufficient viscosity and give an unctuous and oily feel to its water solution and to the hair at all times.

Preferably the material should be of such a nature that the addition of between 5% to 20% by weight of the substance, based on the total weight of the solution will not increase the viscosity of the solution to a degree where it will not pour easily and cannot penetrate the machineless heating pads freely.

A preferred group of organic compounds that fill the above requirements comprises the high molecular weight ethylene oxide polymers commonly referred to as polyethylene glycols and also called polyoxyethylene glycols. These substances have a general formula



The molecular weights that are suitable in carrying out my invention range from about 1000 to about 7000 in which range the compounds are solids. However, any water soluble compound of this group having a molecular weight above 7000

could also be used if it otherwise meets the above viscosity requirement and is sufficiently soluble in water.

Other representatives of the broad group of organic compounds that fulfill the broad definition for the organic compound are the water soluble polypropylene glycols having molecular weights ranging between about 500 and about 6000 and polyvinyl alcohols preferably of "low" viscosity and containing less than 15% unhydrolyzed vinyl acetate groups. Since the molecular weights of the polyvinyl alcohols are difficult to determine with accuracy it is more convenient to use the viscosity in centipoises of a 4% by weight aqueous solution at 20° C., as determined with a Hoeppler viscosimeter, as a means for designating the type of polyvinyl alcohol used. The viscosity of the polyvinyl alcohols suitable for use in compounding my invention ranges from between about 1 and about 25 centipoises at the above conditions.

Aliphatic alcohol ethers of the polymers mentioned above that possess the required water solubility may also be employed. However, compounds that hydrolyze in mild acid solution cannot be used.

The speed with which a water activated machineless pad generates heat is generally dependent upon the rate of solution of the accelerator therein. For this reason the proper selection of the accelerating material to be added to the solution is quite important.

Accelerators may be broadly divided into two groups:

One group of materials that is suitable for accelerators is the water soluble inorganic acid salts of cations which will precipitate in alkaline solution. The acid radical should furthermore be one capable of reacting with aluminum.

A second group of materials that may also be used are the water soluble salts of inorganic acids such as HCl and H₂SO₄ capable of reacting with aluminum, strong water soluble organic acids capable of reacting with aluminum, water soluble aliphatic amine salts of inorganic acids as well as their derivatives capable of reacting with Al, as well as free inorganic acids capable of reacting with Al. Certain of these amine hydrochlorides may be classified functionally in group one, depending upon the properties of the free amine.

The pH of a normal aqueous solution of the accelerator should be below about 5.0.

At least one accelerator from the first group should be present in order to protect the heating pad from the alkaline waving solution and if further acceleration is desired one or more of the accelerators in group two can be added.

Examples of the strongly acidic water soluble inorganic salts are aluminum chloride, aluminum sulphate, ammonium chloride and ammonium sulphate.

Examples of the strong organic acids are citric acid, tartaric acid, lactic acid and other acids of similar strength.

Examples of the water soluble amine hydrochlorides are diethylhexylamine hydrochloride, 1-hydroxyethyl 2 heptadecynylglyoxalidine hydrochloride and similar amine hydrochlorides.

The preferred accelerator because of its cheapness, availability and excellent performance is a mixture of aluminum chloride and ammonium chloride in percentages varying between ½% and 7% by weight of ammonium chloride based on the weight of the total aqueous solution, and

5

2½%-10% by weight aluminum chloride based on the weight of the total aqueous solution.

The incorporation of an additional percentage of an acid-forming salt or other substance into the aqueous activator solution proves beneficial in overcoming any retarding effect caused by the addition of organic compounds to the solution. This may be explained when it is seen that the initiating action of a water activated heating pad occurs in two stages: First the aluminum sulfate is dissolved by the water, and secondly the aluminum sulfate solution formed reacts with the copper carbonate in the pad forming a salt. The presence of any dissolved organic compound tends to lower the rate of solution of the aluminum sulfate, therefore, the time required for the first stage would be increased considerably. The addition of an accelerator such as those described to the solution compensates for this slowing down action by providing a solution that reacts directly on the copper carbonate.

The use of applicators provided with impermeable layers is not desirable when an organic substance that can impart oily properties to the water is used in the activating solution because the impermeable sheet prevents the organic substances from coming in contact with the hair. Up to the present time the use of a permeable applicator pad has been impractical since the highly alkaline waving solution would quickly penetrate the pad and neutralize the acidic constituents destroying their effectiveness.

My novel activating aqueous solution may be used in conjunction with a porous applicator pad since it contains metal salts capable of precipitating insoluble hydroxides such as aluminum hydroxide when the acid metal salt is neutralized by the alkaline waving solution. The metal hydroxide is deposited as an insoluble gelatinous film on the side of the applicator through which the alkaline waving solution must pass thus effectively preventing the alkaline waving solution from reaching the heating pad, at the same time allowing a substantial portion of the organic compounds in the activator solution to be deposited on the hair.

Other compounds that will also serve satisfactorily are colorless acid salts of metals capable of precipitating insoluble hydroxides and releasing acid radicals that will react with the aluminum in the pad. Examples are the salts of magnesium, aluminum, zinc, and titanium such as the chlorides and sulfates.

Another group of chemical compounds that may be also used to prevent the passage of the alkaline waving solution are the water soluble aliphatic amine hydrochlorides and their derivatives which precipitate insoluble free amine when neutralized by the alkaline solutions. Examples of the last-named group of substances are diethylhexylamine hydrochloride, 1-hydroxyethyl 2 heptadecynylglyoxalidine hydrochlorides and similar aliphatic amine hydrochlorides.

The activator solution according to my invention may be broadly compounded within the following approximate limits:

	Per cent
Ethylene oxide polymers (polyoxyethylene glycols, or equivalent) (average molecular weight range between 1000 and 7000)	5 -20
Ammonium chloride	1½- 8
Aluminum chloride	2½-10
Water	About 60 -90

6

A preferred form of the solution is as follows:

	Per cent by weight
Ethylene oxide polymer (polyoxyethylene glycol—average molecular weight 6000)	10
Ammonium chloride	3
Aluminum chloride	4
Water	83

Another preferred form of the invention is as follows:

	Per cent by weight
Ethylene oxide polymer 4000 average molecular weight (polyoxyethylene glycol)	11
Ammonium chloride	3
Aluminum chloride	4
Water	82

On a water free basis the organic material is present in amounts varying between about 30% and about 80% by weight based on the weight of the non-aqueous ingredients. The water soluble acidic constituent is present in amounts varying between about 20% and about 50% by weight based on the weight of the non-aqueous ingredients therefore in the above formulations the $AlCl_3$ will be from about 10% to about 50% by weight of the non-aqueous ingredients and the NH_4Cl will vary between 1% and 20% by weight of the non-aqueous ingredients.

While it has been stated that the average molecular weight of the preferred ethylene oxide polymer ranges between 1000 and 7000 it is contemplated to include within the scope of this invention allied materials having molecular weights exceeding 7000 as long as the material is sufficiently water soluble and is not sticky or tacky when dry. The higher molecular weight ethylene oxide polymers may also have incorporated therein small quantities of lower molecular weight polyethyleneglycols as long as the amount of such substance used does not lower the average molecular weight below 1000. The preferred ethylene oxide polymers that have been generally used are those having average molecular weights of approximately 1500, 4000 and 6000 average molecular weight.

My novel solution possesses the advantage that it is possible to employ the more effective water machineless heating pads with an activator solution containing oily materials capable of imparting desirable properties to the hair without losing any of the heat thus insuring a more satisfactory permanent wave.

Another advantage of my solution is that it permits the use of permeable applicator pads which allow a substantial portion of the organic materials in the solution to become deposited on the hair, yet at the same time prevent diffusion of any of the alkaline waving solution from the hair into the heating pad.

My novel activator solution contains organic substances that impart a lasting gloss and softness to the hair and are not rinsed away on the first washing.

A further advantage of my invention is that the desirable effect of an oil machineless wave can be obtained without the danger of staining or ignition often encountered when the present so-called oil machineless activator solutions are applied to permanganate heating pads.

I claim:

1. An activator solution for use with a normally water-activated machineless hair waving pad, said solution comprising a polyoxyethylene

glycol having an average molecular weight ranging between about 1000 and about 7000 in an amount ranging between about 5% and about 20% by weight based on the weight of the total solution, ammonium chloride in an amount varying between about ½% to about 8% by weight based on the weight of the total solution, aluminum chloride in an amount varying between about 2½% to about 10% by weight based on the weight of the total solution and water in an amount varying between about 60% and about 90% by weight based on the weight of the total solution.

2. An activator solution for use with a normally water-activated hair waving pad, said solution comprising about 11% by weight polyoxyethylene glycol having an average molecular weight of 4000, about 3% by weight of ammonium chloride, about 4% by weight $AlCl_3$, and about 82% by weight water.

3. An activator composition for use with a water activated machineless hair waving pad comprising: a water-soluble organic material selected from the group consisting of polyoxyethylene glycols having a molecular weight above 1000; polypropylene glycols having molecular weights above 500; polyvinyl alcohols containing less than 15% unhydrolyzed vinyl acetate groups, an aqueous solution of said polyvinyl alcohols containing 4% by weight having an average viscosity at 20° C. of between about 1 and about 25 centipoises determined by a Hoesppler viscosimeter; and aliphatic alcohol ethers of said polymers: between about 10% and about 50% by weight, based on the weight of the total non-aqueous ingredients, of $AlCl_3$; and between 0% and about 20% by weight, based on the weight of the total non-aqueous ingredients of an acidic constituent selected from the group consisting of HCl, H_2SO_4 , water-soluble salts of HCl, water-soluble salts of H_2SO_4 , and water-soluble organic acids, an aqueous solution of said acidic constituent, when containing one chemical equivalent per liter, having a pH below about 5.0.

4. An activator composition according to claim 3 wherein said water soluble organic material is present in the proportion between about 30% and about 80% by weight, based on the weight of the total non-aqueous ingredients.

5. An activator composition according to claim 3 wherein between about 60% and about 90% by weight of water, based on the total weight of the solution is added to the non-aqueous ingredients.

6. In machineless hair waving the combination comprising the activator composition of claim 5 and a heating pad comprising a mixture of Al, $CuCO_3$, $Al_2(SO_4)_3$, and $KClO_3$.

7. An activator composition for use with a water activated machineless hair waving pad, said composition containing: a water soluble organic material selected from the group consisting of polyoxyethylene glycols having molecular weights above 1000; polypropylene glycols having a molecular weight above 500; polyvinyl alcohols containing less than 15% unhydrolyzed vinyl acetate groups, an aqueous solution of said polyvinyl alcohols containing 4% by weight having an average viscosity at 20° C. of between about 1 and about 25 centipoises determined by a Hoesppler viscosimeter; and aliphatic alcohol ethers of

said polymers; said composition also containing between about 10% and about 50% by weight of $AlCl_3$, based on the weight of the non-aqueous ingredients; said composition further containing between about 1% and about 30% by weight of ammonium chloride based on the weight of the non-aqueous ingredients.

8. In hair treating employing an applicator pad, a heating pad, and an activating solution, the method of preventing the passage of an alkaline waving solution through said applicator pad which comprises incorporating in said activating solution $AlCl_3$, and precipitating a layer of $Al(OH)_3$ on said applicator pad when said waving solution comes in contact with said $AlCl_3$.

9. In a hair treating process employing an applicator pad, a water activated machineless hair waving heating pad, and an activating solution, the method of preventing passage of an alkaline waving solution through said applicator pad into said heating pad which comprises incorporating in said activating solution a compound selected from the group consisting of $AlCl_3$, $MgCl_2$, $ZnCl_2$, $TiCl_3$, $Al_2(SO_4)_3$, $MgSO_4$, and $ZnSO_4$, and precipitating an insoluble layer on said applicator pad when said alkaline waving solution comes in contact with said compound.

10. An activator composition for use with a water-activated machineless hair waving pad comprising a water-soluble organic material selected from the group consisting of polyoxyethylene glycols having a molecular weight above 1000; polypropylene glycols having molecular weights above 500; polyvinyl alcohols containing less than 15% unhydrolyzed vinyl acetate groups, an aqueous solution of said polyvinyl alcohols containing 4% by weight having an average viscosity at 20° C. of between about 1 and about 25 centipoises determined by a Hoesppler viscosimeter; and aliphatic alcohol ethers of said polymers: between about 10% and about 50% by weight, based on the weight of the total non-aqueous ingredients, of a compound selected from the group consisting of $AlCl_3$, $MgCl_2$, $ZnCl_2$, $TiCl_3$, $Al_2(SO_4)_3$, $MgSO_4$ and $ZnSO_4$; and between 0% and about 20% by weight, based on the weight of the total non-aqueous ingredients of an acidic constituent selected from the group consisting of HCl, H_2SO_4 , water soluble salts of HCl, water soluble salts of H_2SO_4 , and water soluble organic acids, an aqueous solution of said acidic constituent, when containing one chemical equivalent per liter, having a pH below about 5.0.

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