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Evaluation of the Physical Stability of Sunscreen: Application of a Canonical Correlation Analysis for Relating the Temperature and Extensibility

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ABTRACT

In recent years, awareness campaigns on sun exposure have successfully changed the habits of many citizens. However there are people who still do not realize the serious health risks that they can cause the sun without adequate measures. Many times they are driven for the fashion for tanning the skin, but they not carry out the most basic precautions to the exposion the sun. Today people are aware that may have third degree burns and skin cancer when exposed to sunlight. We elaborate a sunscreen in the laboratory of Pharmacy, School of Chemical Sciences of the BUAP. It evaluates the physical stability, pH, their absorption in the ultraviolet and extensibility to 5 ° C, 25 ° C and 45 ° C, with the results obtained are considered two sets of variables: extensibility and room temperature. We will study the relationship between the two sets to determine if they both have a stake in the behavior of the cream, for this analysis will use the technique of Canonical Correlation Analysis is responsible for studying two groups of variables to determine the relationship through its maximum correlation, a situation that allowed us to determine that the behavior of the extensibility of the cream has a relationship with temperature.

Keywords: *TiO_2, ZnO, sunscreen, UV radiation, cosmetics.*

I. INTRODUCTION

In recent years, awareness campaignsonhuman exposures to the sun have successfully changed the habits of many citizens. Currently there are few people who do not take preventive measures before sun exposure. It is also known that even people who are looking for tanning the skin, they must meet certain requirements to avoid the appearance of burns favored by the sun. For a cream can be considered as either sun screen or sun block sun screen active ingredients included in the formula must have certain essential attributes. Thus for example, must absorb abroad range or a specific part of the solar spectrum without decomposition, as this would reduce their efficiency or could lead to the formation of irritating or toxic derivatives. They must possess the characteristics necessary to cosmetic formulation vehicles and be readily absorbed through the skin, water resistant and sweat should not need very frequent application to be effective, must not be toxic, irritating or sensitizing (Wilkinson, 1990. Wilkison, 1990, The Cosmetic 1990. Thompson. J. 2004. Remington, 2003. Davson,1968. Tortora, 2000. Farmacopea, 1994. Grupo Multicolor, 2007).

Currently there are a range of sunscreens in different forms and with different degrees of protection (FPS) (Wilkinson, 1990), which have been commonly used to try to avoid the damage the sun causes in our skin. Although our body produces melanin, which helps protect it from sunlight (Remington, 2003; Davson, 1968). Unfortunately the cost of such products is relatively high, which makes them difficult to acquire for the general population. In the present work we intend to develop a sunscreen that is alternative to commercial creams effective and appropriate on the basis of a mixture of titanium oxide and zinc oxide, whereas the concentrations present in commercial sunscreens. A study of physical stability, using the parameters set in the NOM 073, color, odor, pH, (Norma Official Mexicana 073, 2005). In addition we consider extensibility. Also in this study verify the degree of coverage by characterizing UV radiation in a UV-VIS spectrophotometer. To determine the appropriate behavior of the cream, we established a relationship between the temperatures proposals extensibility of 5°C, 25°C (environment) and 45°C, employing a Canonical Correlation study which is described below (C. Rencher A., 1998).

II. CANONICAL CORRELATION

The canonical correlation involves the partitioning of a collection of variables into two sets.

The goal is to find linear combinations of the type:

$$U = a'X \quad y \quad V = b'Y \qquad (1)$$

Such that U and V have maximum correlation and research converges to getting these new variables whose correlation is high, it will determine the relationship between groups of extensibility and temperature.

III. ANALYTICAL APPROACH

Consider the canonical equations (2):

$$\left.\begin{aligned} U_1 &= a_{11} X_1 + a_{12} X_2 + \ldots + a_{1p} X_p \\ V_1 &= b11 Y_1 + b_{12} Y_2 + \ldots + b_{1q} Y_q \end{aligned}\right\} \qquad (2)$$

The objective is:
Estimate $a_{11}, \ldots$, a1p and $b_{11}, \ldots$, b1q such that C_1 is maximum.

- C_1 is the correlation between U_1 and V_1 called canonical correlation.
- U_1 and V_1 are called canonical variables.

Algorithm

Step (1)
1) U_1 and V_1 are estimated
2) A second set of canonical variable is identified: U_2 and V_2

$U_2 = a_{21} X_1 + a_{22} X_2 + \ldots + a_{2p} X_p$
$V_2 = b_{21} Y_1 + b_{22} Y_2 + \ldots + b_{2q} Y_q$

It is verified that

- The correlation between U_2 and V_2 is maximum.
- U_2 and V_2 are not correlated with U_1 y V_1.

Step (M)

This procedure is repeated to identify the m-th canonical set of variables Um and V_m:

$U_m = a_{m1} X_1 + a_{m2} X_2 + \ldots + a_{mp} X_p$
$V_m = b_{m1} Y_1 + b_{m2} Y_2 + \ldots + b_{mq} Y_q$

So that:

- C_m is maximun:
- $C_{orr}(V_j, V_k) = 0 \quad \forall\ j \neq k$
- $C_{orr}(W_j, W_k) = 0 \quad \forall\ j \neq k$
- $C_{orr}(W_j, V_k) = 0 \quad \forall\ j \neq k$
-

Maximization problem (Step 1)

- Let X a random vector of dimension p
- Let Y a random vector of dimension q
- Let $\sum_{xx}$ the covariance matrix of X
- Let $\sum_{xy}$ the covariance matrix of Y

Let U = a´X and V = b´Y (3) linear combinations of X and Y respectively.

Objective

The objective is to estimate a´ and b´ such that the correlation between U and V $a'\sum_{xy}b$

$$\text{Is maximized subject to the constraints} \left\{\begin{aligned} a'\textstyle\sum_{xx}a=1 \\ a'\textstyle\sum_{yy}a=1 \end{aligned}\right. \qquad (3)$$

The solution a´ for the first step we obtain:

- Calculating the eigenvectors of the matrix $\sum^{-1}_{xx} \sum_{xy} \sum^{-1}_{yy} \sum_{yx}$
- Imposing the condition to a´∑xxa = 1

The solution b for the first step is obtained equation (4):

- Calculating the eigenvectors of the matrix $\sum^{-1}_{yy}\sum_{yx}\sum^{-1}_{xx}\sum_{xy}$
- Imposing the condition to $b'\sum_{yy}b = 1$.

$$\boldsymbol{U = a'X} \text{ and } \boldsymbol{V = b'Y} \qquad (4)$$

linear combinations respectively.

The objective is to estimate that $\boldsymbol{a'}$ y $\boldsymbol{b'}$ such that the correlation between *U* and *V* $\boldsymbol{a'\Sigma_{XY}b}$ is maximal subject to restrictions.

IV. EXPERIMENTAL PART

Table1 shows the amounts of reagents used in the preparation of the cream with sun screen activity, highlighting the concentrations of zinc oxide (ZnO) and titanium oxide (TiO_2) which are the main active ingredients.

Procedure

In a beaker of 100 mL are added 0.16 g of camphor to 6.7 mL of sesame oil to dissolve under constant stirring for 30 min. separately, prepare a homogeneous solution with 0.16 g of menthol and 0.01 mL of glycerin at 70°C, maintaining constant temperature and agitation. This solution is added to the vessel containing the mixture with the sesame oil. Subsequently the emulsion is stirred until all solid components have dissolved completely.

Table 1: Quantities of Active Ingredients and Excipients

Material	Amount
ZnO (Sigma-Aldrich, 99.9%) g	0.5
TiO_2 (Sigma Aldrich, 99.9%) g	0.5
Nipazol (Sigma Aldrich) g	0.01
L-Menthol (Sigma-Aldrich) g	0.016
Alcanfor (Sigma-Aldrich) g	0.016
Eucalyptus (Sigma-Aldrich) mL	3.0
Glycerin (Sigma-Aldrich) mL	0.01
sesame oil (Sigma-Aldrich) mL	6.7
Stearyl alcohol (Sigma-Aldrich) g	2.5

Preparation Of The Cosmetic Cream With Blocking Activity

A suspension is prepared in a container with a mixture of zinc oxide (ZnO), titanium oxide (TiO_2) and nipazol (see Table 1), and suspended in a solution of water and alcohol in a ratio of 5:1 and stirred vigorously. Afterwards are added 2.5 g of stearyl alcohol to the emulsion and heated until dissolved with constant stirring for 30 min. The emulsion is cooled to obtain cosmetic cream with blocking activity. We obtained two batches of cream labeling them as lot 2 and lot 3. Each batch was prepared in duplicate. The emulsion is cooled to obtain cosmetic cream with blocking activity. We obtained two batches of cream labeling them as lot 2 and lot 3. Eachbatchwasprepared in duplicate.

Extensibility

We added 0.5 g of the cream on a glass plate of 12x12 cm and a weight of 404.05 g and previously placed at the bottom of a graph paper. After 5 minutes was measured the distance from the point of application of cream to the edges of a sheet in one direction.

Stability Studio

The cream obtained was placed in three plastic containers (bottles) of 5 ml and was initially determined the color, odor and pH. Subsequent to each container was placed independently of temperature of 5°C, 25°C (ambient) and 45°C. These parameters were evaluated by 14 weeks, by controlling the ambient humidity 60% ± 5% RH.

The pH of the samples was measured every week at a potentiometer mark Mettler-Toledo, previously calibrated with a buffer solution of pH 4 and pH 7.The pH value of the samples is 2 and 3 as shown in table No. 2.

Characterization

A spectrophotometer UV-VIS Varian Cary Model 100 was used with integrating sphere coupled diffuse reflectance coated with MgO as standard reflectance Lab sphere registered trademark with a reflectivity of 100%. This type of spectroscopy was used to test the degree of protection from UV radiation which presents the cream prepared, that means, that the cream made blocks all the area of ultraviolet radiation, from the most harmful (UV-C) to less dangerous to the humans (UV-A).

Findings

Figure 1 shows the spectroscopic study of UV-VIS of the cream. It shows a wide coverage of the region of the ultraviolet spectrum with a wavelength of 424.0 nm with respect to titanium oxide (TiO_2 of Degussa) whose wavelength is 392.5 nm and the zinc oxide (ZnO Becker) of 420.0 nm. The spectroscopic data show that the cream has a broad spectrum of coverage and protection from ultraviolet radiation from UV-C radiation until the UV-A, as shown in Table No. 2.

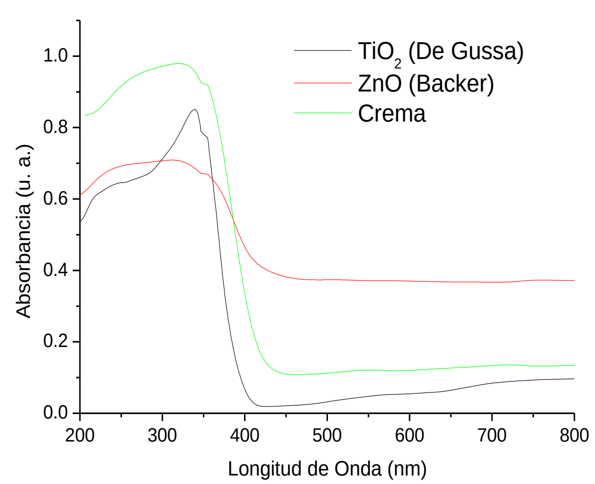

Figure 1: UV-VIS spectra of the cream on the TiO_2 (De-gussa) and ZnO (Backer)

Table 2 shows the cream has a low energy absorption in the region of the electromagnetic spectrum, showing a magnitude of energy band gap Eg of 2.92 eV to the value of ZnO (Eg = 2.95 eV) whose crystalline phase is wurtzite (Jaime Andrés Perez Taborda,2008. Huifeng Li, 2011). The TiO_2 (Eg = 3.16 eV) is presented as anatase (M. F. Brunella, 2007; D., Mendoza-Anaya, 2004). These are typical of semiconductors causing a transition from the maximum of the valence band to the minimum of the conduction band. From the point of view of ligand field theory L. (A. Grunes, 1982), corresponding to transitions of the electronic state of no link (η) and the electronic state Pi (π), the final state of antibonding Pi (π*) (M. Tzompantzi, 2002).

Table 2: Electronic and optical properties of the cream, TiO_2 (Degussa) and ZnO (Becker)

Material	λ. (nm)	E_g (eV)	υ (Hz) ($x10^{14}$)	SpectralRegion
TiO_2	392.5	3.16	7.64	VIS (violet)
ZnO	420.0	2.95	7.14	VIS (blue-violet)
Cream	424.0	2.92	7.08	VIS (blue-violet)

From the view point of molecular orbitals, the upper edge of the valence band is composed of oxygen 2p atomic orbitals, which form link p orbitals, while the bottom of the conduction band, the bands are mainly formed by atomic orbitals 4d of Ti and Zn respectively. The three materials (TiO_2, ZnO and cream), have a frequency of excitation in the visible spectral region, but in a different color, TiO_2 is presented in a violet color and ZnO with the cream between blue and violet colors, demonstrating the wide range of UV coverage featuring the cream, according to table No. 1. Therefore, according to the optical and electronic properties presented in Table No. 1, shows that the cream obtained are optimally efficient full spectrum of ultraviolet radiation.

The key results for this study are extensibility, temperature and pH, which were ordered in two batches, labeled as Lot 2 and Lot 3, as shown in Tables No. 2 and 3. Both pH extensibility decreases within creasing temperature of 5°C to 45°C.

Table 3: Temperature and pH.

Values obtained from the study of stability of the cream of Lot 2 and 3

	Weeks													
T °C (pH)	1	2	3	4	5	6	7	8	9	10	11	12	13	14
5 (2)	7.9	7.6	7.8	7.6	7.8	8.0	7.8	7.9	7.9	7.8	7.9	7.9	7.8	7.8
25 (2)	6.9	6.9	6.9	6.9	6.8	6.7	6.8	6.9	7.0	6.9	7.1	7.3	6.9	6.9
45 (2)	7.0	7.2	6.9	6.9	7.0	6.5	6.7	7.1	7.3	7.1	6.9	6.9	7.1	7.0
5 (3)	7.2	7.4	7.3	7.5	7.6	7.7	7.2	7.3	7.4	7.6	7.4	7.3	7.3	7.4
25 (3)	6.2	6.3	6.2	6.3	6.8	6.8	6.8	6.9	6.7	6.8	7.1	6.9	6.9	6.7
45 (3)	6.8	7.2	6.9	7.0	6.7	6.5	6.8	6.8	6.9	7.2	7.1	6.9	7.2	6.9

Table 4: Temperature and pH

Values obtained from the study of stability of the cream of Lot 2 and 3

	Weeks													
T °C (ext)	1	2	3	4	5	6	7	8	9	10	11	12	13	14
5 (2)	3.8	3.8	3.8	3.8	3.7	3.8	3.8	3.8	3.7	3.8	3.9	3.8	3.8	3.8
25 (2)	3.9	3.9	3.8	3.9	3.8	3.7	4.0	3.9	3.8	3.9	3.8	3.8	3.9	3.9
45 (2)	3.4	3.3	3.4	3.3	3.2	3.5	3.4	3.4	3.6	3.5	3.3	3.5	3.8	3.4
5 (3)	3.6	3.5	3.9	3.9	4.5	4.1	3.6	4.1	3.9	3.9	3.9	3.9	4.0	3.9
25 (3)	3.3	3.5	3.8	4.2	4.4	3.6	3.3	3.8	3.9	4.3	3.5	3.8	4.1	3.8
45 (3)	2.9	2.3	2.8	2.5	2.7	2.8	2.9	2.6	2.9	2.7	2.8	2.9	3.0	2.7

The pH of both groups (2 and 3) tends to decrease when temperature increase of 5°C to 45°C, an average of 7.9 to 7.0 pH during the 14 weeks, see Table No. 2. Active substances presented in the composition cream are TiO_2 and ZnO. These oxides have amphoteric properties of acidity-basicity and according to the periodic properties of elements, the character "acid-base" increases from left to right in the same period. Both elements are in period 4. Ti and their respective oxides are slightly less acidic than Zn and their respective oxides. This leads us to suppose that if the TiO_2 is presented as support and if we consider that the ZnO as impurities presented in the stand, then, the amount of acid-base sites on the surface of TiO_2 tend to be occupied by particles of ZnO and OH^- groups. When the temperature increases, these acid-base centers are activated and species adsorbed onto the surface of TiO_2 are OH^- groups, due to being more reactive with respect to ZnO. By increasing the number of OH groups on the surface of TiO_2, it tends to have more basic character, causing the change in pH to values of 7 approximately as shown in figure 2.

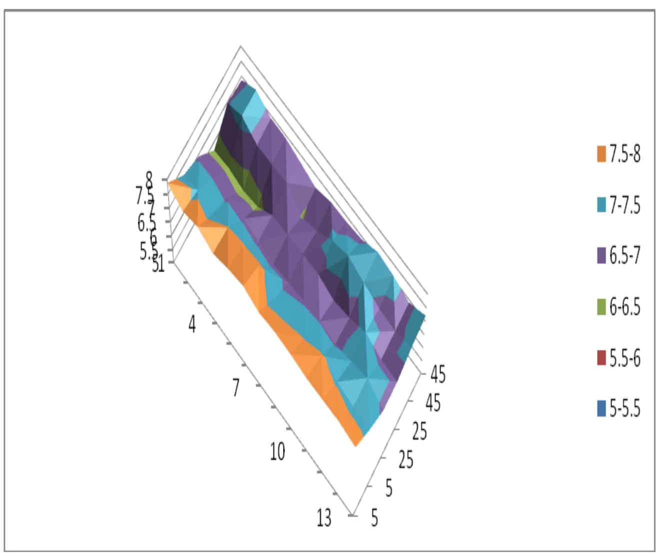

Figure 2: Graph of pH, week and temperature.

Extensibility results from Table 3, shows a deformation measurement threshold of the system, the viscoelastic properties of stearyl alcohol having about the principal active components (TiO_2 and ZnO) present in the cosmetic cream. At a temperature of 45°C decreases the extensibility of 3.8 to 3.4 and this is reflected in the canonical correlation analysis. We infer that his could be due to alcohol, being as thickener agent; to increasing the temperature at 45°C, could influence the properties of TiO_2 and ZnO in such a way that does not allow the agglomeration of these we would suggest that a higher consistency we obtain a lower extensibility.

This decrease of extensibility with respect to temperature can be explained for the active compounds (TiO_2 and ZnO) and stearyl alcohol. Both batches (2, 3) have a reduced extensibility values by increasing the temperature of 5°C to 45°C. It is inferred that the acid-base pairs generated on the surface of TiO_2 are occupied by the dopant ZnO and hydroxyl radicals (OH^-); however most of these species is the OH^- reactive, so that the latter interacts more readily with the active centers of TiO_2 and only a few active sites on ZnO occupying them. OH^- species does not allow the interaction of ZnO more molecules on the surface of TiO_2, which infers a decrease of extensibility. From the physical standpoint, stearyl alcohol increases the viscosity of the material, reducing the contact area between the active sites (acid-base pairs) and there is rapidly occupied by OH^- groups.

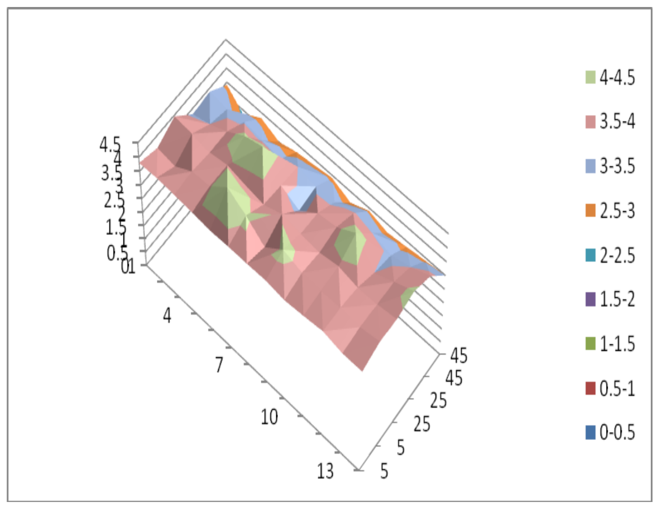

Figure 3: Graphic extensibility, week and temperature

A program was developed to conduct a canonical correlation analysis in order to confirm the correlation between temperature and extensibility. The program was programmed in MATLAB (John H. Mathews, 1999), because of the easily handles of the arrays.

The objective is to obtain the estimate:

$$a' = (a_1, a_2) \quad (5)$$

Then we proceed to calculate the eigenvectors of the matrix . $\Sigma_{XX}^{-1}\,\Sigma_{XY}\Sigma_{YY}^{-1}\Sigma_{YX}$

Covariance matrix of the variables X and Y are:

$$\Sigma_{XX}=\begin{pmatrix}0.0201 & 0.0095 & 0.0016\\ 0.0095 & 0.0464 & -0.0066\\ 0.0016 & -0.0066 & 0.0119\end{pmatrix}$$

$$\Sigma_{XY}=\begin{pmatrix}0.0001 & 0.0022 & 0.0020\\ 0.0058 & 0.0058 & 0.0001\\ -0.0045 & 0.0058 & -0.0008\end{pmatrix}$$

$$\Sigma_{YX}=\begin{pmatrix}0.0001 & 0.0058 & -0.0045\\ 0.0022 & 0.0058 & 0.0058\\ 0.0020 & 0.0001 & -0.0008\end{pmatrix}$$

$$\Sigma_{YY}=\begin{pmatrix}0.0065 & 0.0012 & 0.0002\\ 0.0012 & 0.0242 & -0.0018\\ 0.0002 & -0.0018 & 0.0021\end{pmatrix}$$

From matrix (6) we obtained the matrix:

$$\Sigma_{XX}^{-1}\,\Sigma_{XY}\Sigma_{YY}^{-1}\Sigma_{YX}=\begin{pmatrix}0.3178 & -0.1415 & 0.0693\\ -0.1479 & 0.2070 & -0.0477\\ 0.0205 & -0.0187 & 0.1419\end{pmatrix} \quad (7)$$

To subsequently obtain $a' = (a_1, a_2)$

For equation (7) will get their own values which were

$$a' = \begin{bmatrix}0.4254\\ 0.1076\\ 0.1336\end{bmatrix} \quad (8)$$

This process is repeated to obtain b' and then obtain the linear combinations

$$U_1 = 0.8374X_1 - 0.5885X_2 + 0.0992X_3$$
$$V_1 = -1.0709Y_1 + 0.4501Y_2 + 0.1529Y_3$$
$$U_2 = -0.5105X_1 - 0.8308X_2 - 0.1479X_3$$
$$V_2 = 0.0567Y_1 + 1.0192Y_2 + 0.2770Y_3 \quad (13)$$
$$U_3 = 0.2289X_1 - 0.2012X_2 - 1.0187X_3$$
$$V_3 = 0.0907Y_1 - 0.0403Y_2 - 1.0171Y_3$$

Interpretation of Linear Combinations

The interpretation can be given to the first pair of canonical variables (U_1, V_1) the pair of variables that have the highest correlation and the variables that follow are the pair (U_2, V_2) and so on. We see first that seems to be a contrast in the canonical variable U_1 regarding its variables; namely, variable X_2 against X_1 and X_3 as the first has a positive sign and the last two negative and the same for V_1 where is a contrast between Y_1 and Y_2, Y_3 as the first variable is negative and the latter are positive, it is now apparent that the variables have the greatest contribution to U_1 are X_1 y X_2 as their value exceeded 0.5, the discretion of [20] and to V_1 rises above 0.5 is Y_1. Variables that have a negative sign can be interpreted as follows: variable Y_1 represents the extensibility at room temperature and indicates that a lower extensibility higher temperature represented by the variable X_1 and X_2 that means for temperature at least 5° less extensibility represented by Y_1; the interpretation is consistent with the physical application performed applying the cream to different people at different temperatures, noting a higher temperature the cream evaporates and slides less. For the next pair of canonical variables would apply the same criteria.

V. CONCLUSIONS

The obtained cosmetic cream covers the range from UV radiation as shown in the UV-VIS spectra, having a wavelength of 424 nm. Physically the cream showed different behaviors in different room temperatures, the canonical correlation analysis corroborated there is a relationship between the group of environmental variables and the group of extensibility to make the interpretation for the first pair of canonical variables (U_1, V_1) are those with highest correlation and consequently the most important, we could see first that it seems there was a contrast to the canonical variable U_1 regarding its variables, that contracted respect to the sign X_2 with X_3 and X_1 and the same for V_1 where is also a contrast between Y_1 and Y_2, Y_3, and now it was known that the variables that had greater contribution to U_1 were X_1 and X_2 and for V_1 the variable Y_1 that had a negative sign, the variable Y_1 represents the extensibility at room temperature indicates that the lower extensibility higher temperature represented by the variable X_1 and X_2 means for temperature at least 5° less extensibility represented by Y_1, this interpretation is consistent with the physical application performed applying the cream to different people at different temperatures. We continue to make more practical with the product and the next step is to see if in fact the skin efficiently protects it from exposure to the sun.

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