Sunscreen Formulas with Multilayer Lamella Structure

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Key words

sunscreen, SPF water wash resistance, phosphate emulsifiers, multilayer lamella phase, emulsion rheology, structurally bounded water

Abstract

The multilayer lamellar structure in sunscreens containing phosphate emulsifiers plays key roles in the emulsion rheology and in enhancing deposition of sunscreen oil on skin surface, thereby improving the SPF water wash resistance.

A sunscreen formula's ability to protect the skin from UV damage depends on a wide variety of factors. These factors include chemical structures of UV filters, concentrations of active ingredients in the formula, and importantly, what concentration can be achieved on application to the skin and how much remains during the water wash process. The emulsifier(s) and fatty components in an applied sunscreen emulsion are the principal influences on the product's effectiveness.

In a previous study,[1] we concluded that a new phosphate emulsifier[a] improved the SPF water wash resistance of sunscreen formulations, and the structural characteristics of the emulsion were also very important. The INCI name of this ingredient is cetearyl alcohol (and) dicetyl phosphate (and) ceteth-10 phosphate. Figure 1 shows a drawing of the two phosphate esters.

In general, phosphate esters demonstrate the following chemical properties:

- The ionic phosphate group constitutes a powerful O/W emulsifying agent.
- The ionic phosphate group is shielded by the alkyl chains, hence the "crypto" in the term "cryptoanionic."
- Unlike carboxylic acid esters, the phosphate ester link is very stable at high and low pH.
- The emulsification characteristics of the ester depend on the degree of neutralization of the free-acid groups (ratio of free-acid/mono ester/di-ester).
- The lipophilic character is critically dependent upon the alkyl chain length, chain-length distribution, and number of EO (ethylene oxide) groups in the molecule.
- Fatty alcohols work well in combination with phosphate esters made from these alcohols.

In this article, we present our recent studies on sunscreen emulsions with and without the phosphate emulsifier. We observed the emulsion structure, and we measured emulsion rheology, the content of structurally bound water in the sunscreen formula, and the in vivo fluorescence intensity of the tested sunscreen emulsions applied on human skin before and after the water wash process.

Materials

We prepared sunscreen formulas that provided static SPFs of approximately 30 and approximately 15. In each case we made one version with the phosphate emulsifier and another version in which the phosphate emulsi-

[a] *Crodafos CES, Croda Inc., Edison, NJ USA*

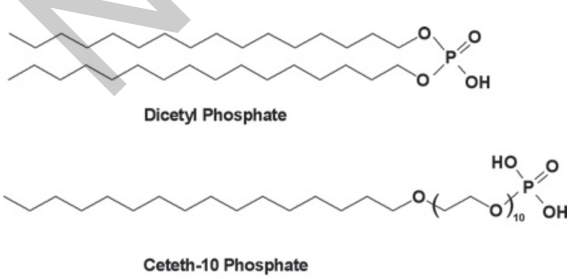

Figure 1. The phosphate esters in a new phosphate emulsifier

fier was replaced with an emulsifying wax. For the SPF 30 formula, we also made a version containing the phosphate emulsifier and 2.5% avocado oil unsaponifiables to enhance the skin moisturization. In this article we'll identify these five sunscreen formulas as follows:

- SPF30P = SPF 30, with 6.5% phosphate emulsifier;
- SPF30PA = SPF 30, with 6.5% phosphate emulsifier and 2.5% avocado oil unsaponifiables;
- SPF30W = SPF ~30, with 6.5% emulsifying wax NF;
- SPF15P = SPF 16, with 6.0% phosphate emulsifier;
- SPF15W = SPF 14, with 5.2% emulsifying wax NF.

The exact SPF of SPF30W was not determined. (It was made only to study the emulsion structure. Because its formula was similar to those of SPF15P and SPF15W, we believe that the SPF value should be approximately 30.) The complete formulations are given in Formulas 1 and 2, where the static SPF and the waterproof SPF (after 80 minutes of water immersion) are also given.

Formula 1. Waterproof SPF 30 sunscreens

	Weight %		
	SPF30PA	**SPF30P**	**SPF30W**
Cetearyl alcohol (and) dicetyl phosphate (and) ceteth-10 phosphate (Crodafos CES, Croda)	6.50	6.50	-
Emulsifying Wax NF (Polawax, Croda)	-	-	6.50
Benzophenone-3 (Rona)	5.00	5.00	5.00
Octyl methoxycinnamate (H&R Group)	7.50	7.50	7.50
Octyl salicylate (H&R Group)	5.00	5.00	5.00
Menthyl anthranilate (H&R Group)	5.00	5.00	5.00
Octyl stearate (Crodamol OS, Croda)	5.00	5.00	5.00
Avocado oil unsaponifiables (Crodarom Avocadin, Croda)	2.50	-	-
Sodium hydroxide, 10%	1.54	1.54	1.54
BHT	0.10	0.10	0.10
Carbomer (Carbopol 981, BFGoodrich)	0.13	0.13	0.13
Propylene glycol (and) diazolidinyl urea (and) methylparaben (and) propylparaben (Germaben II, ISP)	1.00	1.00	1.00
Water (aqua), deionized	60.73	63.23	63.23
Static SPF	**31.66**	**31.66**	N/D
Waterproof SPF	**30.31**	**30.31**	N/D

Formula 2. Waterproof SPF 15 sunscreens

	Weight %	
	SPF15P	**SPF15W**
Cetearyl alcohol (and) dicetyl phosphate (and) ceteth-10 phosphate (Crodafos CES, Croda)	6.00	-
Emulsifying Wax NF (Polawax, Croda)	-	5.20
Mineral oil	8.00	8.00
Ethylhexyl methoxycinnamate (Escalol 557, ISP)	7.50	7.50
Petrolatum	4.50	4.50
Steareth-10 (Volpo S-10, Croda)	1.00	1.00
Steareth-2 (Volpo S-2, Croda)	0.50	0.50
Cetyl alcohol (Crodacol C-70, Croda)	0.50	0.50
TEA, 99%	0.30	-
Propylene glycol (and) diazolidinyl urea (and) methylparaben (and) propylparaben (Germaben II, ISP)	1.00	1.00
Water (aqua), deionized	70.70	71.80
Static SPF	**16.20**	**14.3**
Waterproof SPF	**13.60**	**11.2**

Methods

Emulsion structure: The phase structure of emulsions depends on various factors, such as the emulsion type, concentrations of surfactants and other ingredients, the molecular structures of emulsifiers and the preparation process (shearing speed and temperature). Generally speaking, micelles exist in two-component systems and their shape can be spherical, lamellar, and multilayer lamellar (Figure 2).

At higher concentrations, surfactant or mixed surfactant solutions can form liquid crystals – lamellar and hexagonal phases. These liquid crystals can be observed using an optical microscope with crossed polarizers.[3-4] It is our interest to look at two unique multilayer lamellar phases: unilamellar and multilamellar phases.

Particles containing only one bilayer have been termed "unilamellar vesicles" (ULV), among which small unilamellar

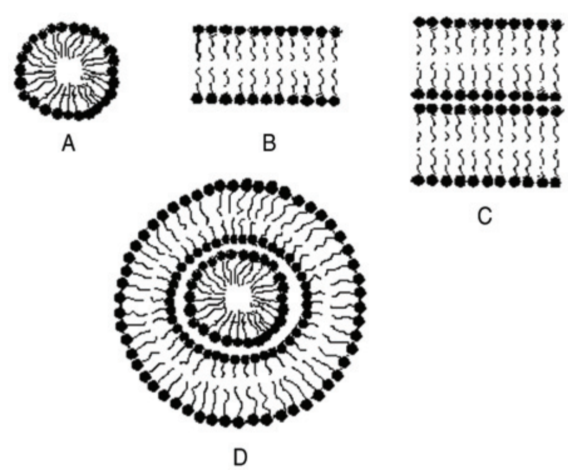

Figure 2. Schematic representations of emulsion particles
A = spherical micelle
B = lamellar micelle
C = multilayer lamellar micelle
D = multilayer lamellar vesicle

vesicles (SUV) and large unilamellar vesicles (LUV) can be differentiated. Particles containing two and more bilayers have been termed "multilayer lamellar vesicles" (MLV). The MLV have been widely used in pharmaceutical as well as in cosmetic applications as a delivery system for active ingredients. The major benefits obtained from a MLV delivery system are:[2]

- Improved dispersion of difficult-to-solubilize compounds;
- Microencapsulation in a vehicle that may enhance penetration into skin;
- Improved adhesion on the skin surface and sustained release;
- Reduced skin toxicity/irritation from the carrier/solubilizer system.

In our experiments, sunscreen emulsion samples were placed on glass slides with cover glasses on a thermal stage with a constant temperature of 25°C. The image of the emulsion was captured using a polarizing microscope[b] with crossed polarizers and later subjected to computerized image analysis[c].

Emulsion rheology: Rheology of an emulsion is of fundamental importance, because flow is always involved in both making and using emulsions. Rheological measurements provide very useful information about the effect of temperature on the viscosity of the emulsion, the influences of ingredients on the emulsion stability and shelf life, and the response of the finished products to different shear rates (i.e., dispensing and application to the skin). These are factors used by the consumer to create a perception of quality and value.

The correlation between shear rate, shear stress and viscosity of liquids can be expressed as the power law:[5]

$$\tau = KD^n \quad [1]$$

$$\eta = \tau/D = KD^{n-1} \quad [2]$$

where D is the shear rate (1/s), τ is the shear stress (Pascal), η is the calculated viscosity (mPa.s), K is the consistency index, and n is the flow index. K and n are characteristic constants of the material. Liquids with a value of n greater than 1 are shear thickening (viscosity increases with an increase in shear rate) while those with n less than 1 are shear thinning (viscosity decreases with an increase in shear rate). The smaller the n value, the quicker the viscosity decreases with increasing shear rate. When n = 1 and η = K, then η is the Newtonian viscosity, and the viscosity remains constant at various shear rates.

It has been reported[6,7] that the multilamellar vesicles can be formed from regular lamellar phase by shear-induced processes. Three main orientations have been described: At very low shear rate (below 1 s^{-1}) the lamellar layers are mainly parallel to the flow. At very high shear rates, the orientation of lamellae is similar. For intermediate shear rates, the lamellar phase organizes itself into multilamellar vesicles, which are close-packed and fill up space.

The rheological profiles of our sunscreen samples were determined using a rheometer[d] at constant temperature of 25°C. The data analysis was performed using computer software[e].

Determination of structurally bound water in an emulsion: Water, as the continuous phase, is a major component in an O/W emulsion. The water molecules in an emulsion are of two types: "structurally bound" and "free." The "structurally bound" water molecules are defined as chemically associated with other molecules in the emulsion. The "free" water molecules, in fact, are strongly bound themselves together through inter-molecule hydrogen bonding.

It has been reported[8] that differential scanning calorimetry (DSC) can be used to determine the temperature and the enthalpy of a phase transition (freezing/melting) of water during a heating or cooling process. In fact, water molecules contained in emulsions have relatively higher free energy than those in pure water. This means that structurally bound water molecules in emulsions need less activation energy to escape from the emulsion (evaporation), and therefore, they should have lower melting temperature and smaller enthalpy of fusion than those in pure water. The melting point is 0°C and the enthalpy of fusion of pure water is 333.6 Joule/gram,[9] which reflects the highest energy required to break the hydrogen bonding between associated water molecules.

When a portion of water molecules is bound to other molecules of ingredients in an emulsion, the determined enthalpy of fusion of water should be always smaller than the standard value. Increasing the amount of bound water will mean fewer free water molecules and a lower melting/freezing enthalpy

[b] *Nikon Optiphot-Pol Polarizing Microscope, Nippon Kogaku KK, Tokyo, Japan*
[c] *Image-Pro Plus 4.5 image analysis software, Media Cybernetics, Silver Spring, MD USA*

[d] *DV-III Rheometer, from Brookfield Engineering Lab, Inc., Middleboro, MA USA*
[e] *Rheocalc 2.3, from Brookfield Engineering Lab, Inc., Middleboro, MA USA*

value. Therefore, it is possible to use the determined value of freezing enthalpy of water in an emulsion to calculate the percent of bound water (PBW) and free water (PFW) in the emulsion:

$$PBW\ (\%) = [1-(H_1/H_0)] \times 100\% \quad [3]$$

$$FBW\ (\%) = (H_1/H_0) \times 100\% \quad [4]$$

where H_0 is the standard water freezing enthalpy, 333.6 Joule/gram, and H_1 is the determined freezing enthalpy of water in the emulsion sample (Joule/gram). The calculated PBW/FBW value can be used to estimate the emulsion stability. The higher the content of structurally bound water, the more stable the emulsion.

In this paper, the PBW of our emulsion sample was determined instrumentally[f]. About 2 mg of emulsion sample was placed in a hermetic pan and cooled to -20°C. The sample then was heated at 2°C/min of heating to 25°C and the melting point and the enthalpy of fusion of water were calculated.

Quantitative assessment of sunscreen application by in vivo fluorescence spectroscopy: A group of scientists from the UK has conducted extended studies on evaluation of sunscreen performance using fluorescence spectroscopy.[10-13] They have found that the feasibility of using fluorescence spectroscopy for in vivo quantitative assessments of sunscreen substantivity depends on selecting a suitable fluorescent agent, which should be nontoxic, mix readily with sunscreens and be excited in the UV/visible region of the spectrum. They have observed that the fluorescence from Neutrogena Sunblock was sufficiently intense for use as a tool for in vivo measurements of substantivity. This product achieves SPF 15. Its active ingredients are octyl - methoxycinnamate, octyl salicylate and menthyl anthranilate.

Based upon the same technique, we determined the fluorescence intensity of our test SPF 30 sunscreens (SPF30P,

[f] DSC (differential scanning calorimeter) Q-100, TA Instruments, New Castle, DE USA

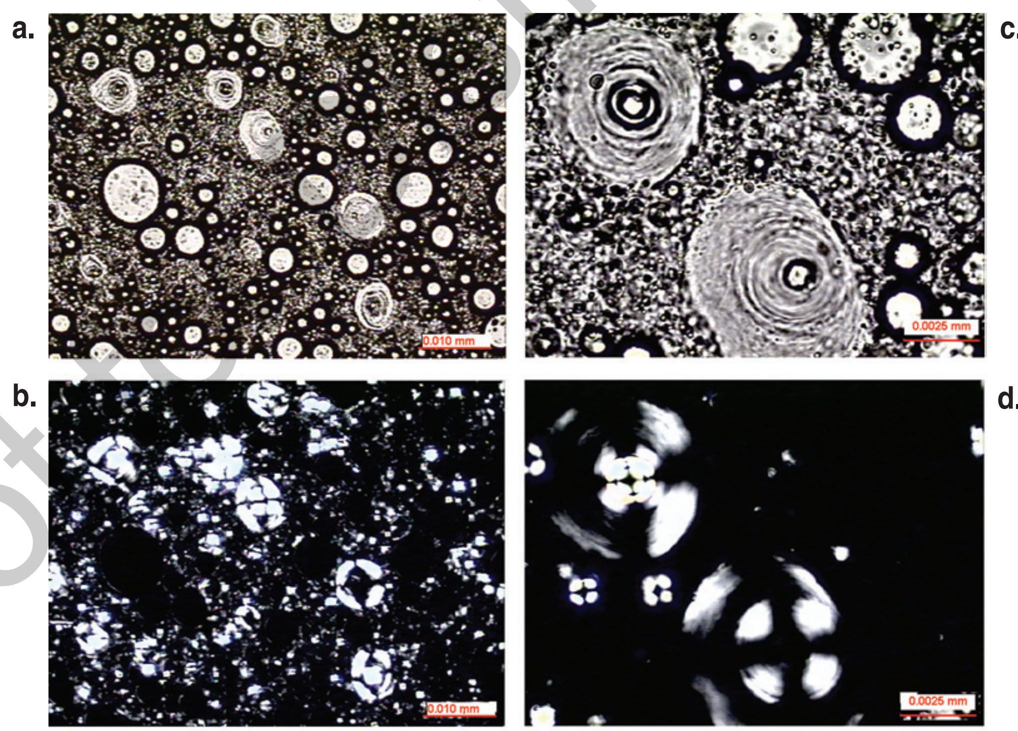

Figure 3. Micrographs of phosphate-emulsified SPF 30 sunscreen formula (SPF30PA) with avocado oil unsaponifiables
a = X100, no polarizer
b = X100, under crossed polarizer
c = X400, no polarizer
d = X400, under crossed polarizer

SPF30PA and SPF30W) and found that the intensities were strong enough for in vivo measurements. The fluorescence intensity of sunscreen on human skin was calibrated and determined using a spectrofluorometer[g] coupled to a bifurcated optical fiber cable. Radiation from the exit slit of the excitation monochromator was conducted via quartz optical fiber to the skin. The optical fiber collected the fluorescent radiation from the skin and conducted this to the entrance slit of the emission monochromator. The signals were processed and the data displayed using appropriate software[h].

For the water wash test of sunscreen formulas, the main experimental procedures include:

1. Finding the optimum excitation and emission monochromators and respective bandwidths for the applied sunscreen formula on the skin surface.
2. Establishing the calibration curve, which is the relationship between sunscreen density and fluorescence intensity for the applied sunscreen.
3. Applying a certain amount of sunscreen on the determined skin area and allowing it to dry for 30 minutes.
4. Water wash step: set the running tap water at 30°C with a flow rate of 2.5 liter per minute; water wash time: 30 seconds; dry the skin for 15 minutes. Repeat the washing and drying steps for two more cycles.
5. Determining the fluorescence intensity after the water wash step and calculating the remained sunscreen density on the skin.
6. Comparing the original sunscreen density to the remained density after water wash and calculating the remained sunscreen percentage.

[g] *Fluorolog-3 spectrofluorometer, ISA Instruments SA, Inc, Edison, NJ USA*
[h] *DataMax software from ISA Instruments SA Inc, Edison, NJ USA*

Results on Emulsion Structure

Micrographs of sunscreen formulation SPF30PA (with the phosphate emulsifier and avocado oil unsaponifiables) are presented in Figure 3. From Figures 3a and 3c (no polarizer; x100 and x400, respectively) it is clearly observed that SPF30PA contains particles having multilayer structure. Figures 3b and 3d (cross polarizer; x100 and x400, respectively) show typical patterns of liquid crystals of these particles and clearly demonstrate the multilayer lamellar phase in the formula. The observed sizes of large multilayer lamellar droplets are in the range 0.5-5.0 µm

Sunscreen formula SPF30P (with the phosphate emulsifier) showed the same patterns of micrographs as SPF30PA and was similarly composed of multilayer lamellar vesicles.

A micrograph of the corresponding formula SPF30W (using Emulsifying Wax NF as the emulsifier) is presented in Figure 4. It can be seen that the sizes of droplets in the formula are smaller and more uniform, but no liquid crystal was observed under crossed polarizers.

A similar difference in the emulsion structure was observed for the SPF15 sunscreen formulas: SPF15P showed multilamellar vesicles and SPF15W did not.

These experimental results strongly indicate that the phosphate emulsifier plays a key role in the formation of the multilayer lamella liquid crystals of the formula. In fact, phospholipids have been widely used to form multilayer lamellar vesicles in both pharmaceutical and cosmetic applications (see sidebar).

Results on Emulsion Rheology

Change in viscosity with shear rate: Plots of viscosity versus shear rate of sunscreen formulas SPF30P and SPF30W are presented in Figure 6. It can be seen that these two formulas demonstrated similar rheological characteristics but with different parameters:

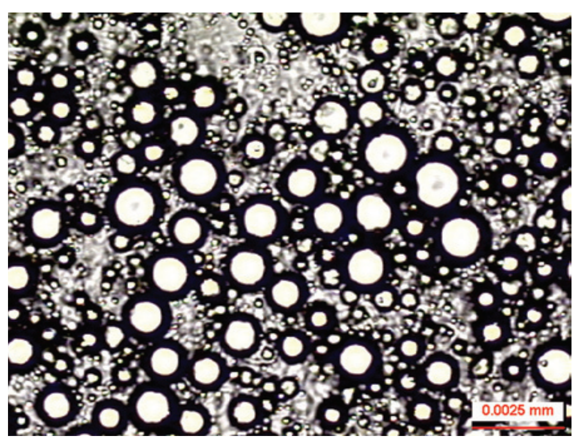

Figure 4. Micrograph of wax-emulsified SPF 30 sunscreen formula (SPF30W) at X400, no polarizer

Effect of Emulsifier Molecular Structure on Emulsion Structure

It is interesting to study the effect of modification in molecular structure of a phosphate emulsifier on the emulsion structure of sunscreen formulas. A sprayable sunscreen lotion (Formula 3) with a phosphate emulsifier has been developed. The lotion has low viscosity and the micrograph of the emulsion is presented in Figure 5.

It can be seen that the average droplet size is small and the density of the droplets is low in the lotion. The low viscosity of the formula can be attributed to the increased number of ethylene oxide groups in the molecule. The larger the EO group number in the molecule, the more flexible the molecular configuration, and the more difficult the formation of lamellar structure.

Formula 3. Sprayable sunscreen lotion

Cetearyl alcohol (and) dicetyl phosphate (and) ceteth-20 phosphate (Crodafos CS 20 Acid, Croda)	4.00% wt
Xanthan gum	0.20
Glycerin	5.00
TEA 98%	0.10
C12-C15 Alkyl benzoate	3.00
Di-PPG-3 Myreth-10 adipate	5.00
Ethylhexyl methoxycinnamate (Octinoate, ISP)	7.50
Ethylhexyl salicylate (Octisalate, H&R Group)	5.00
Benzophenone-3 (Oxybenzone, H&R Group)	5.00
Propylene glycol (and) diazolidinyl urea (and) methylparaben (and) propylparaben (Germaben II, ISP)	1.00
Water (aqua), deionized	64.20
Static SPF	**16.35**
Waterproof SPF	13.25

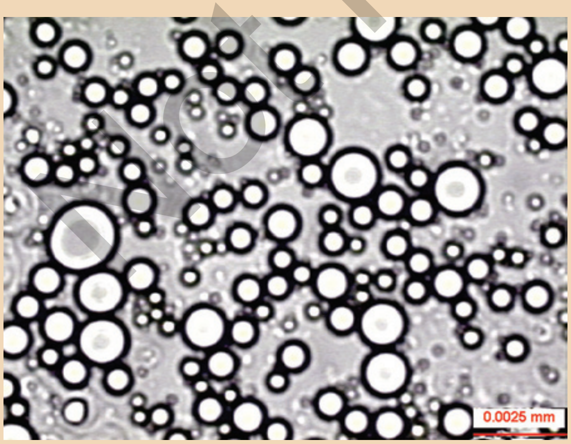

Figure 5. Micrograph of phosphate-emulsified SPF 15 sprayable sunscreen lotion (Formula 3) at X400, no polarizer

- Both formulas were viscoplastic materials and demonstrated thixotropic behavior; their viscosity decreased with an increase in shear rate.
- The phosphate-emulsified formula showed more pronounced thixotropic characteristics: it had higher initial viscosity at low shear rate and lower viscosity at high shear rates, compared to the wax-emulsified formula.

The differences in their rheological profiles can be attributed to their different emulsion structures. Indeed, viscosity is a measure of the hydrodynamic radius of particles of liquid under shear stress. The larger the average hydrodynamic radius, the higher the liquid viscosity will be. As mentioned earlier, SPF30P contains multilamellar vesicles with larger average size compared to SPF30W. It is not surprising that SPF30P should have higher initial viscosity at the low shear rate. On the other hand, the shear-thinning rate is related to the deformation of the emulsion structure under the high shear rate. The faster the change in emulsion structure, the higher the shear-thinning rate should be. Since SPF30W does not have multilayer lamellar structure, the change in emulsion structure for SPF30W at high shear rate can be expected to be much less than the change for SPF30P at a similar shear rate. Therefore, the viscosity for SPF30W should be less affected by an increase in the shear rate.

Power Law and flow index: According to the Power Law,

$$\tau = KD^n \qquad [1]$$

$$\log \tau = \log K + n \log D \qquad [5]$$

where K, again, is the consistency index and D is the shear rate. Plots of logarithm of shear stress (log τ) versus logarithm of shear rate (log K) for the SPF30P and SPF30W sunscreen formulas are shown in Figure 7.

It can be seen that the rheological profiles of the two samples fit the Power Law very well. The flow index (n) is 0.2413 and 0.3745 for sunscreen formulas SPF30P and SPF30W, respectively. This result indicates that the sunscreen formulation containing phosphate emulsifier showed faster decreasing rate (smaller n) in viscosity with an increase in shear rate than the corresponding wax-emulsified formulation. This is consistent with our predictions based upon the differences in their emulsion structure.

In practical applications, when applying the sunscreen product to skin, we always apply the shear stress to the product in order to evenly distribute the product on the skin. The less viscous after the applied shear stress the sunscreen product becomes, the easier it should be to flow and form a uniform layer of product on the skin. Therefore, it is expected that the phosphate-emulsified formula should generate a more uniform layer when applied on the skin.

Results on Structurally Bound Water

Differential scanning calorimetry melting curves of SPF30P and SPF30W emulsions are presented in Figure 8.

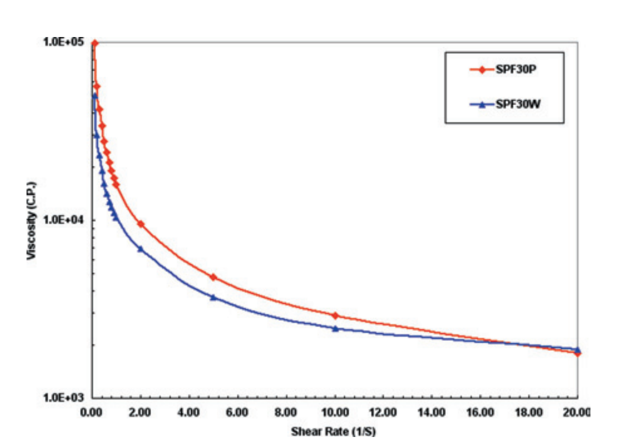

Figure 6. Change in viscosity with shear rate of phosphate-emulsified and wax-emulsified SPF 30 sunscreen formulas (SPF30P and SPF30W, respectively)

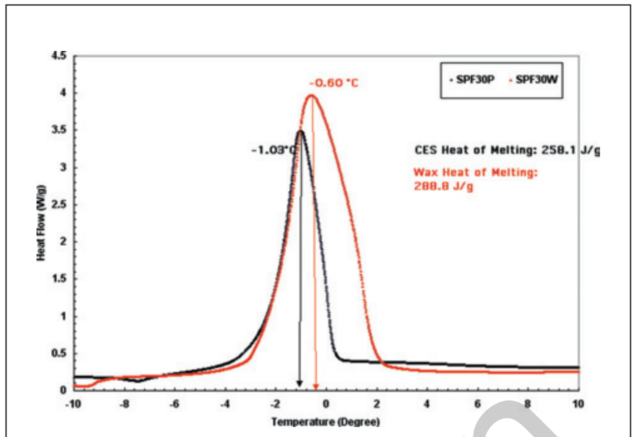

Figure 8. DSC curves of phosphate-emulsified and wax-emulsified SPF 30 sunscreen formulas (SPF30P and SPF30W, respectively)

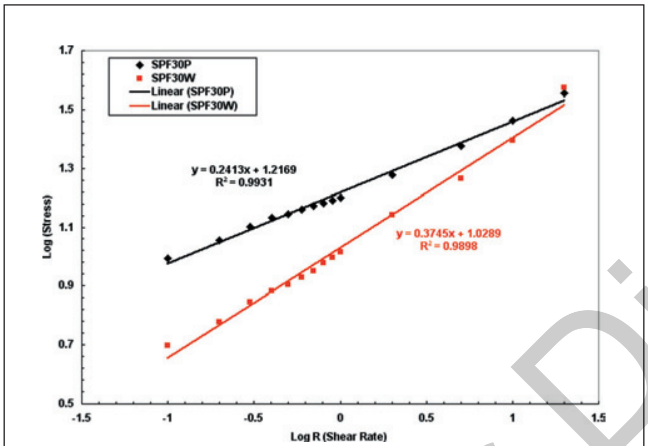

Figure 7. Power law and flow indexes of phosphate-emulsified and wax-emulsified SPF 30 sunscreen formulas (SPF30P and SPF30W, respectively)

It is observed that the phosphate-emulsified sunscreen formula showed lower melting point and smaller enthalpy of fusion of water compared to the corresponding wax-emulsified formula. The measurements suggest that the SPF30P emulsion contains more structurally bound water than the SPF30W does.

This experimental result correlates well with our observations of the multilamellar structure existing in the SPF30P sunscreen formula. Using equations [3] and [4], we are able to calculate the percent of structurally bound water in the two emulsions.

PBW (phosphate) = (1 – 258.1/333.6) × 100% = 22.6%

PBW (wax) = (1 – 288.8/333.6) × 100% = 13.4%

The calculated percentages of free water in the emulsion are 77.4% and 86.6%, respectively, for SPF30P and SPF30W sunscreen emulsions. In our previous study,[1] we reported the different water evaporation rates for phosphate and nonionic systems. The phosphate system showed higher water evaporation rate than the nonionic system. This result can be explained by the different content of structurally bound water in the two emulsion samples. The phosphate emulsion contains more structurally bound water and the structurally bound water molecules are in higher free energy state compared to those in the nonionic emulsion system. Therefore, these water molecules need less energy to evaporate from the emulsion and their water evaporation rate is greater than that for nonionic emulsion system.

Results on Water Wash Resistance

We determined the responses of fluorescence intensity versus the sunscreen concentration on the skin of three female panelists; the obtained calibration curves were very similar. A calibration curve of fluorescence intensity versus applied sunscreen concentration on skin is presented in Figure 9. We applied a known amount of sunscreen on the skin. After washing the skin with water, we measured the fluorescence intensity of sunscreen on the skin surface, and then used this calibration curve to obtain the concentration of sunscreen on the washed skin. From that we calculated the remained percent of the applied sunscreen on the skin surface.

Plots of the remaining percent of sunscreen concentration on skin after water washing for formulations SPF30P and SPF30W are shown in Figure 10. It can be seen that the phosphate-emulsified formula demonstrated better water wash resistance than the corresponding wax-emulsified formula.

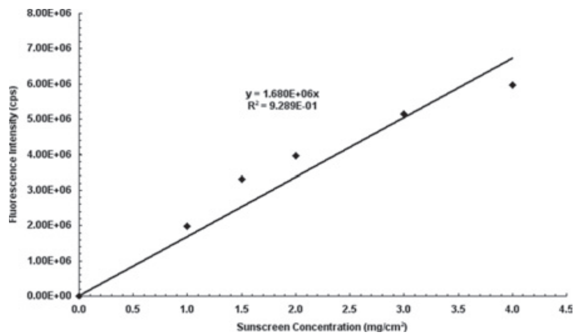

Figure 9. Response of fluorescence intensity vs. sunscreen concentration on skin

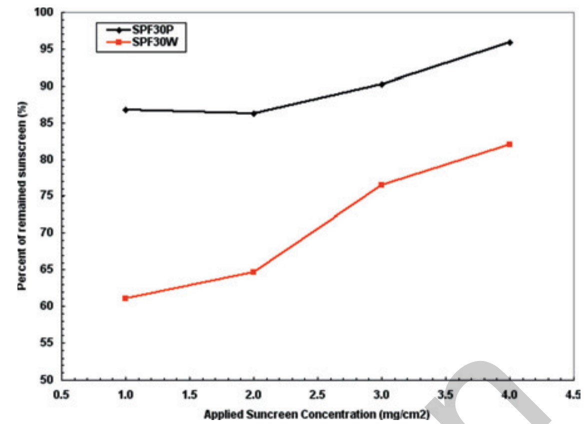

Figure 10. Water wash resistance of phosphate-emulsified and wax-emulsified SPF 30 sunscreen formulas (SPF30P and SPF30W, respectively)

These experimental results are consistent with SPF water wash resistance measurements obtained from panelist testing conducted by AMA Laboratories.[14] The results also strongly indicate the correlation between sunscreen water wash resistance and the emulsion structure.

As we mentioned before, the multilayer lamellar vesicles are very good delivery systems for active ingredients: they improve the dispersion of difficult-to-solubilize compounds, such as sunscreen oil and the adhesion on the skin surface and sustained release of the active ingredients. As a result of these improvements, the phosphate-emulsified

SPF30P sunscreen formulation exhibited better water wash performance than the corresponding wax-emulsified formulation.

Conclusions

The phosphate-emulsified sunscreen emulsions formed multilayer lamella structure with large particle size, while the corresponding wax-emulsified emulsions demonstrated small particle size without multilayer lamella structure.

The phosphate-emulsified sunscreen emulsions had a higher amount of structurally bound water and exhibited a higher viscosity shear-thinning rate compared to the corresponding wax-emulsified emulsions.

The phosphate-emulsified sunscreen emulsions left a higher amount of sunscreen concentration on the skin surface where they were applied and demonstrated better water wash resistance compared to the corresponding wax-emulsified emulsions. This was attributed to the multilayer lamella structure in the formula.

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