# OPTIMIZATION OF POWDER MAKE-UP PRODUCTS FORMULATION BY MEANS OF THE INSTRUMENTAL ANALYSIS OF POWDERS ABSORPTION AND FLOWABILITY PROPERTIES

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**Key Words**: Powders, Rheometer, Characterization, Shear stress, Oil absorption, Pigments, Pearlescent Pigments, Texture

## Abstract

Make up products in powder form are based on a mixture of pigments, pearls, texturizing ingredients, binders and preservatives. The variable content of pigments and pearls allows to create the final shades of a product but differences in texture can occur in a color line-up. The aim of this study is to characterize the powder cosmetic ingredients in terms of absorption and flowability, in order to maintain the texture features within a color palette. In fact, the physical and chemical differences of the color phase ingredients affect the products in terms of finish and performances, therefore the remaining ingredients of the formulation must be counterbalanced to preserve the texture. The ratio between the dry (powdery) and the binding (oily) phases is based on the determination of the powders oil absorption value measured with Brabender absorptometer. Moreover, through absorptometer analyses has been proved that the absorption of a powder mixture is very different from the sum of the contribution of every single powder: the behavior of powders mixture is not predictable in a theoretical way knowing the properties of the single ones, because their relative action plays a primary role. To go deeper in the optimization of powders formulation, other characteristics have been evaluated: the shear stress properties have been investigated using a powder rheometer and the resultant flowability trend has been compared to the sensory evaluation. Therefore, it has been demonstrated that cohesivity, represented by shear stress value, of fillers, pigments, pearls and dry phases, is a suitable property to predict the texture of a pressed powder because the flowability data trend of the tested samples and their sensory evaluation trend turned out to be comparable. Future studies will focus on the integration of powders absorption and cohesion values in order to obtain a more precise equation to optimize the formulation of wide color range palette.

## 1. Introduction

Cosmetic powders are based on a mixture of pigments and pearls interspersed in fillers or functional ingredients as binders, preservatives, fragrances [1]. Each pigment, pearl and filler differentiates itself for fundamental properties (shape, size, porosity, superficial area) and derived properties (flowability, apparent density, packing arrangement and specific superficial area). The variable amount of pigments and pearls within a cosmetic formulation

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allows to create the entire color line-up, but a high concentration of the variable portion (color phase) generates texture differences between shades. The current eye-shadows market trend dictates very high coverage and then formulations with high amount of color phase; due to the physical and chemical differences within the pigments and pearls, the remaining ingredients of the formulation must be counterbalanced to preserve comparable texture within a color line-up. Therefore, the characterization of each powder, especially pigments and pearls, is important in the first instance to manage the product formulation and secondly to evaluate the conformity of finished product or intermediate during the production process. To date, cosmetic powders are characterized in terms of particle size, shape, superficial area and density but, since these properties are not enough to predict ingredients behavior inside each formulation, powders oil absorption and flowability data were studied to investigate their possible correlation with the finished product sensorial evaluation. Cosmetic formulations in powder form are obtained through a wet granulation process [2] and can be divided in two big categories: referring to the absorption graph in Fig.-1, we define as "Left Formulation" (LF) the formulas with low binders amount and "Right Formulation" (RF) the formulas with high binders amount. More in detail, on the X-axis is represented the quantity of binder added in 100g of dry powder and on the Y-axis the Torque (mNm) necessary to mix the bulk, obtained through Brabender absorption analysis. At the beginning, there is only dry powder and no binder; increasing the binder amount, so moving to the right part of the chart, wet granulation process begins and powder particles aggregate so that the force (Torque) needed to move the mixture increases until a maximum value (OAN) that represents the point of maximum absorption: to its left, the mixture can be assimilated to a powder (Left Formulation) and, to its right, to a paste (Right Formulation).

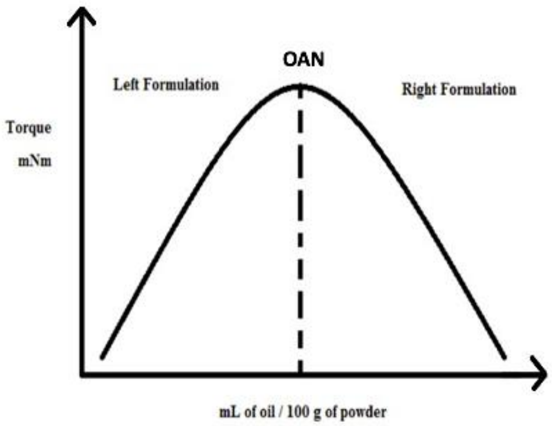


*Fig.-1. Schematic representation of typical Brabender absorption profile graph*

For RF, the texture of the finished product is strictly related to the absorption properties of the powders involved, due to the high percentage of binder, and in the first part of this work we used Brabender absorptometer analysis to find out an equation to balance the powder and binder ratio to maintain the texture within a color line-up. Indeed, for the LF the absorption behavior has not such an impact on the finished product texture and the second part of this work was dedicated to better investigate the cohesivity properties of powders, especially the shear stress value through the mean of the powder rheometer FT4 (Freeman technology). The raw materials object of study are fillers: talc, mica and zinc stearate; pigments: iron oxides, titanium dioxide, and carmine; pearly pigments: natural mica-based and glass-based.

## 2. Material and methods

### 2.1 Right formulations study by means of oil absorption analyses

According to previous work [3], the oil absorption analyses have been performed by means of Brabender Absorptometer "C", that offers a valid method to replace manual measurement and guarantees accurate and reproducible results. The principle of the absorptometer consists in measuring the resistance which the studied powder put up against the rotating blades during oil addition and in determining its oil absorption number. The high-precision burette adds liquid to the powder sample in the mixing chamber. Upon absorption of sufficient liquid, particles begin to adhere to each other forming agglomerates. Resistance to mixing rises, indicated by a sharp increase in torque up to a maximum corresponding to the OAN [4]. In the first experimental part of this study an eyeshadow formula composed by 44% of binding phase and 56% of dry phase **(**Table-1, Table-2 and Table-3**)** has been studied: the green shade was the first one to be developed and it represents the standard for texture and performance. According to the equation $Ax$ (%$DPx$)/(%$OPx$) = (%$DPstd$)/(%$OPstd$) $Astd$ (Equation 1), knowing the oil absorption of a standard formulation with given percentage of dry phase and oil phase, and measuring the oil absorption value of an unknow formulation, it's possible to calculate the correct ratio of dry and oily phases to maintain the texture and performance of the standard one. The oil absorption profile of green, purple and gold dry phases has been analyzed and the finished product, formulated in accordance with the mathematical formula, was evaluated from a sensorial point of view. The sensorial analysis was conducted through a panel test with seven people of different ages with expertise in powder products and the results were expressed using a scale from 1 (soft) to 5 (hard).

*Table-1 Green dry phase composition*

| GREEN DRY PHASE | % |
|---|---|
| FILLERS | 18 |
| MICA AND TITANIUM DIOXIDE (CI 77891) AND FERRIC FERROCYANIDE (CI 77510) | 44 |
| MICA AND TITANIUM DIOXIDE (CI 77891) AND FERRIC FERROCYANIDE (CI 77510) | 15 |
| MICA AND IRON OXIDE | 18 |
| MICA AND YELLOW 5 | 5 |

*Table-1 Purple dry phase composition*

| PURPLE DRY PHASE | % |
|---|---|
| FILLERS | 18 |
| MICA AND IRON OXIDE | 25 |
| SYNTHETIC FLUORPHLOGOPITE AND IRON OXIDES (CI 77491) | 35 |
| MICA AND TITANIUM DIOXIDE (CI 77891) | 21 |

*Table-2 Gold dry phase composition*

| GOLD DRY PHASE | % |
|---|---|
| FILLERS | 18 |
| SYNTHETIC FLUORPHLOGOPITE | 8 |
| MICA AND IRON OXIDES (CI 77941) | 11 |
| BRONZE POWDER (CI 77400) AND SILICA | 63 |

*Equation 1 Mathematical formula to normalize textures through oil absorption analyses*

$$\begin{cases} Ax\,\dfrac{\%DPx}{\%OPx} = \dfrac{\%DPstd}{\%OPstd}Astd \\ \%DPx + \%OPx = 100 \end{cases}$$

*DPx% : percentage of Dry Phase in the "unknown" formulation*

*OPx%: percentage of Oily Phase in the "unknown" formulation*

*DPstd%: percentage of Dry Phase in the standard formulation*

*OPstd%: percentage of Oily Phase in the standard formulation*

*Ax: absorption value of the "unknown" formulation*

*Astd: absorption value of the Phase in the standard formulation*

To verify the consistency of this equation for every powder formula, the same study has been conducted on a LF composed by only 15% of binders and 85% of powders (filler and natural mica-based pearls) and two different shades, orange and brown, have been object of study. The two different natural mica-based pearls and the related powdery phases showed comparable oil absorption values (see results), but the resulting finished product textures were not comparable as expected. Since we couldn't uniform the texture of LF using the previous approach, much related to the relations between powders and binders, the second part of the study focused on the characterization of the powdery ingredient itself, especially on its flowability properties.

### 2.2 Left formulations study by means of Shear stress analyses

Basing on previous works [5] FT4 Powder Rheometer from Freeman Technology has proved to be the instrument of choice to study the flow properties; it's a universal powder flow tester largely used in pharmaceutical field, with four categories of methodologies, defined as Bulk, Dynamic Flow, Shear (in accordance with ASTM D7981) and Process [6]. The analytical methodology considered in our study has been the Shear one and basing on Freeman technology expertise, the Shear Cell analysis (Fig.-2) has been elected as the best way to define the powder cohesivity profile.

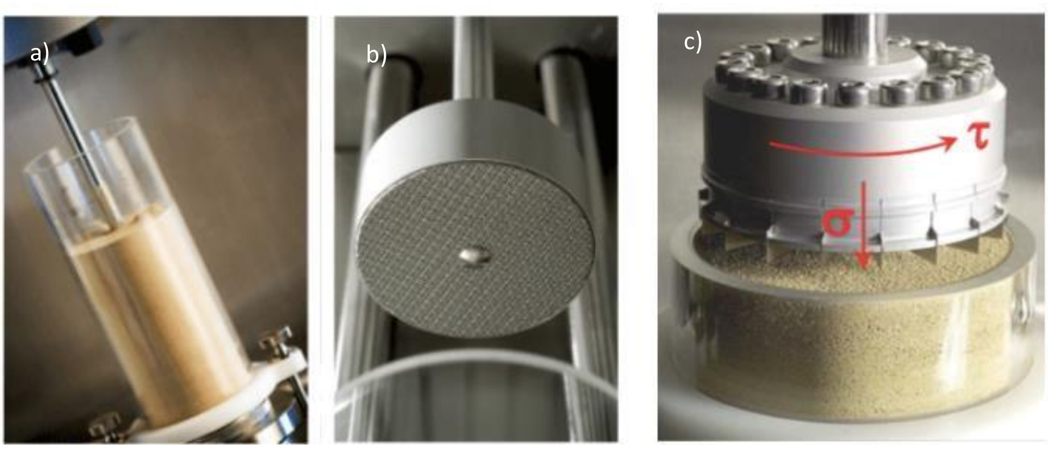


*Fig.-1 Shear Cell analysis ASTM D7981. a) FT4 blade, b) vented piston, c) shear head. The two forces represented on shear head are: τ = Shear Stress, σ = Normal Stress.*

The powder is initially conditioned using the standard FT4 blade to produce a homogeneous sample; (Fig.-2) the vented piston is used to induce a precise consolidation stress to press the sample; the vessel is then split, and a shear head induces both vertical ($\sigma$ = Normal Stress) and rotational stresses ($\tau$ = Shear Stress).

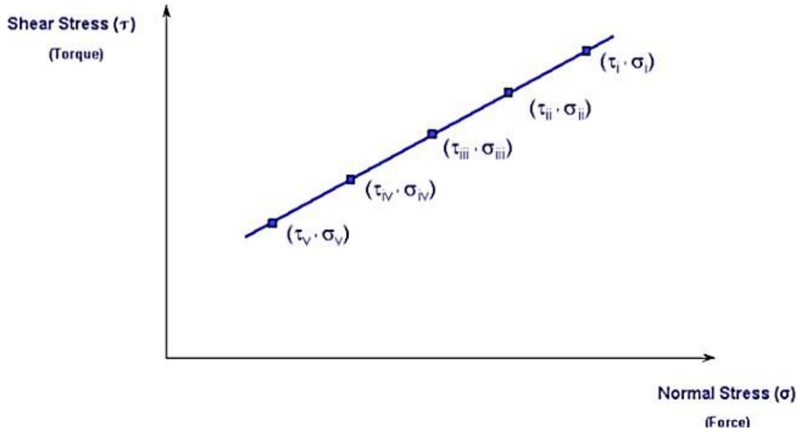


*Fig.- 2. Typical yield Loci, obtained plotting every incipient failure point against their corresponding normal stresses*

For every ingredient examined, the shear stress analysis has been conducted setting a scale of applied normal stress $\sigma$ from 0 to 9 kPa and within this range the rotational stress increases until the powder begins to flow: this point is the yield point of the powder and corresponds to the shear stress value $\tau$ **(**Fig.**-**3). According to FT specialists, we considered as output of the analysis the shear stress value measured at 7 kPa of applied normal stress considered as the most representative point to differentiate the powders. The obtained values can be considered reliable because the instrument repeats the analysis until two subsequent shear stress values (measured at 7 kPa) give a standard deviation lower than 0.1%. Different kinds of pearls, pigments, fillers and final formulations as free granulate have been evaluated; all the analyses have been conducted on powders after sieving.

Pearlescent Pigments

Two different categories of pearls have been analyzed: different color shades of mica-based pearls and glass-based pearls; that implicates two variables: the influence of the pearl substrate, mica or glass, and its color coating, for example pigment lakes or titanium dioxide.

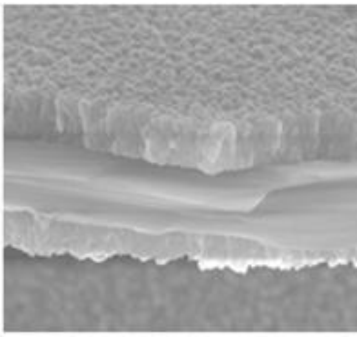

*Fig.-3. SEM image of natural mica based pearlescent pigments, composed by a substrate coated with a double layer of pigments*

Every single pearlescent pigment (pearl) has been analyzed by means of the rheometer and the resulting finished product **(**Table-4**)** has been evaluated from a sensorial point of view; since pearly pigments don't have good compacting properties, they needed to be conveyed in a finished formula. The sensorial analysis was conducted through a panel test with seven people of different age with expertise in powder products and the results were expressed using a scale from 1 (soft) to 5 (hard).

*Table-3 Percentage of components in final pearly pigments formulation*

| **Components** | **%** |
|---|---|
| Fillers | 50 |
| Pearls | 35 |
| Binders | 15 |

Pigments and fillers

In a similar way, matte pigments and fillers have been evaluated and thanks to their good compacting properties, the sensorial evaluation has been conducted on the single raw materials pressed in a pan.

Final Formulation

Finally, a monochromatic final formulation in granulate form **(**Table-5**)** has been analyzed by means of the rheometer, then pressed and evaluated from a sensorial point of view.

*Table-5. Percentage of components in final monochromatic formulation*

| **Components** | **%** |
|---|---|
| Fillers | 64 |
| Pigments | 24 |
| Binders | 12 |

## 3. Results and discussions

### 3.1 Right formulation study by means of oil absorption analysis results

The Fig.-5 represents the output of Brabender analyses of the Green, Purple and Gold formulation and the extrapolated values have been entered into the Equation 1 to calculate the ratio of binders and powders (Table-6); through the sensorial evaluation, the textures of the three finished products have been judged as comparable.

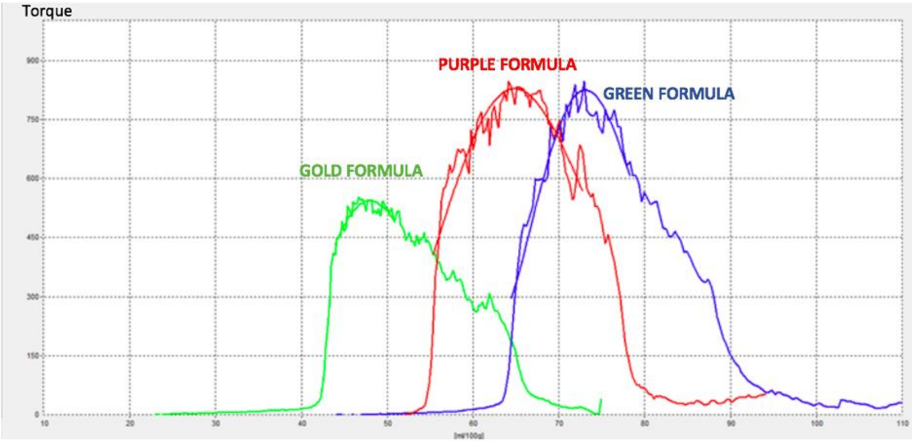


*Fig.-4 Oil absorption profile of the three dry phases analyzed, where the green formula is the standard*

*Table-4 Oil absorption value extrapolated from the above graph (Fig.-10), OP% and d0% and Texture evaluation for the three shades analyzed*

| | **STD Green formula** | **Purple formula** | **Gold formula** |
|---|---|---|---|
| **OAN (g/100g)** | 61.8 | 56.4 | 50.2 |
| **OAN CV%** | 1.2 | 0.1 | 0.2 |
| **% Oil Phase** | 44.2 | 42.1 | 33.7 |
| **% Dry Phase** | 55.8 | 57.9 | 66.3 |
| **Sensorial Evaluation(1-5)** | 3.0 | 3.0 | 3.0 |

Following this approach all the shades belonging to this RF have been aligned in order to obtain the same texture and performances. On the other hand, the same experiment conducted on the LF composed by 15% of binders and 85% of powders gave different results (Table-7): brown and gold dry phases showed comparable oil absorption curves, but the finished product formulated with the same amount of binding phase gave different results in terms of texture and cosmetic performance. This confirms that formulas with low binder content cannot be studied by means of oil absorption analysis.

*Table-5 Oil absorption value and sensorial evaluation, with their respective CV% of brown and orange pearls.*

| Name | Inci | OAN [g/100g] | OAN CV % | Sensorial Evaluation (1-5) | SE CV % |
|---|---|---|---|---|---|
| Brown | Mica and Iron Oxide | 59 .0 | 0.8 | 1.6 | 14.9 |
| Orange | Mica and Titanium Dioxide and Iron Oxide | 60.1 | 4.8 | 3.6 | 6.7 |

## 3.2 Left Formulation study by means of Shear stress analyses results

Natural mica-based pearlescent pigments

The output of the FT4 Rheometer for the natural mica-based pearls is shown in the Fig.-6 and the obtained values are summarized in the Table-8 with sensorial analyses.

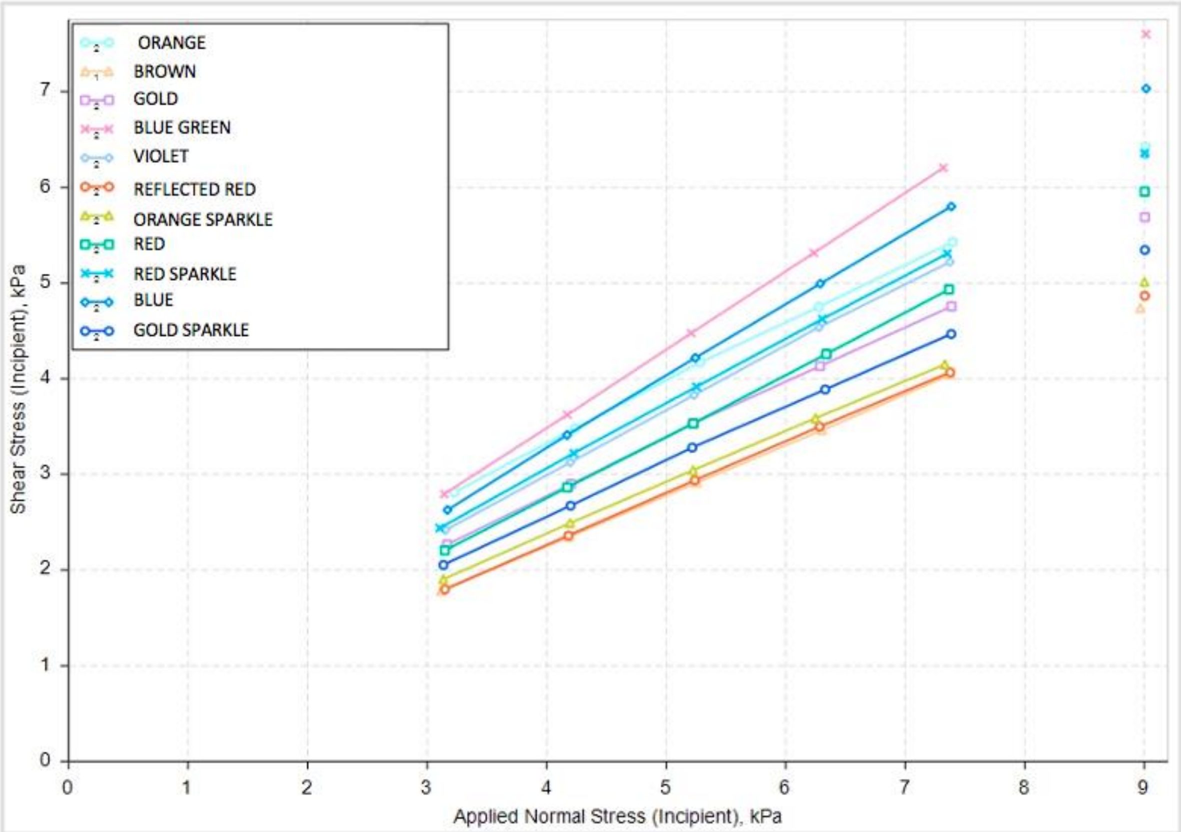


*Fig.- 5 Results of Shear Cell analyses on Natural mica-based pearls*

*Table-6 Shear stress and sensorial evaluation of natural mica-based pearls*

| Name | Inci | Shear stress kPa | Sensorial Evaluation (SE) (1-5) | SE Std Dev | SE CV % |
|---|---|---|---|---|---|
| BROWN | MICA AND IRON OXIDE (CI 77941) | 4,0 | 1,6 | 0,2 | 12,2 |
| REFLECTED RED | MICA AND IRON OXIDE (CI 77491) | 4,1 | 1,8 | 0,2 | 13,6 |
| GOLD SPARKLE | MICA AND TITANIUM DIOXIDE (CI 77891) AND IRON OXIDE (CI 77491) | 4,5 | 2,1 | 0,7 | 32,2 |
| RED | MICA AND TITANIUM DIOXIDE (CI 77891) AND TIN OXIDE | 4,9 | 2,3 | 0,5 | 21,3 |
| VIOLET | MICA AND TITANIUM DIOXIDE (CI 77891) | 5,2 | 2,6 | 0,4 | 16,1 |
| GOLD | MICA AND TITANIUM DIOXIDE AND YELLOW IRON OXIDE | 4,8 | 2,8 | 0,3 | 9,7 |
| ORANGE SPARKLE | MICA AND TITANIUM DIOXIDE | 4,2 | 3,1 | 0,7 | 22,0 |
| SPARKLE RED | MICA AND TITANIUM DIOXIDE (CI 77891) | 5,3 | 3,3 | 0,5 | 14,9 |
| ORANGE | MICA AND TITANIUM DIOXIDE (CI 77891) AND IRON OXIDE (CI 77491) | 5,4 | 3,6 | 0,2 | 5,5 |
| BLUE | MICA AND TITANIUM DIOXIDE AND FERRIC FERROCYANIDE | 5,8 | 4,0 | 0,5 | 12,0 |
| BLUE GREEN | MICA AND TITANIUM DIOXIDE AND FERRIC FERROCYANIDE | 6,2 | 4,1 | 0,3 | 6,5 |

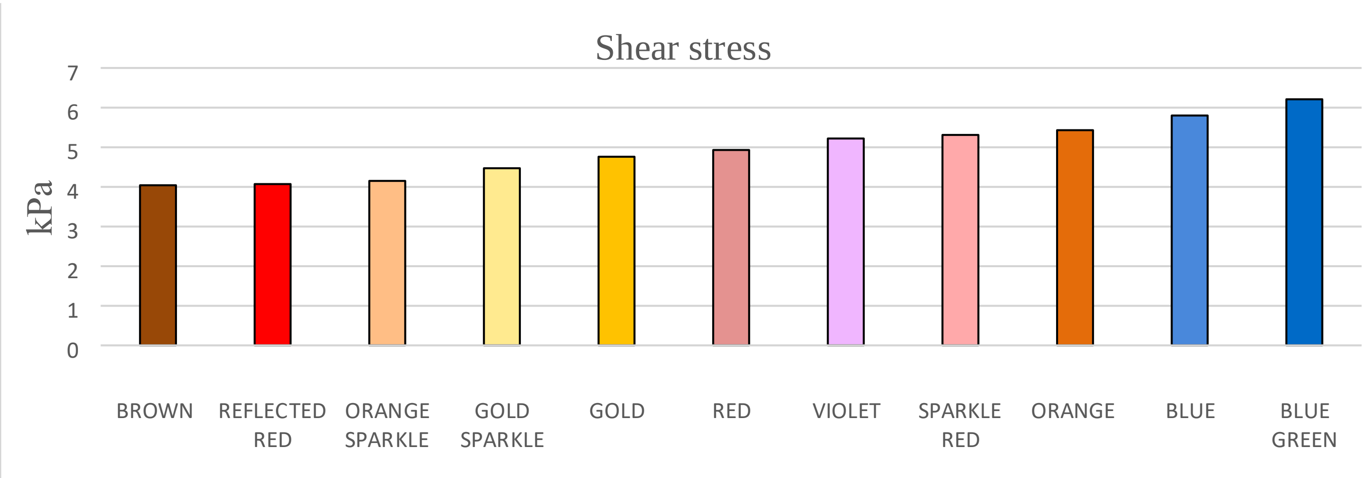


*Fig.- 6 Graphic presentation of mica-based pearls, Shear stress value.*

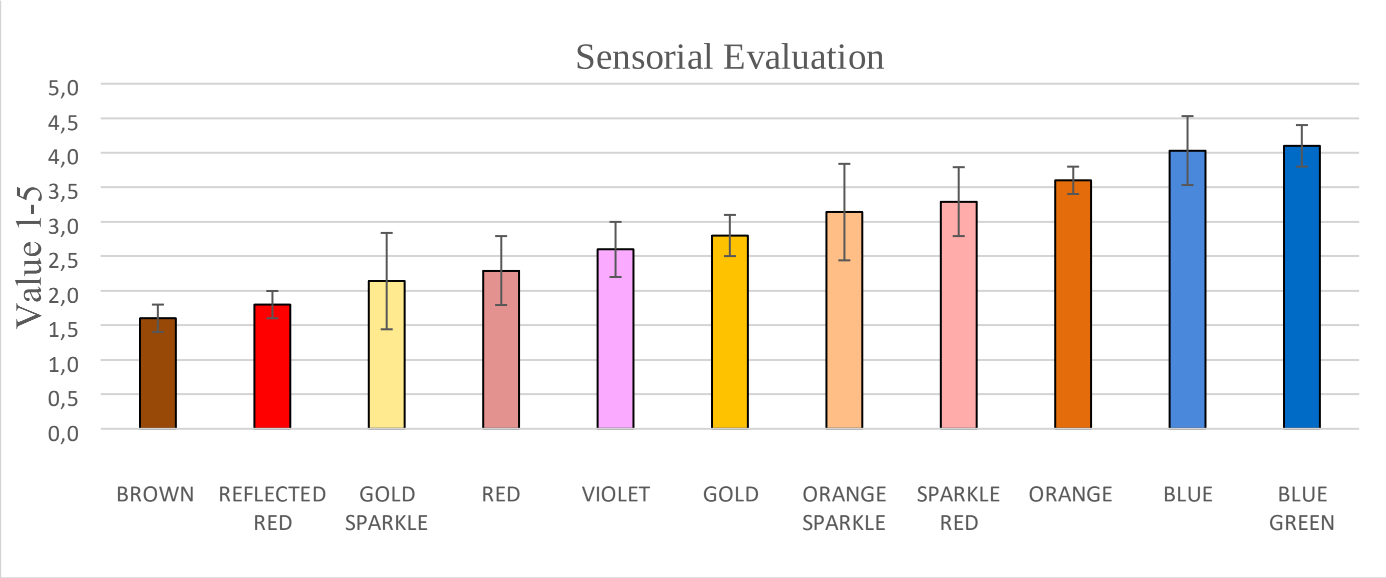


*Fig.-7. Graphic presentation of Natural Mica based pearls, Sensorial evaluation.*

Comparing the shear stress and sensorial evaluation data plotted in Fig.-7 and Fig.-8, a strong match has been proved; moreover, there is a correlation between pearls with similar INCI. In particular, pearls coated with iron oxide are very smooth and show low shear stress values (Brown and Reflected Red); on the contrary, pearls with titanium dioxide and ferric ferrocyanide are very hard and show high shear stress values **(**blue and blue green)[7] The subjectivity of the sensorial evaluation is shown by the big standard deviation in Fig.-8**,** demonstrating the importance of finding an objective and more precise method to differentiate similar textures.

Glass-based pearlescent pigments

Glass-based pearls are the second category taken into consideration and the FT4 rheometer output can be seen in Fig.-9; shear stress and sensorial evaluation data are summarized in Table-9.

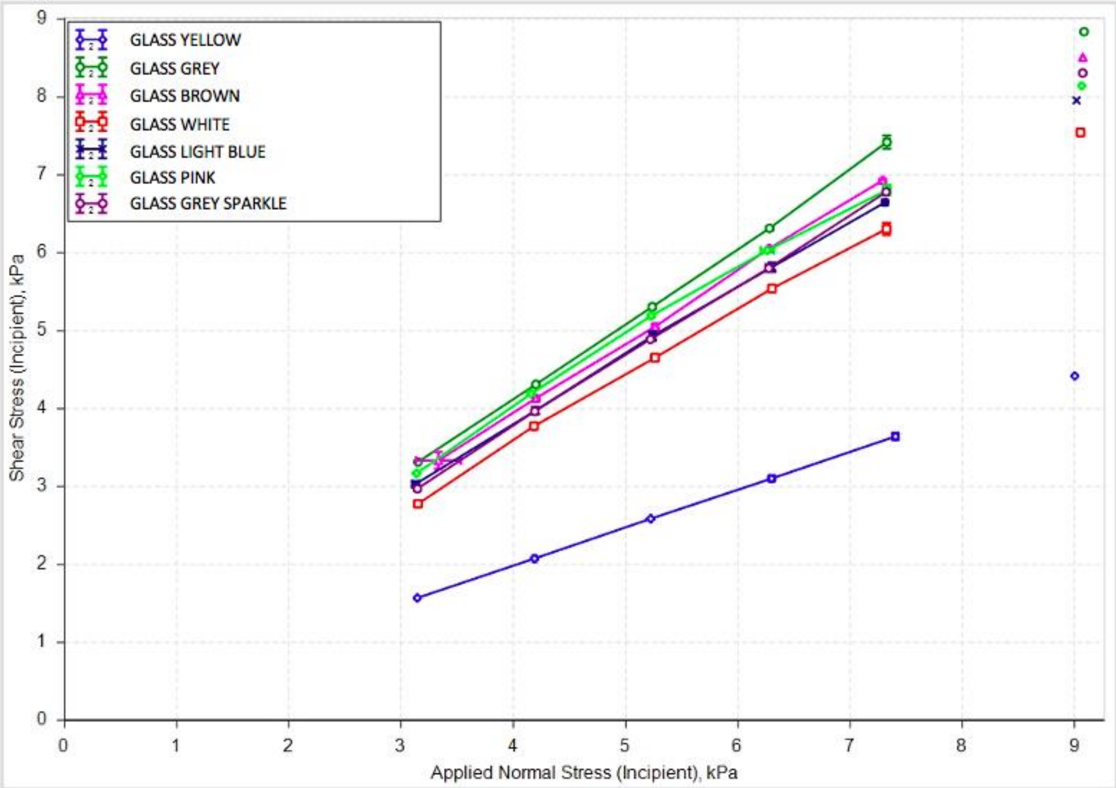


*Fig.- 8 Results of Shear Cell analyses of Glass based pearls*

*Table- 7 Shear stress and sensorial evaluation of glass based pearls*

| Series Name | Inci | Shear stress kPa | Sensorial Evakuation (SE) (1-5) | SE Std Dev | SE CV% |
|---|---|---|---|---|---|
| GLASS GREY SPARKLE | CALCIUM ALUMINUM BOROSILICATE AND TITANIUM DIOXIDE (CI 77891) AND TIN OXIDE | 6,7 | 1,0 | 0 | 0 |
| GLASS PINK | CALCIUM ALUMINUM BOROSILICATE AND IRON OXIDES (CI 77491) | 6,8 | 1,6 | 0,5 | 34,0 |
| GLASS YELLOW | CALCIUM ALUMINUM BOROSILICATE AND TITANIUM DIOXIDE (CI 77891) AND TIN OXIDE | 3,6 | 1,7 | 0,7 | 39,5 |
| GLASS WHITE | CALCIUM ALUMINUM BOROSILICATE AND TITANIUM DIOXIDE (CI 77891) AND TIN OXIDE | 6,3 | 3,8 | 0,5 | 13,9 |
| GLASS LIGHT BLUE | CALCIUM ALUMINUM BOROSILICATE AND TITANIUM DIOXIDE (CI 77891) | 6,8 | 4,3 | 0,5 | 11,4 |
| GLASS BROWN | CALCIUM ALUMINUM BOROSILICATE AND IRON OXIDES (CI 77491) | 6,9 | 5,0 | 0,0 | 0,0 |
| GLASS GREY | CALCIUM ALUMINUM BOROSILICATE AND TITANIUM DIOXIDE (CI 77891) AND TIN OXIDE | 7,4 | 5,0 | 0,0 | 0,0 |

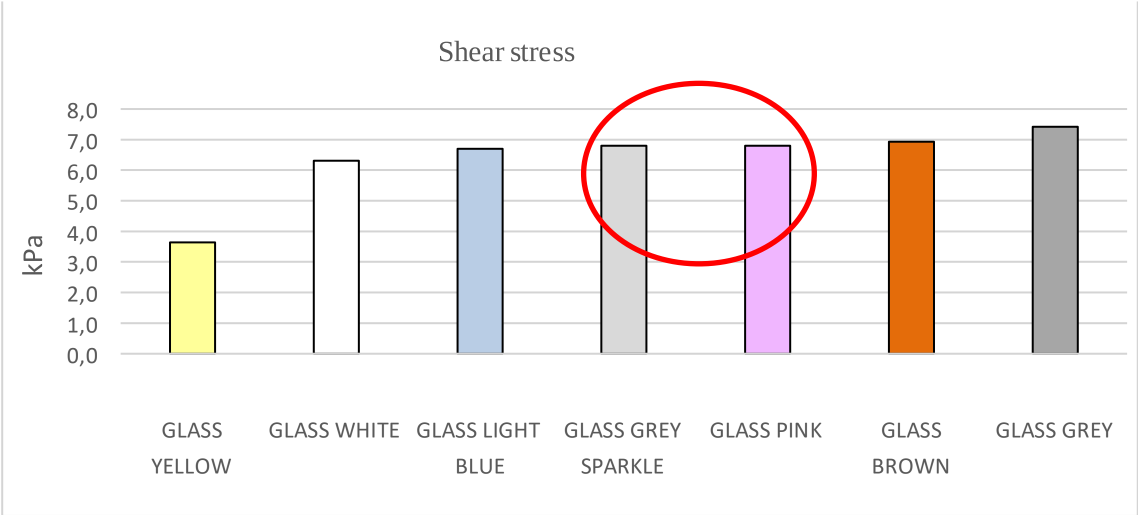


*Fig.-9 Graphic presentation of Glass based pearls, Shear stress value*

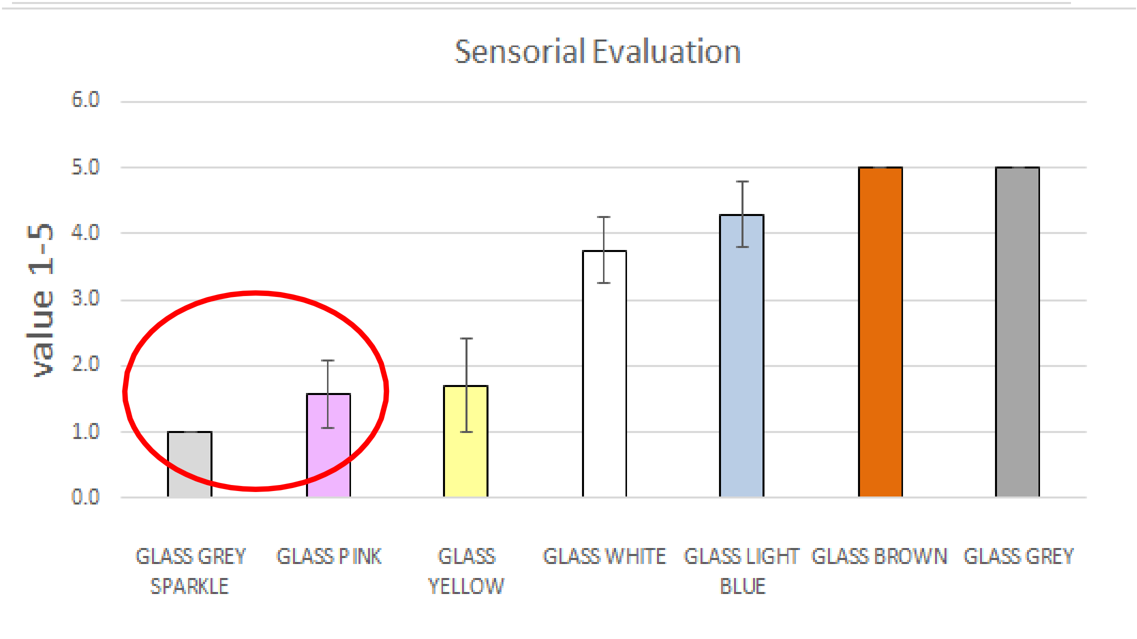


*Fig.- 10 Graphic presentation of Glass based pearls, Sensorial evaluation*

Here too, shear stress and sensorial data have been plotted in Fig.-10 and Fig.-11 and a correlation between the shear stress value and sensorial evaluation has been proved. However, we can see that two pearls (Grey Sparkle and Glass Pink) that show a high shear stress value have been evaluated as smooth and soft to the touch; future studies will be focused on finding a correlation between flow behavior and absorption profile.

<u>Pigments and fillers</u>

Pigments and fillers have been analyzed by means of FT4 Rheometer and the output can be seen in Fig.-12; shear stress and sensorial evaluation data are summarized in Table-10.

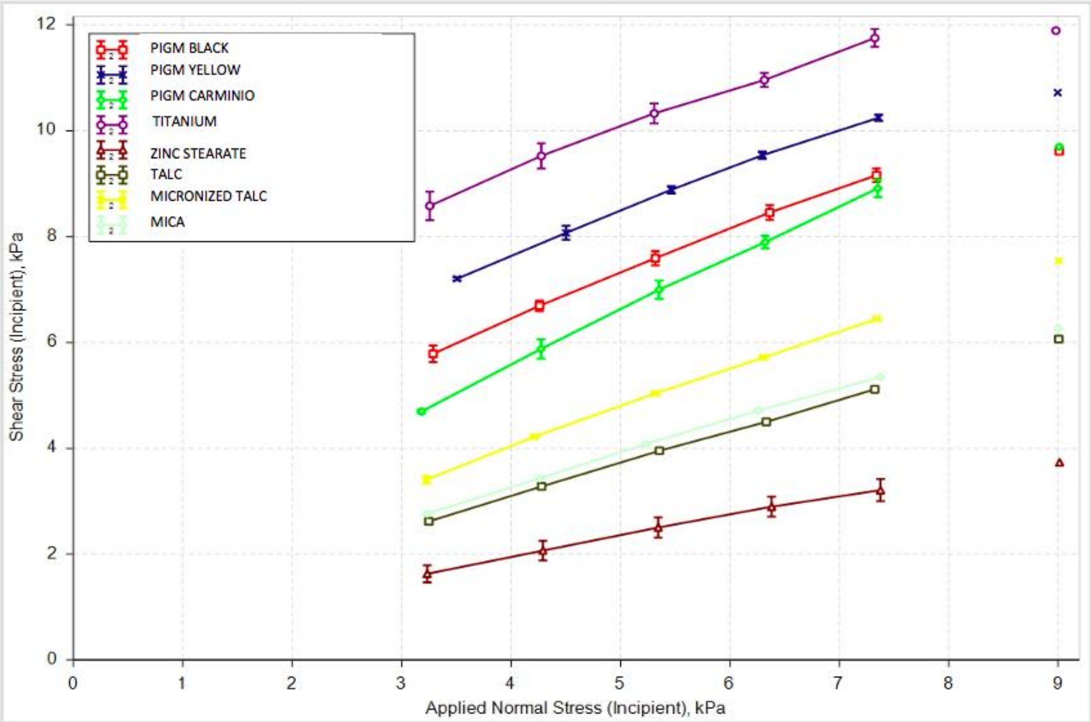


*Fig.- 11 Results of Shear Cell analyses on Pigments and Fillers*

*Table- 8 Shear stress and sensorial evaluation of Pigments and Filler*

| Series Name | Inci | Shear Stress kPa | Sensorial Evaluation (SE) (1-5) | SE Std Dev | SE CV% |
|---|---|---|---|---|---|
| ZINC STEARATE | ZINC STEARATE | 3,2 | 1,0 | 0,0 | 0,0 |
| TALC | TALC | 5,1 | 1,0 | 0,0 | 0,0 |
| MICA | MICA | 5,4 | 1,0 | 0,0 | 0,0 |
| MICRONIZED TALC | TALC | 6,5 | 2,0 | 0,0 | 0,0 |
| CARMINE | CARMINE | 8,9 | 3,8 | 0,3 | 7,7 |
| YELLOW PIGMENT | IRON OXIDE | 10,3 | 4,5 | 0,0 | 0,0 |
| WHITE PIGMENT | TITANIUM DIOXIDE | 11,8 | 5,0 | 0,0 | 0,0 |

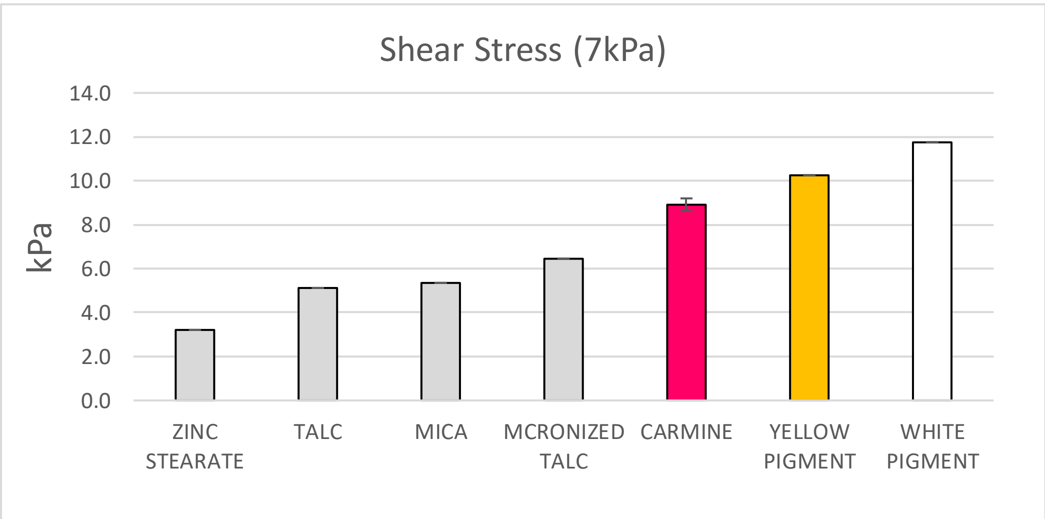


*Fig.- 12 Graphic presentation of pigments and fillers, Shear stress value*

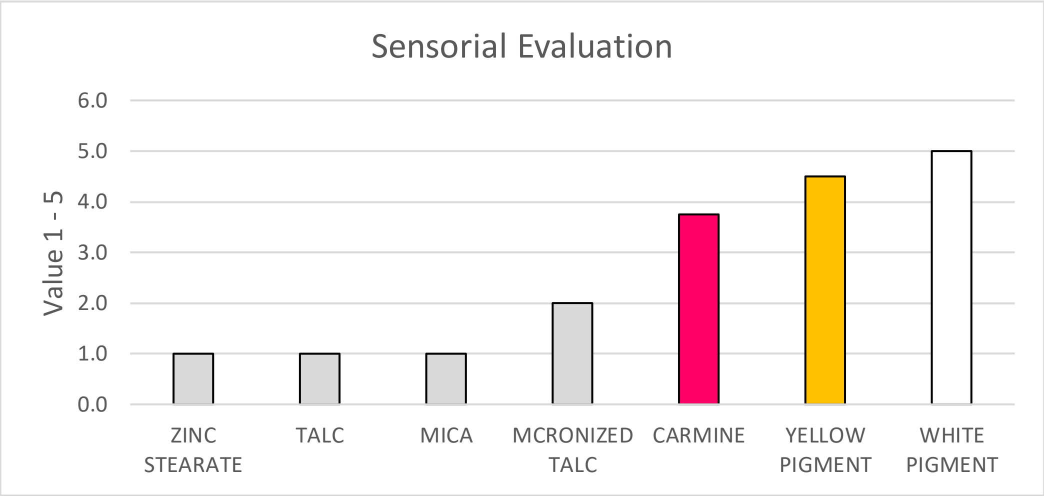


*Fig.- 13 Graphic presentation of Pigments and Fillers, Sensorial evaluation*

Shear stress and sensorial data have been plotted in Fig.-13 and Fig.-14 and a correlation between the cohesion value and sensorial evaluation of the pressed powders has been proved; moreover, talc and micronized talc showed different results, meaning that there's a connection between texture and particle size.

<u>Final formulation</u>

Finally, complete formulations (powders plus binders) have been analyzed by means of FT4 rheometer and the output can be seen in Fig.-15; shear stress and sensorial evaluation data are summarized in Table-11.

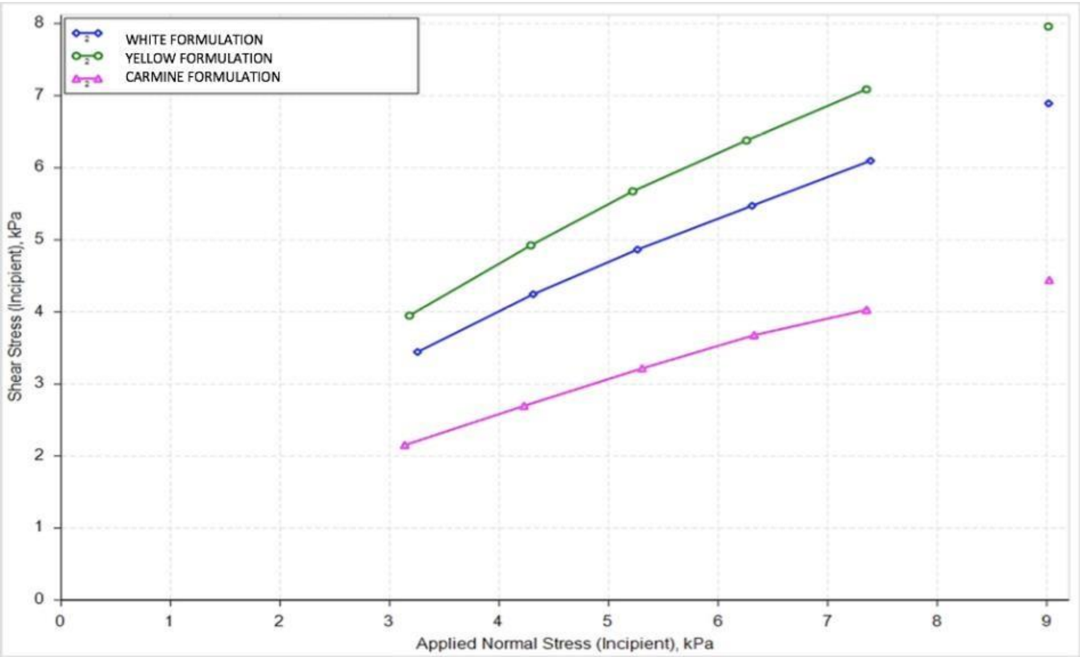


*Fig.-14 Results of Shear Cell analyses on Final formulation*

*Table-9 Shear stress and sensorial evaluation of Final formulation*

| Series Name | Inci | Shear stress kPa | Sensorial Analysis (SE) (1-5) | SE Std Dev | SE CV% |
|---|---|---|---|---|---|
| CARMINE FORMULATION | CARMINE | 4,1 | 2,5 | 0,5 | 22,0 |
| WHITE FORMULATION | TITANIUM DIOXIDE | 6,1 | 3,5 | 0,5 | 15,6 |
| YELLOW FORMULATION | IRON OXIDE | 7,1 | 4,5 | 0,5 | 12,1 |

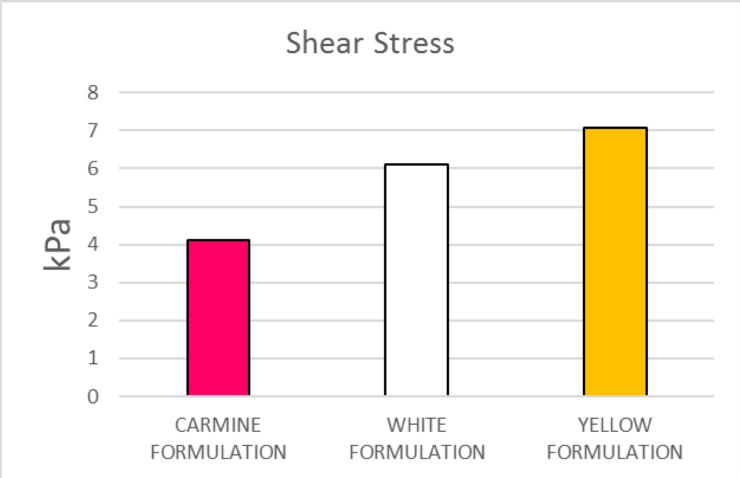


*Fig.-15 Graphic presentation of Final formulation, Shear stress value*

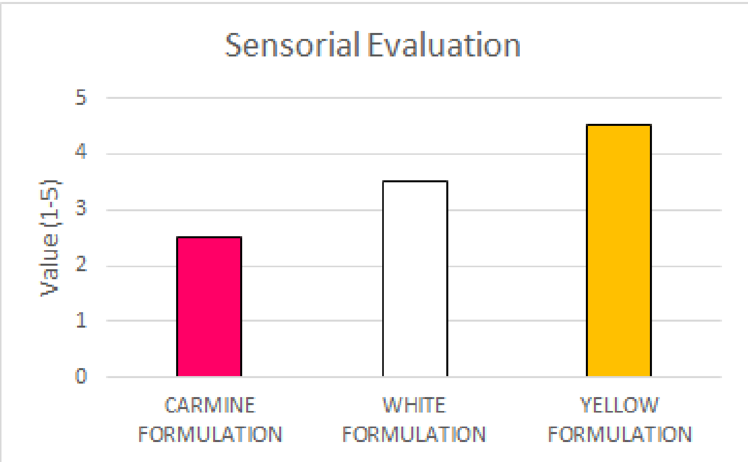


*Fig.-16 Graphic presentation of Final formulation, Sensorial evaluation*

Shear stress and sensorial data have been plotted in Fig.-16 and Fig.-17. Here too, the same correlation among cohesivity and sensorial profile has been found. Comparing to the previous studies on the single ingredients (pearls, pigments, fillers) and on the production intermediates (dry phases), the study of the final formulation granulate is particularly significant because it takes into consideration all the variables linked to the powder and the binder phases.

## 4. Conclusions

In conclusion, through this work we can consider the Brabender oil absorption analysis as a valid and reproducible method to manage the formulation of powder cosmetic products with a high binder content, defined as Right Formulation RF. Hence, it has been shown that using oil absorption value in the appropriate mathematical formula (Equation 1) it's possible to normalize the texture within a color palette, ensuring a wide range of color shades without compromising the product performances. Instead, for formulations with a low content of binder defined as Left Formulation (LF) the Powder Rheometer FT4 shear cell analysis has proved to be useful in correlating the cohesivity of the powders with the sensorial evaluation of the finished product. Furthermore, Powder Rheometer analyses demonstrated that cohesivity, expressed as shear stress value, of fillers, pigments, pearls, dry phases and final formulation granulates represents a suitable property to predict the texture of a pressed powder; indeed, the flowability data trend of the tested samples and their sensorial evaluation trend were comparable. Future studies will focus on the integration of the shear stress analyses data with the absorption equation to obtain a more precise number to simplify the formulation of wide color range palette, moving from a subjective formulation approach to a more objective one.

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