The invention relates to a manufacturing process for the treatment of hair and hair-bearing epithelium, which preparation is therefore suitable for treating the hair of the head and beard, for example before using an electric razor. It is for example known to use hair lotions, hair fixatives, setting creams, liquids containing alcohol, such as Eau de Cologne, and similar preparations for these purposes. By hair lotion is understood a perfumed alcoholic liquid which is diluted with water and which can contain certain additives for nourishing the hair and hair-bearing epithelium such as glycerine, lecithin, cholestrin and patent extracts, for example camomile and nettle.

By setting creams are understood perfumed emulsions of the water-in-oil or oil-in-water type, which in addition to the additives used in hair lotions, can also contain additives which make the hair suitable for waving, impart gloss thereto and enable the waves to last for a relatively long time.

By hair fixative is understood pleasantly perfumed and usually aqueous solutions, primarily of substances which impart a thinnest possible lustrous film to the hair, this film holding the hair for a certain time in the required setting, for example, polyvinyl alcohol, alkali alginates, tragacanth, tylose (carboxymethyl cellulose).

The invention is concerned with a universal agent for the treatment and care of the hair, this agent having the surprising and novel property of combining the effects of known treating agents, such as hair lotions, setting creams and hair fixatives, and being at the same time in such a form that it can be packed in tubes and consequently can be easily handled.

The agent according to the invention for the treatment and care of hair and hair-bearing epithelium contains an alcoholic gel of a synthetic, insoluble, lightly cross-linked carboxylic polymer in addition to at least 40% of alcohol, and is in the form of a paste or jelly.

The lightly cross-linked carboxylic interpolymers which are useful for preparing the products of this invention are described in U.S. Patents Nos. 2,798,053 and 2,858,280. The carboxylic acid component of interpolymers can be defined as an alpha-beta monomolecularly unsaturated acid. This includes monomers such as acrylic acid, methacrylic acid, ethacrylic acid, alpha-phenyl acrylic acid, crotonic acid, beta-acryloxy propionic acid, hydroxysorbic acid, sorbic acid, cinnamic acid, beta-styril acrylic acid, hydromucoic acid, lactic acid, citraconic acid, mesaconic acid, muconic acid, glutaric acid, anhydride, umbellic acid, maleic acid, fumaric acid and maleic anhydride.

It is known that maleic acid, fumaric acid, the beta-substituted acrylic acids and maleic anhydride will not homopolymerize to produce high molecular weight polymers and so when such acids are employed it is essential to use an additional monomer which will either homopolymerize or which will copolymerize with the maleic acid, fumaric acid or maleic anhydride to form an essentially linear water-soluble polymer. The comonomers which will copolymerize with maleic acid, fumaric acid or maleic anhydride include such monomolecularly unsaturated monomers as alkyl vinyl ethers having from 1 to about 8 carbon atoms in the alkyl groups, acrylic acid, methacrylic acid, ethacrylic acid, acrylic esters of lower monochloralalkylalcohols having about 1-8 carbon atoms, ethylene, isobutylen, butylene, styrene, vinyl esters of lower saturated aliphatic carboxylic acids, having from 1 to about 8 carbon atoms, vinyl benzoate, vinyl chloride, vinylidene chloride, vinyl pyridine, vinyl carbazole and other monoolefinic monomers which are known to copolymerize with the maleic or fumaric acids or maleic anhydride to form linear polymers.

The homopolymerizable acids, such as acrylic, methacrylic or other alpha lower alkyl substituted acrylic acids can also be used in admixture of at least 50 mole percent by weight of such acid with the other monomers mentioned above.

Mixtures of homopolymerizable acids can be used in any proportion.

The cross-linking agents are those which have an average of more than 2 terminally unsaturated vinylidene groups on the molecule. These include compounds such as the polyunsaturated ethers described in U.S. Patent No. 2,798,053 and the solvent-soluble diene polymers or copolymers having a plurality of vinylene or vinyl side chains, as described in U.S. Patent No. 2,858,281.

These polysaturated ethers are polyalkenyl polyethers of polyhydric alcohols containing more than one alkoxyl group per molecule, the parent polyhydroalcohol containing at least 4 carbon atoms and at least three hydroxyl groups. The alkonyl group has a terminal CH=—C< structure and contains from 2 to 4 carbon atoms. Thus, the alkonyl group can be vinyl, allyl or methallyl.

The polyhydric alcohol can be a butane triol, a tetrose, pentose or hexose sugar, an algalanoseharide, reduced derivates of said sugars, often termed sugar alcohols, or a "sugar acid."

The cross-linking agents of U.S. Patent 2,858,281 are soluble in solvents such as benzene and are made by polymerizing a monomeric conjugated diene hydrocarbon or a mixture containing at least 50% of a conjugated diene hydrocarbon and another monomer polymerizable with the diene in an inert solvent with an alkali metal catalyst. Representative dienes are butadiene-1,3, isoprene, piperylene and 1,2-dimethylbutadiene. Representative comonomers include styrene acrylonitrile, methyl methacrylate, methyl acrylate, vinylidene chloride and vinyl pyridine. This class of homo and copolymers has a high proportion of residual saturation present as vinyl side chains.

The amount of cross-linking agent used will vary somewhat depending on the properties desired in the final interpolymer, but usually from 0.1 to about 5% by weight of the combined weight of the other monomers, of which at least 50 mole percent is a carboxylic monomer. The remaining 50 mole percent of the monomer mixture is immaterial, and if a homopolymerizable carboxylic acid or a mixture of such acids is used, then only the cross-linking agent and the said acid or mixtures thereof need be used.

The preferred carboxylic acid monomer is acrylic acid and the preferred cross-linking agent is a polyalkyl succinates having from 5 to 20 such repeating groups per succo molecule. The preferred range of acid to cross-linking agent is 98-99% of acid and 1.0 to 2.0% cross-linking agent.

Especially suitable alcohols for use in the agent according to the invention are low aliphatic alcohols, such as ethyl isopropyl alcohol or other liquid physiologically acceptable alcohols. Other conventional substances for
nourishing the scalp or promoting hair growth can be added to the hair-treating agent. Thus for example stearins such as cholesterol, phosphatides, for example lecithin, pantethene acid or others, as well as for example perfumes and the like can be added to the alcohols. On the other hand, greasing and softening agents, such as glycerine, glycol or castor oil, can be added to the aqueous solutions of the gel-forming substances.

For the production of the agent for treating hair, such as beard or head hairs, and hair-bearing epithelium the gel-forming substance is introduced into a liquid mixture containing water and at least 40% of alcohol, and left to swell for a sufficient time, for example overnight. The gel former in this case is a finely divided powder, which can easily be dispersed in the water-alcohol mixture, for example by stirring.

As is usual with the swelling of gel formers, an acceleration of the swelling process can be obtained by mechanical movement during the production of the jelly, i.e. during the swelling. After the gel former has been swollen, it is advisable to stir again thoroughly and thereafter to neutralize the gel with the necessary quantity of a basic compound. Physiologically unobjectionable basic compounds, such as those which have for example previously been used in the cosmetic art, are suitable for this neutralization. As examples, there are mentioned alkali and alkaline earth carbonates, amines, such as triethanolamine and especially fatty acyl alkylamides.

Surprisingly, it was found that the described acid amides can serve to neutralize or form an addition compound with carboxylate polymers which forms a clear gel in a mixture containing a very high alcohol content. This activity is surprising because the NH₂ group in the amide is essentially neutral, and has lost much of its basic character because of its attachment to the group. Indeed, it is known that amides are unstable in the presence of mineral acids and that they are subject to hydrolytic cleavage in such systems. It was therefore unexpected that the fatty acid amides would thicken a mucilage of the cross-linked acidic interpolymer to form a firm gel in an aqueous mixture containing at least 40% alcohol by forming addition compounds with or neutralizing the polymer.

Typical fatty acyl alkylamides are those obtained by reacting fatty acids from natural fats or mineral or vegetable oils with an alkyl amine having at least one replaceable hydrogen on the nitrogen atom. The fatty acids contain from 8 to about 18 carbon atoms or more particularly from about 12 to 18 carbon atoms.

Representative amino alcohols that can be reacted with the fatty acids are mono-ethylamine, diethylamine, monopropanol amine, dipropylamine, monothanolamine, monopropanol amine, or other mono- or dialkyl amines in which the alkyl has from 2 to about 4 carbon atoms. The amides have the generic structure

\[
\begin{align*}
O & \quad \text{R} \quad \text{N} \\
\text{R}_1 & \quad \text{R}_2 \\
\end{align*}
\]

in which R is an aliphatic hydrocarbon radical of from 7 to about 17 carbon atoms, R₁ and R₂ each represents hydrogen, an alkyl or a polyalkyl group.

Concentrates of the N-alkyl substituted fatty acid amides have been used heretofore as foam stabilizers in shampoos. In the composition of this invention they supply fatty ingredients to the hair and scalp.

The amount of fatty acid amide can vary between about 0.5 and about 6.5% and particularly between about 0.75 and 5.0% based on the finished product. If desired, small amounts of triethanolamine 0.1 to 0.2% based on the finished product can be used in addition to the amide.

The amount of acidic interpolymer in the gel is relatively small and can vary between about 0.5 and 2% by weight of the finished product and preferably 0.7 to about 1.5%. This small amount of polymer forms a very thin film on hair or scalp so that the residue after frequent and repeated applications is not troublesome nor is it perceptible to touch.

The gel which is formed is clear, it gives a high gloss and is extremely stable.

By comparison with the prior known agents for hair treatment, the agent according to the invention in the form of a paste offers considerable advantages. Since the agent is a paste which can be packed in tubes, the handling thereof is extremely simple. By comparison with a lotion, it offers for example the advantage that it does not run out of badly sealed containers. Due to the high alcohol content, it has a disinfecting, astrigent and refreshing action in the same way as a conventional agent with a high alcohol content for the treatment of the skin and the scalp. After evaporation of the liquid, the selected gel former remains as a scarcely perceptible residue on the hair and on the skin. This residue is present in the form of a thin film, which has the property of not being brittle, but of being flexible and firmly adhering, so that when it is used as a fixative, a comparatively large quantity of the hair treatment agent can gradually be applied between the individual shampoos without any possibility of the hair being disturbed as a result of the gel former which had been applied becoming detached because of breaking of the film. After the gel has been applied, the hair feels soft and silky and no sticky or other undesirable residues are left on the hands after application. It is further shown that the agent according to the invention for the treatment and care of the hair can be applied over an unlimited period without any secondary properties detrimental to the use thereof becoming apparent. Due to the film formed on the hair and the hair bed, the particular gel former imparts a high lustre to the hair and also gives the hairs a certain rigidity. When the hairs have for example been brought to a particular position, they tend to remain permanently in this position, so that the hair can be more easily and better curled, although the new agent does not have a greasy action.

When used as a shaving auxiliary, more especially before using an electric razor, it is shown that the agent according to the invention produces a certain protection against mechanical irritation due to the film thereof formed on the skin. Due to having a film of the film, the surface of the skin is smoothed and the individual hairs of the beard are erected, whereby electric shaving can be carried out more easily. On the whole, a coherent and contracting film is produced, by which the difficulties which usually arise with electric shaving are obviated. This greater strength makes it possible to shave more easily.

The novel agent for treating and caring for the hair consequently combines the action of the various hair treating agents, such as hair lotion, hair fixative and setting cream. The use of the new preparation also makes the use of oil superfluous. Furthermore, the preparation offers the advantage that it can be used as a frictional agent in the same way as the known hair lotions.

It is known that water-containing jellies can be produced by the gel former employed according to the invention. By adding relatively large quantities of alcohol, for example 20 to 35%, so that with a water-base the gel former is precipitate. Thus it occurs in the form of a solid lump which cannot be further employed and it is impossible in this way to produce jellies with a relatively high alcohol content. Consequently, it is very surprising that it is possible by using the process according to the invention to produce gels with a high alcohol content which can in principle contain more than 40% of alcohol and if desired even 50%, 60%, 70% or even more
alcohol without the gel-forming properties of the gel former which is employed being thereby deleteriously affected. On the other hand, it has been found that these gels with a high alcohol content are clear, stable products which give a high gloss and are excellently suitable for the purposes according to the invention.

The invention is further illustrated by the following non-limiting examples:

Example I

1% of an interpolymer of 99% glacial acrylic acid and 1% allyl sucrose containing an average of about 5.8 allyl groups per sucrose molecule is added while stirring to a normal hair lotion consisting for example of 50% of isopropl or ethyl alcohol, 47% of water and 3% of perfume oils. The polymer is allowed to swell overnight, stirred again thoroughly on the following day and neutralized for example with 0.15% of triethanolamine (based on the quantity of hair lotion), for example to a pH value of 6. There is obtained a lustrous gel in the color in the hair lotion, which is extremely stable and with which it is possible to fill tubes. After evaporation, scarcely any residue is left, and the hair feels soft and silky after the gel has been applied. Moreover, after application, no sticky or other undesirable residues are left on the hands.

Example II

1 g. of the polymer described in Example I was added to 74 g. of a perfumed water-isopropanol mixture containing about 56% by volume of the alcohol and then allowed to swell. To the mucilage was added a solution of 3 g. of coconut oil diethanol amide in 22 g. of the above-described water-isopropanol mixture, while the mucilage is stirred vigorously. There results 100 g. of a clear and consistent gel.

Example III

A mucilage made from 0.75 g. of the polymer of Example I and 74.25 g. of a perfumed water-isopropanol mixture containing about 56% by volume of the alcohol was mixed, by the procedure described in Example II, with 0.75 g. coconut oil polyethanol amide dissolved in 24.25 g. of the water-isopropanol mixture described above. There resulted 100 g. of a gel form of hair treating material.

Example IV

75 g. of the mucilage described in Example II were mixed with a solution of 5 g. of lauric acid diethanol amide in 20 g. of the described water-isopropanol mixture and stirred vigorously for a short time. There resulted a clear very viscous gel which is particularly useful for treating dry and difficulty curlable hair.

Example V

A mucilage containing 0.75 g. of the polymer of Example II in 74.25 g. of a perfumed water-ethanol mixture containing about 55% by volume of the alcohol, was mixed in the manner described in Example II with a solution of 0.13 g. of triethanolamine and 1.5 g. of coconut oil diethanolamide dissolved in 23.37 g. of the water-ethanol mixture. There were obtained 100 g. of a clear gel form of hair dressing material.

It is to be understood that the other hydrophilic carboxyl groups have a high degree of cross-linking and the interpolymers can be substituted within the range of 0.5–2% by weight of the finished compositions of this invention to obtain gel forms of hair treating material. Thus, acrylic acid cross-linked with polyallyl pentaerythritol, allyl sorbitol, allyl raffinose, allyl inositol or a polybutadiene polymerized in a predominately 1,2 structure to be suitably used for part for part in the above examples, Also, acrylic acid, methacrylic acid interpolymer can be substituted with the cross-linking agents can be so substituted. In addition, interpolymers of the acrylic acid maleic acid or anhydride or fumaric acid, lightly cross-linked as described, can be used in place of the polymers of the examples. Among the lightly cross-linked interpolymers made from maleic anhydride and another monomer that is copolymerizable therewith in substantially equimolar proportions those which are specially useful in this invention are the maleic anhydride-ethylene and maleic anhydride isobutylene cross-linked interpolymers.

We claim:

1. An agent for the treatment of hair and hair bearing epithelium, which comprises an aqueous-alcoholic gel of from about 0.5 to about 6.5% based on the weight of the finished composition of (A) an interpolymer of (1) at least 50 mol percent of an alpha-beta, monoelectronically unsaturated carboxylic acid having from 3 to 10 carbon atoms and from 0 to 50 mol percent of a different monoelectronically unsaturated monomer copolymerizable with said acid and (2) from 0.1 to about 5% by weight, based on (1) of a cross-linking agent selected from the class consisting of (I) a hydrocarbon soluble alkali metal-catalyzed homopolymer of a butadiene-1,3 and (II) polyalkenyl polyethers of polyols having at least 3 hydroxyl groups and at least 4 carbon atoms, said polyalkenyl groups being present on the average of more than 2 per polyol molecule and being terminally unsaturated vinylidene groups of from 2 to 3 carbon atoms, and (B) at least 40% and up to 70% by weight based on the weight of the finished composition of a liquid physiologically acceptable lower monohydric alcohol, the said composition being neutralized to a pH of at least 6 with at least one member selected from the class consisting of triethanolamine and an amide of the structure

\[ R - N - (\_)_{n} - R \]

in which R is an aliphatic hydrocarbon of from 7 to 17 carbon atoms and R1 and R2 each is selected from the class consisting of hydrogen, an alkylol group and a polyalkol group.

2. The composition of claim 1 in which the cross-linking agent in the interpolymer is allyl sucrose containing an average of from 5 to 6 allyl groups per sucrose molecule.

3. The composition of claim 1 in which the interpolymer consists of from 98–99% by weight of acrylic acid and 1 to 2% by weight of allyl sucrose having an average of from 5 to 6 allyl groups per sucrose molecule.

4. The composition of claim 1 in which the interpolymer consists of substantially equimolar quantities of (A) maleic anhydride and (B) isobutylene cross-linked with (C) from about 1 to 5% by weight based on the combined weight of (A) and (B) of a solvent soluble sodium polymerized polybutadiene.

5. The composition of claim 1 in which the interpolymer consists of from 98 to 99% by weight of acrylic acid and from 1 to 2% by weight of allyl pentaerythritol containing an average of more than 2 allyl groups per molecule.

6. The composition of claim 1 containing in addition at least one member selected from the class consisting of steearins, phosphatides, glycerol, glycol and carbor oil.

7. The composition of claim 1 containing from 0.5 to 2.0% based on the weight of the finished composition of the cross-linked interpolymer.

8. The composition of claim 1 in which the monohydric alcohol is an alkane of from 2 to 3 carbon atoms.

9. A process for preparing an agent for the treatment and care of hair and hair bearing epithelium, which comprises adding the interpolymer of claim 1 to a mixture of water containing at least 40% and up to 70% by weight of a liquid physiologically acceptable lower monohydric alcohol, allowing the interpolymer to swell therein and thereafter neutralizing to a pH of at least 6 with
3,178,353

7. A member selected from the class consisting of triethanolamine and an amide of the structure

\[
\begin{array}{c}
\text{O} \\
\text{R} \\
\text{N} \\
\text{R_1} \\
\text{R_2} \\
\text{R_3}
\end{array}
\]

where R is aliphatic hydrocarbon of from 7 to 17 carbon atoms and R_1, R_2, and R_3 each is selected from the class consisting of hydrogen, an alkyl group, and a polyalkylol group.

8. The process of claim 9 in which the monohydric alcohol is an alkanol having from 2 to 3 carbon atoms.

9. The process of claim 9 which comprises effecting neutralization by adding triethanolamine.

10. The process of claim 9 which comprises effecting neutralization with coconut oil polydiethanolamide.

11. The process of claim 9 which comprises effecting neutralization with coconut oil diethanolamide.

12. The process of claim 9 which comprises effecting neutralization with a fatty acid from 8 to 18 carbon atoms.

13. The process of claim 9 which comprises effecting neutralization with椰子油聚二乙醇酰胺.

14. The process of claim 9 which comprises effecting neutralization with coconut oil diethanolamide.

15. The process of claim 9 which comprises effecting neutralization with coconut oil polydiethanolamide.

16. The process of claim 9 which comprises effecting neutralization with lauric acid diethanolamide.

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