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Sunscreen Cream Formulation with Natural Ingredients, including Arabic gum and Beeswax Foundation

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Abstract

The aim of this research was to develop sunscreen cream formulation with natural ingredients and calculated sun protection factor (SPF) for it. The sunscreen is prepared using water phase that includes distilled water as a main solvent, glycerine as a moisturizer, Arabic gum as a thickener, and citric acid as a preservative. The oil phase is composed of one of the following oils: paraffin oil, olive oil, sesame oil or pond oil, and beeswax foundation as emulsifier. Zinc oxide and titanium dioxide are both employed in sunscreen as inorganic physical sun blockers. The best cream texture was obtained in the case of using beeswax foundation as emulsifier by 8%. The best solubility of sunscreen cream is obtained using equal proportions of hexane and ethanol. An in vitro SPF (sun protection factor) of used samples is calculated according to Mansur's method. Moreover, Mansur's method calculates only SPF values of organic substances (triglyceride oils) but physical sun blockers (zinc oxide and titanium dioxide) cannot be calculated by Mansur's method. By comparing SPF values for triglyceride oils, the best protection value is obtained using olive oil. For other oils were found to be around 6. Therefore it can be founded that triglyceride oils have absorbency in UV region so that these oils can be used in the formulation of sunscreens as emollients and sun blockers. This formulation of sunscreen cream is focused on using natural ingredients, creamy texture, and efficacy..

Keywords: *SPF, Sun protection factor, Titanium dioxide, Zinc oxide, Olive oil, Triglyceride oils.*

1. Introduction

There is agreement between the scientific and medical societies that exposure to sunlight is a main reason to damage the skin.[1] An electromagnetic radiation in sunlight called ultraviolet (UV). Ultraviolet light is artificially divided into three ranges: UVA (320-400 nm), UVB (290–320 nm), and UVC (200–290 nm)[1,2]. Sunscreens are the most common products that used for skin protection against solar UVB radiation which causes sunburn, photoaging, skin cancer, formation of telangiectasia, and pigmentation irregularities[2,3] Both UVA and UVB can cause sunburn, photo ageing, erythema and inflammation.[4] Generally, UVC does not have harmful effects on the skin[2]

Sun blocking chemicals can be classified according to the type of protection they afford to the following categories:

a. Inorganic (physical blockers)

The two primary inorganic UV filters are Zinc oxide (ZnO) and titanium dioxide (TiO_2) white particles which used in the cosmetic and pharmaceutical industries. [5] Moreover, Titanium dioxide is somewhat more effective in UVB protection while zinc oxide absorbs more broadly in the UVA range.[6] Both these filters can block UV light through reflection and scattering properties (Figure 1)[6]. Their maximum concentration authorized is concentration of 25% in a UV filter.[5]

b. Organic (chemical absorbers)

Organic UV filters such as benzophenones, absorb UV radiation with excitation to a higher energy state [7]. Excess energy is dispersed by emission of higher wavelengths or relaxation by photochemical processes, for example isomerisation and heat release (Figure 1) [7]. Their absorption range and their strength are affected by the chemical structure and type of substituents.[5]

c. Natural (chemical absorbers)

"Natural chemicals like polyphenols (flavonoids, tannins), carotenoids, anthocyanidins, few vitamins, triglyceride oils, volatile oils from vegetables, fruits, medicinal plant parts (leaves, flowers, fruits, berries), algae and lichens are more effective over synthetic chemicals which is due to their long term beneficial effects especially against free radical generated skin damages along with UV-rays blocking" [9]. Moreover, Oils have been a part of human lifestyles for ages, and their safety has been evaluated by millions of users down through the centuries [8].

For designers and manufacturers of sunscreen requirements can be summarized in the following four basic requirements[11, 12].

i. Effectiveness, choose the correct UV filters Mix and other key ingredients to accomplish desired performance.
ii. Safety, whether objective or simply conceived by the media and the consumer,
iii. Registration, which is most important if the sunscreen, will be distributed to the world.
iv. Patent Freedom, i.e. "freedom of action" with respect to the third intellectual property rights (IP)

The effectiveness of a sunscreen is usually expressed by sun protection factor (SPF) which is the ratio of UV energy required to produce a minimal erythemal dose (MED) in protected skin to unprotected skin [2]. High SPF numbers give the false impression they can provide enhanced protection when that is not the case.[2] A well-formulated sunscreen with an SPF 30 still only protects your skin from about 97% to 98% of the sun's rays [2].

A simple, rapid and reliable in vitro method of calculating the SPF is to screen the absorbance of the product between 290-320 nm at every 5 nm intervals. SPF can be calculated by applying Mansur equation (1) [13-15].

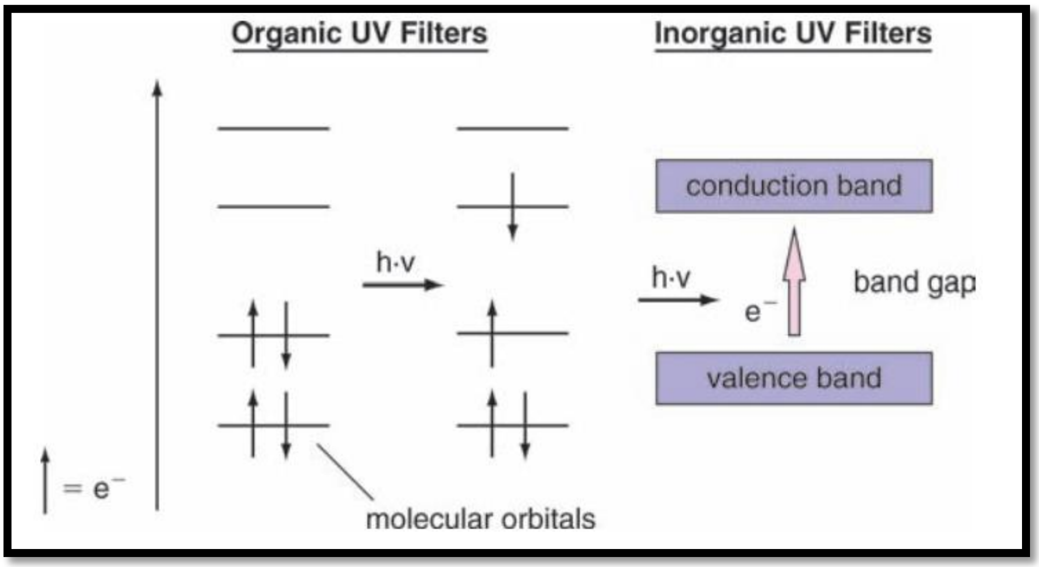

***Figure 1*.** Action mode of organic (left) and inorganic (right) UV filters.

2. Materials And Methods

.2.1 Chemicals and equipment**:**

Paraffin oil was purchased from Carlo Erba Reagents, Spain. Beeswax foundation was purchased from Madybees, Egypt. Ethanol and hexane were purchased from BDH. Glycerine was bought from Fluka chemika. Titanium oxide and Zinc oxide were purchased from Merk. All used natural oils; citric acid and Arabic gum were purchased from local distributors in Libya and used without further modification. Spectrophotometric determination of UV absorbance was carried out in 1 cm path length cuvette (quartz), using JENWAY6305 UV/Visible spectrophotometer (single beam). Samples mixing were carried out using Vortex mixer (Bio Cote). pH measurements were performed using a pH Benchtop meter (Orion 2 star, Thermo Scientific)

2.2 Preparation of sunscreen product formulation

The sun protection cream was prepared on the basis of following percentages for the total weight of the sample (5 gr) as shown in Table 1**:**

Table 1. The weights of each ingredient of sunscreen preparation are given as well as the percentages of them to the total weight of sunscreen cream's sample (5 gr)

Total Percentage	Ingredient Name	Percentage	Weight
Water phase, total percentage = 68%	Distilled water	58%	2.90 gr
	Arabic gum	5%	0.25 gr
	Glycerine	5%	0.25 gr
Oil, total percentage = 20%	paraffin oil	20%	1.00 gr
Emulsifier, total percentage = 8%	Beeswax foundation	8%	0.40 gr
Sunscreen, total percentage = 3.5%	ZnO or TiO_2	3.5%	0.18 gr
Preservative, total percentage = 0.5%	citric acid	0.5%	0.03 gr

After the weighting of ingredients (Table 1), the following steps are taken**:**

i. Both of the water phase and the oil phase are heated separately to 70 °C for 15 minutes. This will destroy any bacteria that may be present in both phases**.**

ii. The water phase is gradually added to the oil phase with the stirring. Then the solar blocker and the preservative are added with good mixing using vortex**.**

iii. After cooling the cream pour into a box and close well and covered with a white tissue until the measurement of SPF**.**

The pH of any cream or lotion can be tested and then pH level will be adjusted with adding citric acid to be pH 6 to 6.5, which is the appropriate pH level for adult skin **.**

.2.3 Preparation of sunscreen sample for SPF measurements

200mg of each sample was weighed, transferred to a 100 mL volumetric flask, diluted to volume with 50% hexane in ethanol and followed by vigorous vortexing. Then, it is filtered through filter paper, rejecting the first 10 mL. A 5.0 mL aliquot was transferred to 50 mL volumetric flask and diluted to volume with 50% hexane in ethanol. Then a 5.0 mL aliquot was transferred to a 50 mL volumetric flask and the volume completed with 50% hexane in ethanol. The final concentration of each diluted sample is 20 ppm in 50% hexane in ethanol**.**

The absorption spectra of samples in solution were obtained in the range of 290 to 320 nm using 1 cm quartz cell, and 50% hexane in ethanol as a blank. The absorption data were obtained in the range of 290 to 320 (the range of UVB) every 5 nm.

3. Results And Discussion

The preparation of the sunscreen depends on three main factors:

I. Emulsifier (chemical energy): A key factor to gather both water and oil phases together is the emulsifier. Beeswax foundation is used as a main emulsifier in this research. It melts at about 60- 63 °C. It is chosen to form the emulsion and can also be used for emulsion stabilization.

II. Heat (thermal energy): Melting the solids in oil phase (bees wax foundation) to facilitate the mixing with water phase's ingredients by heating and mixing.

III. Mixing (mechanical energy): one of the most important factors that make creamy texture.

The used ingredients in the preparation of the sunscreen's cream and their respective purposes were briefly summarized in Table 2. Paraffin oil (mineral oil) is colourless and odourless. It consists of light mixtures of higher alkanes.[16] Emulsified mixtures of liquid paraffin make excellent skin creams.[16]

Table 2. A brief summary about the ingredients that used in the preparation of the sunscreen cream.

Ingredient Name	Purpose	Phase	Typical Use Level
Arabic gum	It is stabilizer, dissolves in the water phase and when mixed with the oil phase, it helps to stabilize the emulsion over a long time.	Aqueous	0.5-3%
Glycerine	It is used as a humectant where helps to retain moisture.	Aqueous	2-5%
Beeswax foundation	Emulsifier and thickener	Oil	3-10%
Stearic acid and palmitic acid	Thickener.	Oil	3-10%
Triglyceride Oils	Emollients.	Oil	8-20%
Citric acid	Preservatives.	Aqueous	0.1-1%
Titanium Dioxide and Zinc Oxide	Inorganic sunscreens.	Oil and aqueous	1-10%

3.1. Getting the best texture:

To obtain the best cohesive creamy texture, the previous ratios in Table 1 were adjusted as well as the percentage of water and emulsion were varied, as shown in Table 3, to obtain a good texture.

Table 3. Attempts to get the best creamy texture.

Ingredient Name	Texture 1	Texture 2	Texture 3	Texture 4	Texture 5
Distilled water	58%	58%	57%	58%	58%
Beeswax foundation	4%	8%	9%		
Stearic acid	4%			8%	
Palmitic acid					8%
Paraffin oil	20%	20%	20%	20%	20%
Arabic gum	5%	5%	5%	5%	5%
Glycerine	5%	5%	5%	5%	5%
Zinc oxide	3.5%	3.5%	3.5%	3.5%	3.5%
Citric acid	0.5%	0.5%	0.5%	0.5%	0.5%

In Texture 1, mixing of stearic acid with beeswax foundation in equal ratios led to the light texture. Likewise, when fatty acids were used as emulsifiers (Textures 4 and 5), it also led to a lighter texture which is not coherent to the required degree of creamy texture. Furthermore, the best cream texture was obtained in the case of using only beeswax foundation as emulsifier by 8% (Texture 2). While in the case of texture 3, in which the proportion of emulsion in the oil phase (9%) is increased, and the proportion of water (57%) is reduced, that led to solidify the cream to undesired texture. Consequently, texture 2 was used as the main texture for the preparation of samples (A to J) in this research.

3.2. Preparation of samples:

The sun protection samples were prepared with fixed ratios for the substances that mentioned in Table 4. Only the used oils, which included olive oil, pond oil, corn oil and sesame oil, were adjusted (Table 5) to test the effect of these oils on the sun protection's values.

Table 4. Ingredients that are used with fixed percentages in samples preparation (A to J).

Ingredient Name	Distilled water	Arabic gum	Glycerine	Citric acid	Beeswax foundation	ZnO or TiO_2
Percentage	%85	5%	5%	0.5%	8%	3.5%

Table 5. Percentage of oils and inorganic sun-blockers (ZnO and TiO_2) that are used in the preparation of samples A to J.

Ingredient Name	A	B	C	D	E	F	G	H	I	J
Paraffin oil	20%	20%								
Corn oil			20%	20%						
Sesame oil					20%	20%				
Pond oil							20%	20%		
Olive oil									20%	20%
ZnO	3.5%		3.5%			3.5%		3.5%	3.5%	
TiO_2		3.5%		3.5%	3.5%		3.5%			3.5%

These oils in samples (C to J) contain unsaturated fatty acids, in which there is at least one double bond in their structures so that they can absorb wavelengths from 290–320 nm to achieve the desired SPF. These purified oils are used in approximately 20% as emulsions and sunscreens.

3.3. Solubility of sunscreen cream:

To obtain the best solubility of the prepared samples, a different mixtures of ethanol (polar solvent) and hexane (non-polar solvent) were used as shown in Table 6 (entries 1-4). In brief, the best solubility of sunscreen cream is obtained using equal proportions of hexane and ethanol (entry 3).

Table 6. Results of the solubility of sample of sunscreen cream.

Entry	Solvent mixtures	Solvents ratios	Observation
1	Hexane : Ethanol	1 : 4	Very little solubility
2	Hexane : Methanol	2 : 3	little solubility
3	Hexane : Ethanol	2.5 : 2.5	Good solubility
4	Ethanol : Water	1 : 4	Very little solubility
5	Hexane : Ethanol : Water	2.5 : 2 : 0.5	Two separate layers

3.4. Calculations of pH for sunscreen samples:

The acidity of some samples (Table 7) can be attributed to the use of citric acid as a preservative in the preparative method. Acidification can be adjusted with the addition of a small percentage of sodium bicarbonate while, the basicity can be adjusted with the addition of small amounts of citric acid.

Table 7. PH values for samples (A to J).

Samples	A	B	C	D	E	F	G	H	I	J
PH	5.52	5.08	8.04	8.29	7.28	7.34	5.31	7.31	8.24	8.22

Calculations of solar protection factor (SPF)

The absorbance of prepared solutions (20 ppm in 50% hexane in ethanol) is measured in the range of 290-320 nm, each time the wavelength range is changed by 5 nm in each measurement. The Mansur mathematical equation (1) is used to calculate the SPF values of the samples (A- J).[13-16]

$$\mathbf{SPF} = \text{CF x} \sum_{290\,nm}^{320\,nm} EE(\lambda) \text{ x } I(\lambda) \text{ x } ABS(\lambda) \qquad (\mathbf{1})$$

Where: CF is the correction factor (=10); “EE”, the erythemal effect of radiation at wavelength λ; “I”, the intensity of the solar spectrum; and “ABS”, the absorbance at wavelengths 290-320 nm. “EE”, “I”, and “ABS” are values obtained or applied for every wavelength (λ). The values for each of the [EE(λ) x I(λ)] are constants have been reported by the authors as normalized on the basis of the work by Sayre et. al., and are shown in Table 8.[13-15]

Table 8. The values of EE x I as they were determined by Sayre et al (1979).

Wave length (nm)	290	295	300	305	310	315	320
EE x I	0.0150	0.0812	0.2874	0.3278	0.1864	0.0837	0.0180

Appling absorbance values in Mansur equation (1) to calculate the SPF values for these prepared samples (A-J) is shown in Table 9.

Table 9. The SPF values for prepared samples (A-J).

Samples	Active ingredients (organic filter and inorganic filter)	Calculated SPF
A	Paraffin oil and zinc oxide	6.84
B	Paraffin oil and titanium oxide	6.22
C	Corn oil and zinc oxide	6.74
D	Corn oil and titanium oxide	6.01
E	Sesame oil and titanium oxide	6.20
F	Sesame oil and zinc oxide	6.81
G	Pond oil and titanium oxide	6.15

H	Pond oil and zinc oxide	6.10
I	Olive oil and zinc oxide	7.03
J	Olive oil and titanium oxide	7.11

It can be observed from Table 8 that the SPF values found for triglyceride oils were in between 6 and 7. By comparing SPF values for triglyceride oils, the best protection value is obtained using olive oil with both inorganic filters (zinc oxide or titanium oxide) as shown in both Figures 2 and 3. For other oils were found to be around 6. Therefore it can be founded that triglyceride oils have absorbency in UV region so that these oils can be used in the formulation of sunscreens as emollients and sun blockers.

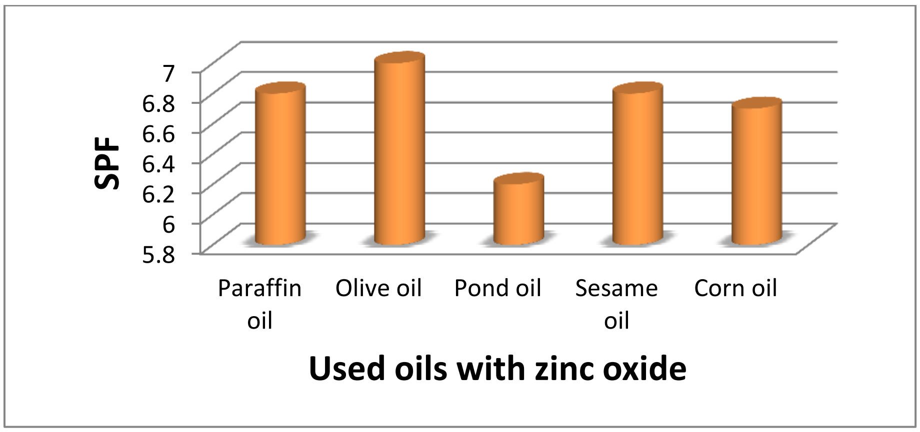

Figure 2. Relationship between SPF values and the used oil with inorganic filter Zinc oxide.

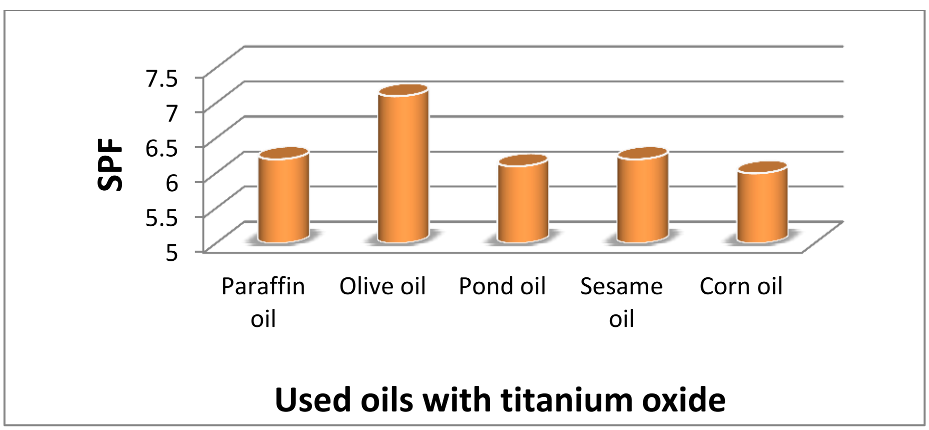

Figure 3. Relationship between SPF values and oil used with inorganic filter titanium oxide

4. Conclusions

The preparation of a sunscreen cream carried out using inorganic filters and five kinds of different oils. These fixed oils can be formulated in the form of cosmetics formulation due to their superior acceptability, less irritant nature and also these are less costly. The used beeswax foundation is less costly and available. The used Arabic gum is completely nature and inexpensive. The preservative was citric acid and no organic filter was used except triglycerides oils. The used spectrophotometric method, to calculate SPF, is an inexpensive and easy to apply. Moreover, this method can calculate SPF for organic filters but it cannot used to calculate SPF values for inorganic filters, such as zinc oxide and titanium oxide, as an active ingredient. Then, this spectrophotometric method evaluates only cosmetic product that contains organic filters.

5. Recommendations

To a prepare a cream must be the availability of certain conditions, including a good emulsion, pure oil (free of impurities and odorless) and high speed mixer to obtain the best texture. One of the best shakers recommended is Silverson Mixer. It is also preferable to measure the viscosity of the cream produced using the viscometer.

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