A New Biopolymer Film-Former for Personal Care Applications
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Abstract: Film-forming agents are very common ingredients in personal care products where they are used in hair styling, skin care, and color cosmetics. A continuing trend in personal care products, indeed in many other markets as well, is the sustainability of the sources of those ingredients used. Asensa® NFF 11 is a corn starch based film-former that has been shown to work well in hair styling gels and lotions as well as in skin care to provide tightening. Its use in color cosmetics is being investigated.

Film-Formers in Personal Care
Personal care products are often in the form of emulsions or gels. There are many ingredients used in creating personal care products from the oily phase to the aqueous phase and all manner of additives to hold the two together. Many additional compounds are used to provide a special benefit or effect once the product is applied to the consumer’s skin or hair. One such added component is the film-former. These are used to coat the skin to prevent transepidermal water loss, to maintain a good barrier for ultraviolet radiation protection, to prevent chapping of the skin in cold, dry weather, etc. Film-formers are used in hair products where they can help to style the hair or to hold the style in place. In color cosmetics, film-formers are used in lipstick, eyeliner, mascara and many other applications. Of course, film-formers can be soluble in the oil or the water phase; the desired effect or benefit dictates which phase to use.

Typically in lipstick applications or in skin care formulations, where a water resistant film is desired to hold a sunscreen film on the skin, an oil soluble film-former is used. In hair styling or certain facial preparations, water solubility is desired.

People have been styling their hair and using products to keep the style in place for centuries. Products used for styling generally consist of a material that can be applied to the hair and that will hold the hair in place. Initially, the styling aids were natural fats and greases most likely from animal sources. Eventually, these fats were emulsified and fragrances added to make more elegant products that were widely accepted by both women and men. These waxy, greasy materials held the style by coating the hair with physically immovable substances that prevented the individual hairs from separating from one another. Of course, the greasy nature of these materials also held on to dust and dirt particles in the air and also rubbed off onto clothing and upholstery. In order to prevent this greasiness, scientists looked for other substances that could hold hair styles in place that did not rely on greasy materials. One of the first hair styling products that started the trend away from the more greasy appearance and feel was, again, a natural product; shellac. Animal derived, shellac was the first resin used in hair styling. It actually came from the coatings industry where it was used to protect wood. It was dissolved in alcohol and then it could be applied to hair and actually coat the hair fibers. Where two
(or more) fibers touched each other, a weld would form where, as the alcohol evaporated, the hairs were essentially glued together. In certain respects, it was a vast improvement over previously used products. It wasn’t greasy. It could be sprayed. It offered excellent humidity resistance. However there was one major problem, it was impervious to removal by all but the harshest of shampoos. In fact, it was generally brushed out.

Around the middle of the twentieth century, BASF developed a new polymer that found its way into hair styling. This was polyvinylpyrrolidone (PVP) and synthetic polymers have been used in hair styling products ever since. For more than 50 years, companies such as BASF, National Starch (Akzo Nobel), International Specialty Products (ISP) and others led the field in developing one new resin after another to offer benefits unheard of previously. Each new molecule offered some new benefit or property to satisfy a need brought about by consumer preferences or (more likely) regulatory pressure.

These various materials were based on a myriad of monomers and so a wide range of polymers were produced. As already mentioned, PVP was first followed by copolymers of vinylpyrrolidone with vinyl acetate to improve humidity resistance. Subsequently, other polymer types were created including methylvinylether copolymers with maleic anhydride which were then esterified. An almost endless variety of acrylic acid monomers led to many new polymers for hair setting. These were especially used in hair sprays when low volatile organic compounds (VOCs) were starting to be regulated because of their deleterious effects on the atmosphere.

Asensa® NFF 11

Then, in the beginning of the twenty first century something strange occurred. Consumers suddenly demanded a return to nature and products based on sustainable resources. In the court of public opinion, synthetic ingredients were now labeled as bad and consumers were willing to give up some of the benefits for a product that came from a natural or sustainable source. Products based on gums and other polysaccharides were offered but these did not perform to even minimal standards. The most noticeable problem with these materials was their lack of curl retention under high humidity conditions, a problem that had been easily solved with synthetic resins years before.

Now a new material has been developed that not only is essentially 100% natural and from sustainable resources, but also solves the curl retention problem. Asensa® NFF 11 biopolymer is a corn starch based natural polymer with both adhesive and film-forming properties, making it an excellent choice for hair styling applications. Like other products before it, this material was originally developed for industrial applications.

Asensa NFF 11 biopolymer is made through a patented process starting with corn starch. The resulting material is a coarse off-white powder that easily disperses in water to make a latex which can then be incorporated into hair styling preparations such as gels, lotions, mousses, etc. imparting hold, frizz control, and shine to the hair. Truly “green” products can be made with the Asensa NFF 11 biopolymer.

Asensa NFF 11 biopolymer is quite easy to use. It disperses readily in water to
give a slightly hazy dispersion. The use of a small amount of sodium carbonate or other base facilitates the dispersing.

The characteristics of Asensa NFF 11 biopolymer are given in the table below.

<table>
<thead>
<tr>
<th>Property</th>
<th>Asensa® NFF 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>INCI name</td>
<td>Hydrolyzed Corn Starch</td>
</tr>
<tr>
<td>Appearance</td>
<td>Off white, fine powder</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>4 – 10.5%</td>
</tr>
<tr>
<td>Bulk Density (kg/l)</td>
<td>0.5 – 0.7</td>
</tr>
<tr>
<td>Average Particle Size (µm)</td>
<td>~ 330</td>
</tr>
<tr>
<td>Brookfield viscosity, 25% solids, RTP, (mPa·s)</td>
<td>150 – 250</td>
</tr>
</tbody>
</table>

These parameters are not to be taken as specifications.

**Evaluations**

**Hair Styling**

One of the most common film-formers currently used in gel type styling products is still PVP; that synthetic polymer invented some 60+ years ago. But it is not a natural ingredient and it does have a particular problem when it comes to humidity resistance. Asensa NFF 11 biopolymer was compared to PVP in a typical gel (see Formulation I below) and subjected to both a salon in-use study as well as a curl retention study.

**In-use Study**

Product Treatment Protocol:

The stylist applied a commercial clarifying shampoo, lathered and rinsed according to manufacturer instructions. Following the shampoo treatment, the stylist applied a commercial daily conditioner to wet hair, distributed evenly to the ends and left on the hair for 2 minutes prior to rinsing. After rinsing away the conditioner and towel drying hair, the stylist parted the panelist’s hair and applied gel A to one side and gel B to the other side. Application of gel A and gel B was randomized between left and right sides of panelist’s heads. Refer to Appendix for Randomization Table. Equal amounts of gel A and gel B were applied on each side. The gel treated hair was styled according to hair type. Straight-hair panelists were curling iron styled after blow drying and curly/wavy panelists were scrunch styled while blow drying. (Full study report is available.)
Results

**Stylist Evaluation**

The results show that there are minimal differences between the two products and in some properties, the control (PVP) is better, whereas in other properties, Asensa NFF 11 is better.

**Panelist Evaluation**

Again we see a mixed response, but also one of minimal differences. While the differences are statistically significant, they do indicate that Asensa NFF 11 is a viable material for hair styling and it is based on sustainable resources.
Curl Retention Study

Curl retention is a test to see how a styling product resists humidity. Some resins will absorb moisture from the air and lower their glass transition temperature to below room temperature. This causes the resin to relax and the hair style to droop. We knew that PVP did not have very good curl retention, so if Asensa NFF 11 performed better than PVP we would know we had an improvement.

Procedure

Sample Treatment (Five tress replicates were used for each treatment)

1. Treat each tress with 1 cc gel product and wrap on ‘orange’ convex-shape perm rod (approx. 2 cm diameter, 6.3 cm circumference).
2. Dry wrapped tresses under hood drier for 2 hours until completely dry.
3. Remove curled tress from rod carefully (do not break film) and mount with binder clips to rod.

Curl Retention Measurement

1. Rod with mounted tresses was placed in an equilibrated chamber set at 90-95% Relative Humidity and 78 – 82 °F with positioning of top of tress at/near “0” mark.
2. Measurements of curl length were taken initially, at 30 minute intervals up to 4 hrs, 5 hrs, 6 hrs, 24 hrs and 48 hrs. Photographs were taken at each time point for comparison only (camera was aligned at a different vantage point from actual measurements).
3. Curl Retention was calculated using the following formula:

   \[
   \% \text{ Curl Retention} = \frac{(Lt - Lf)}{(Lt - Li)} \times 100\%
   \]

   Where:
   - \(Lt\) = Length of tress fully extended – 5.8"
   - \(Lf\) = Length of tress at each time interval
   - \(Li\) = Length of tress at initial

Results

In the curl retention study, Asensa NFF 11 biopolymer outperformed PVP and, in fact, the curls remained intact after 2 days in the humidity chamber. The results are shown below. (Asensa NFF 11 is on the left and PVP is on the right.)
With these results, we are convinced that we have a great new material for hair styling products.

**Skin Care Applications**
In the area of skin care, consumers are often looking for a tightening effect on the skin to help reduce the appearance of fine lines, especially around the eye area. There are a few different types of materials used in this application. In some cases, a film-former based on albumin is used since it provides a tightening effect as the water in the formulation evaporates from the skin. Some other, synthetic polymers behave similarly. Another technique to make fine lines and wrinkles seem to disappear is to use a mild irritant that makes the skin swell a little, thereby giving a smoother appearance. With the Asensa NFF 11 biopolymer, this type of product can be made with a sustainable polymer that is not animal derived, causes no irritation and is not based on petroleum products.

**Results**
In an initial screening study, panelists reported that they felt the tightening effect on the skin. (See Formulation IV below) The material was applied to the “crow’s foot” area of the eye as a simple formulation using xanthan gum to provide some body. A reduction in wrinkles and pore size was also observed. Further studies are being designed to follow up on these initial results.

**Color Cosmetic Applications**
In color cosmetics, film-formers are also used to keep the applied color in place on the skin or eyelashes, so eyeliners and mascaras can also be produced using the Asensa NFF 11 biopolymer to provide a more natural product. We are currently evaluating the material in these areas.
Summary
We have introduced a new, naturally based polymer into the personal care market. It shows utility in both hair care and skin care as a film-former. The results of evaluation tests indicate that it performs very well in hair styling and wrinkle reduction products. We are currently testing its performance in color cosmetics.

Formulation I
Spike Your Curls (Used in curl retention and in-use studies)
Honeywell Concept Formulation (F103)
Phase A:
- Water 75.74
- Carbomer (Carbopol 980) 0.60
Phase B:
- Glycerin 1.50
- 1,3-Propanediol (Zemea) 1.45
Phase C
- Asensa® NFF 11 (30 % Aqueous dispersion) 20.00
Phase D
- TEA 0.41
Phase E
- Glydant Plus 0.30

Procedure: Disperse Carbomer in the water. Add Phase B. Add Asensa NFF 11 dispersion. Neutralize with Phase D and then add preservative.

Acknowledgement
I would like to thank Mark Wheeler and John Clay for editorial suggestions, valuable discussions, and proofreading the final copy.

Formulation II
Keep Your Curls
Honeywell Concept Formulation (F102a)
Phase A:
- Water 85.25
Phase B:
- Xanthan Gum 1.50
- Glycerin 1.50
- 1,3-Propanediol (Zemea) 1.45
Phase C
- Asensa® NFF 11 (30 % Aqueous dispersion) 10.00
Phase D
- Glydant Plus 0.30

Procedure: Disperse xanthan in the glycerin and propanediol and add to water. Add Asensa NFF 11 dispersion and then add preservative.
Formulation III

Hair Styling Lotion

Honeywell Concept Formula (F105)

Phase A:
- Water 50.16

Phase B:
- Xanthan Gum 1.50
- Glycerin 1.50
- 1,3-Propanediol (Zemea) 1.45

Phase C
- Water 40.00
- Sodium Carbonate 0.09
- Asensa® NFF 11 5.00

Phase D
- Glydant Plus 0.30

Procedure: Mix each phase separately, add B to A with stirring until homogeneous and then add C with continued mixing. Add D and E, mix and package. The entire process can be carried out at room temperature.

Formulation IV

Eye Tightening Serum (Used in wrinkle reduction and pore size studies)

Honeywell Concept Formula

Phase A:
- Water 59.45
- Disodium EDTA 0.15
- Glydant Plus 0.20

Phase B
- Xanthan Gum 0.20

Phase C:
- Water 27.91
- Sodium Carbonate 0.09
- Asensa® NFF 11 12.00

Procedure: Mix each phase separately, add B to A with stirring until homogeneous and then add C with continued mixing.