Abstract:
The compositions imparting curling keratinous fibers are described. A consumer package comprises a composition, applicator and instructions for curling keratinous fibers.

Title: COMPOSITIONS AND METHODS FOR CURLING KERATINOUS FIBERS

Fig. 3e

Abstract: Compositions comprising materials with certain wetting and contractile properties, as defined herein, are capable of imparting a long lasting curl to keratinous fibers. The composition does the work of curling after it is applied to the hair. The compositions are applied to one side of the hair fibers, only. Safe and effective methods of curling keratinous fibers are also disclosed, as is a consumer package that comprises a composition, applicator and instructions for curling keratinous fibers.
COMPOSITIONS AND METHODS FOR CURLING KERATINOUS FIBERS

This application claims priority from US provisional application 61/085,140, filed July 31, 2008.

Technical Field

The invention is in the field of methods for curling keratinous fibers such as eyelashes or hair and related products and packages.

Background of the Invention

Imparting Curl To Hair

Curl Retention Methods

Long, curled eyelashes are very desirable to women. When eyelashes are curled the eyes may appear larger and more dramatic. It is known to impart a temporary curl to hair by curling hair fibers with a mechanical force, and while in the curled state, applying a curl retention agent. This method can be effective, but it is a two step process, first curling, then applying a curl retention agent.

In the case of eyelashes, it is known to use a mascara brush to tease the upper lashes in the upward direction, while simultaneously applying a highly viscous, fast drying mascara. The mascara acts as a curl retention agent. With each stroke of the brush, the lashes are curled upward a little more, and another coat of mascara is applied to retain some of that curl. When the mascara dries completely, some relatively small amount of curl has been achieved. This method may be thought of as curl retention, since the mascara composition does not actually impart curl to the hair. This method is a one step process, but is somewhat tedious and often gives only a so-so result.

It is also known to curl eye lashes by heating them and applying a mechanical force. The eyelashes are heated and bent into a curled shape. Bending the lashes is usually done with
a tool designed for the purposes (i.e. an eyelash curler), but may be done with a finger or even a spoon. The heat may be supplied by the eyelash curler or some other source. Presumably, the curling effect is the result of a rearrangement of hydrogen bonds in the hair fiber structure. However, the curl will only last for a relatively brief period of time, after the eyelash curler is removed, unless a curl retention agent is employed. Thus, it is known to apply mascara to the lashes while the lashes are still in a curled state. When the mascara dries, the lashes are maintained in a curled state, relative to their pre-treated condition, by the highly viscous mascara. This method may give better results than curling with a mascara brush alone, as described above. However, heating the lashes may damage them, especially if done repeatedly, day after day. Also, a separate heating device is needed and the process takes longer than simply brushing the eye lashes, because it is a two step process, first curling, then applying a curl retention agent.

A curl retention method may also be employed when curling other keratinous fibers. For example, using hair spray to hold a curl in head hair or wax to hold a curl in a moustache. Like the mascara, the hair spray or wax do not impart the curl; they merely hold the curl in place after a mechanical force has been used to induce a curl.

US2004/0151685 discloses curl retention methods comprising applying to the keratinous material a retention effective amount of a transglutaminase enzyme.

Generally, with curl retention methods, the curl retention agent (i.e. mascara, hairspray, wax, transglutaminase) is applied liberally, to all sides of hair fibers. No intentional effort is made to consistently apply a curl retention agent unevenly, on one or more sides of each hair fiber. By "consistently apply", we mean that more curl retention agent is applied to the same side of each adjacent fiber and significantly less or none is applied to the opposite side of each adjacent fiber.
Another method of curling keratinous fibers is to "perm" the fibers. In this method, hair is treated with a reducing agent to open up the disulfide bonds in the hair, then bent into a curled shape, and then treated with an oxidizing agent to reform new disulfide bonds. The hair fibers remain curled until they grow out. This is unlike the curl retention methods above, which provide a relatively brief effect, typically no more than one day. Furthermore, unlike lashes mechanically curled and held in place by mascara, permanent eyelash curling persists even after swimming, showering, crying or sweating. The drawback of this method is the use of certain reactive agents in close proximity to the eye, the relatively complicated and long process needed to achieve a simple aesthetic effect. Also, the chemicals used to effect oxidation and reduction of protein bonds are potentially harmful to human hair. Thus, there is a need for a product, method, and/or device that is maximally effective in curling keratinous fibers and that is long lasting. In particular, there is a need for a product and method and/or device, that is maximally effective in curling eyelashes, that is long lasting even when mascara or other curl retention agents are not used, and that is safe and easy to use.

**Other Methods**

US2004/0151685, mentioned above, also states that transglutaminase can be used to enhance or impart curl, perhaps by forming covalent crosslinks between lysine and glutamine, two of the more common amino acids in hair. However, the present invention curls hair without forming covalent crosslinks between lysine and glutamine, and without altering the natural covalent bond structures in the hair. This a benefit, since such alterations may have short or long term negative side-effects on the health of the hair. US2004/015 1685 does not disclose the methods described herein, specifically, methods of applying a curl-imparting composition to only one side of the hair fibers.

**Objects of the Invention**

3
A main object of the invention to provide compositions that impart curl to keratinous fibers, safely and effectively.

Another main object of the invention is to provide compositions that impart curl to eyelashes, the compositions being safe for use in the eye area.

Another main object of the invention is to provide safe and effective, one-step methods of curling keratinous fibers, that do not involve oxidation and reduction of protein bonds.

A further object of the invention to provide a consumer package that comprises a composition, applicator and instructions for curling keratinous fibers.

**Summary of the Invention**

It has been found that compositions comprising materials with certain wetting and contractile properties, as defined herein, are capable of imparting a long lasting curl to keratinous fibers, such as eyelashes, head hair, moustaches, etc. There is no need to first curl the hair with a mechanical force supplied by a user, and then apply a curl retention agent. The composition does the work of curling after it is applied to the hair. The compositions are unique in that they are designed to be applied to one side of the hair fibers, only. To the extent that the compositions are applied to both sides of the hair fibers, the curling effect is diminished or lost. Therefore, the invention is also directed to a novel method for curling hair fibers. The method comprises applying a useful contractile agent consistently, but unevenly to adjacent hair fibers. The amount of useful contractile agent applied and the degree of uneven application must be sufficient to curl hair fibers. Curling may be followed by applying a makeup color composition to the hair fibers, but this is not required.

**Description of the Drawings**

Figure 1 is a plot of percent eyelash curling verses concentration of Flexan® II.
Figure 2 is a plot of percent eyelash curling verses ratio of Flexan® II to Antara® 430, at several total concentrations.

Figure 3a is a photograph of untreated eyelashes.

Figure 3b is an eyelash treated with mascara alone.

Figures 3c-3g show eyelashes treated with a composition according to the present invention.

Figure 3c is a low curl application.

Figure 3d is a medium curl application

Figure 3e is a high curl application.

Figure 3f is an extreme or excessive curl application.

Figure 3g shows that mascara may be easily applied after the lashes have been curled according to the present invention.

Figures 4 illustrates application of a liquid contractile agent composition to the upper surface of the upper eyelashes, with a beaded applicator.

Detailed Description

The present invention makes use of materials that we call useful contractile agents.

We focus on a preferred form of contractile agents that we call "liquid contractile agents", but the principles of the invention may be extended to contractile agents that fall outside the realm of liquid contractile agents. In this description, we identify several critical parameters or properties that define what is a useful liquid contractile agent. Working and preferred ranges of these parameters or properties are also disclosed. These critical parameters include: wetability, contractile strength, application amount, drying time, wet and dry adhesion and internal structure.

Methods of the invention also consider the number of passes through the hair to complete an application and the need for uneven coating of the hair. Packages of the invention also consider the type of applicator and how much liquid contractile agent it can deliver.
In the phrase "liquid contractile agent", the term "liquid" refers to a material that continually deforms (flows) under an applied shear stress. This may include liquids in the conventional sense, as well as other materials, such as gels. It may include materials that are in a liquid phase at room temperature or that can be maintained in liquid phase by the application of heat. The term "liquid" also allows for the presence of solid materials in the liquid, as a dispersion or solution. The need for flowability under applied shear, is to allow the contractile agent to be spread with an applicator, over a portion of the hair fiber surface.

Although the liquid contractile agent is applied as a liquid, it dries when exposed to the open air. Therefore, in the phrase "liquid contractile agent", the term "contractile" implies that the material shrinks as it dries, when no shear is being applied.

In the phrase "liquid contractile agent", the term "agent" may be a single material having the requisite properties, as described herein, or it may be a composite material, wherein one or more individual components do not have the requisite properties, but the composite does have the requisite properties, as described herein.

Throughout the specification, the term "comprise" means that a collection of objects is not necessarily limited to the items explicitly recited, and may include items not explicitly recited.

1. Liquid Contractile Agent Must Provide Suitable Wetting

"Wetting" is a measure of the ability of the liquid to maintain contact with a substrate. The degree of wetting of the substrate by the liquid is manifested in the shape of the liquid as it rests on the surface of the substrate. In general, when a liquid contacts a substrate, such as the surface of a solid or the surface of a thin polymer film, intermolecular interactions arise between the liquid and the substrate. These intermolecular interactions between the liquid and the substrate are adhesive forces that tend to pull the liquid into a less spherical, more spread
out shape. Working against the adhesive forces are cohesive forces within the liquid, which tend to minimize contact with the substrate by drawing the liquid into a more spherical shape.

When a liquid is at rest on a substrate, we can define two interfaces; the interface between the air and the liquid, and the interface between the liquid and the substrate. The "contact angle" is the angle at the intersection of these two interfaces, inside the liquid. A smaller contact angle means that adhesive forces dominate cohesive forces (i.e. the liquid spreads out on the substrate surface), and the liquid is deemed "more wetting". A larger contact angle means that cohesive forces dominate adhesive forces (i.e. the liquid beads on the substrate surface), and the liquid is deemed non-wetting or "less wetting". Of course, even a less wetting liquid can be spread out over a substrate surface, if some other force is applied to accomplish this purpose. For example, by applying pressure, a drop of water on a substrate surface may be spread out well beyond where it normally spreads from adhesion and cohesion alone. But once the pressure is removed, the water may retreat in an attempt to revert to a more drop-like state. Another way to think about contact angles is that a larger contact angle between two materials means that the two materials are dissimilar in hydrophilicity/hydrophobicity. A smaller contact angle means that two materials are similar in this hydrophilicity/hydrophobicity.

In describing liquid contractile agents useful in the present invention, it is important to distinguish between two different contact angles. First, we can talk about the contact angle that a drop of water makes on the liquid contractile agent. This contact angle is a measure of the hydrophobicity or hydrophilicity of the liquid contractile agent. The smaller (larger) the contact angle between the water and the liquid contractile agent, the more hydrophilic (hydrophobic) is the liquid contractile agent.

Second, we can talk about the contact angle between a liquid contractile agent and a fiber of hair. Hair is naturally hydrophobic. If the liquid contractile agent is also hydrophobic, or to the degree that it is hydrophobic, the liquid contractile agent will spread out on the hair
fiber. If the liquid contractile agent is hydrophilic, or to the degree that it is hydrophilic, the liquid contractile agent will not spread out on the hair fiber, and may bead up. In the present invention, a balance must be struck between too much and too little hydrophobicity. On the one hand, a liquid contractile agent needs form significant adhesion to the hair fiber so it can pull the hair fiber as it contracts. On the other hand, too much adhesion might cause the liquid contractile agent to migrate all around the hair fibers, thus failing to curl the fibers.

Therefore, in the context of wetting, a simply preferred and useful liquid contractile agent is one that, after being spread on the hair fibers by an applicator, may spread out a little further, but only to a degree that the contractile agent is still able to impart a noticeable or cosmetically acceptable curl to the fibers. Thus, after a liquid contractile agent is spread on the hair fibers, the adhesive forces of the liquid contractile agent form a significant bond with the hair fiber, but the cohesive forces do not allow the liquid contractile agent to spread much further.

In the context of wetting, a more preferred and useful contractile agent is one that, after being spread on a hair fiber by an applicator, does not spread out any further, and retreats only to a degree that the contractile agent is still able to impart a noticeable and cosmetically acceptable curl to the hair fibers. By not spreading any further, the liquid contractile agent does not migrate to portions of the hair fiber where it should not go. By not retreating, or only retreating a small amount, we can be sure that the liquid contractile agent is forming a significant bond with the hair fiber.

In the context of wetting, a most preferred liquid contractile agent is one that, after being spread on a hair fiber by an applicator, remains in place, not spreading any further, nor retreating.

By "suitable wetting" or the like, we mean that a liquid contractile agent is one of preferred, more preferred, or most preferred, as just described.
Wetting Tests

To compare wetting characteristics of different liquid contractile agents, a simple wetting test may be conducted. 1 ml of a liquid contractile agent is spread on a 10 cm x 10 cm glass plate using a 2 mil (thousandths of an inch) standard draw down bar, forming a film. The film is allowed to dry for 15-30 minutes. Using a Sony CCD camera model SSC-DC 5OA or similar device, acquire a digital image of the intersection of the air-liquid interface with the liquid-glass interface. The contact angle between the film and glass plate may then be measured through the use of digital image software, which are well known in the art and widely available. Because the glass plate is hydrophobic, a larger contact angle would imply that the liquid contractile agent is more hydrophilic.

Similarly, to compare the hydrophobicity or hydrophilicity of different liquid contractile agents, 1 ml of a liquid contractile agent is spread on a 10 cm x 10 cm glass plate using a 2 mil (thousandths of an inch) standard draw down bar, forming a film. The film is allowed to dry for 15-30 minutes. A defined amount of water is placed on the film of liquid contractile agent. Using a Sony CCD camera model SSC-DC 5OA or similar device, acquire a digital image of the intersection of the air-water interface with the water-film interface. The contact angle between the film and water droplet may then be measured through the use of digital image software, which are well known in the art and widely available. Because water is hydrophilic, a smaller contact angle implies a more hydrophilic liquid contractile agent.

The tests described here are merely examples, and other suitable tests may substituted for these. Once the contact angle of a test sample is known, that angle may be compared to the contact angle of one or more standard liquid contractile agents, known to be useful for the present invention. A similar contact angle implies that the test sample may perform similarly to the standard liquid contractile agent, as least as far as wetting is concerned. Of course, suitable wetting of keratinous fibers, is just one necessary characteristic of a useful liquid
contractile agent. For example, a liquid contractile agent that displays preferred wetting, yet has little strength to curl hair fibers, is not useful in the present invention.

II. Liquid Contractile Agent Must Provide Suitable Curling

"Suitable curling" implies that the liquid contractile agent has produced a desired visible effect in the shape of the hair fibers to which the agent was applied. In the beauty field, suitable curling implies that an improvement in aesthetic appeal of the eye lashes or head hair or moustache etc., has been achieved.

In general, the radius of a curl should not be too large or too small. If the radius is too large, the curling effect may not be sufficiently dramatic. If the radius of the curl is too small, the effect may be a weird, unnatural appearance (see figure 3f). That which is too little radius or too much radius are subject to some individual interpretation. However, there are accepted norms in society that give guidance on what is too much or too little curl in the eye lashes, or moustache, for example. Persons of ordinary skill in the art or persons skilled in marketing such products, can readily determine that which is too little and too much curl. Of course, the standard, or the meaning of "suitable curling", will vary with whether the hair fibers are eye lashes, head hair, a moustache, etc.

For a more objective assessment, methods of measuring the degree of curl can used. For example, the following method works well for shorter fibers, such as eyelashes. Before curling, the straight line distance between the free end and the insertion end of a hair fiber is measured. After curling, that distance is measured again. The percent curl is computed as:

\[
\text{Percent Curl} = \frac{\text{Initial distance} - \text{Final distance}}{\text{Initial distance}} \times 100\%
\]

By this method, a product developer could designate different ranges of percent curl as "Low Curl", "Medium Curl", "High Curl" and "Extreme Curl" or any similar designations.
For example, in our experience, we designate 10 - 30% as Low Curl, 30-50% as Moderate Curl, 50-70% as High Curl and above 70% as Extreme Curl. With compositions and methods of the present invention, curls above 90% are possible. It is even possible to make the fibers curl back on themselves (100% curl or more), but from a commercial beauty standpoint, such extreme curl may not be useful. Although, such extreme curls may find uses in fields outside of the beauty industry, such as in the performing arts.

A useful liquid contractile agent, from a curling point of view, is one that is able to provide suitable curling when applied to hair fibers according to the methods of this invention. Two main factors to consider are the strength of the liquid contractile agent and the amount of contractile agent applied. Unlike prior art methods of curling, the contractile agents of the present invention do all the work of curling. It is not necessary to apply a mechanical force to the hair fibers before a composition of the invention is applied. This means that application of too much contractile agent can result in too much curling. Also, application of too little liquid contractile agent can result in too little curling, although this may be correctable by applying more contractile agent. Thus, the degree of curling depends on the strength of the contractile agent and the amount of contractile agent applied.

A main focus of the present invention is curling eyelashes, although the principles of the invention readily adapt to moustaches, beards, hair of the head, etc. While it is difficult to control how much product a consumer may apply to her eye lashes, a sense of this may be gotten from experience in the field of eye lash makeup. For example, to apply mascara to the eye lashes, a woman may dip a brush into mascara and draw the brush through a wiper, as is well known in the art. She may then draw the loaded brush over each eye lash from about one to about ten or twenty times. Thus, not wanting to burden a consumer with more than that which she is already accustomed, a preferred and useful liquid contractile agent of the present invention, is one that is able to impart a suitable curl to the eyelashes, when an applicator loaded with the liquid contractile agent is drawn over each lash, at least ten to no more than
twenty times. A more preferred and useful contractile agent is one that is able to impart a
suitable curl to the eye lashes when the loaded applicator is drawn over each lash at least five
to no more than ten times. A most preferred and ideal contractile agent is one that is able to
impart a suitable curl to the eyelashes when the loaded applicator is drawn over each lash no
more than five times. Of course, the number of passes through the lashes will depend on how
much product a given applicator can retrieve from the product reservoir, but it is well within
the ability of a person of ordinary skill in the art, to choose a suitable combination of
contractile agent and applicator, after he or she has been made familiar with the various
critical parameters as identified, herein.

III. Liquid Contractile Agent Must Have Suitable Drying Characteristics

"Suitable drying" means several things. (I) A liquid contractile agent dries in no more
than about fifteen minutes; (2) as it dries, the liquid contractile agent contracts, and remains
adhered to the hair fibers as it contracts; (3) after it is dry, the liquid contractile agent
continues to adhere to the hair fibers, and has enough internal structure to hold the shape of the
hair fibers.

In terms of drying time, useful liquid contractile agents dry in about ten to about fifteen
minutes. Preferred liquid contractile agents dry in five or about five minutes to ten minutes.
More preferred liquid contractile agents dry in two or about two minutes to five minutes. The
most preferred liquid contractile agents dry in one or about one to two minutes. Additionally,
"suitable drying" means that a liquid contractile agent of the present invention should not dry
so fast that a user does not have time to thoroughly apply the agent to her lashes. About one
minute may be enough time to thoroughly apply the agent to the lashes. If consumer testing or
other information suggests that more time is needed, then a person of skill in the art can adjust
the dry time of the liquid contractile agent accordingly.
In terms of wet adhesion, the adhesion between the hair fiber and the liquid contractile agent must be sufficient to withstand the forces of contraction within the liquid the contractile agent.

In terms of contraction, a liquid contractile agent must exert a force strong enough to bend the hair fibers to which it adheres. The reshaping of the hair fiber is mechanical, but all of the work is done by the liquid contractile agent. The contraction may occur along one or more principle axes, or it may occur more generally, along all directions (i.e. isotropically). At a minimum, the liquid contractile agent must contract along the direction of the length of the hair fibers, so that the free end of the fibers are pulled toward the insertion point of the fibers. More preferably, the liquid contractile agent contracts much more along the direction of the length of the hair fibers, than in any other direction.

After the liquid contractile agent has contracted and dried, it is preferable for a curl to remain in the hair for at least eight hours after application. More preferably, the curl is able to remain in the hair for at least sixteen hours after application. Most preferably, the curl is able to remain in the hair for as long as the dried contractile agent is on the hair. The degree of curl retention depends largely on the internal molecular structure of the dried liquid contractile agent. Gravity and forces within the hair, may tend to undo the curl. To counteract those forces, the liquid contractile agent must be able to hold its molecular arrangement. Thus, the more internal structure in the dried liquid contractile agent, the longer a curl will remain in the hair.

A Contractile Test

Identification of agents that that have the necessary contractile strength for use in the methods and products of the invention, may be ascertained by performing a simple contractile test as follows. Using a 2 mil draw down bar, 1 ml of a test liquid contractile agent is applied to a 5 cm x 20 cm piece of standard white paper, to form a film. The paper may be, for example, the
type used in photocopier machines (for example, International Paper Hammermill® Copy Plus). The film is allowed to dry for 15-30 minutes. The degree of curling of the paper sample indicates the contractile ability of the agent. For example, if the dried film does not curl the paper, the agent may not have sufficient contractile properties. If the paper curls, the agent may be suitable. The degree of curling is directly proportional to the curling effectiveness of the agent. The direction(s) of curl may also be noted. Once the degree and direction of paper curling is known, that curled paper may be compared to the paper curling test results of one or more standard liquid contractile agents, known to be useful for the present invention. A similar degree of paper curl implies that the test sample may perform similarly to the standard liquid contractile agent, as least as far as curling is concerned.

The test described here is merely an example, and other suitable tests may substituted for this one. For example, a similar test may be performed on hair samples. When performed on hair samples, the percent curl can be measured as described above. Of course, suitable curling of keratinous fibers, is just one necessary characteristic of a useful liquid contractile agent. For example, a liquid contractile agent that displays good curling in the paper test, yet has too much wetting (so that it spreads around all sides of the hair fiber), is not useful in the present invention.

IV. Liquid Contractile Agent Must Have Sufficient Structure To Retain Shape

As noted, a suitable liquid contractile agent of the present invention is one that, after it is dry, has sufficient internal structure to retain a curl for a desired amount of time. Internal structure is molecular level property. In general, materials with a high degree of crosslinking, and/or a high degree of non-covalent intramolecular forces (i.e. ionic bonds, hydrophobic interactions, hydrogen bonds, Van der Waals forces, i.e. "London dispersion forces", and dipole-dipole bonds) may have significant internal structure.

Polymers: Charge density, Young's Modulus, etc.
In general, polymers have good non-specific adhesive affinity to various surfaces. This is due to the accumulation of numerous Van der Waals interactions along a polymeric chain. Also, in general, polymers withstand substantial deformation without destruction of the material, and, due to their viscosity, thin films are readily obtainable. These features may suggest that polymers, in general, would make good liquid contractile agents. However, there are factors to consider, and not all polymers found in the personal care or hair care field are suitable as a liquid contractile agent of the present invention. For example, Table I lists 29 polymers that were tested for their ability to curl eye lashes. Only four were effective.

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>Company Name</th>
<th>CAS Name</th>
<th>Ionicity</th>
<th>% Curling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flexan II</td>
<td>National Starch</td>
<td>Sodium Polystyrene Sulfonate</td>
<td>Anionic</td>
<td>High Curling</td>
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<tr>
<td>XL PVA</td>
<td>Lipo Technologies</td>
<td>Crosslinked PVA</td>
<td>Non-ionic</td>
<td>No Curling</td>
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<tr>
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<td>BASF</td>
<td>PVP</td>
<td>Non-ionic</td>
<td>No Curling</td>
</tr>
<tr>
<td>XL PVA</td>
<td>Lipo Technologies</td>
<td>Crosslinked PVA + 10% Ethanol</td>
<td>Non-ionic</td>
<td>No Curling</td>
</tr>
<tr>
<td>Pharmadur</td>
<td>Alzo International</td>
<td>Poly(N,N dimethylacrylamide AA, EthylMA PS</td>
<td>Anionic</td>
<td>No Curling</td>
</tr>
<tr>
<td>Aquaflex FX-64</td>
<td>International Specialty Products</td>
<td>Poly(Isobutylene-co-maleic anhydride)</td>
<td>Amphoteric</td>
<td>No Curling</td>
</tr>
<tr>
<td>Aquaflex XL-30</td>
<td>International Specialty Products</td>
<td>Low MW Poly(Isobutylene-co-maleic anhydride)</td>
<td>Amphoteric</td>
<td>No Curling</td>
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<td>AQ 38S</td>
<td>Eastman</td>
<td>Polyester 5</td>
<td>Anionic</td>
<td>No Curling</td>
</tr>
<tr>
<td>Syntran PC5100NP</td>
<td>Interpolymer</td>
<td>Polyacrylate 21/Acrylates/DMAMA</td>
<td>Anionic</td>
<td>Low Curling</td>
</tr>
<tr>
<td>Syntran PC 5227</td>
<td>Interpolymer</td>
<td>Ethylene/Amino Acrylate Copolymer</td>
<td>Anionic</td>
<td>No Curling</td>
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<td>Avalure UR450</td>
<td>Noveon</td>
<td>Polyurethane</td>
<td>Non-ionic</td>
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<td>Gaffix VC 713/ Advantage S</td>
<td>International Specialty Products</td>
<td>Vinyl Caprolactam/PVP/DM AEMA</td>
<td>Non-ionic</td>
<td>High Curling</td>
</tr>
<tr>
<td>Avalure AC 120M</td>
<td>Noveon</td>
<td>Acrylate-Ethylene Glycol Monophenil Ether Copolymer</td>
<td>Anionic</td>
<td>No Curling</td>
</tr>
<tr>
<td>Gafquat</td>
<td>International</td>
<td>Quaternized Vinyl</td>
<td>Cationic</td>
<td>No Curling</td>
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</tbody>
</table>
Therefore, when the liquid contractile agent includes a polymer, there are some important parameters to consider, such as, surface charge density, stiffness of the polymer,
dispersability in polar solvents, stability at cosmetically acceptable pH, and viscosity in
solution. Safety is also an issue, especially when the polymer may be used around the eyes.
More on this below.

Charge Density

Useful polymers have a surface charge density of 1 to 10%, more preferably from about 2 to 8%, as measured by X-ray fluorescence. Preferred polymers are anionic with a rigid hydrophobic backbone, while cationic polymers are less preferred. This is because many cationic polymers tend to plasticize the medium in which they are dispersed, which means the medium deforms easily and may not support initial curling and/or curl retention, very well. Also, cationic, non-ionic, zwitterionic and amphoteric polymers are not a priori excluded from use in the present invention, but their selection and incorporation into a useful hair curling composition may be more difficult. Ultimately, their suitability is determined by the curling results.

Stiffness

Human eye lash fibers have an elastic modulus on the order of 4 GPa, say about 1-7 GPa. Therefore, preferred polymers have a stiffness characterized by an elastic modulus (or Young's modulus) ranging from about 1 to 12, preferably from 4 to 8, more preferably about 6 GPa, as measured by ASTM test methods D638, D882 or E1875. This amount of stiffness (internal structure) is required to transmit the contracting force that curls the hair fiber and retains the curl for a desired amount of time.

Dispersability

A suitable polymer may be applied by itself, to the hair fibers (i.e. neat) or they may be dispersed in a solvent. Preferred polymers are dispersible in polar solvents, such as aqueous or aqueous/alcoholic solutions or dispersions.
A preferred polymer is one that is stable at the pH of its environment. For example, personal care and cosmetic products often have a pH in the 5-7 range. Thus, for a product of this type, the polymer used should be stable in the 5-7 range. If the polymer is not stable at that pH, then formulating a useful product may be more difficult. The length of time over which the polymer must be stable also depends on the intended use. In the personal care industry, stability often implies that a product does not degrade for at least 6 months, preferably at least 1 year, more preferably at least 2 years.

**Viscosity**

When polymers are to be used in solution or dispersion, we have found that the viscosity of solution is preferably about 1-3 poise. This viscosity allows spreading the polymer solution over the fibers, but provides enough internal resistance to prevent the polymer solution from migrating to the opposite side of the fiber.

**Addressing Safety Concerns**

As noted, safety is an issue, especially when a liquid contractile agent, such as a polymer, will be used around the eyes. Polymers have residual monomer units, left over from processing. In excessive concentrations, these residual monomer units may be health hazard. For applications around the eyes, preferred polymers are those that have residual monomer levels of less than 20ppm. For polymers having residual monomer levels in excess of 20ppm, it may be possible to use a concentration of liquid contractile agent that is safe around the eyes, and yet, stills gives an acceptable curl. However, it may be that at concentrations that are safe, the resulting curl is unacceptable. This would be because the amount of liquid contractile agent is insufficient to form a good adhesion with the hair fiber or does not have enough structure to hold the curl. When this is the case, it may be possible to supplement the adhesion of the polymer to the hair fiber and the internal structure of the liquid contractile agent, by adding a material that does not contribute to the residual monomer level.
In general, a liquid contractile agent of the present invention may adhere directly to the hair fibers, so that when the liquid contractile agent contracts, the hair fibers are bent. Alternatively, it may be possible that some other material in the composition adheres to the hair fibers. In this case, the contraction of the liquid contractile agent in the composition would have to be transmitted to the hair fibers through some additional structure in the composition.

We have discovered that the addition of one or more clays to an anionic polymer allows us to reduce the concentration of the anionic polymer to cosmetically safe levels, while still achieving a high degree of curl. For example, Flexan® II (sodium polystyrene sulfonate) at 30% concentration produces a high degree of eye lash curl (about 60% or more), but that level of Flexan® II may be unusable around the eye area. When we reduced the level of Flexan® II to 10%, the degree of curl was unacceptable. This was due to an insufficient amount of adhesion between the polymer and the hair fiber. The Flexan® II, even at 10%, is strong enough to curl a hair fiber, but it cannot get a good grip on the fiber, so to speak.

We have discovered that by combining certain clays, Laponite® clay for example, with 10% Flexan® II, a high degree of curl is again achieved. However, we have also noted that not all clays are useful. For example, bentonite and hectorite were unable to restore acceptable curling results.

Laponite® platelets are about 20 to 50 nm in size, and provide over 700 m² per gram of surface area populated by Na⁺ ions. In general, these ions may participate in ion-dipole and ion exchange interactions with a liquid contractile polymer. Other interactions may occur between the polymer and oxygen, silicon, Mg, Li, or OH groups near the surface of the Laponite®. At the same time, Laponite®, has good adhesion to hair fibers and significant internal structure. As a example, a water base composition of the Flexan® and Laponite®, effectively and safely curls the eyelashes. One side of the Laponite® platelets adhere to the Flexan® polymer. The other side adheres to the hair fibers. When the Flexan® contracts, it
pulls on the clay, which pulls on the hair fibers. The Laponite clay has sufficient structure to be able to transmit the force of the contracting polymer to the eyelashes. Clays that adhere to the contractile polymer and to the hair fiber, but that lack the necessary internal structure to transmit the force of contraction, will not be useful in the present invention. On the other hand, clays that have the necessary internal structure, but that lack the necessary adhesion to hair fiber and/or polymer will not work, either. Thus, by incorporating Laponite clay into the composition, we can reduce the concentration of Flexan® II from 30% to about 10%, while still achieving a high degree of curl. This is unlike anything in the prior art. The amount of clay used may vary as needed and may be determined by trial and error. A rough guide may be that liquid contractile agents of the invention may comprise from about 1% to about 50% of one or more clays.

Summary Of Suitable Liquid Contractile Agents

To summarize, the present invention makes use of materials that we call contractile agents or liquid contractile agents. In this description, we have identified several critical parameters that define what is a useful contractile agent. These critical parameters include: wetability, contractile strength, contractile direction, application amount, drying time, wet and dry adhesion, internal structure, safety concerns. For polymers, we discussed charge density and Young's modulus. Working ranges of some of these parameters were also disclosed.

While it may be possible to devise a battery of tests that conclusively categorize a material as a useful or non-useful liquid contractile agent, that approach is likely to be overkill and not commercially feasible. Rather, having the set of critical parameters or properties identified herein, and having ranges of those parameters, a more reasonable approach from an economic and commercial standpoint, is to screen a number of candidate materials for these critical parameters. After identifying one or more materials that meet the criteria herein described, those materials, in varying concentrations, may be used to curl keratinous fibers and the results
may be noted. Through routine experimentation, and by making comparative judgments about the results, a person of ordinary skill in the art may identify one or more suitable materials, in commercially feasible concentrations.

5 Hair Curling Compositions

A hair curling composition according to the present invention must contain at least one useful contractile agent. A material having the properties described, herein, in the working ranges described, herein, is a useful contractile agent, specifically, a liquid contractile agent. A hair curling composition may comprise only the useful contractile agent(s), or it may comprise other ingredients in addition to the useful contractile agent(s), so long as those other ingredients do not interfere with the ability of the useful contractile agent(s) to curl keratinous fibers.

A hair curling composition of the invention comprises from about 0.1 to 100%, more preferably from about 1-95%, most preferably from about 1 to 90% by weight of the total composition of liquid contractile agent(s). The other ingredients present may include water, polar non-aqueous solvents such as mono-, di-, or polyhydric alcohols, and the like. If present, suggested ranges for the water or polar non-aqueous solvent are from about 0.1 to 99%, preferably from about 0.5 to 75%, more preferably from about 1 to 60% by weight of the total composition. The liquid contractile agent(s) may be dispersions or solutions of useful contractile agents in water or non-aqueous polar solvents. Preferably, the compositions are aqueous solutions or dispersions of the liquid contractile agent in a cosmetically safe concentrations.

Suitable Contractile Agents

Suitable contractile agents include natural or synthetic compounds, polymers, mixtures of natural ingredients, and the like, so long as they behave within the critical parameters
defined above. The term "natural" means that the agent is naturally occurring, for example, the agent may be found in resins, gums, or extracts from plants. Examples include, but are not limited to various botanical extracts and plant exudates, such as gums or resins.

Polymers

Any polymer having the properties of a useful contractile agent, as described herein, may be suitable for use in the invention. Preferably, the polymers are charged, that is they may be negatively or positively charged such as anionic, cationic, zwitterionic, or amphoteric polymers.

In one preferred embodiment, the charged polymers are anionic and have a charge density in the range of about 1 to 10%, more preferably from about 2 to 8%, as measured by X-ray fluorescence. In this embodiment, the polymers have a preferred elastic modulus (or Young's modulus) of about 6 GPa. Also, the polymers of this embodiment are water soluble or dispersible, and the polymers or polymer solutions are stable at a pH of about 5 to 7.

Examples of suitable polymers include, but are not limited to:

(1) Sodium polystyrene sulfonate, one type being an anionic polymer sold under the trademark Flexan® II by National Starch Personal Care, which comprises about 90-100% polymer and about 1-10% water. Figure 1 shows the effects achievable with Flexan® II.

(2) Styrene/acrylates/ammonium methacrylate copolymer, one type being an anionic polymer sold by Interpolymer Corporation under the trademark Syntran® PC5 100NP, which comprises about 25% solids in aqueous solution comprising sodium laureth sulfate, C11-15 pareth-7, butylene glycol, phenoxyethanol, potassium sorbate, caprylyl glycol, and water.

(3) Vinyl caprolactam/VP/dimethylaminoethylmethacrylate copolymer, one type being a nonionic polymer sold by International Specialty Products under the trademark Gaffix® VC-713 which comprises about 35-40% polymer and the remainder ethanol.
(4) Sodium polystyrene sulfonate and PVP styrene copolymer, one type being a mixture of anionic and nonionic polymers, such as those sold by National Starch Personal Care under the trademark Flexan® II and International Specialty Products under the trademark Antara® 430. Figure 2 shows the effects achievable with Flexan® II/Antara® 430. Also useful is the mixture Flexan® II/Polectron® 430. Polectron® 430 (from ISP) is a "cleaner" version of Antara® 430 in that the residual monomer level of Polectron® 430 is significantly lower than the residual monomer level of Antara® 430. For this reason, Polectron® 430 may be preferred over Antara® 430, for eye products or anytime that safety is an issue.

(5) Another useful liquid contractile agent comprises a combination of Flexan® II and one or more clays. Specifically, Flexan® II with Laponite® clay.

(6) Likewise, Flexan® II/Antara® 430 has been used effectively, in combination with Laponite® clay.

Example I is a composition according to the present invention which achieves a high degree of curl.

Example I

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>q.s.</td>
</tr>
<tr>
<td>PVP/styrene copolymer</td>
<td>23.00</td>
</tr>
<tr>
<td>sodium polystyrene sulfonate</td>
<td>5.00</td>
</tr>
<tr>
<td>sodium manganese silicate (Laponite®)</td>
<td>10.25</td>
</tr>
<tr>
<td>phenoxyethanol / caprylyl glycol / potassium sorbate / water / hexylene glycol</td>
<td>1.00</td>
</tr>
<tr>
<td>phenoxyethanol</td>
<td>0.50</td>
</tr>
<tr>
<td>ethylhexylglycerine</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>-------</td>
</tr>
<tr>
<td>citric acid</td>
<td>0.30</td>
</tr>
<tr>
<td>glycercyl stearate / PEG-100 stearate</td>
<td>2.00</td>
</tr>
<tr>
<td>steareth-20</td>
<td>0.75</td>
</tr>
<tr>
<td>steareth-21</td>
<td>0.50</td>
</tr>
<tr>
<td>beeswax</td>
<td>2.00</td>
</tr>
</tbody>
</table>

Utilizing compositions of the present invention, 60-70% curling is achievable.

Because the preferred compositions are aqueous and the liquid contractile agent is water
soluble, the composition may be easily rinsed from the hair. This is especially useful, if too
much composition is applied, and the user wants to start over. Another useful feature is that
the composition can be applied over a previous, dried application, either hours or even days
later.

Figure 3a is a photograph of an untreated eyelashes. Figure 3b is an eyelash treated
with mascara alone. Figures 3c-3g show eyelashes treated with a composition according to the
present invention. Figure 3c is low curl, 3d is medium curl, 3e is high curl and 3f is extreme
or excessive curl. Figure 3g shows that mascara may be easily applied after the lashes have
been curled according to the present invention. The mascara may add to the curl retention
provided by the composition of the present invention, but the mascara is not required.

With the teachings provided herein, a person of ordinary skill in the art, through
routine experimentation, could refine compositions of the present invention to suit a particular
user or classes of users. Hair varies from person to person and ethic group to ethic group. The
parameters identified herein allow the present invention to be used by anyone. However, by
taking into account differences in hair fiber structure and hair fiber chemistry between
subpopulations (i.e. differences in elastic modulus, surface tension, degree of cross linking), it
may be possible to develop curling compositions that are more effective for each sub-
population.

Methods

In methods of the invention, a composition having wetting and contractile properties as
described above is provided. A critical feature of the invention is the step of applying the
composition unevenly over the surface of one or more keratinous fibers so that sufficiently
more of the composition is applied to one side of the fiber. By "sufficiently more" we mean
that the excess curling composition on one side of a fiber is enough to curl the fiber toward
that side, and the amount of curl is visible to the naked eye. Preferably, one side of the fiber
receives at least twice as much curling composition as the opposite side of the fiber. More
preferably, one side of the fiber receives at least three times as much curling composition as
the opposite side. Most preferably, one side of the fiber receives an effective amount of
curling composition, and the opposite side of the fiber receives none.

For purposes of this discussion, we will describe methods in relation to eyelashes. To
curl the upper eyelashes upward, sufficiently more of the composition must be placed on the
upper side of the eyelashes than on the lower side. If the curling composition is applied with a
mascara applicator, then the applicator is first loaded with curling composition, and then the
applicator is brought into contact with the upper side of the upper eyelashes. As this is done,
care is taken to keep the composition from accumulating on the underside of the upper lashes.
Thus, a curling composition of the present invention should not be able to spread so easily,
that it flows, via gravity, to the underside of the lashes. And yet, a certain amount of
wetability is required to get good coverage over the upper sides of the lashes using an
applicator. Curling compositions having the appropriate wetting characteristics have been
described above. Thus, if care is taken to avoid contacting the underside of the upper lashes
with the applicator, then the uneven application of curling composition, that is required for
curling the lashes, will be achieved. The composition, once applied properly as described herein, will do the work of curling. In principle there is nothing that prevents compositions of the present invention from being used on the lower lashes.

In one method of the invention, a liquid contractile agent is applied to a portion of the keratinous fiber where it is desired to form a concave surface. In the case of eyelashes, the contractile agent is applied to the upper surface of the upper eyelashes. This may be unusual for those mascara users who routinely apply mascara only to the undersides of the lashes. Figure 4 shows application of the contractile agent composition to the upper surface of the upper eyelashes using a beaded applicator. While a beaded applicator is depicted in figure 4, any other applicator known to be effective in the hair care field, may be used to apply a composition of the present invention, including but not limited to those set forth in provisional application US61/085,140, herein incorporated by reference, in its entirety. For example, effective curling of eyelashes has been achieved with conventional bristle brushes, well known in the mascara field. Vibrating applicators, such as those disclosed in US patent 7,465,114, (herein incorporated by reference in its entirety) may also prove useful. Devices that crimp the eyelashes will be effective when the contractile agent is applied to the crimp surface that contacts the upper surface of the upper eyelashes, and not applied to the crimp surface that contacts the under side of the upper lashes.

Optionally, methods of the invention include the step of treating the hair fibers with a color or treatment product, prior to or after, the step of applying a liquid contractile agent. The color product may be any type of mascara that does not interfere with the curling action of the liquid contractile agent. The treatment product may be any product that does not interfere with the curling action of the liquid contractile agent, such as a lengthening or volumizing product.

When a color product is to be applied to the hair fibers before applying the liquid contractile agent composition, then it is preferable if the liquid contractile agent composition is
translucent or transparent, to allow the color to show through. Preferably, however, the hair fibers are treated with a color or treatment product after the step of applying a liquid contractile agent. More preferably, the hair fibers are treated with a color or treatment product after the liquid contractile agent has dried on the hair fibers. For example, a user dips a mascara-type applicator into a vial of liquid contractile agent composition; draws the applicator out of the vial, through a wiper; draws the loaded applicator five times, over the top surface of her eyelashes; waits at least two minutes for the applied composition to curl the eyelashes and dry; applies eyeliner in her usual fashion; and applies mascara to the curled eyelash in her usual fashion.

Methods of the invention include applying a liquid contractile agent to the same hair fibers, one or more times per day.

For example, optionally, prior to applying a composition of the invention, the hair fibers may be rinsed or cleaned with water alone or with a mild, common cleanser, to remove residual liquid contractile agent from a previous application. Preferably, no special cleanser is needed. This is convenient for a user who applies a composition to her eyelashes, allows the composition to dry, and then realizes that she wants less curl in her lashes. Being able to clean the lashes easily with water alone, makes the process fast and inexpensive. After the lashes are rinsed or cleaned, the user simply applies a fresh coat of the composition, this time applying less composition to get a less dramatic curl. This process may be repeated until the user is satisfied with the curl.

Optionally, a fresh application of liquid contractile agent may be applied over a previous application of liquid contractile agent. This is convenient for a user who applies a composition to her eyelashes, allows the composition to dry, and then realizes that she wants more curl in her lashes. Without having to clean the lashes, she simply applied another coat of the composition to gain even more curling. This process may be repeated until the used is satisfied with the curl.
Packages

A package of the invention provides a reservoir for storing and applying the contractile agent composition. One embodiment of the invention is directed to a package for use in curling keratinous fibers containing a composition comprising a contractile agent and an applicator for application of the composition to a portion of the keratinous fibers in an amount sufficient to curl the fibers. With a little practice, a user may quickly gain a feel for how much curling composition to apply, how many strokes are needed, how many times to dip the applicator, etc. However, some guidance may be provided on a package in which the composition and/or applicator is sold. Thus, a package for consumer sales that comprises a liquid contractile agent of the type described herein, and instructions for using the liquid contractile agent according to the methods disclosed herein, is novel and non-obvious over the prior art.

In another aspect of the packaging, a reservoir that holds a curling composition may be a type that requires an applicator to be dipped into it, to retrieve some the composition. Alternatively, it may be the type that is integrally connected to an applicator surface via a flow path from the reservoir to the applicator surface. Various arrangements of these two systems are well known in the art.

Heretofore, compositions that curl keratinous fibers when applied to one side of the fibers were unknown. Methods associated with such compositions were also unknown. The benefits achieved with the compositions and methods herein described were not previously achievable by other methods. The main benefit is the ability to impart long lasting curl to keratinous fibers, in one-step, without heating the fibers and without subjecting the fibers to oxidation and reduction of protein bonds. The compositions and methods are safe for use in the eye area.
WE CLAIM:

1. A method for curling keratinous fibers comprising applying a liquid contractile agent unevenly over the surface of one or more keratinous fibers, so that more of the composition is applied to one side of the fibers.

2. The method of claim 1 wherein the one side of fibers, is the upper surface of eyelashes.

3. The method of claim 2 wherein at least twice as much liquid contractile agent is applied to the upper surface of the eyelashes compared to the lower surface of the eyelashes.

4. The method of claim 2 wherein the resulting curl is between 10 and 100%.

5. The method of claim 4 wherein the resulting curl is between 30 and 90%.

6. The method of claim 5 wherein the resulting curl is between 50 and 70%.

7. The method of claim 1 wherein the liquid contractile agent comprises an anionic polymer.

8. The method of claim 7 wherein the anionic polymer has a charge density of 1 to 10%, an elastic modulus of 1 - 12 GPa, are water soluble, and stable at a pH of about 5 to 7.

9. The method of claim 7 wherein the liquid contractile agent is selected from the group consisting of:

   (a) Sodium polystyrene sulfonate,

   (b) Styrene/acrylates/ammonium methacrylate copolymer,

   (3) Vinyl caprolactam/VP/dimethylaminoethylmethacrylate copolymer,

   (4) Sodium polystyrene sulfonate and PVP styrene copolymer; and

   (5) mixtures thereof.

10. The method of claim 2 wherein the liquid contractile agent comprises sodium polystyrene sulfonate and Laponite® clay.

11. The method of claim 2 further comprising the steps of immersing an applicator in a receptacle of a liquid contractile agent, and thereafter, contacting the upper surface of the eyelashes with the applicator.

13. The composition of claim 12 wherein the liquid contractile polymer is an anionic polymer.

14. The composition of claim 13 wherein the anionic polymer has a charge density of 1 to 10%, and an elastic modulus of 1 - 12 GPa.

15. A package comprising:
   a reservoir containing a contractile agent composition;
   an applicator for application of the composition to keratinous fibers; and
   instructions for using the liquid contractile agent to curl keratinous fibers.
Effect of Flexan II on Eyelash Curling

Fig. 1

Effect of Antara 430:Flexan II on Eyelash Curling

Fig. 2
Fig. 3d

Fig. 3e

Fig. 3f
High Curl Treatment 2
+ Mascara

Fig 3g

Fig. 4