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INNOVATION IN THE PRODUCTION OF A CREAM BASED ON THERMAL WATERS FROM THE SURROUNDIGS OF THE ARENAL VOLCANO IN COSTA RICA

German L Madrigal Redondo[1*], Rolando Vargas Zúñiga[2], Gustavo Carazo Berrocal[3], Nils Ramírez Arguedas[4]

[1]Associate Professor, [2,3]Professor, [4]Director,
Researcher at The Laboratory of Biopharmacy and Pharmacokinetics (LABIOFAR) of The Institute of Pharmaceutical Research (INIFAR), and The Pharmaceutical Chemistry Laboratory of The Faculty of Pharmacy University of Costa Rica, Rodrigo Facio Campus, San Jose, Costa Rica.

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***Correspondence for Author**
German L Madrigal Redondo
Associate Professor, Researcher at The Laboratory of Biopharmacy and Pharmacokinetics (LABIOFAR) of The Institute of Pharmaceutical Research (INIFAR), and The Pharmaceutical Chemistry Laboratory of The Faculty of Pharmacy University of Costa Rica, Rodrigo Facio Campus, San Jose, Costa Rica.

ABSTRACT

Introduction: Since 2009 the University of Costa Rica, through the Faculty of Pharmacy, is dedicated to promote a model of development in cosmetics in small and medium industries in rural or poorest areas of Costa Rica, in which female heads of household are leading the company,. aA successful example of this model is microenterprise Biosphere, located in the province of Alajuela, canton of San Carlos, District Fortune, which produces cosmetics based on hot springs and peloids obtained in the surroundings of the Arenal Volcano, which are characterized and formulated at the Institute of Pharmaceutical Research (INIFAR). Objective: Formulate a cream based on hot springs with renewable natural resources, cosmetic features, and high in content of minerals and high in content of minerals and not physicochemically unstable due to this composition. Methods: the raw materials and formulations were characterized by physicochemical tests such as pH, rheology, density, and organoleptic tests, and a formula were selected due to this characterized attributes. Results and conclusions: an stable formulation at high mineral content, HLB 6.82 , thixotropic adequate bed-wetting characteristics, pH 5.0 -7.0 , and without overheating with the friction, useful as the base was obtained for massage spas were obtain.

KEYWORDS: Hot Springs, physicochemical properties, cosmetics, Social Development, microenterprise, peloids, SMEs, link Partner Enterprise-University -Society.

INTRODUCTION

Since very ancient times mud and thermal waters were used for cosmetic and therapeutic uses such as: skin problems (psoriasis), inflammation (arthritis), infections (fungi), among others. There are places such as the baths of Trajan in Rome or the spas of Geller in Budapest and the hot springs of La Fortuna in San Carlos, Costa Rica, where have historically been used these resources for esthetic and therapeutic purposes. This practice has increased in recent times, leading to a growth in the production and marketing of cosmetic products based on thermal and peloids.[1]

All around the world there is a great interest in developing and patenting new cosmetic formulations. Data from the year 2011 of the World Intellectual Property Organization (WIPO) registration documents of 8819 patents registered. In figure 1 and 2 show that since 1980 there has been an exponential increase in the registration of patents in this field, from 4 patents in 1980 to 763 in 2010.[2]

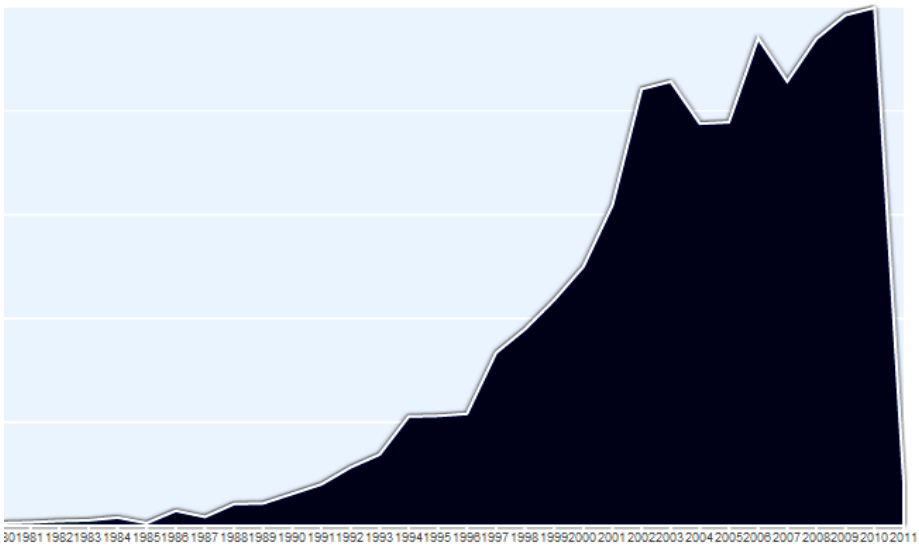

Figure 1: Number of patent applications per year for the cosmetics area worldwide, according to the data of the World Intellectual Property Organization (2) .Source 2

The area of cosmetic formulations is still a very new field, according to data from WIPO,; in the year 2010 is were submitted 763 patent applications in cosmetics in contrast to the 4121.

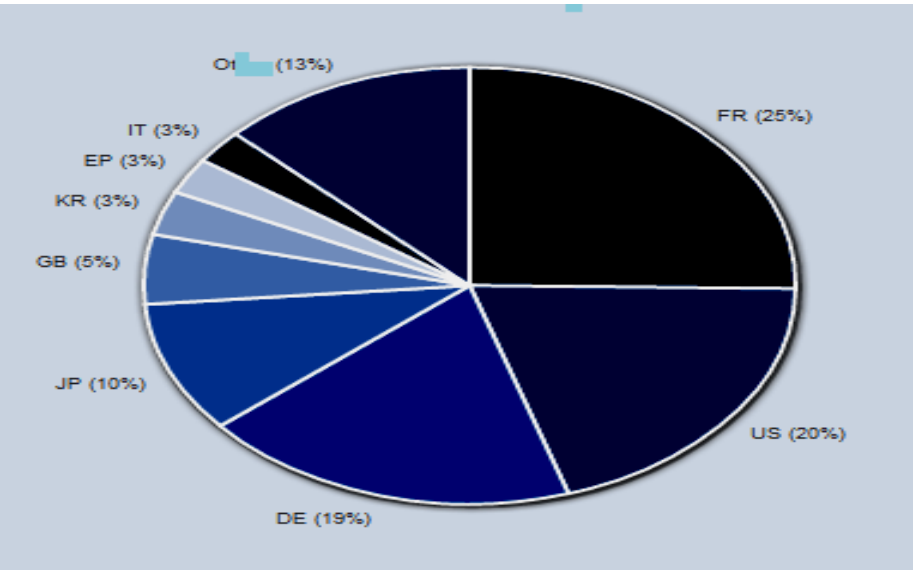

Figure 2. Percentage of patent applications by country of origin for the cosmetics sector of the year 1980 to January 2011oOrganizacion according to the world of Intellectual Property (2) Source 2.

Applications in the field of medicines, which represents only 18.51 % of the total number of requests for pharmaceutical products. It is important to emphasize that the countries of origin of patent applications in the area are mainly France (FR) and United States of America (US, United States) and in third place Germany (DE) as shown in Figure 2.[2]

In Costa Rica since the beginning of the twentieth century, the work of Gustavo Michaud, Manuel Quiros, Elias Jimenez Rojas, Indalecio Saenz, Otton Luthmer Jimenez, among many others about natural products research has to be highlighted. For example, in the year of 1905, Fidel Tristan and Gustavo Michaud discovered, isolated and identified the carbohydrate agavosa, from an agave plant of the garden of the house of Mauro Fernandez, today the National Museum. Many of these works were published in The Journal of American Sciences. The Faculty of Pharmacy of the University of Costa Rica founded in the year of 1899 has played a very important role in the development of research in the pharmaceutical and cosmetic fields, taking advantage of the natural resources of the country and applying them to the improvement of the health of the population.[3; 4]

A more precise review of WIPO on the status of applications in the cosmetics sector shows that in Latin America the main countries where innovations are protected in the cosmetics sector are Argentina, Mexico and Colombia. It is remarkable the case of Spain with 4184 patent applications in the cosmetics sector.[2] For January 2011, in the case of Argentina,

there are 436 applications, Mexico 1833 and Colombia 129 registered. Other countries with registered patents are: Guatemala 16, Uruguay 9, Cuba 8, Peru 7, Costa Rica and Panama 2. These data reflect the importance of the countries for advancing the study and protection of pharmaceutical dosage forms cosmetic (2; 5). It is clear that the Latin American market is growing and diversifying, for example in the year 2007 Brazil had sales of $10.100 million; Argentina won $1492 million dollars. However, Europe and the United States are the major markets of the cosmetics in both; its production and consumption.[5; 6; 7]

According to the Ministry of Trade Exterior of Costa Rica, global spending on personal care products in the period 2008-2012 ascends to 849,771 million USD as annual average. For that period, for each $100 you spend a consumer, 2.3 USD correspond to personal care products; also is important that according to estimates by Euromonitor, for the period 2013-2017 is expected a annual growth of 3.1 per cent in spending.[8] For example in the field of the creams for skin care the same trend has been followed as shown in figure 3, and that's why the development of new products in this niche has been increase.[9]

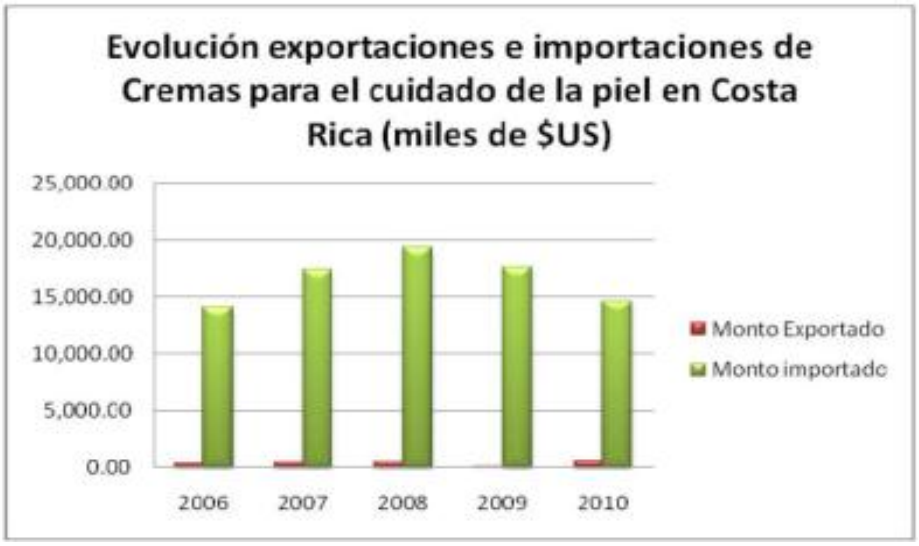

Figure 3. Comparison of sales in thousands of US dollars between personal care creams of exported and imported in Costa Rica from 2006 to 2010. Source.[9]

A study conducted in 2004 by Proexport Colombia on the cosmetic market in Costa Rica, showed that the Costa Rican market for 2002 was approximately $100 million per year, while in 2012 according to data of Procomer, reached a volume of 350.5 million[8;10], however Costa Rica exported only in this period a total of $5.6 million. This study confirms that although competition within this sector is important SMES have advantages for its growth,

because the flexibility of the production, the knowledge of the domestic market, an expanding market, margins of considerable utility, national technical support, in addition to natural resources for domestic raw materials abundant and virtually untapped.[8;10]

One of the advantages of Costa Rica is that it has an important source of natural resources for the development of cosmetics. Peloids, mud and thermal waters are used for esthetic and therapeutic purposes, its use has increased in recent decades, constituting a possibility for the development of small and medium-sized companies.[8; 9; 10]

According to Juan Francisco Romero Sánchez, the evaluation of medicinal peloids as therapeutic elements, is given on the basis of their composition and physical-chemical and bacteriological properties. That's why parameters such as are pH, moisture, presence of organic and volatile substances, presence of biogenic elements, mineralization and ionic phase composition, among others, are fundamental for this type of materials.[11]

Prior research has established that is very important to study the physicochemical characteristics of the thermal springs with medicinal properties in order to be able to classify them. This type of material can be defined, from a physic-chemical point of view, as heterogeneous systems consists of a suspension of solid phases of organic and inorganic natural matter in a liquid phase (water).[12] For this reason is that the density, conductivity and viscosity are fundamental properties to be evaluated in this type of systems.

It is precisely by this composition and this characteristics of the thermal source that they can produce specific therapeutic or cosmetic effects in the skin[1; 12], by knowing these properties we can modify or enhanced them, using an adequate dosage form and standardize their qualities in the time.[12]

The Cuban standard NC 93-18-01:218 (1995) defines mineral waters as water with a high content of certain mineral salts and their relative proportions, as well as trace elements and other useful components in the human metabolism. It is obtained directly from natural sources or perforated groundwater aquifers of strata, is considered thermal mineral water when in the point that arise has 4 degrees Celsius higher than the average annual environmental.[15, 13]

The classification of the mineral waters can be summed up as follows.

Table I Classification of the Mineral Waters.

Denomination	Clasification	Detail
Use	Non Energetic	Balneologicas and therapeutic Human consumption Domestic
	Industrial	Energetic Calefaction Agricultural
	Multiple uses	Other uses
Origin	Sea waters	From the sea
	Meteorics waters	Precipitation waters Ground waters Superficial underground waters
	Congenit waters	Sea waters Other origin
	Metamorphic waters	Witn high content of CO2 and Bore Other waters
	Magmatic water	Originated from the low depth magmas
	Plutonic water	Originated from the high depth magmas
	Young waters	Magmatics Others
Temperature	Hiperthermals	More than 4°C of the ambiental media temperature.
	Ortothermals	Same as the ambiental media temperature.
	Hipothermals	Less than 4°C of the ambiental media temperature
	Cold	Less than 20°C
Tonicity	Hipertonics	More than 325 mOsmol /L
	Isotonics	325 mOsmol/L
	Hipotonics	Less than 325 mOsmol/L
pH	Strong acid reaction	pH less than 3.5
	Moderate acid reaction	pH between 3.5-5.5
	Light acid reaction	pH between 5.5-6.8
	Neutral reaction	pH between 6.8-7.2
	Strong alkaline reaction	pH above 9.5
	Moderate alkaline reaction	pH between 8.5-9.5
	Light alkaline reaction	pH between 7.2-8.5
Mineralization	Oligo-minerals	Dry residue less than 100 mg /L
	Low Mineralization	Dry residue between 100-500 mg/L
	Medium Mineralization	Dry residue from 500 to 1500 mg/L
	Strong Mineralization	Dry residue above 1500 mg/L

Chemical composition	Chloride	More presence of chloride in comparison to sulfates and carbonates
	Sulphates	More presence of sulphates in comparison to chlorides and carbornates
Chemical composition	Carbonates	More presence de carbonates in comparison to chlorides and sulphates
	Anionic Mixes	Proportionally the same amount of chlorides, carbonates and sulphates
	Sodium	More presence of sodium in comparison to calcium and magnesium.
	Calcium	More presence of Calcium in proportion to sodium and magnesium
	Magnesium	More presence of Magnesium in comparison to sodium and calcium.
	Cationic Mixes	Proportionally the same amount of calcium, sodium and magnesium.

Source.[11; 15; 13; 14]

The INIFAR® of the Faculty of Pharmacy of the University of Costa Rica, has been developing in recent years a series of projects in the field of development of cosmetics development that allows it to contribute and play a leadership role in the application of scientific knowledge in the service of the pharmaceutical and cosmetic national industry national, and also cooperate with the remote areas of the central valley that are little industrially developed and, therefore, generate a social impact in supporting people with few job opportunities and local scientific development.

The cosmetics industry in Costa Rica is very incipient and not always has the support of a professional to make and also perform the quality control of these products, which affects the growth of this type of industries (3).

The need to improve, develop and optimize based formulations of peloids and thermal is based on the fact that the company Biosphere sells products in restaurants, hotels, and supermarkets,; however these products present problems of shelf stability in the shelf, which affects negatively in the commercialization of their productos for a long time.

Another need of the company is to generate new cosmetic products, to expand its market; these products must also be stable, to ensure your marketing and registration with the

Ministry of Health. The stability of the products is essential to your marketing, not only in Costa Rica, but also in other markets, particularly in Europe, either by means of tourists who buy the products, or directly by exporting them.

The creams are oil dispersions in water or water in oil with a high viscosity,; the ones that are brewed with hot mineral waters have stability problems due to its high content of ions that affect the zeta potential of the particles, wichwhich dehydrates cells in favor of hydrate ions. To Sstabilize this type of formulations is extremely difficult, so achieveing this type of formulations is a significant technical advance, mainly because depending of the origin of the thermal water its properties and chemical composition vary. The obtained creams of thermal waters is a benefit because it increases the absorption properties of the elements in them that are in addition to obtaining the specific properties of their composition that attach to the skin, these properties can be cosmetic or therapeutic.[15, 16]

OBJECTIVE

Formulating and characterize a cream with innovative mineralo-medicinal thermal water originating in the foothills of the Arenal Volcano in Costa Rica that is physic-chemically stable for a year to its marketing to national and international level.

MATERIALS AND METHODS

Reagents: Thermal Water taken in the foothills of the Arenal Volcano, vegetable oil, Beeswax, Tween 80, Lanolin, Sodium borate, Mineral Oil Polyethylene glycol 40, Methylparaben, Propylparaben, stearic acid, Cetilic Alcohol, Tween 20, Triethanolamine, Glycerin, stearylic alcohol, Astek floral fragrance. A series of test formulations where prepared with the excipients mentioned above, to this formulations were applied a basic procedure in formulation that is combining the excipients in a oily phase and bring them to 80 °C and the hydrophilic excipients in the aqueous phase also at 80 °C and then mixed in continuously agitation for 20 minutes to form a homogeneous dispersion, is cooled to room temperature and finally packaged. From these formulations were selected a one base formulation that hold up the test of centrifuge at 5000 revolutions per minute for 15 minutes to evaluate its stability at hyper accelerated conditions. Equipment: pH metro Denver Instrument ® pb 11, membrane electrode glass, Rheometer LV DV III® Brookfield spindle 18 and 25 Analysis Software Reocal®, Pycnometer of stainless steel, Analytical Balance of four decimals, Flame Atomic Absorption Spectrophotometer Vary SpectrAA-220FastSecuential with accessories for graphite furnace and hydride generation. Analyzers

CHNS-O EA-1108 y EA-1112, centrifuge generic desktop speeds from 1000 to 10000 rpm. In the case of pH and specific gravity, three samples were analyzed of the natural peloid and also from the reference and were measure, in the case of pH close to 15 grams of the sample were placed in a beaker and then measured after calibrating the instrument with patterns of 4.0 , 7.0 and 10.0 ; the temperature analysis was 25 °C, in the case of the specific gravity empty pycnometer, pycnometer filled with distilled water and finally pycnometer filled with the mixture were weight on an analytical balance at 25 °C. The centrifuge test involves placing six samples in test tubes for 15 minutes at 5000 rpm, then a water soluble dye is added to check whether or not there is separation of phases. In the conductimetry test, samples are placed in a glass beaker with an electrode and wait for the signal to stabilize.[17] Elemental Analysis: The samples were nebulized and then transferred to an energy system consisting of a flame obtained by combustion of acetylene, who supply to the molecules the amount of energy required to break their bonds. For the refractory elements, which require more energy input (Al, Si, Ti, Va), is often used the flame caused by nitrous oxide and acetylene.[18] The loss of weight test was carried out by drying three samples in refractory furnace at 110 °C for 24 hours and weighted by difference in an analytical balance. For the rheological tests a ramp of six speeds from 5 rpm up to 50 rpm and then repeated downward were used, the spindles used were 18 and 25 and the container R18, the working temperature was 22 °C. The data were analyzed by the software Reocal®.[17,18]

RESULTS

Listed below are the results of the characterization of the mineral-medicinal thermal water and the formulation of a cream of thermal water.

Table II: Selected formulation for the physicochemical characterization.

Oil phase	**Aqueuos phase**
Bee wax 10 g **Vegetable oil 10 g** **Lanoline 3,1 g**	Borax 0.8 g
	Tween 80 5 g
	Triethanolamine 1 g
	Thermal water c.s.p 100 g
Perfume and preservant	

Table III. Elemental determination of the thermal water of the slopes of the Arenal Volcano Costa Rica.

Chloride (mg/mL)	**Bromide (mg/mL)**	**Nitrite (mg/mL)**	**Nitrate (mg/mL)**	**Fluoride (mg/mL)**	**Sulphate (mg/mL)**	**$CaCO_3$ (mg/mL)**	**Phosphate (mg/mL)**
335	0.45	0.06	319	12.4	0.39	175	0.53

Table IV. Results for pH of thermal water.

Sample	pH
Thermal water sample 1	8.15
Thermal water sample 2	8.20
Thermal water sample 3	8.30
Mean	8.22 ± 0.08

Source 19

The test result of weight loss for the thermal water produce a dry residue of 1,320 mg/L ± 35 mg/L and the electrical conductivity of the thermal water was 1.923 µS/cm ±15 µS/cm (19). For the cream of thermal water selected

Table V: Results for pH and specific gravity of thermal water cream of the study.

Sample	pH	Specific gravity
Thermal water cream sample 1	8.14	0.841435171
Thermal water cream sample 2	8.13	0.840594131
Thermal water cream sample 3	8.10	0.841321858
Mean	8.12± 0.21	0.841117± 0.000456

Source 19.

The results of the rheologic study are shown below.

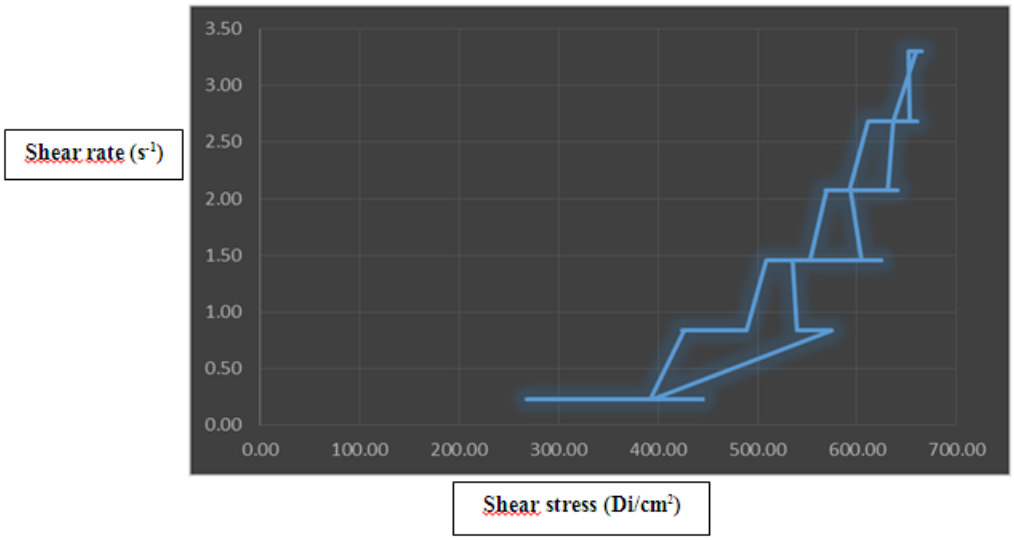

Figure 4 Analysis of thixotropy of the cream of thermal water source 19.

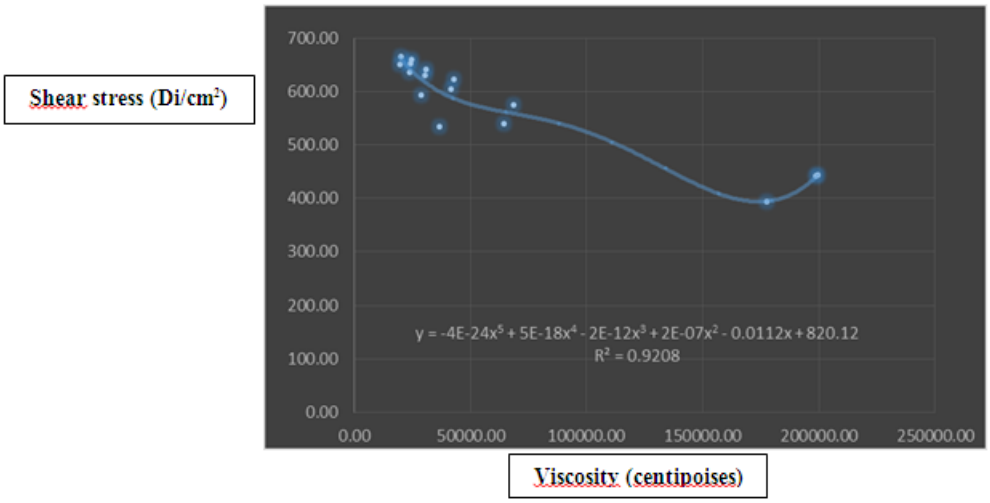

Figure 5. Analysis of plasticity of the thermal water cream.

Source 19.

The electrical conductivity of the cream of thermal water was 1.014 ± 24 µS/cm (19).

DISCUSSION AND CONCLUSIONS

Based on the results of the tables I, III, IV, the thermal water used in the present study can be classified as mineral-medicinals waters, of the type hyper thermal because the temperature of the source from where it was obtain is 42 °C, a pH basic moderate reaction, which is explained by the high carbonate content, magma type because they come from magmas of aquifers from low depth or superficial.[1, 13, 14]

By its mineralization can be indicated that it is of high mineralization if it is considered for human consumption, or animal, however from a geological point of view is weakly mineralized already that the dry residue of 1320 mg/L, its chemical composition is mainly chlorides, nitrates and carbonates, which categorizes as a hypertonic chloride water, however can be used for various uses, such as agriculture, human or animal consumption, spas, therapeutic or industrial.[1, 13, 14]

Characterize the mineralo-medicinal water to be used in the test, its useful for formulating a vehicle in moisturizing emulsion with cleaning capacity due to its basic pH with an external aqueous base to take maximum advantage of the mineral content and also to be used as a vehicle for massages or body therapies such as wraps.[15,16]

The high content of fluoride makes it ideal for the formulation of mouthwashes and rinses, which already makes it possible to provide an essential element for the dental protection.[15]

The formulation of table II was selected out of 10 based on the formulations which changed the proportion of oils and waxes of the oily phase for a dispersion that will pass the test of the centrifuge, a test that allows you to identify quickly if there will be separation of the phases, only one of the formulations was able to pass the test, this due to the high electrolyte content of the water used that prevents the stabilization of the emulsified globules, as this is the problem were preferred the use of non-ionic surfactants in order to not increase the loads of zeta potential of the formulation.[15, 20]

Table V shows the characteristics of the formulation selected (table II), with a moderate basic pH 8.12 which allow it to be use as a skin cleaner, mainly for oily skin with acne, and also useful for massage. Its low density (0,841 g/cm3) provides a smooth feeling for the skin. The rheological study of the formulation in figure 4 shows a thixotropic plastic flow with a high critical shear stress of 350 fluence dinas/cm, the figure shows that the formulation has a high thixotropy what contributes to its stability because it decrease the possibility of phases separation according to the Stockes Law, decreasing the cremation speed, and also the high thixotropy that shows the hysteresis loop corresponds to a smooth application on the skin because it tends to disperse at high speeds of shear after you get the fluence point for example in massaging creams.[15.20]

The easy application or the collapse of the viscosity before high shear efforts is clearly shown in figure 5, it goes from 2000 poises at low shear stress to 200 poises at high shear stress, which ensures that while the formulation is in the shelf the high values of viscosity avoids the separation. However due to its high thixotropy and plasticity, you can obtain a soft application on the skin surface.[15, 20]

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The Reocal® software allows you to perform the approximation mathematical model, which is in accordance to the data obtained. According to these results, the best fit is obtain by the Casson model: $\sqrt{t} = \sqrt{\eta D} + \sqrt{t^0}$

The result of the model gives a plastic viscosity ηof 2487 cp and a yield stress τ^0 of 387.5 dinas/cm, with a approximation percentage to the model of 96 %, shown by the equation: $\sqrt{t} = \sqrt{2487\ \chi\pi\ *D} + \sqrt{387.5} Dinas/cm$

In addition we calculated the melt flow index and the index of consistency according to the Law of the power of Ostwald the outcome of this trial determined a flow rate "n" of 0.23 which shows their high degree of plasticity index and the consistency of "K" was estimated at 50754 cp, which shows the high degree of stability having a great consistency at rest. The degree of approximation for this model was 92 %.

It is concluded that the water used in formulations is a mineral-medicinal high mineralization water for human or animal consumption and weak geological level of mineralization with a high content of chlorides, nitrates and carbonates by which is defined as chlorides water and it can be used in the formulation of cosmetic creams for massages. Its basic pH 8.22 makes it suitable for the formulation of cleansers. The thermal water cream has a suitable consistency for its application in skin thanks to its high plasticity and low specific gravity. It has a plastic thixotropic flow that contributes to its stability under rest conditions and its high plasticity allows for easy application at high shear rates, for example for massage therapies. Also its basic pH makes it ideal for cleaning therapies as in facial cleaning. Its high content of minerals allows it to provide trace elements to the skin which are more easily absorbed by a dispersion.

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