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MALEIC ANHYDRIDE AND ETHYLENE OXIDE COPOLYMERS IN HAIR PREPARATIONS

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This invention relates to new and useful improvements in the treatment of fibers or fibrous material containing keratin such as hair or wool, and it is particularly concerned with treatments for aiding the setting and styling of such substances and for the treatment of keratin-containing materials in or before finishing operations.

The invention resides in the particular arrangements and relationship of the various elements of the formulations as exemplified in the detailed disclosure hereinafter set forth wherein the objects of the invention, as defined in the paragraphs below, will be apparent.

The formulations hereof relate fundamentally to wave sets although it is to be understood from the outset that same can also be used as resins in other types of hair preparations inasmuch as they possess possibilities of advantageous use in same. That is, the formulations hereof possess definite conditioning powers or characteristics and accordingly may conceivably be incorporated as a conditioner in almost any type of hair preparation such as shampoos, cold wave preparations, and/or the like.

My invention essentially comprises a composition for providing the aforementioned setting and styling result and consists of the product of the composition which possesses the characteristics, properties, and relation of constituents, and the method of use thereof, all as exemplified in the detailed disclosure hereinafter set forth.

The existing practices in the trade, as exemplified by the prior art heretofore known, all have certain common and obvious objections. Many kinds of preparations for setting waves or curls in human hair have been proposed. Most of same have been based on sticky or mucilaginous substances with the natural gums tending to displace other materials, because they are more readily applied. Yet the natural gums do not possess all of the desired and required properties for a successful wave set or for a preparation to hold human hair in any desired form. They are usually insufficiently effective in very thin layers, lack adhesion, flake off, dry hard and turn white consequently dulling luster, discolor the hair, impart to some degree an undesirable stiffness and brittleness and/or exhibit other faults. Also detrimental is the use of alcoholic solutions of gums or of various proteins since high percentages of alcohol are drying to both hair and scalp. The solid gel-like preparations have other objections in that they dry to a brittle stage so as to render hair wire-like and stiff. The dried films become flaky and do not regain moisture rapidly.

In contradistinction, I have devised a novel product whereby these difficulties and objections are overcome. I accomplish this by the provision of compositions which may be readily applied to human hair and which are free from the disadvantages of the sticky or mucilaginous substances referred to above as being heretofore used.

It is an object of this invention to provide a product and process for shaping and setting hair with a minimum amount of coating material and with no chemical attack on the hair.

It is a further object hereof to provide compositions and methods for treating hair and at the same time for giving hair a neat and well groomed appearance.

Still another object of the invention is to provide a composition of the above type which is relatively inexpensive and which can produce novel results heretofore unobtainable.

These objects are attained in a highly satisfactory manner by applying to hair a thin deposit or coating of a solution of a base thickener of maleic anhydride and ethylene copolymers combined with additives consisting of a lubricant, preservative, anti-foam agent, and aromatic and coloring ingredients.

After an aqueous solution of the same is applied to the hair as by brushing, combing, spraying or similar procedure, the hair is formed into a plastic mass to which may be imparted a desired form capable of being retained when the hair is dried, leaving thereon a thin, transparent flexible film, which is highly adhesive yet free from tackiness.

These objects and other incidental ends and advantages will in part be obvious and apparent and will in part be more fully pointed out in the progress of the disclosure, and to the end of attaining these and any other object and advantage hereinafter reasonably appearing, it will be explained that the invention consists substantially in the formulations as described in detail hereinafter, and as defined with particularity in the appended claim forming a part hereof.

The protection which is sought for this invention is covered by the language of the specification and the spirit represented thereby and same is limited only by the prior art and the scope of the appended claim.

It will be apparent however that the physical embodiment delineated is only indicative of but one of the various ways, albeit the preferred exemplification, in which the principles of the invention may be employed and in which the component ingredients may be combined and arranged. Some is submitted as one best known embodiment of the invention in accordance with the patent statutes and is given with a view to illustrating and explaining the precise nature of the principles of the invention and their embodiment for practical use, in order that others skilled in the art may be enabled to adapt and modify them in numerous embodiments, variations and modifications, each as may be best adapted to the conditions of any particular use.

The novel features which I consider to be characteristic of my invention will be best understood from a consideration of the following detailed description forming a part of this specification; nevertheless it is to be understood that the invention is not confined to such disclosure and that the precise formulation need not be slavishly followed, the invention being susceptible of such changes and modifications as shall define no material departure from the salient features of the invention as expressed herein.

The following gives one specific example of an end product forming the basis of this invention, it being understood that other adjuvant materials may be similarly incorporated and that the quantities and types of substances added to the materials mentioned herein may be varied.

It has been found that the formulated resin hereof possesses properties making it particularly suitable for this use. These properties impart to the hair some hygroscopicity which preserves flexibility, prevent excessive stiffness and brittleness, avoid harshness and hardening of the coated hairs, and keep the deposit adherent and coherent. Thereby flaking, powdering and discoloration, particularly by the deposit's turning white, do not result. At the same time, the hair is not sticky and the deposit may be easily removed by washing with water.

The desiderata in formulations of the types herein envisioned are that they be capable of setting the hair, have a safe pH, be non-reactive with other hair prepara-

tions, be non-grippy, be easy to apply, offer good slippage and penetrating power, produce no flaking, create no dragging or snarling of the conditioned hair, be of pleasant odor, add lustre to the hair, be resistant to humidity, be safe for use, and costwise successfully serve as a competitive item on the commercial market. As a further objective, the formulation preferentially must be capable of being atomized as a spray from a pressurized container without being chemically inactivated.

The formulations of the present invention meet these specifications in every respect, they providing novel and remarkably efficacious hair compositions.

The invention resides in the use of a cosmetically acceptable viscous composition comprising generally maleic anhydride and ethylene copolymers as a base preparation and an ethylene condensate of a high molecular weight fatty alcohol for providing lubricity in combination with additives comprising a preservative, an anti-foam agent, and aromatic and coloring ingredients as necessity dictates all of which are distributed in an aqueous medium.

Depending upon the amount of water used, and also depending on the amount of the thickening agent used, the consistency of the product may vary from a rather fluid liquid state to a relatively solid gel-like state. The viscosity of the product may therefore be varied, depending on the requirements of the manufacturer and/or user.

By the formulations hereof, an end-use product is herein provided as is a concentrate thereof which is capable of being diluted so as to resemble the end-use product.

The demand of beauty salons has been for a concentrated wave set which is dilutable. This has been for reasons of economy, the shipping expenses and attendant costs obviously presenting aggravating problems.

The formulations hereof offer unusual versatility so as to permit operation within a wide variety of ranges, it being a notorious fact that individual beauty salon operators have individual concepts as to what is the desideratum in a wave set. By way of illustration, different beauty salon operators desire differing degrees of plasticity on the hair as they work therewith. Too, being creative artisans, they prefer to adjust the head to their respective methods of working. As a result thereof, they prefer to dilute a commercially available base to their individual tastes.

When used in a cold wave preparation, the composition functions as a mechanical aid and serves to thicken the solution. It is to be here explained that all cold wave lotions or neutralizers are not of the same consistency. Where and as it may be desired to vary a specific consistency, the formulation hereof may be successfully employed.

The following example is illustrative of the type of wave set formulations which have been found to achieve the objects of this invention:

Example I

A wave set formulation was made up of the following constituents:

	Percent
Maleic anhydride and ethylene copolymer	0.30
Ethylene condensate of a high molecular weight fatty alcohol	0.80
Methyl ester of hydroxybenzoate	0.30
Dimethyl siloxane	0.05
Coloring	0.03
Perfume	0.10
NaOH (5% sol.)	0.70
Water, q.s. 100%.	

The method of compounding involves the heating of the resin and water combination to a temperature approximating 95° C. for substantially 20 minutes to effect solution and then adjusting the pH with the base.

In large scale manufacture however, such a procedure would represent excessive production costs.

The methyl ester of parahydroxybenzoate when used at the indicated high concentration of 0.3% is preferentially incorporated into the formulation at temperatures in excess of 70° C.

Accordingly, a preferred manufacturing procedure involves the heating one-half of the water to a temperature of 75° C. followed by the addition of the resin and 0.2% base thereto. Thereafter the temperature is maintained during a 20 minute cycle of agitation. There following, the other half of the water, heated to a temperature of 60° C., is added, followed by the addition of the remaining raw materials as the resultant mass cools. During the course of the cooling, the pH is adjusted.

The maintenance of a proper pH is a critical factor in the control of the viscosity.

The sodium hydroxide functions to bring the batch to the desired pH of approximately 4.75.

The advantages of the invention as here outlined are best realized when all of its ingredients are combined, but useful embodiments may be produced involving less than the whole.

The base of the formulation hereof is a copolymer composed of maleic anhydride and ethylene. That is, it is the reaction between maleic acid and ethylene gas. Preferentially it is the anhydride of a resin which, in water, forms a dicarboxylic acid and has a pH of about 2.30 at about 25° C. The maleic anhydride-ethylene copolymer is of the type disclosed in U.S. Letters Patent 2,913,437, issued to John H. Johnson on November 17, 1959, and titled Low Molecular Weight Olefin/Maleic Anhydride Copolymers Made in Special Solvent Systems. As this acid is neutralized with sodium hydroxide, the viscosity of the solution increases. Ammonium hydroxide may be substituted for the sodium hydroxide.

This resin, when used in the hair preparations envisioned herein, has demonstrated capacity for setting the hair in such manner as to make same easy to style. It enhances the luster thereof, imparts humidity resistance thereto, and does not flake. Nor does it effect the color of the hair. From an economic viewpoint, it is highly efficient. It is compatible with other preparations normally employed in hair cosmetics, possesses good curl retention capabilities, is not sticky and is easily removable. Hair treated therewith can be wet and reset with improved results over the use of water alone.

Same is used at a very low concentration (in a range from 0.01–1.00% in a water base at pH 4.5–8.5) offering a product possessing good hair holding properties which, following drying, does not leave the hair coated, delustered or tacky.

The ethylene condensate of a high molecular weight fatty alcohol is a surface-active agent of a non-ionic nature. It is a product having a carbon chain of from C_{12} to C_{18} and an ethylene oxide ratio of from 5–50 mols. It has the capacity for increasing the lubricity or slip making the hair easier to set and style. It decreases the wet snarl making wet hair easier to comb. It provides a good spread or dispersal of the resin on wet hair, allowing it to penetrate the hair crop, nullifies static electricity on dry hair, and leaves the hair soft and manageable. Without its addition, the formulations would exhibit tendencies toward grippiness.

Microbiological growth having been detected in solutions of maleic anhydride and ethylene copolymers, growth inhibition has been an admitted problem. The exhibited potentiality of the resin as an excellent substrate for molds and motile bacilli necessitated the search for a commercial inhibitor, such mold growth being obviously unacceptable from a finished product sales acceptability standpoint.

Optimum results have been obtained with a methyl ester of parahydroxybenzoate as a preservative, it having a capacity for arresting the bacteria growth.

Because of a tendency of the formulations hereof to foam, dimethyl siloxane is employed as a valuable additive, same having a capacity to eliminate the foam which some user might understandably consider objectionable.

It further has the capacity to enhance the lubricity of the combination of ingredients, producing no deleterious eye and skin effects and serving as a useful component of any protective or barrier cream.

To give the preparation of pleasing odor, a small amount of a perfume or aromatic ingredient may be incorporated in the composition as desired. In order to give the preparation a pleasing appearance, it may be slightly colored by a harmless coloring matter.

It will be understood that the proportions of the previously described chemical compounds employed in the cosmetics may be widely varied depending upon various factors such as the nature of the particular cosmetic, the effectiveness of the particular chemical compound selected, the specific results sought, and the like.

The formulations hereof offer definite advantages over gum wavesets of the known prior art. They are not sticky, or tacky or stringy or flaky, as are the known gum wavesets. Whereas gums require from 4 to 8 hours to set up, the formulations of the present invention can be used immediately in their formulated form or can be diluted and likewise used immediately. These formulations in no way impair the luster of the hair on which used, have a longer life than the known gum wave sets and leave the hair softened and with a more natural feeling than the known gum wave sets. Too, they possess superior hair holding properties under high humidity conditions.

The formulations hereof offer definite advantages over the water-thin, non-dilutable type wavesets. Firstly, they are easier to apply, the increased viscosity thereof offering better control of distribution on the head. They are not as stiff and tacky as are some of the known wavesets in the aforesaid category; they leave the hair softer and provide it with a more natural feeling. Too, they can be more economically prepared, they being dilutable. They do not flake as do some of the known wavesets and they do not dull the luster of the hair as do some of these.

Hair which has been treated with the composition of this invention holds for a long time the form or shape which has been given to it. Because of the hygroscopic properties of the treated hair, as has been explained, the hair remains flexible and retains its normal luster and color. The flexible film on the hair gives it a smoothness which is not attained with gums. The solutions possess a unique advantage in that they are somewhat thixotropic and pseudo-plastic so that they are easily worked into the hair. They have the further advantage in drying of not passing through the sticky stage which makes many other materials very difficult to apply properly and allows hair to be more easily arranged. The films which are deposited are relatively thin yet highly effective. This preserves a natural appearance of the hair.

If desired, a concentrated form of the preparation may be prepared for convenience in shipping and to which water may subsequently be added to prepare it for use.

When the preparation is applied to the hair and then dried, a durable coating is formed about each strand of hair. Each strand is thus provided with its own individual sheath of dry but resilient material which is transparent and highly glossy and enhancing to the appearance of the hair.

Without further analysis, the foregoing is intended to so fully reveal the gist of my invention that others can, by applying current knowledge, readily adapt it for various applications without omitting features which, from the standpoint of prior art, fairly constitute essential characteristics of its generic and/or specific aspects. The substitution of equivalents and other changes, modifications and alterations as circumstances may suggest or render expedient, are contemplated since the invention is susceptible of such without departing from its real spirit or underlying principles. Stated otherwise, it is not desired to limit this invention to the exact composition described as the objects hereof may be attained by the use of formulations different in certain respects from that disclosed.

Having thus described my invention and the best manner of practicing the new process for forming the novel composition thereof, all without limiting myself to the order of steps of such process recited, or to the proportions of parts employed therein, or to the precise ingredients named therein, as it is evident that each of these ingredients named therein has a considerable range of equivalents and as it is further evident that the order of steps and proportions of parts employed may be varied without departing from the scope and purpose hereof, what it is desired to claim and secure by Letters Patent of the United States is:

A process of shaping human hair comprising the steps, applying to the hair an aqueous solution containing, a salt selected from the group consisting of sodium and ammonium salts of a copolymer of ethylene oxide and maleic acid in a concentration of less than 1.00% neutralized by the addition of an alkali, an ethylene oxide condensate of oleyl alcohol containing 5–50 mols of ethylene oxide to oleyl alcohol, a methyl ester of parahydroxybenzoate, and dimethyl siloxane, said solution forming a pliable mass, working and shaping said mass into a desired form, and drying the shaped mass for depositing upon the hair a thin hygroscopic coating substantially free of tackiness and flaking tendencies.

References Cited in the file of this patent

UNITED STATES PATENTS

2,055,456	Eichwald	Sept. 22, 1936
2,378,629	Hanford	June 19, 1945
2,387,755	Hanford	Oct. 30, 1945
2,396,785	Hanford	Mar. 19, 1946
2,766,214	Erchak et al.	Oct. 9, 1956
2,913,437	Johnson	Nov. 17, 1959
2,930,775	Fordyce et al.	Mar. 29, 1960
2,938,016	Johnson	May 24, 1960

OTHER REFERENCES

Lourie: Soap, Perfumery and Cosmetics, April 1940, pp. 238–242, 244 and 264.

Greenberg: Handbook of Cosmetic Materials, Interscience Publ., Inc., New York (1954), p. 176.

Schimmel Briefs, No. 272, November 1957, 1 p.

D and C, Drug and Cosmetic Industry, 83:5, November 1958, p. 662.