**Hair conditioning foams formulations**

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**Introduction**

There are a number of substances used as hair conditioning agents. Those include fatty substances, ethylene glycols, silicones, protein hydrolysates, cationic surface-active agents, vitamins and other [1:6]. They are mainly applied to products such as: rinses, foams, creams, balms, lotions, gels, pomades, hair oils, shampoos [7].

Hair washing and care are among the most fundamental hygienic activities. Conditioning agents and shampoos are one of the most crucial and most competitive segments of the cosmetics market. Consumers appreciate the benefits of nice-looking and easily combed hair, and in recent years the conditioners market has witnessed the most rapid growth in the whole industry [7]. Hair conditioners are supposed to facilitate combing of wet and dry hair, provide antistatic and moisturizing effect, increase the hair shine and volume, as well as repair the damaged hair shafts.

Hair foams can be used as conditioners and/or styling agents. Foam products can be applied to both wet and dry hair. As with most conditioners, they can either be left on the hair until next washing or be rinsed after some time. The foam created by the propellant allows for even coverage of the hair with the product, thus ensuring easy combing, conditioning properties and hairstyle duration.

Foam products soften the hair, at the same time providing excellent stabilisation for the hairstyle. Applying the abovementioned products allows the consumers to instantly change their hairstyle; the products can change the direction of locks and waves, increase hair volume or give the hairstyle a wet appearance. Foam products differ from other styling products in that they do not leave the hair stiff and sticky. Applying hair foam is very easy and convenient, therefore products in the foam form are appreciated by a wide group of consumers [8].

First hair styling foam products were introduced to the market in 1970, however, they were not particularly popular at the time. Only in 1973 did Helene Curtis introduce a product line for professional styling under the name „Balsam & Body”. Other products by that company include: „Last Word” and „Heats On Self – Heating Foam Conditioner”. Those products were applied to wet hair and left until next washing. In Europe foams were introduced to retail in 1983 (L’Oreal). At the same time, foam styling product „Valence” was introduced to the American market. The product intended solely for conditioning was „Flone”, introduced by L’Oreal Paris. The product was available in two versions: moisturizing, whose aim was to replenish and retain moisture in the hair, and volume-enhancing. The years 1986-1987 saw further growth in foam products production. Increasingly higher consumer demands and changing hairstyle trends pushed foam products off the market and gave way to hairsprays. Hairsprays provided hairstyle stabilisation, something the foams were unable to do [8]. The general foam composition is as follows: solvent, active ingredients/polymers, propellant/s, emulsifier/polymer, stabilisation for the hairstyle. Applying the abovementioned products allows for even coverage of the hair with the product, thus ensuring easy combing, conditioning properties and hairstyle duration.

The aim of this study was to develop a formulation for a hair foam with conditioning and styling properties, at the same time retaining good organoleptic and utility parameters. Furthermore, the image of hair structure prior to and after application of keratine solution was made, using SEM technique.

**Experimental part**

Basing on the analysis of foam product formulations [9] and the information on cosmetic raw materials provided by manufacturers [10], a base formulation was developed. The formulation was then used to produce 7 foams with conditioning and styling properties. Each formulation contains ingredients (INCI) provided in Table 1.

In the comparative study market products with the following composition were used:

**Market product 1 (INCI):**

*Water, Glycerin, Cetrimonium Chloride, Polyquaternium-11, PVP/VA Copolymer, Ceteareth-20, PEG-25 LUminosan, Polyquaternium-11, PVP, Dimethicone, Octyl Methoxycinnamate, Hydrolyzed Keratin, Parna Glutamic Acid, Ceteareth-20, Propylene Glycol, Parfum.***

**Market product 2 (INCI):**

*Water, Alcohol Denat., Butane, Propane, VP/VA Copolymer, Polyquaternium-11, Panthenol Conditioner Water-soluble.***

**Market product 3 (INCI):**

*Water, Alcohol Denat., Butane, Propane, VP/VA Copolymer, Polyquaternium-16, Cetrimonium Chloride, Isobutane, Parfum, Phenoxy ethanol, Benzyl Acetate.***

**Table 1**

<table>
<thead>
<tr>
<th>Ingredients of the hair foam formulations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Trade name</strong></td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>Cetrimonium chloride</td>
</tr>
<tr>
<td>Polyimide – 1</td>
</tr>
<tr>
<td>Hydrolyzed Keratin</td>
</tr>
<tr>
<td>Polysorbate – 20</td>
</tr>
<tr>
<td>PEG-12 Dimethicone</td>
</tr>
<tr>
<td>Cocamidopropyl Betaine</td>
</tr>
<tr>
<td>PEG - 25 PABA</td>
</tr>
<tr>
<td>Freebase</td>
</tr>
<tr>
<td>VP/VA Copolymer</td>
</tr>
<tr>
<td>PVP</td>
</tr>
<tr>
<td>Citric acid</td>
</tr>
<tr>
<td>Propane/Butane</td>
</tr>
<tr>
<td>Panthenol</td>
</tr>
<tr>
<td>D – Panthenol USP</td>
</tr>
<tr>
<td>Dimethylaminomethane</td>
</tr>
</tbody>
</table>

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The obtained foam bases (75 cm³) were then placed in aluminium containers and kneaded; the containers were filled with propellant. The formulations of the obtained foams are provided in Table 2.

### Table 2

<table>
<thead>
<tr>
<th>Trade name</th>
<th>P 1</th>
<th>P 2</th>
<th>P 3</th>
<th>P 4</th>
<th>P 5</th>
<th>P 6</th>
<th>P 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>WATER</td>
<td>87.73</td>
<td>86.93</td>
<td>91.30</td>
<td>86.93</td>
<td>88.76</td>
<td>88.65</td>
<td>90.98</td>
</tr>
<tr>
<td>Propane/Butane</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Luviskol K30</td>
<td>2.78</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aquaflex XL 30</td>
<td>5.56</td>
<td>5.56</td>
<td>1.11</td>
<td>1.11</td>
<td>1.11</td>
<td>1.11</td>
<td>1.11</td>
</tr>
<tr>
<td>PVP W 635</td>
<td>-</td>
<td>-</td>
<td></td>
<td>5.56</td>
<td>5.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartamin 60W30</td>
<td>5.56</td>
<td>5.56</td>
<td>1.11</td>
<td>1.11</td>
<td>1.11</td>
<td>1.11</td>
<td>1.11</td>
</tr>
<tr>
<td>Kerasol</td>
<td>3.33</td>
<td>-</td>
<td>2.22</td>
<td>2.22</td>
<td>-</td>
<td>2.22</td>
<td>-</td>
</tr>
<tr>
<td>DC 193 Fluid</td>
<td>1.11</td>
<td>1.11</td>
<td>0.56</td>
<td>0.56</td>
<td>0.56</td>
<td>0.56</td>
<td>0.56</td>
</tr>
<tr>
<td>Ercasorb 2020</td>
<td>0.56</td>
<td>0.56</td>
<td>0.56</td>
<td>0.56</td>
<td>0.56</td>
<td>0.56</td>
<td>0.56</td>
</tr>
<tr>
<td>Fragrance</td>
<td>0.56</td>
<td>0.56</td>
<td>0.56</td>
<td>0.56</td>
<td>0.56</td>
<td>0.56</td>
<td>0.56</td>
</tr>
<tr>
<td>Citric acid</td>
<td>0.48</td>
<td>-</td>
<td>0.25</td>
<td>1.89</td>
<td>2.22</td>
<td>0.11</td>
<td>-</td>
</tr>
<tr>
<td>Panthenol</td>
<td>0.28</td>
<td>0.28</td>
<td>0.28</td>
<td>0.28</td>
<td>0.28</td>
<td>0.28</td>
<td>0.28</td>
</tr>
<tr>
<td>Tego Betaine ZF</td>
<td>0.22</td>
<td>0.22</td>
<td>0.22</td>
<td>0.22</td>
<td>0.22</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>EUXYL KS10</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>Uvinul P25</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Foam liquefaction time was measured by weighing out approx. 3 g of the given foam on a watch glass and then, using a stopwatch, the time was measured until the foam was liquefied.

The study of electrostatic properties of hair was conducted on the basis of hair volume measurement [12, 13]. This comprises measuring the width of the shadow cast by the hairpiece on a graph paper sheet, after prior washing of the hairpiece, applying the foam and drying in a hot air stream. On the basis of the shadow width measurement we can infer the efficacy of electrostatic charge reduction by the given conditioner.

Prior to measurements, hairpieces were washed in shampoo, carefully dried with a towel and combed bottom-up with a plastic fine-tooth comb. This activity was repeated 14 times. After applying the foam (0.5 g), the hairpiece was mounted on a tripod and dried completely with a hairdryer. The hair was then again combed (14 times) and the width of the shadow cast by the hairpiece on graph paper was measured. The width of the shadow was read out on the millimetre scale. In order to standardize results, the readout is carried out at 6 cm and 13 cm from the top of the hairpiece.

The obtained results are provided in Table 3.
• European, non-dyed, dark-brown hair
• single hairpiece weight approx. 2 g, length 17.5 cm
• all hairpieces made from the same hair type.

In order to acquire locks with proper curl, metal rollers with 1.5 cm in diameter were used. Prior to curling, the hairpieces were washed in 10% solution of a market shampoo, drained (in a paper towel) and then placed into a holding oven (45°C) for the night in order to dry off.

In the study of one foam type, 6 hairpieces were used plus one for the so-called blank test. 0.5 g of foam was rubbed into each of the 6 hairpieces; the hair was then curled on the roller. It is important for the hair to be curled strongly and tightly adhere to the roller. Curled hair was secured against uncurling with the use of clips. Identical procedure was applied to the blank test, using distilled water instead of foam. The prepared rollers were placed into the holding oven for 2 hours at 45 oC. After that time the hairpieces were removed of foam. The prepared rollers were placed into the holding oven where: L – length of fully straightened hair [cm]; L0 – length of hair prior to high humidity exposure [cm]; L t – length of hair after high humidity exposure over time t, cm.

The degree of hairpiece straightening was marked on the scale on the chamber wall after each readout. The hair shape retention was calculated using the following formula:

\[
\% \text{ of hair shape stability} = \frac{L - L_0}{L_t - L_0} \times 100\% 
\]

where: L – length of fully straightened hair [cm]; L0 – length of hair prior to high humidity exposure [cm]; L t - length of hair after high humidity exposure over time t, cm.

The obtained mean results of hair curl retention for the tested products are provided in Table 4.

### Table 4

<table>
<thead>
<tr>
<th>TIME</th>
<th>P 1</th>
<th>P 2</th>
<th>P 3</th>
<th>P 4</th>
<th>P 5</th>
<th>P 6</th>
<th>P 7</th>
<th>MP 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
<tr>
<td>15</td>
<td>82.58</td>
<td>78.77</td>
<td>91.58</td>
<td>90.29</td>
<td>92.68</td>
<td>91.13</td>
<td>89.10</td>
<td>85.79</td>
</tr>
<tr>
<td>30</td>
<td>75.00</td>
<td>68.77</td>
<td>84.72</td>
<td>81.97</td>
<td>83.41</td>
<td>83.64</td>
<td>81.24</td>
<td>77.03</td>
</tr>
<tr>
<td>45</td>
<td>68.41</td>
<td>63.42</td>
<td>80.75</td>
<td>77.36</td>
<td>78.91</td>
<td>80.37</td>
<td>77.22</td>
<td>70.24</td>
</tr>
<tr>
<td>60</td>
<td>65.55</td>
<td>60.78</td>
<td>77.74</td>
<td>73.81</td>
<td>74.79</td>
<td>77.94</td>
<td>74.66</td>
<td>68.55</td>
</tr>
<tr>
<td>90</td>
<td>61.17</td>
<td>58.28</td>
<td>75.48</td>
<td>69.66</td>
<td>69.82</td>
<td>75.49</td>
<td>72.20</td>
<td>64.77</td>
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<tr>
<td>120</td>
<td>57.57</td>
<td>55.57</td>
<td>72.90</td>
<td>66.83</td>
<td>64.27</td>
<td>73.86</td>
<td>68.67</td>
<td>64.18</td>
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<tr>
<td>150</td>
<td>55.28</td>
<td>53.76</td>
<td>70.90</td>
<td>66.83</td>
<td>63.55</td>
<td>73.86</td>
<td>68.11</td>
<td>61.88</td>
</tr>
</tbody>
</table>

The analysis of the hair structure image was carried out with SEM technique, using the JEOL JSM-5410 scanning electron microscope with an EDS detector by NORAN. The analysis was carried out on „bundles” of dyed, dark-brown European hair. Next, the hair was subjected to harsh conditions by placing it into a market hair lightener with 9% distilled water for 12 hours.

Prepared hair was then placed on the so-called holders and dusted with gold, and placed in the apparatus to conduct measurements. Finally, the hair was immersed in Kerasol solution with 0.39% concentrated keratine.

### Discussion

All acquired foams contain a conditioning agent (Quartamin 60W30 – cetrimonium chloride). Aside from the abovementioned quat, also keratine hydrolysates were added to four foams (1, 3, 4, 6). Foam 2 was the placebo (did not contain keratine hydrolysate). Both foam 1 and 2 did not contain conditioning and styling resins. Foam 3 contained Luviskol K30 resin, foams 4 and 5 contained Aquaflex XL 30, and foams 6 and 7 contained PVP W 635 resin.

The pH values of foam base 1 with conditioning agent (keratine), not containing stabilizing resin, was 5.70 and required correction. The foam base 5 (4/8, 14), based on Aquaflex XL 30 resin, required a minor addition of citric acid solution. The PVP W 635 resin in foam 6 reduced the base pH. In bases with keratine (pH approx. 5.84) higher pH values were observed than in bases without keratine (pH approx. 5.14). Foam 3 with Luviskol K30 resin had the pH of 6.04. Similarly, bases with PVP W 635 and Luviskol K30 resins required minor additions of citric acid solution to reduce the pH value. The lowest pH value was observed in the foam base 2 (3.80).

Comparing the density of acquired products, it was established that the highest reduction of foam base density was caused by PVP W 635 (PVP/VA) resin.

The dry mass indicator informs on the causalities of production and the quality of the given foam product. Low solid content value of other foams might indicate the absence of resin from the formulation; with higher SC value the foam is considered to have better conditioning and styling properties. This is not entirely correct, since high presence of volatile ingredients might distort the results. Those ingredients might escape at the measurement temperature (105°C) and thus be absent from the solid content. The analysis of solid content (Fig. 1) shows that the lowest solid content value (0.61) was observed in the market product 1, which was most likely caused by high content of volatile ingredients therein.
2, 5, 7 (not containing keratine – Kerasol) exhibited liquefaction time 
of (15.30; 16.10 min), whereas the liquefaction times of foams with 
keratine (1, 3, 4, 6) were shorter and amounted to (15.13; 16.40; 
9.20; 15.41 min respectively). The liquefaction time values of foam 
products acquired in the laboratory (with the exception of foam 4, 
containing Aquaflex XL30, Quartamin 60W30 and Kerasol resins) were 
characterised by comparable liquefaction times to market product 1.

Electrostatic properties of hair are often the crucial parameter 
determining the demand for the given product on the market.

Electrostatic properties

It is important that the electrostatic properties of hair are significantly 
reduced after applying the foam. Figure 2 presents the impact of the 
studied products on the electrostatic properties of hair. The diagram 
indicates that the lowest electrostatic properties are exhibited by 
foam 1 (without resin), containing a conditioning mixture of keratine 
hydrolysates (3%) and cetrimonium chloride (5%). When foam 1 
was applied, a considerable reduction in the hairpiece shadow width 
was observed from 60 to 39 cm. In the case of foams containing resins, 
the lowest electrostatic properties of hair is attributed to foam 6 with 
a 5% PVP W 635 addition and conditioning agents: keratine 2% and 
Quartamin 60W30 1% (shadow width reduction from 60 to 45 cm). 
In general, all of the studied products exhibit very good antistatic 
properties, comparable to market foam (MP1).

Figure 3 presents the curl retention of hairpiece, depending on the 
applied resin or absence thereof.

The highest curl retention rate was observed for foam 6 (5% PVP/ 
VA), exhibiting curl retention of 73.86%, higher than the rate for foam 
7 (68.11%) which contains similar ingredients, with the exception of 
keraatine hydrolysates. In the case of foams based on Aquaflex XL30 
resin, the addition of keratine had increased the CR value. Foam 5, 
with similar content of Aquaflex XL30 but without Kerasol, had lower 
CR value (CR = 63.55%) than foam 4, containing 2% Kerasol (CR = 
66.83%). Foams based on Aquaflex resin provide lower curl retention 
rate than foams containing PVP/VA.

High curl retention rate (70.90%) was also observed in 
hairpieces treated with foam 3, containing 2.5% Luviskol K30 resin 
and 2% Kerasol.

The CR value for foam 1, containing 3% keratine hydrolysates, 
is (55.28%), while for foam 2, which was the placebo, the value was 
(55.76%). In both those foams the keratine hydrolysates exhibit no 
positive impact on the curl retention rate.

SEM analysis of the hair structure has confirmed the layer 
structure. Photographs 1 and 2 present the exterior hair layer – 
the cuticle. On photograph 2 we can see jagged, fractured and open 
hair scales, indicating that the hair is considerably damaged.

Fig. 2. Effect of the antistatic agent on electrostatic properties of hair

Photo. 1. Open hair scales

Photo. 2. A broken hair scale is indicated

Photo. 3. SEM image of hair interior after removal of cuticle
In order to examine the conditioning impact of keratine, a hair sample was immersed in 0.39% solution of keratine hydrolysate (Kerasol) for 3 minutes. After drying the sample was observed under a microscope. Photographs 5 and 6 show the image of the hair sample after conditioning. As we can see, the keratine with low hydrolyse degree (M = 125,000) creates a protective film, covering the open scales and cortex.

Conclusions

When using keratine hydrolysate solution as the hair conditioning agent, it is important to select the appropriate pH of the foam base (optimum pH = 5.00).

The solid content (SC) of the ready product (foam) depends on its composition. The lowest SC value was observed for foams containing extremely volatile ingredients.

The curl retention (CR) depends on the type and concentration of resin used in the foam. The addition of PVP, PVP/VA or Polyimide – 1 (2.5% of mass) resins allowed for achieving average CR rate. The highest CR rate (73.86%) is provided by foam 6 (5% PVP/VA).

The cationic surface-active agents effectively reduce the electrostatic properties of hair. A 64% (1.5% cetrimonium chloride) and an average 59% (0.3% cetrimonium chloride) reduction of hairpiece shadow was observed after applying products containing that complex.

AquaFlex XL 30 (Polyimide – 1) in 2.5% mass concentration failed as ingredient in hair styling foam products.

Keratine with high molecular weight (M=125,000) creates a protective film on the hair surface, instead of penetrating the interior.

Literature


Jan OGONOWSKI – Professor (Ph.D., Eng) is a graduate of the Faculty of Chemistry of the Silesian University of Technology (1996). Currently He is employed as Head of the Organic Technology and Refining Processes Chair on the Faculty of Chemical Engineering and Technology, Cracow University of Technology. Specialization: organic technology, biotechnology, catalytic processes.

Marta OLSZANSKA – Ph.D., (Eng), is a graduate of the Faculty of Chemical Engineering and Technology of the Cracow University of Technology (1971). Currently She is employed at the Institute of Organic Chemistry and Technology. Specialization: low-tonnage products technology, cosmetic chemistry and technology.

Rafal SADOWSKI – Ms.Sc., (Eng), is a graduate of the Faculty of Chemical Engineering and Technology of the Cracow University of Technology (2010).