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ABSTRACT OF THE DISSERTATION

„ Identification of factors influencing the uncontrolled crystallization of chemical UV filters/stabilizers in cosmetic formulations and development of inhibitors for selected systems"

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Designing multifunctional cosmetics containing sunscreens can lead to formulation difficulties. Sunscreen filters burden the formulation, increase viscosity, cause a sense of heaviness, a whitening effect on the skin, and can also lead to various types of destabilization of the end product. One of the significant problems is the recrystallization of chemical sunscreen filters. They precipitate from the composition in the form of visible crystallites on the surface of the cosmetic mass and/or are perceptible as small granules within the volume of the product during sensory testing. The crystallization of parts of the filters primarily affects the reduction of sun protection effectiveness; an additional unfavourable aspect is the decline in product quality due to emerging instabilities in the mass (crystallization, discolorations, leaks, phase separation) which worsen its aesthetics in the packaging, potentially leading to a negative perception of the product. Cosmetics are complex multi-component systems of raw materials, which is why the proper selection of ingredients is crucial to achieve a high-quality product. A crucial element of pre-market cosmetic research is aging tests, as they enable a relatively quick assessment of potential defects, allowing issues to be detected early and formulation changes to be introduced in a timely manner to prevent the appearance of instability-related flaws.

The aim of this thesis was to develop formulations for an anhydrous makeup fluid with a high sun protection factor, in which the issue of crystalline precipitates would either not occur or would be significantly delayed (i.e., extending beyond the standard "shelf life" of the product, which is 37 months). This involved identifying crystalline precipitates that appear in anhydrous makeup formulations containing both chemical and physical sunscreens (carefully selected to provide an SPF50 level of protection), as well as identifying factors that promote the crystallization of these filters within the cosmetic mass and determining the mechanism of their formation.

The research for this doctoral thesis was divided into several stages. In the first stage, production cosmetic masses were subjected to testing, during which crystalline formations appeared on the cosmetic's surface and fine crystals were detected throughout the mass during sensory analysis. In a subsequent stage, these crystals were isolated from the cosmetic masses and subjected to diffraction analysis (XRD), spectroscopic analysis (infrared spectroscopy and Raman spectroscopy), and microscopic analysis (scanning electron microscopy with EDS microprobe for identifying the chemical composition of the crystals). Additionally, in order to examine phase transitions and determine characteristic temperatures for the crystallizing substances, thermal studies were conducted using differential scanning calorimetry.

It has been determined that crystalline formations in cosmetic products occur due to the co-crystallization of one of the organic sun filters along with waxes present in the cosmetic mass. The crystallization process is initiated on the surface of titanium dioxide and/or zinc oxide particles, whose silicone coatings have been partly damaged by friction caused by shear forces during the homogenization process. Exposed active sites on the titanium dioxide and/or zinc oxide particles catalyze the isomerization and dimerization reactions of avobenzone molecules. Both the enol form of avobenzone and chelating dimers interact with the exposed titanium and/or zinc ions, forming a layer on the particle's surface. Such particles act as nuclei for crystallization and over time, layers of crystallizing avobenzone along with other formulation ingredients (waxes) build up around them, resulting in spherical crystals ranging in size from hundreds of micrometers to millimeters.

Simultaneously, during the research on crystalline precipitates, preliminary work was conducted on developing a recipe for a product free from the issue of post-production crystallization of sunscreens. As part of these efforts, solvent mixtures were prepared with organic filters and other liquid materials. The prepared mixtures underwent aging under controlled conditions (identical to the conditions of accelerated aging of cosmetic masses), and the formation of crystals was observed in various cases. Based on the results of preliminary studies, modifications to the fluid mass recipe were developed, including changes such as substitution, addition/removal of selected materials, and adjustments to ingredient proportions. In the next stage, based on the modified recipes, laboratory samples of fluid masses were prepared. The obtained masses were observed during aging tests. From the laboratory tests that did not show signs of destabilization after aging tests, formulations were selected for implementation at a semi-technical scale from the R&D laboratory level. Fluid masses were prepared using the selected formulations, and their samples were also subjected to aging tests to determine the impact of environmental factors.

Furthermore, to assess the effect of modifications to the base recipe on the applicative properties of the tested materials, rheological studies were conducted on laboratory samples as well as the implemented masses. Based on the conducted rheological studies, it was determined that the introduced modifications affect rheological properties, particularly evident in changes to parameters such as yield stress, flow point, and creep compliance.
In the case of the implemented masses, it was observed that their rheological properties differed from the rheological properties of corresponding laboratory samples. This implies that the technological process, when scaled up, does indeed impact the rheological properties of cosmetic masses, but their quality parameters remain within the intended ranges.
Aging tests conducted over a specified period under controlled temperature conditions confirmed that the cosmetic masses did not exhibit tendencies for the crystallization of sunscreens, nor were there any visible discolorations or leaks. Rheological studies conducted on aged masses confirmed that their quality would not deteriorate within the intended product shelf life (i.e., 37 months).

The outcome of this doctoral work is the development of 10 stable anhydrous cosmetic fluid formulations with the addition of a sunscreen filter system providing a level of protection against radiation at SPF50. The following modifications to the base recipe prevent the crystallization of organic filter in the tested products: exchange of ingredients such as emollients (INCI (International Nomenclature of Cosmetic Ingredients): phenyl trimethicone for C12-15 alkyl benzoate or propylene glycol dibenzoate) which provided additional solvent for the crystalline filters, removal of crystalline filters to see if other types of precipitates (e.g. waxes), replacement of waxes (INCI: copernicia cerifera cera with oryza sativa (rice) bran wax), addition of an active ingredient (INCI: ascorbyl palmitate) to improve the stability of the formulation, changing the proportions of liquid organic filters and solvent to match the solubility of the crystalline organic filters, the introduction of an additional filter (INCI: ethylhexyl methoxycinnamate) to improve the photostability of avobenzone, the elimination of other raw materials such as the filters *bis*-ethylhexyloxyphenol methoxyphenyl

triazine (INCI), ethylhexyl salicylate (INCI) or the solvent dibutyl adipate, and the use of raw materials in which avobenzone was in dissolved form.

An exemplary mechanism for delaying/eliminating the crystallization of an organic sunscreen in anhydrous fluid cosmetic masses is proposed.

Keywords: anhydrous cosmetic fluid, crystallization, UV filters, stability tests, rheology

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