

## INFLUENCE OF NATURAL POLYMER DERIVED FROM STARCH AS A SENSORY MODIFIER IN SUNSCREEN FORMULATIONS

ROBERTA B RIGON<sup>1</sup>, ADRIELLE R PIFFER<sup>2</sup>, ALINE A S LIMA<sup>2</sup>, APARECIDA E BIGHETTI<sup>2</sup>, MARLUS CHORILLI<sup>1</sup>

<sup>1</sup>Pharmaceutical Sciences Schools, Department of Drugs and Medicines, Universidade Estadual Paulista Júlio de Mesquita Filho, Rodovia Jau-Araraquara, Km 1, 14801-902, Araraquara - SP, Brazil, <sup>2</sup>San Francisco University of Bragança Paulista, USF, Av. São Francisco de Assis, 218, Bragança Paulista, São Paulo, Brazil.

Received: 07 Nov 2012, Revised and Accepted: 13 Dec 2012

### ABSTRACT

**Background:** Nowadays, there has been increased incidence of skin cancer, which is mainly related to increased sun exposure. Although sunscreen products may prevent the appearing of this disease, consumers may not use them due to some factors, including the sensory properties. The *Aluminum Starch Octenylsuccinate* (Dry-Flo<sup>®</sup> Pure, Akzo Nobel), an aluminum salt produced by the reaction of anhydride octenylsuccinic with starch, is able to improve the spreadability on the skin and reduce the oiliness of the formulation.

**Objective:** To verify volunteers' acceptance for sunscreen formulation with natural polymer, compared with a control formulation (without polymer).

**Methods:** To carry out the sensory analysis a formulation with or without 2.0% *Aluminum Starch Octenylsuccinate* was prepared. Formulations had FPS 15, with critical wavelength of 353 nm, determined by testing *in silico* using the BASF<sup>®</sup> Sunscreen Simulator. Sensory analysis was performed on 60 students of both sexes, aged between 18 and 25 years, regular users of sunscreen products.

**Results:** The results suggested that the polymer was able to promote a very soft and velvety feel on the skin when used in a sunscreen formulation, and it was able to mitigate and noticeably reduce the oiliness of the skin. Of the 60 volunteers who participated in the study, 45 volunteers (75%) considered that the polymer formulation provides little brightness or did not notice the difference in brightness of the skin after application.

**Conclusions:** It was able to improve the sensory of the product, contributing to greater volunteers' acceptance.

**Keywords:** Sensory analysis; Sunscreen; Sensory modifier; Aluminum Starch Octenylsuccinate.

### INTRODUCTION

Recently, there has been increased incidence of skin cancer, including melanomas and basocellular and spinocellular carcinomas, causing great concern for public health officials, who have conducted many campaigns for prevention and early diagnosis[1]. This increased incidence is related mainly to increased sun exposure.

In addition to skin cancer, exposure to solar ultraviolet radiation (UV) is a very important factor in the pathogenesis of various skin diseases, including skin aging and hyperpigmentation acquired[2].

UV radiation can be divided into three spectrums: UVA (320-400 nm), UVB (280-320 nm) and UVC (<280 nm).

UVA radiation can penetrate the epidermis, reaching the dermis, where it induces the formation of singlet oxygen and free radicals that can damage cellular macromolecules such as proteins, lipids and deoxyribonucleic acid (DNA) [3].

UVB radiation can induce a variety of biological effects, including inflammation, sunburn, hyperpigmentation, immunological changes and induction of oxidative stress, which when combined, can promote the formation of skin cancer[4].

Thus, various skin changes resulting from chronic exposure to UVB radiation can cause photoaging, which is mainly related to the degradation of skin extracellular matrix and hyperpigmentation; immunosuppression and photocarcinogenesis that is involved in the accumulation of genetic alterations as well as modulation of the immune system and the development of skin cancer[5].

Given the harmful effects caused by UVA and UVB radiation and considering the need for prevention of these effects on the skin, several *in vivo* and *in vitro* studies have been conducted to demonstrate that the use of sunscreen products may prevent the appearance of such diseases[6].

Currently, researchers at the University of Queensland, Australia, found in a randomized study that the use of sunscreen SPF 15 or higher, in a period of 5 years, in adults aged 25 to 75 years, reduced

the incidence of new primary melanomas for up to 10 years after the end of the study. In addition, the protective effect was also evident in invasive melanomas, which showed a decrease of 73% in those patients who received sunscreen daily. Thus, the researchers concluded that melanoma can be prevented by regular use of sunscreen also in adults[7].

Another study confirmed that sunscreens prevent UVA radiation-induced transcriptional expression of five genes studied. These results indicate the high effectiveness of broad-spectrum sunscreens protect the human skin against the gene response induced by UVA[8].

Furthermore, Moroccan investigators found excellent tolerance of broad-spectrum sunscreen products (SPF 50+, UVA-PF 28) when used by pregnant women for 12 months, and demonstrated that the use of this product reduced the occurrence of chloasma. From 185 pregnant women who completed the study, chloasma was observed in only 5 of them, an occurrence of 2.7%. In colorimetric essays, whitening of skin and reduction of pigmented areas in late pregnancy were observed[9].

Even with numerous benefits associated with the use of sunscreen, it is known that adherence to sunscreen is low. A Brazilian study found that only 23% of survey respondents used sunscreen[10].

Sunscreens are available in the market since 1928, and the industries in the sector have focused on developing new formulations that have increased solar protection factor (SPF) and protection against both UVA and UVB radiation through combinations of filters or use of new substances, with the aim of increasing the effectiveness of their products[6].

Nevertheless, it is observed that even with scientific advances, many currently marketed sunscreen products have not been well received by the general public due to inadequate sensory properties that they have[11].

It is known that some typical characteristics of sunscreens can reduce the interest of consumers, i.e. increasing the greasy feel and whitish or 'ghost' effect promoted by physical sunscreens[12].

Thereby, in order to increase consumers' adhesion in daily application of sunscreen products, various substances have been used in formulations in order to improve sensory quality of final product. Moreover, there is a growing search for replacing synthetic by natural and organic substances, since they are safer and more sustainable for the environment[13].

Standing out among numerous materials currently used, the *Aluminum Starch Octenylsuccinate* (Dry-Flo® Pure, Akzo Nobel), an aluminum salt produced by the reaction of anhydride octenylsuccinic with starch[14]. It is a polymer that improves spreadability on the skin and reduces the oiliness of the formulation, promoting silky and velvety sensory characteristics to the product.

Usually, companies perform sensory analysis to verify the acceptance of a certain product in the market. Sensory characteristics are as important to consumers as efficacy and safety tests, and are the motivation for consumers to buy and continue using the product[15].

Beyond that, sensory analysis provides reliable information for research, development and production of cosmetic products, in order to anticipate the impact of this in the market. Likewise, marketers can verify if the sensory properties are compatible with the intended goals and publicity[16].

The aim of this study was to verify the volunteers' acceptance for sunscreen formulation containing natural polymer hydrophobically modified starch-based, compared with a control formulation (without polymer).

## MATERIALS AND METHODS

### Formulation Development

To carry out the comparative test of sensory evaluation of sunscreen, it was used a formulation containing glyceryl monostearate, cetostearyl alcohol; octyl metoxicinamate, octyl salicylate, avobenzone, homosalate; phenonip® (INCI name: *Phenoxyethanol, Methylparaben, Ethylparaben, Butylparaben, Propylparaben, Isobutylparaben*, Clariant, United Kingdom), disodium EDTA and deionized water, with the addition of: (A) 2.0% *Aluminum Starch Octenylsuccinate* (Dry-Flo® Pure, Akzo Nobel) or (B) without the addition of polymer (Table 1). The emulsions were prepared melting the separate phases: phase O (oil) and phase A (aqueous) at a temperature of 75° - 80° C under constant mechanical stirring. After the two phases reach the same temperature the aqueous phase was poured into the oil phase. Agitation and temperature were maintained for 15 minutes. Then, shut down the heating and stirring was maintained until cooling. The pH was adjusted to 6.5 with triethanolamine and the formulations were allowed to settle for 24 hours, capped and at room temperature.

**Table 1: Sunscreen formulations for sensory evaluation**

| Components                              | Concentration (%) |               |
|---|-------------------|---------------|
|   | Formulation A     | Formulation B |
| Glyceryl monostearate                   | 0.5               | 0.5           |
| Cetostearyl alcohol                     | 2.0               | 2.0           |
| Octyl metoxicinamate                    | 7.5               | 7.5           |
| Octyl salicylate                        | 5.0               | 5.0           |
| Avobenzone                              | 2.0               | 2.0           |
| Homosalate                              | 10.0              | 10.0          |
| Phenonip®                               | 0.5               | 0.5           |
| Disodium EDTA                           | 0.04              | 0.04          |
| Deionized water                         | qs* 100           | qs* 100       |
| Triethanolamine                         | qs* pH 6.5        | qs* pH 6.5    |
| <i>Aluminum Starch Octenylsuccinate</i> | 2.0               | ---           |

\*qs - Means adding a quantity sufficient to achieve a stated function.

### SPF Determination of formulations tested

SPF determination of formulations was performed *in silico* test using the BASF® Sunscreen Simulator. This program is an alternative to estimate the SPF *in vitro*, based on the properties of ultraviolet absorption of sunscreens in the formulation[17].

The reliability of the program is based on the reproducibility of the *in vitro* SPF of three sunscreens patterns, with *in vivo* SPF values known, determined in accordance with the European protocol[17].

### Consumer Panel

This study was approved by the Research Ethics Committee of the San Francisco University of Bragança Paulista, protocol 0119.0.142.000-09/2009. Sensory analysis was performed on 60 students of both sexes, regular users of sunscreen products. Participants were aged between 18 and 25 years and belonging to the University San Francisco, located in Bragança Paulista, SP, Brazil. The sample was randomly divided in 2 groups of 30 volunteers.

### Acceptance Test

Consumers received 2 photoprotective cosmetic products, which were stored in plastic tubes of 60 mL, coded with 3 random digits, in this article represented only as product: (A) Basic formulation of sunscreen with natural polymer derived from starch (Dry-Flo® Pure - INCI name: *Aluminum Starch Octenylsuccinate*) and (B) Basic formulation of sunscreen without polymer (control).

The volunteers were instructed to apply the formulation in the forearm, in the previously demarcated area with dimensions of 4 cm x 8 cm each. The test coordinator requested that each consumer placed 2.0 g of each product in the center of one of the cycles and with 15 rhythmic movements applied in the direction of the wrist to the antecubital fossa.

Consumers were instructed to describe the intensity of the attributes, according to a 5-point hedonic scale (Table 2), and data were collected in paper ballots through self-administered questionnaire containing the sensory attributes (texture, spreadability, absorption, tackiness, brightness, softness and greasiness). The tests were conducted in a sensory laboratory and the evaluations were performed under artificial lighting, controlled temperature (between 22 and 24° C) and air circulation.

**Table 2: Hedonic scale of volunteers' acceptance**

| Hedonic Scale     | Points |
|-------------------|--------|
| Like very much    | 5      |
| Like a little     | 4      |
| Not sure          | 3      |
| Dislike a little  | 2      |
| Dislike very much | 1      |

Before the assessments, consumers were given an explanation of the test. The two formulations were evaluated in a single session of approximately 30 minutes.

### Analysis of Results

The results were statistically analyzed to detect significant differences between the sensory analyses for each formulation. Tests were conducted with a significance level of 5% in order to determine the type of distribution of sample data, and the degree of homogeneity. For this, data were compiled in Origin software. Were considered normal probability plots, distributions that follow approximate the pattern of a straight line. Thus, the distribution can be considered 'not normal', when the distribution of points on the right is below the straight line determined by the rest of the points[18]. From the verification of normality was carried out using ANOVA followed by Tukey's test.

## RESULTS AND DISCUSSIONS

### SPF Determination of Formulations

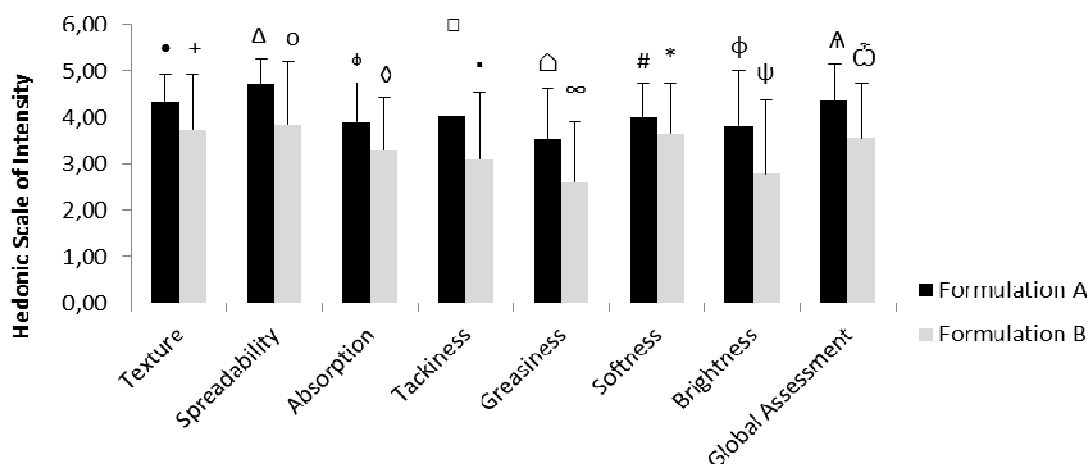
The test *in silico* carried out in the BASF® Sunscreen Simulator[17] showed that formulations had 15 FPS, with critical wavelength of 353 nm.

### Sensory Analysis

Through the questionnaire responses, it was possible to evaluate different sensory aspects of the analyzed formulations. Table 3 shows the mean score and standard deviations related to the sensory attributes evaluated by the volunteers on each formulation.

**Table 3: Volunteers' sensory analysis in each sunscreen formulation, according to hedonic scale of intensity**

| Sensory Attributes | Formulation A | Formulation B |
|--------------------|---------------|---------------|
| Texture            | 4.33 ± 0.60   | 3.75 ± 1.19   |
| Spreadability      | 4.72 ± 0.56   | 3.85 ± 1.36   |
| Absorption         | 3.90 ± 0.84   | 3.28 ± 1.15   |
| Tackiness          | 4.05 ± 1.41   | 3.10 ± 1.46   |
| Greasiness         | 3.53 ± 1.10   | 2.62 ± 1.29   |
| Softness           | 4.00 ± 0.74   | 3.67 ± 1.07   |
| Brightness         | 3.82 ± 1.19   | 2.78 ± 1.60   |
| Global Assessment  | 4.35 ± 0.80   | 3.55 ± 1.17   |



The same symbols on top of the averages indicate that the difference among them was not statistically significant ( $P > 0.05$ ).

**Fig. 1: Statistical analysis of data ( $p < 0.05$ ) in relation to the sensory attributes evaluated**

For a sunscreen has high adhesion among consumers, it is necessary that the formulations complies with certain requirements, such as: reasonable price, high resistance to water, non-sticky feel[20]. It is observed in Figure 1 that Formulation B has lower spreadability and tackiness when compared with Formulation A, which contain the natural polymer, differing to the results found by Parente, Gámbaro and Ares (2008)[21]. These researchers found in their results that the increase in solid content is directly proportional to the increased difficulty of spreading and stickiness of a formulation.

The difficulty of spreading may be related to properties that depend on the interaction between the skin and the product during the mechanical movement of application[21]. According to Parente *et al.* (2005)[22], the difficulty of spreading and skin adhesion can be related also to the physicochemical properties of the formulation, i.e. the viscosity, which measures the resistance to flow.

Moreover, the spreadability of the formulation A probably performed better due to the physical characteristics of the polymer to possess fine and uniform particles. In sunscreens, good spreadability is extremely important since it is closely related to the mode of application and it should promote a uniform layer on the skin and ensure the SPF[23].

The excess of oily feeling in the formulations can be reduced through the use of 3%, more preferably 1.5% to 2.5%, of raw materials that absorb oil, i.e. the *Aluminum Starch Octenylsuccinate* (Dry-Flo® Pure, Akzo Nobel)[24]. This effect could be observed, because the

In all evaluated attributes, there is a high standard deviation (0.56 to 1.60), which indicates a wide variation between assessments of consumers. According to Parente, Ares and Manzoni (2010)[19], this indicates that consumers do not have similar references to the evaluated attributes, suggesting heterogeneity in scores of consumers. This behavior can be explained by the absence of training for evaluation of cosmetic products and also be affected by the fact that there are no references during the evaluation.

Figure 1 shows that formulations were statistically different ( $p < 0.05$ ) for all evaluated parameters, according to hedonic scale of intensity.

Formulation A, which contained 2.0% of this raw material, decreased oily sensation significantly when compared to the Formulation B.

A study performed in Montevideo, Uruguay, showed that a correlation exists between the terms 'easy to apply' and 'soft' as well as the terms 'sticky', 'oily' and 'heavy'. In addition, the texture was correlated with the ease of application, indicating that more viscous emulsions are more difficult to apply to the skin and more difficult to be absorbed through the skin, leaving a larger residual, and present oily feel[19]. The same could be observed in this study. It appears that the Formulation A, which was easier to apply, provides softness to the touch as well as texture superior than Formulation B. Moreover, as already shown above, Formulation B shows more oily and sticky feel than Formulation A.

The brightness is an important attribute to be evaluated in sensory analysis, because it is related to the appearance of the skin. The complete absence of brightness can make the skin look like dry appearance, while the brightness can contribute to an unattractive skin, due to the oily-look[25]. The volunteers felt that the conventional sunscreen formulation (Formulation B) promotes increase in perceived brightness of the skin (Figure 1). Of the 60 volunteers who participated in the study, 35 (58.33%) considered that the skin is too bright or moderately bright after the application of Formulation B. While 45 volunteers (75%) considered that Formulation A provides little brightness or did not notice the difference in brightness of the skin after application (Table 4).

**Table 4: Evaluation of volunteers' perception with respect to brightness after product application**

| Evaluation of Brightness   | Number of Volunteers |               |
|--|----------------------|---------------|
|  | Formulation A        | Formulation B |
| Very bright  | 1                    | 17            |
| Moderate bright  | 14                   | 18            |
| Little bright  | 25                   | 11            |
| There is no difference in the brightness of the skin after application of the product. | 20                   | 14            |

Results show that volunteers assigned to Formulation B as having greater stickiness, oilier feel and higher brightness and Formulation A as having better spreadability, softness and global assessment.

The results suggest that the sensory modifier polymer added in the formulation, *Aluminum Starch Octenylsuccinate* (Dry-Flo® Pure, Akzo Nobel), was able to promote softness and velvety feel to the sunscreen, and it was able to mitigate and noticeably reduce the oiliness of the skin produced by the other components. In addition, the starch showed a soft and dry sensory of the skin, while also improving spreadability of the product. Thus, it was able to improve the sensory characteristics of the analyzed sunscreen, contributing to greater acceptance by the volunteers.

#### ACKNOWLEDGEMENTS

The authors wish to thank CAPES, PADC, FAPESP and CNPq for the financial support.

#### REFERENCES

- Mendonça GAS. Risco crescente de melanoma de pele no Brasil. *Rev Saude Publ* 1992; 26(4):290-4.
- Ndiaye M, Philippe C, Mukhtar H, Ahmad N. The grape antioxidant resveratrol for skin disorders: promise, prospects, and challenges. *Arch Biochem Biophys* 2011; 508(2):164-70.
- Katiyar SK. Grape seed proanthocyanidines and skin cancer prevention: inhibition of oxidative stress and protection of immune system. *Mol Nutr Food Res* 2008; 52 Suppl 1:S71-6.
- Williams KA, Kolappaswamy K, Detolla LJ, Vucenik I. Protective Effect of Inositol Hexaphosphate Against UVB Damage in HaCaT Cells and Skin Carcinogenesis in SKH1 Hairless Mice. *Comp Med* 2011; 61(1):39-44.
- Matsumura Y, Ananthaswamy HN. Toxic effects of ultraviolet radiation on the skin. *Toxicol Appl Pharm* 2004; 195(3):298-308.
- Sambandan DR, Ratner D. Sunscreens: an overview and update. *J Am Acad Dermatol* 2011; 64(4):748-58.
- Green AC, Williams GM, Logan V, Stratton GM. Reduced melanoma after regular sunscreen use: randomized trial follow-up. *J Clin Oncol* 2011; 29(3):257-63.
- Marionnet C, Grether-Beck S, Seité S, Marini A, Jaenicke T, Lejeune F et al. A broad-spectrum sunscreen prevents UVA radiation-induced gene expression in reconstructed skin *in vitro* and in human skin *in vivo*. *Exp Dermatol* 2011; 20(6):477-82.
- Lakhdar H, Zouhair K, Khadir K, Essari A, Richard A, Seité S et al. Evaluation of the effectiveness of a broad-spectrum sunscreen in the prevention of chloasma in pregnant women. *J Eur Acad Dermatol* 2007; 21(6):738-42.
- Lima AG, Silva AMM, Soares CEC, Souza RAX, Souza MCMR. Fotoexposição solar e fotoproteção de agentes de saúde em município de Minas Gerais. *Rev Eletr Enf* 2010; 12(3):478-82.
- Clares B, Gálvez P, Gallardo V, Ruiz MA. Elaboration, characterization, and stability study of a sunscreen emulsion for use as a towelette application in pediatric photoprotection. *J Cosmet Sci* 2011; 62(4):371-82.
- Puizina-Ivic N. Skin aging. *Acta Dermatovenerol Alp Panonica Adriat* 2008; 17(2):47-54.
- Lyrio ES, Ferreira GC, Zuqui SN, Silva AG. Recursos vegetais em biocosméticos: conceito inovador de beleza, saúde e sustentabilidade. *Natureza on line* 2001, 9(1):47-51.
- Nair B, Yamarik TA. Cosmetic Ingredient Review Expert panel. Final report on the safety assessment of aluminum starch octenylsuccinate. *Int J Toxicol* 2002; 21 Suppl 1:1-7.
- Zague V, Nishikawa DO, Silva DA, Baby AR, Behrens JH, Kaneko TM et al. Influence of storage temperature on cooling intensity of topical emulsions containing encapsulated menthol. *J Sens Stud* 2008; 23:26-34.
- Cruz AG, Cadena RS, Walter EHM, Mortazavian AM, Granato D, Faria JAF et al. Sensory Analysis: Relevance for Prebiotic, Probiotic, and Synbiotic Product Development. *Compr Rev Food Sci F* 2010; 9(4):358-373.
- Herzog B. Prediction of sun protection factors by calculation of transmissions with a calibrated step film model. *J Cosmet Sci* 2002; 53(1):11-26.
- Freund JE, Simon GA. *Estatística Aplicada: Economia, Administração e Contabilidade*. 9th edn. Porto Alegre: Bookman; 2000.
- Parente ME, Ares G, Manzoni AV. Application of two consumer profiling techniques to cosmetic emulsions. *J Sens Stud* 2010; 25(5):685-705.
- Maier H, Schmalwieser AW. Sunscreens and occupation: the Austrian experience. *Photochem Photobiol Sci* 2010; 9:510-515.
- Parente ME, Gámbaro A, Ares G. Sensory characterization of emollients. *J Cosmet Sci* 2008; 23(3):149-61.
- Parente ME, Gámbaro A, Solanas G. Study of sensory properties of emollients used in cosmetics and their correlation with physicochemical properties. *J Cosmet Sci* 2005; 56(3):175-82.
- Borghetti Gs, Knorst MT. Desenvolvimento e avaliação da estabilidade física de loções O/A contendo filtros solares. *Braz J Pharm Sci* 2006; 42(4):531-7.
- Krafton TJ. The Gillette Company. Antiperspirant Emulsion. US Patent 4,499,069, filed Feb. 7, 1983, and issued Feb. 12, 1985.
- Fujii M, Misaki Y, Sasaki I. Application of image processing technique for facial gloss evaluation. *Int J Cosmetic Sci* 2010; 32:163-16.