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PREPARATION FOR WASHING LIVING HAIR

Ehrhart Franz, Leipzig, Germany

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1 Claim. (Cl. 252—161)

This invention relates to a process for washing living hair and to agents adapted to carry out this process.

It is a continuation in part of applicant's United States patent application, Serial No. 656,594 of February 13, 1933, on Process of washing living hair.

It is an object of this invention to provide an agent, which effectively cleanses living hair; but the agents shall not injure the hair; i. e. they shall not cause loss of vitality; nor render the hair unduly sensitive nor change its normal behavior in respect to light, weather or exudations of the body; nor shall such agents unfavorably affect the physical behavior and properties, or the chemical composition of the hair.

The invention concerns treatment of the living hair with washing agents comprising organic compounds of hexavalent sulphur of the general formula $R—SO_3—Me$, in which:

R represents an organic radical of the aliphatic series, particularly a straight aliphatic chain having more than 10 carbon atoms; R may be substituted, e. g. by a nitrogenous radical; and it may comprise for connection with the $SO_3—$ radical an oxygen atom or certain organic groups.

Me stands for a metal of the alkalies or a nitrogenous radical that is salifiable.

Compounds of this class have been applied before for washing textiles, but only together with soap which is added to a solution of such a detergent or formed in the textile material from the oleic acid or a salt thereof due to greasing. However, a neutral or acid washing process with the compounds in question has never been adopted by the textile industry; the usefulness of these compounds was thus restricted to a few limited, special applications, in connection with which their defects and costs were favorably offset by certain advantages; and for that reason they were used in preference to other agents.

My experiments have revealed, however, that the compounds referred to excel at a surprising degree in the treatment of living air in the presence of certain substances which possess protecting and conserving characteristics, and their use in this respect constitutes a considerable advance in the art.

It is well known that animal and especially human hair is seriously injured when treated with the usual washing agents. Such substances, which rely on an alkaline action, attack the protein molecules of the hair, the micellar structure is loosened, and the hair loses its luster, becomes brittle, hard and inelastic, and at times even changes in color. The harm which is thus caused cannot be counteracted and overcome by the most thorough rinsing, nor by after-treatments with acids, which are to remove the adsorbed alkali.

Hair consists of very complex protein molecules which are arranged like threads to form micellae. The diversity and complex arrangement of the elements aggregating such molecules involves great exposure to attack, and in the protein molecule numerous chemical reactions find an opportunity to set in. The inner structure of the molecule, i. e. the grouping of basic and acid radicals, insures interior neutralization of the intramolecular kind, and only the sum of such intramolecular neutralizations affects the outer character of the molecule and thus of the hair.

Normal hair has an isoelectric point corresponding to a pH value of 4.6, so that the compound is comparatively strongly acid. Aqueous washing solutions having such a pH value exert no influence upon the hair because it remains neutral and indifferent to them. But solutions of lower and higher pH values are capable of reacting upon the hair, for example they cause a swelling of the hair. Such swelling, however, is harmful and a start of further and greater damage.

On the other hand, all the ordinary washing agents show a greater washing power at a higher pH value; but if aqueous solutions of such higher pH value are used in treating hair, particularly human living hair, extraordinary injury will be inflicted, even though the hair may be exposed to their action for only a very short period of time. Under these conditions such washing agents should have a pH value of less than 7. If we use, for instance, soap at a pH value of 7, and thus face the fact that a certain amount of the damage will be done to the hair, the cleansing effect is not only practically nil, but in addition, the hair will be soiled by fatty acid which has separated. Therefore soap and products containing soap are not suited all for acid washing living hair.

The use of soap involves additional disadvantages: Frequent washing of living hair irritates the capillary matrix and causes excessive secretion on the part of the sebaceous glands. This is due not only to excessive degreasing of the capillary matrix and the hair, but all solutions which react alkaline lead to similar phenomena. Such abnormal activity of the sebaceous glands expedites the greasing of the hair which proceeds from the root in the direction of the tips of the hair; there is new cause for soiling of the hair, so that the hair will have to be washed again after a short time and the new irritation stimulates the sebaceous glands still more. It finally becomes necessary to wash the hair every other or third day. It has been attempted to overcome this drawback by adding astringents, such as weak tanning agents like tannin, acids, etc.; but without much success, because the astringent effect of such agents is known to be quite low in the higher pH range, and the washing action of soap is limited to pH values over 7.

The marked degreasing effect of the new washing agents of this invention, which is still greater than that of soap, raised the presumption that in their use on hair the above-mentioned drawback would become still more pronounced than in case of soap. It is surprising, that the opposite could be proved: The irritation of the sebaceous glands is greatly reduced. This is due to the constitution of the new washing agents, which insures an astringent effect by virtue of the neutral acid state of the aqueous solutions.

The washing agents of this invention can be used in the range of pH values below 8 so that they act as tanning substances. That effect can be intensified by suitable additions of acids and the like to the extent of excluding any excessive secretion of fat. A shortage in the secretion of fat can be offset by the addition of fatty substances to the washing agent or by greasing the hair during or after washing.

Comparative tests with modern washing agents employed in washing wool and other dead hair do not shown any superiority over soap, except that the washing time is sometimes shortened a little and the washing material is opened more. Inventor's experiments, which have been confirmed by many other authors, show that neither the elastic properties nor the ductility, length and thickness of the hair are differently influenced by one or the other of the groups of washing agents. It was therefore quite surprising to find out that conditions are totally different in respect to living, and more particularly to human hair.

Washing agents for living hair, such as shampoos, act not only on the hair that has come out of the root, but also on the root itself, at least upon the upper part thereof, as well as on the papilla and the capillary matrix. In so far as the customary washing agents contain alkali or lipoid-soluble substances, such as organic solvents or lipoid-soluble by-products, there is always danger that not only the hair, but also the growth of the hair, i. e. the root and the capillary matrix, will be injuriously affected.

Their excellent cleansing action notwithstanding, all organic solvents must therefore be eliminated. It cannot even be predicted whether the water-soluble solvents, as polar compounds, still possess too much solubility in lipoid and thus might injure the centers of growth of the hair.

Organic solvents are capable of separating the intra-capillary and intramicellar fat from the hair; they replace this fat to a large extent in the intermediate spaces where they are difficult to remove, so that it is not possible duly to supply fat to the spaces occupied by them. It has been found out long ago that too much degreasing means enormous damage to the hair. Such degreasing is not possible, when we wash in an acid medium.

Furthermore, when washing with the new washing agents of this invention, especially in a medium of lower pH value, a fat or a fatting agent may be added to the washing agent or the washing mixture. During such a washing, the new washing agents, as complex molecular substances, are unable to enter the interior of the hair. The surface only is degreased, and by adding fat to the washing agent undesirable degreasing is avoided.

For washing a highly sensitive material like living hair, special preparations of the agents in question should be used, from which inorganic and organic impurities have been substantially removed. With such preparations it is possible to wash at pH values which approach very closely the iso-electric point pH=4.5 of the hair, especially at pH values at which washing with soap is out of question.

Soap causes further injuries. Hard water, i. e. water containing lime, magnesium salts or others, leads to the formation of sebacic fatty acid salts insoluble in water while the lime liberates alkaline hydroxide; the precipitated salts embed in the surface capillaries and cracks and are capable, by pressure of crystallization of loosening the hair. The embedded salts also promote trituration of the hair, due to mechanical stressing. The magnesium and lime soaps, which are produced, also have the disadvantage of being filtered off in the hair, of reducing its luster and of decreasing the speed of drying.

In the treatment of living hair with mixtures of this invention the hair retains its chemical composition and its physical and biological properties and is merely freed of dirt and excess fat. The applicability of the washing agents of this invention under the conditions and for the purpose stated could not be foreseen and had to be ascertained by methodic and exact experiments. All agents found to be suitable have the common feature that they contain more than 11 carbon atoms preferably arranged in an aliphatic chain.

From the point of view of physical chemists the compounds represent polar compounds, i. e., they possess a group insuring solubility in water and a complex pyridine-like rest. There are first the sulphuric esters or their salts which can be produced from acids like lauric, myristic, palmitic, stearic and oleic acid, by means of a reduction of said acids to the corresponding alcohols, or directly from the alcohols. Compounds containing an uninterrupted chain 12, 14, 16, 18 of carbon atoms in the molecule are suited. Compounds with less than 11 carbon atoms are no washing agents proper, though they may be useful as foaming additions. Compounds with 11, 13, 15, 17 and 19 carbon atoms do not come into question because they are not commercially available. In other configurations compounds with more carbon atoms may be considered, but in the straight line chain only the first mentioned compounds with 12, 14, 16 or 18 carbon atoms come into question, e. g. butylmethylcyclohexanol sulphuric acid; octadecenoylmethylaminoethanol sulphuric acid or its sodium salt; hexadecoyloxyethanol sulphuric acid or its ammonium salt, dichlor-octadecoylaminopropanol sulphuric acid or salts thereof, chloroctadecanol sulphonic acid salts, similar halogen salts, etc.

Such compounds, so-called sulphuric acids or sulphates, should be in their pure state; in particular lipoid-soluble by-products, such as the di-alkyl-sulphates, must be eliminated. Furthermore, inorganic by-products developed during production, especially sodium sulphate, should be removed from the preparation to a predetermined extent. The presence of such salts must be carefully limited, since any loading of the living hair with such inorganic products is undesirable; they represent or lead to injury.

Particularly useful are the above mentioned sulpho acids, or salts thereof, corresponding for example, to the sulphuric esters mentioned, as they can easily be obtained from these esters with the acid of sodium sulphite, though the sulpho salts are somewhat less soluble than the corresponding ester salts. However, such sulpho acids, unlike any of the esters, cannot decompose under the action of catalysers and enzymes by dividing into the alcohol and the sulphuric acid. That would cause considerable injury and irritation to the living hair. Therefore the said sulpho acids as well as their salts are generally to be preferred. But that does not preclude esters, which have been carefully prepared to prevent decomposition, or which are protected against decomposition by suitable additions, as known.

It is further possible to employ compounds which carry in the aliphatic rest a carboxyl group which should be closed by esterification preferably with the aid of butyl alcohol.

Among the suitable sulpho acids and their salts those are particularly useful which contain, besides the sulpho group, a hydroxyl-like radical which has a slight polar effect. As such radicals serve, above all, the carbonamides and sulphamides. Examples of compounds with sulpho groups and acid amide groups with an uninterrupted aliphatic chain with a straight series of more than 11 carbon atoms are oleic acid-amide-sulpho acid, oleoylamidethane-sulpho-acid, oleoylmethylamidoethane-sulpho acid, dodecoylamino-propanesulpho-acid, tetradecylsulphamidoethanesulpho acid, methionic acid-monocethylamide, and the corresponding carbonamide of the sulphopropionic acid (sulphopropionylethylamide). An equally useful compound containing an aromatic residue is oleoylaminosalicylsulpho acid, in which between the sulpho group and the aliphatic chain the salicyl radical has replaced the ethylene radical.

Excellently suited are further the aliphatic thiosulphates, compounds which may be regarded as sulphuric esters of aliphatic thioalcohols or salts thereof. They can be readily obtained by conversion of the above mentioned sulphuric esters with sodium thiosulphate, or from the corresponding alkyl halides by conversion with sodium thiosulphate. Such compounds are much more stable than the corresponding alcohol sulphuric esters. Special mention of this series deserves sodium dodecyl-thiosulphate, sodium hexadecanthiosulphate. The last-mentioned compounds are effective for preventing scale, and this effect may be imparted to the washing agents also by the addition of compounds like resorcin ether, cystin and the like.

All the compounds mentioned can be applied in the form of their salts, of which the alkali and ammonium salt are especially useful, though the salts of other organic bases, like the salt of triethanolamine or ethanolamine or aminoglycerine, can be employed also.

When the acids are used, or, generally, for the purpose of preventing too low a pH value, the addition of buffer substances, such as sodium bicarbonate, phosphates (ortho-, pyro- and metaphosphates) borates, tartrates, citrates and the like, may be advisable. By use of the salt the buffer agent may become a weak acid or an acid salt. The use of washing acids (W—SO$_3$H) together with buffering salt is the same as the use of washing salt together with buffering i. e. weak acids

$$\text{W—SO}_3\text{H}+\text{Na borate}\rightleftarrows\text{W—SO}_3\text{—Na}+\text{boric acid.}$$

Together with ester salts it is preferable to add a salt of a weak acid for neutralizing, i. e. as a buffer against whatever sulphuric acid or acid sulphates may be generated.

Together with said washing agents or washing agents and buffers we may use compounds which diminish or make possible an attack upon the material; they suit such purpose if they either increase the washing effect, or have protective characteristics of the order found in the above-mentioned fatty agents and fats.

As agents for enhancing the washing effect may be used compounds like sodium octanolsulphate, Turkey red oil, isobutylnaphthalenesulphonate; certain inorganic salts, e. g. sodium sulphate and metaphosphates; or substances capable of a bleaching action such as sodium perborate or an alkali salt of isobutylnaphthalenepermonosulphuric, permonosulphuric acid, or dodecyl-sulphuric acid; or substances which give off hydrogen peroxide like urea peroxide.

As preserving agents protein compounds are particularly suitable, or protein decomposition products like sodium lysalbinate or protalbinate or sebacinate. Compounds like these are useful because they displace the isoelectric point of the hair in the direction of higher pH-values; they also act as buffers, because they counteract the destructive effect of larger amounts of alkali.

For the same purpose albuminous products like gelatin and glue may be used. Other water-soluble compounds yielding solutions which are to a large extent colloidal, such as sugar and sugar-like products, have a similar effect.

Examples

(1) Angora rabbit hair is dusted with sodium dodecyl-sulphate, containing 1% tartaric or citric acid. By the use of lukewarm water, the preparation is caused to foam in the hair until foaming ceases. The wash is allowed to act for some time, and then it is rinsed in lukewarm water. The hair will be found to be perfectly clean; it has been sufficiently but only superficially degreased; and it is loose and soft.

(2) Living animal hair is treated with a solution containing 2% of hexadecylsulphonic acid and 1% of sodium borate or borax at about 30° to 35° C. After treatment the hair is thoroughly rinsed, and dried as usual. As necessary, fat may be introduced into the hair.

(3) Human hair is treated with a 1% solution of sodium oleoylmethylaminoethanesulphonate at 40° to 50° C., containing preferably a weak acid or an acid salt, such as sodium bicarbonate or bitartrate. A heavy foam is produced, and is allowed to remain 3 to 5 minutes in intimate contact with the hair. Then the hair is thoroughly rinsed with lukewarm water. It is advisable to add to the hair during or after washing a certain amount of fatty substance, especially when the hair is poor in fats. Instead of the sodium salt an organic salt of the sulpho acid may be used, such as the triethanolaminates of such an acid.

Preparations for treating living hair should be used in as pure a state as possible; such state can be effectively and simply attained as follows:

The commercial preparation is boiled with 6 to 10 times the amount of ethyl alcohol, so that the organic salt passes into solution, all inorganic impurities forming the residue. In order to economize in solvents, the preparation may be extracted by means of a suitable extracting device; when the alcohol cools off, the organic salt will usually divide out. After evaporation of the alcohol, the product is dried and then treated with benzine, benzene or the like in order to remove water-insoluble impurities. One of the greasing agents mentioned above, e. g. wool grease, and/or a buffer such as weak acid or an acid salt of such weak acid to the washing salts, or a salt of weak acid to the washing acid may be added, and the washing process cannot possibly harm the hair. Even if this reduces the washing power to a slight extent, it also prevents excessive removal of fats from the surface of the hair.

(4) 40 parts by weight of sodium dodecanol sulphate (freed of organic impurities by dissolving in alcohol), or like parts of ammonium tetradodecyl alcohol sulphuric sulphate are dissolved in 100 parts of water. While stirring well approximately 4 parts by weight of the hydrophile portion of wool fat (lanolin) are added, and so much citric acid, as necessary to start litmus paper to turn red. By suitable addition the resultant colloidal solution may be colored and/or scented, as circumstances may require. The product is an excellent solution for washing hair, and is particularly useful for hair lacking fat. When hydrogen-peroxide is admixed to the hair washing solution, we obtain an excellent hairwash for combined bleaching and washing effects.

(5) Like the sodium dodecanol sulphate we may also purify triethanolamine, or sodium octadecenoylmethylaminoethanesulphonate, or sodium octadecenoyloxyethane sulphonate by dissolving in alcohol and by extraction of a watery solution with petroleum ether or benzene. The sulphate or any one of the other compounds so purified is reduced with water to a paste, using substantially the aforementioned proportions.

Instead of the salt we may use the corresponding acid in whole or in part, adding as a buffer the salt of a weak acid, say 10 parts of sodium tartrate.

Into such a paste we work burdock oil, until a saturation point has been reached, such a point being indicated in a diluted sample by the formation of oily drops. Into the resultant paste we may introduce a perfume, as customary. This kind of a preparation is particularly suited for giving a second wash to hair, from which too much fat had been removed when it was washed the first time. But the fatty contents of the preparation may also be adjusted in order to render it suitable for a general hairwash, by reducing or increasing the fatty contents in the case of normal hair or of hair which is short in fat, respectively.

(6) 100 parts by weight of sodium dodecyl sulphonate, which may have been purified as suggested above, are mixed with 30 parts in weight of sodium octylsulphate, and they are pulverized in a suitable container. They are mixed together with 10 parts in weight of finely ground commercial sodium bicitrate or with 5 parts in weight of citric acid powder.

Very fine powder of bran of wheat may also include some colloidal clay. The hair is dusted with the resultant hair-washing powder, moistened and worked until a foam of fine structure is formed, which is allowed to remain in contact with the hair for a short period of time. For a rinse a 0.1% solution of sodium dodecyl sulphate is advisable to use. An emulsion of lanolin in a solution of sodium dodecyl sulphate or sodium hexadecyl sulphate, hexadecyl alcohol may be added, may be applied to and worked into the hair, before it is finally rinsed with clear water.

(7) 30 parts by weight of purified sodium tetradecanol sulphonate, which has been well dried and comminuted or which has been reduced to a fine powder by simultaneously atomizing and drying a watery solution thereof, are mixed with 25 parts by weight of soluble, completely dry starch. 15 parts of well dried di-sodium phosphate and 20 parts of sodium bicarbonate are added.

This hair washing preparation yields a very fine, dense foam, the formation of foam being enhanced by the effervescence of carbon dioxide. The above-mentioned purified washing agent may be others, e. g. ammonium dodecanol sulphate or sodium dodecanol sulphate. Such a washing powder is preferably sprinkled in a dry state unto the hair which is in a dry or slightly moistened state. The powder may be scented, if so desired.

(8) 40 parts by weight of purified, well dried sodium dodecanol sulphate or triethanolamine are well mixed with 30 parts by weight of sodium bicarbonate, 15 parts of soluble starch and 15 parts by weight of acid sodium pyrophosphate, and may then be suitably scented. This preparation has characteristics similar to those of Example 7.

The washing agent may be replaced by others, or we may use a mixture of several washing agents. For such substitution or mixture we may also use the sodium salt of the sulphuric acid ester of cocoanut oil. Not particularly useful by itself, but excellent in mixture is the sodium salt of the sulphuric acid esters of blubber (hexadecanol palmitate).

Not all similar compounds having corresponding constitutions can be used, but only those that, in aqueous solutions, show a certain colloidal condition externally indicated by foaming. Some of these compounds are capable of foaming at low temperature, e. g., 18° C., but at higher temperature they will pass into genuine solutions and lose their foaming capacity. Only acids and salts which are capable of foaming at both 18° and 50° C. can be used. This foaming and washing power is not exclusively dependent upon the acid, i. e., the anion, but also upon the cation. Sodium salt for instance sometimes foams in colloidal solution, whereas the more easily soluble potassium or ammonium salt will be in genuine solution and not foam any more. Only the sodium salt will then be useful, though, on the other hand, a difficultly soluble salt might be useless simply because of this difficulty and because it tends to precipitate from the solution at low temperature, so that only solutions of higher temperature can be used. Foaming capacity can be ascertained in a very simple manner. All that is necessary is to fill a 1%-2% solution of the washing agents into a half-filled cylinder at the temperatures stated, shake it for 30 seconds and allow it to stand. The foam should keep for at least 2 to 3 minutes.

All preparations of this invention react acid upon phenolphthalein. Such washing agents give a hair of excellent properties. Especially the lustre of the hair is brilliant and the fresh parts of the hair directly over the papille, being not yet horned, are not affected.

What I claim is:

An acid preparation free of organic solvents and soap, serving for washing living hair and comprising as the washing agent a stable aliphatic compound having the formula R—SO_3—Me, wherein Me is selected from the group consisting of sodium, potassium and ammonium, and R is an alkyl radical having an aliphatic series upward from 11 carbon atoms. connected to the SO_3 by way of a link taken from the group consisting of —O—, —S—, —CO—NH—R'—, —CO—NR''—R'—, —CO—O—R'— and —O—R'—, wherein R' stands for an alkylene radical and R'' for methyl or ethyl, in combination with a weakly acid ingredient of a quantity sufficient to render the whole preparation acid in reaction.

EHRHART FRANZ.