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HAIR CURLING PROCESS

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This invention relates to compositions which have utility in developing a more or less permanent set to hair, as conveniently applicable for hair curling in cosmetic usages, for treatment and manufactures, etc.

A large number of chemicals have been used in the general field of hair curling and hair waving. These operations are designated in cosmetic practice by such terms as "permanent waving," "finger waving," "curling" and the like. Originally, such cosmetic operations were carried out by professional operators, and in rather luxurious establishments known as beauty parlors. A recent trend as a result of technological advances has been the development of a variety of compositions which more or less simply enable the individual to carry on the manipulations at home with techniques so simplified that the services of a professionally trained operator are unnecessary.

The art of hair curling or waving has proceeded along a variety of paths all stemming initially from the permanent wave processes. Permanent waving in the traditional sense is almost completely mechanical and is based on the fact that hair stretches very substantially when wet or steamed. In a mechanical type permanent waving, the hair is curled when wet around suitable forms and the heating continued until the operation is completed. This operation takes advantage of the fact of non-uniform stretching as the result of flattening an otherwise uniform cross section of hair, thus giving rise to the well recognized fact that round cross section hair is not curly and flat cross section hair is curly. Curling is developed as a result of a production of a strain on one side of the hair shaft and not on the other.

Hair waving through use of chemicals is accomplished in a variety of ways. A very common procedure in the finger wave process is the use of gums or resins, a small amount of gum dissolved in a suitable menstruum being applied to the hair during the curling process and the curl is then set by evaporation of the solvent. This process may be further modified by the addition of weak alkalies. Such weak alkalies have a profound softening effect on hair or fur. Softening makes the hair more plastic, thus taking the curl more readily, and the gum acts as the setting or stiffening agent. A simplified procedure eliminates the use of gum and depends almost entirely on organic alkalies such as ethylenediamine, alkalies based on ammonium such as ammonium hydroxide or ammonium carbonate, and fixed alkalies such as sodium hydroxide, sodium borate, and sodium phosphate or sodium carbonate. A third group of reagents sometimes used for hair waving are sulphites of ammonium, soda, and a variety of organic amines. These sulphites are invariably used in combination with alkalies. The action of the sulphites is not completely clear, but appears to be due to a reaction between the cystine, the sulphur-containing component of hair, and the sulphite radical. Another group of materials now coming into prominence for home waving are the so-called "permanent cold waves." These are primarily based on dithioglycolic

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acids and their alkali derivatives. Such materials evidently act through reaction with cystine. A final group of preparations is designated as "instant curl." Such combinations usually involve the use of mixtures of iron sulphate and citric acid in which the citric acid is the softening agent and the iron sulphate is the setting agent.

The essence of a hair waving procedure thus has involved two general steps. First, a means for softening or plasticizing the hair so that it will take a set, and second a means for more or less permanently establishing the distortion thus produced. In the case of mechanical permanent waving, this softening is accomplished through use of water or steam and the setting developed as a result of drying such plasticized hair under tension. In the case of the "finger waving," the softening is accomplished through the use of alkalies and the setting obtained through use of drying on suitable forms with the aid of a gum or resin solution. In the case of the sulphite type curling, the softening is again accomplished through the use of alkali and the permanent setting develops after drying through the reaction of hair material and the sulphites resulting in unequal stresses. In the case of the "home type permanents," the softening and setting is accomplished through use of thioglycolic acid derivatives, the permanent sets being obtained as a result of chemical reaction between thioglycolic acid and the hair material. In the case of the "instant hair curling" devices, the citric acid is the softening material and the iron sulphate develops the set.

All of these procedures are subject to a number of disadvantages. For example, the chemical type of permanent waving is very expensive, and in addition, its continued use tend to make the hair brittle and lifeless. The "finger wave" procedures involving the use of gums or combinations of gums with alkali softeners have the disadvantage that the drying time is of the order of 60 minutes under a warm air dryer and the gums used tend to deposit white flakes or scales and develop a somewhat unsightly condition. In the case of hair lacquers, where the resin contents are substantially higher, the hair comes out quite harsh and stiff. For the types of solution involving sulphites, these are based on the presence of cystine and as a result, the sulphite type combinations will not develop permanent set in bleached hair, hair which has been exposed to sun for extended periods, or the hair of pregnant women, such hair being substantially entirely lacking in cystine. The same sort of drawback exists in the thio-derivatives, which are considered dangerous since these materials are sometimes powerful skin irritants and develop long standing skin irritations and skin inflammations in individuals who are allergic or sensitive to such chemicals. The "instant hair curling" devices described above are not universally effective; that is, for as yet unexplained reasons they will not develop curl in all types of hair or fur. In addition, however, in view of the colored nature of the salt, light colored hair such as white, gray, blond, and bleached types, tend to be discolored, and sometimes in a streaky fashion.

In accordance with the present invention, a preparation may be had which eliminates the disadvantage of the various combinations heretofore available, and is furthermore effective on all types of hair, whether colored or not, and the setting is also more direct than with materials heretofore customary. And withal, the method of application is very simple, requiring no particular skill, heat being unnecessary.

To the accomplishment of the foregoing and related ends, the invention, then, comprises the features herein-after fully described and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these

being indicative, however, of but a few of the various ways in which the principle of the invention may be employed.

I have found that zirconium in suitable soluble form is a protein precipitant and is also a curliness-inducing agent if applied to hair, and the end product of the action is water-insoluble. Once this action takes place, a stable, permanently soft, water-insoluble or water-resistant product results. As vehicle or carrier for the zirconium agent, I employ a liquid providing organic hydroxyl and carboxyl groups. Thus, the essential zirconium agent may be zirconium in a form dissolvable, this being the essential component, and soluble salts of zirconium, i. e., mineral acid salts or organic acid salts may be applied, as, for instance, such mineral acid salts as chloride, oxychloride, nitrate, sulphate, etc., and zirconium compounds with somewhat milder action or not quite so astringent, such as the double salts, e. g. sodium, potassium, or ammonium zirconium sulphate; sodium, potassium, ammonium, calcium or magnesium zirconium chloride, or similar derivatives of the nitrate. Again, milder and even less astringent zirconium compounds available are the organic acid salts, e. g. acetate, lactate, gluconate, etc.

As indicated, the vehicle includes organic hydroxyl and carboxyl groups, and most conveniently these may be supplied by a hydroxy carboxylic acid, sometimes called alcohol acid, as for instance citric, tartaric, glycollic, hydroxypropionic, lactic or hydracrylic, glyceric, gluconic, etc. Depending upon the particular hair, some range in use of materials is available. Thus, where the hair is relatively coarse, a higher concentration of the zirconium compound is more useful than where the hair is relatively fine. Correspondingly, the concentration of zirconium compound and hydroxy carboxylic acid may vary from about 1 to 20 parts of the zirconium compound to 2 of the acid, or in general, about 10-35 per cent of zirconium. Variations extending beyond this range are feasible, but not so desirable. Where using a double salt of zirconium, as, for instance, the sodium zirconium sulphate above-mentioned, by reason of the lower zirconium content the amount of such double salt in the composition should be increased, as for instance by about one-fourth.

Preferably, there is also included an agent which is surface-active in acid medium, as this adds to the effectiveness of the treatment. In general, such surface-active agents are alkali metal sulphates of long-chain alcohols or modified esterified higher fatty acids. Illustrative agents are sodium alkyl naphthalene sulphonate, polyoxyethylene ethers of higher fatty alcohols and alkyl phenols, sodium 2-ethyl hexanol sulphate, etc., such being commercially available under the trade names, for instance, "Alconox," "Igepal," "Tergitol," etc.

In applications involving cosmetic usages, in order to avoid skin irritation, the acid concentration of the solutions should not be greater than about that equivalent to a pH of 3.5. If, however, such a concentration is exceeded, the pH may be adjusted into the range around 3.5, as up to 5.5, by the addition of borax or sodium acetate.

In applications involving animal hair, as in the treatment and preparation of furs, there is no limitation as in the case of cosmetic usages, and stronger solutions can be applied.

The manner of application is simple. After washing the hair, one or two ounces of the mixture of preferred composition is dissolved in a quart of hot water, and this solution is applied as a rinse. Again, there may be first a treatment with the organic acid solution, then a rinsing, and then treatment with the zirconium compound. Where it is preferred, the hair may first be washed or shampooed, and a solution on the order of, for instance, an ounce of the essential zirconium ingredient per pint of solution may be applied by a comb or brush. Or, in some cases, such solution may be applied without the preliminary shampoo. The solution may be sprayed on

the hair until thoroughly dampened, and the usual curlers or like mechanical holders may be applied. Or, curlers consisting of an absorbent cloth wound on a wire may be immersed in the solution and the hair curled wet around the device and allowed to remain in contact for several minutes, after which it is removed and the hair is rinsed in clean water. As a result of the washing step, the excess soluble salt is washed out, and no residue remains, and the hair is then set. The nature of the material is such that skin irritation does not occur, and the procedure is economical and simple and may be carried out rapidly without hazard.

Where dealing with animal hair or fur, it is desirable to first thoroughly wash the hair with a detergent shampoo to remove oily matter, then, after rinsing, the excess water is wiped off, and while the fur is still wet it is treated with a solution of a mineral salt of zirconium together with an agent which is surface-active in acid medium. The concentration of the zirconium salt may be in general 5 to 10 per cent. The animal fur is set with curlers or like mechanical devices, is allowed to remain thus for about an hour, and the fur is water rinsed and is dried.

In a slightly different manner of procedure, the fur after shampooing is treated with a 5 to 10 per cent solution of citric acid, and then is curled by the usual mechanical devices, and in this curled form is then treated with the zirconium solution described about, the surface-active agent being desirably included in both the citric acid bath and the zirconium compound bath. After about an hour, the fur is water-rinsed and dried.

Again, the fur may be treated with the organic acid and zirconium compound in one bath, convenient proportions being, for instance, 10 to 20 parts of zirconium compound to 1 part of citric acid or the like. After shampooing, the fur is thoroughly wetted with this solution, and is put up in curlers or like mechanical devices and is allowed to stand for about an hour, being dried without removing the mechanical curling devices. After thoroughly washing with water, and drying, the mechanical curling devices are removed.

Illustrative examples are as follows:

I. Five parts of dry powdered zirconium sulphate is mixed with two parts of powdered citric acid. One ounce of this material dissolved in a quarter of warm water is the setting solution for home waving.

II. Two parts of citric acid powder is mixed with one part of zirconium sulphate powder.

III. Same as Examples I and II except that zirconium oxychloride is substituted for the sulphate.

IV. Same as Examples I and II except that zirconium nitrate is substituted for the sulphate.

V. 6.25 parts of sodium zirconium sulphate is mixed with two parts of powdered citric acid.

VI. Two parts of citric acid is mixed with 1.25 parts of sodium zirconium sulphate.

VII. Same as V and VI except that ammonium zirconium sulphate is substituted for the sodium derivative.

VIII. Same as VII except that sodium zirconium chloride, ammonium zirconium chloride or potassium zirconium chloride or magnesium zirconium chloride or calcium zirconium chloride is substituted for the sodium zirconium sulphate.

IX. Same as I or II except that the organic acid is tartaric.

X. Same as I or II except the organic acid is glycollic or lactic or glyceric or gluconic, or hydracrylic. In these cases, the effective reagent is supplied in the form of a concentrated solution in which a solution consisting of 25 parts of the combination and 75 parts of water is used.

Other modes of applying the principle of the invention may be employed, change being made as regards the detail described, provided the features stated in any of the following claims, or the equivalent of such, be employed.

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I therefore particularly point out and distinctly claim as my invention:

1. In a process of treating hair for imparting curliness thereto, the step of subjecting it to a solution of a zirconium compound and a hydroxy-carboxylic acid.

2. In a process of treating hair, imparting curliness thereto by subjecting it to a dissolved zirconium compound and a hydroxy-carboxylic acid and an agent surface-active in acid medium.

3. In a process of treating hair for imparting curliness thereto, the step of subjecting it to the action of a solution of a zirconium salt and a hydroxy-carboxylic acid and an agent surface-active in acid medium.

4. In a process of treating hair for imparting curliness thereto, the step of subjecting it to the action of a solution of a zirconium salt and citric acid.

5. In a process of treating hair for imparting curliness thereto, the step of subjecting it to the action of a solu-

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tion of a zirconium salt and citric acid and an agent surface-active in acid medium.

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