Formulation Enhancement Through The Use of Gelled Emollients

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Synopsis:

A look at common cosmetic formulation problems (rheology, stability, suspending ability) and various formulation solutions.

Introduction

While the term 'emollients' is difficult to define[1], it is clear that this word refers to various skin care ingredients which are used to modify the feel of a finished consumer product. In general, emollients impart a desirable skinfeel during both application and rub-in, as well as after application. The emollients described in this article are commonly used skin care ingredients which meet this description, such as oils and esters.

Many years ago, cosmetic products used for improving skinfeel ('emolliency') were generally anhydrous (such as petroleum jelly) or water-in-oil (w/o) emulsions (often based on a beeswax-borax emulsifying system). Given this limited scope of products, the everyday formulation problems encountered by cosmetic scientists were not very extensive.

Today, knowledge in the field of cosmetic science has increased dramatically, and formulations once thought impossible are now easily prepared. This is due to the proliferation of new and unique ingredients, as well as an overall better understanding of product formulation. Besides baby oil and petroleum jelly, anhydrous systems now include silicone-based lotions and facial treatment products, as well as silicone-oil emulsions. The typical skin care emulsion is now more likely to be oil-in-water (o/w) than w/o. Technology has advanced to the point where water-in-oil emulsions can be prepared at room temperature, multiple emulsions and microemulsions are possible, and stable, surfactant-free skin care emulsions can be made.

As different product forms emerge in cosmetics and toiletries, new formulation issues also arise. This article will focus on several formulation problems which can occur with todays products, and how gelled emollients can minimize or eliminate these problems.

Problem: Low Viscosity

Penreco has developed a series of gelled emollients under the Versagel™ trade name. these products include *transparent* gels based on virtually any nonpolar oil: mineral oil, synthetic hydrocarbons (such as hydrogenated polyisobutene and isohexadecane), esters (e.g., isopropyl palmitate), and vegetable oils (jojoba oil). The patented technology behind the gelling process allows us to provide an essentially unlimited range of viscosities for each of these products. Thus depending on the concentrations of other ingredients added to a cosmetic formulation, the ultimate desired viscosity can be obtained.

Anhydrous Products

Two common anhydrous skin care products are baby oil and suntan oil. Each of these products is typically based on light mineral oil and is designed to add certain emollient properties to the skin when used, such as lubrication and moisturization. However, the product's form (thin liquid) can create some disadvantages when applied to the skin. The oil can easily spill or spread too far over the skin, dripping onto clothes, towels, diapers, and the floor. A simple solution to this problem is to increase the viscosity of the product without diluting its light feel. The oil would then stay where it is applied.

Adding petrolatum or waxes to the oil would not be feasible methods for thickening these specific products, since the oil's light feel would be lost, and the products would no longer be transparent. However, by incorporating a Versagel product, the viscosity problem is solved.

Benefits from using the Versagel material in this instance include the following:

- Product viscosity is increased.
- The light feel of the product is retained.
- The product remains transparent.

Examples of baby oil gel and suntan oil gel formulations are shown in Tables 1 and 2. In each case, esters have been added to give an even lighter, less oily feel to the products.

In addition to solving problems with current products, gelled emollients have enabled formulators to develop new products which otherwise would be very difficult to create. One example of this is a squeezable clear gel lip gloss.

While high viscosity polyisobutenes can be used to formulate clear gel lip glosses, the finished product may have a poor feel due to the tackiness of these ingredients. Adding an ester or other material to reduce tack may also lower the product's viscosity unacceptably.

Table 1. Baby Oil Gel

INGREDIENT	WEIGHT %
A. Mineral Oil (and) Ethylene/Propylene/Styrene Copolymer	
(and) Butylene/Ethylene/Styrene Copolymer*	74.60
Isopropyl Isostearate	13.00
Propylene Glycol Isoceteth-3 Acetate	10.00
B. Isopropyl Isostearate	2.00
Propylparaben	0.10
C. Fragrance	0.30
	100.00%

*Versagel™ M750

PROCEDURE: Mix part A ingredients at 70°C until uniform. Heat part B to 60°C until clear. Add premixed part B to part A and mix at 70°C. When uniform, let cool to 45°C and add part C. Mix well.

Table 2. Suntan Oil Gel

INGREDIENT	WEIGHT %
A. Mineral Oil (and) Ethylene/Propylene/Styrene Copolymer	
(and) Butylene/Ethylene/Styrene Copolymer*	73.80
Octyldodecyl Neopentanoate	14.00
Tocopheryl Acetate	0.50
Fragrance	0.10
B. Octyl Methoxycinnamate	7.50
Benzophenone-3	2.00
Octyl Salicylate	2.00
Propylparaben	0.10
	100.00%

*Versagel™ M750

PROCEDURE: Mix a at 60°C until homogeneous. Heat B to 60°C until clear. Add B to A with moderate mixing at 60°C until unifom. Cool to room temperature.

Table 3. Clear Gel lip Gloss

INGREDIENT	WEIGHT %
Hydrogenated Polyisobutene (and) Ethylene/Propylene/ Styrene Copolymer (and) Butylene/Ethylene/Styrene Copolymer*	81.50
Octyl Palmitate	10.00
Tridecyl Neopentanoate	5.00
Isostearyl Isotearate	3.00
Isopropylparaben (and) Isobutyparaben (and) Butylparaben	0.50
	100.00%

*Versagel™ ME750

PRODCEDURE: Mix all ingredients and heat slowly to 70-75°C with stirring until the mxture is uniform. Cool to 45°C and add flavour and colour if desired, then fill containers.

Since gelled emollients can be created from esters and oils with minimal stickiness, clear lip glosses with improved feel can be easily created. A mineral oil free clear gel lip gloss formula is shown in Table 3.

Emulsions

Due to their more frequent use, discussions in this article involving emulsions will refer to macroemulsions (typically white, opaque products with particle sizes in the range of 0.1-50+ microns) rather than microemulsions, which have particle sizes around 0.01-0.08 microns[2].

Skin care emulsions which are considered 'lotions' are generally pourable at room temperature[3]. Thus, increasing the viscosity of a cosmetic emulsion can allow one to formulate a cream rather than a lotion. In general, stable creams are easier to formulate, since the product's viscosity helps prevent phase separation over time[4]. A common and very efficient way to increase the viscosity of an o/w emulsion is to thicken the external or continuous phase (water). This can be done by adding gums or cellulose derivatives, as well as with synthetic water-swellable/water-soluble polymers. Increasing the viscosity of the internal phase is almost never done, because

1. it is usually not as efficient as thickening the external phase,
2. it often changes the feel of the product (since the water evaporates over time and the internal oil phase is what is left on the skin), and
3. there are few methods to do this apart from adding waxes and clays to the oil phase.

We have found that by using gelled emollients, the viscosity of an emulsion can be increased, even when the emollient is an internal phase ingredient. The flexibility afforded by gelled emollients allows the scientist to create a thickener around one specific ingredient, rather than being limited to one type of generalized thickener. Ease of formulation is another benefit, since the thickener is already 'pre-blended' with one of the emollients; extra ingredients are not required.

Table 4 shows the formulas for two brushless shave creams. In both formulas, it should be noted that the emollient (mineral oil or Versagel M1600, a gelled mineral oil) is present at only 3 wt%. Brookfield viscosity studies have indicated that the formula which contains the gelled mineral oil rather than mineral oil has a viscosity which is measurably higher (Figure 1).

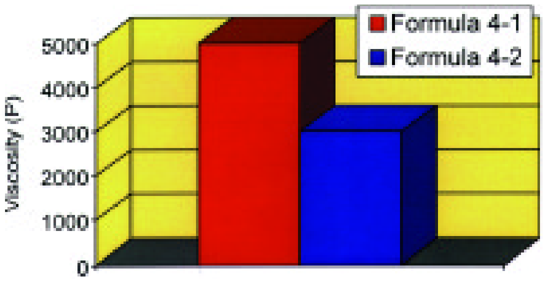

Figure1. Brushless Shave Cream Viscosities

These results are quite surprising, given the small percentage of gelled emollient which is used. In addition, Formula 4-1 had a clearly different feel, being a dense, rich cream, while Formula 4-2 was smooth but much lighter-feeling.

Table 4. Brushless Shave Gel

INGREDIENT	WEIGHT %	
	Formula 4-1	Formula 4-2
A. Deionized Water	76.50	76.50
Glycerin	2.00	2.00
Triethanolamine, 99%	1.50	1.50
B. Stearic Acid	12.50	12.50
Propylene Glycol Stearate	3.50	3.50
Mineral Oil (and) Ethylene/Popylene?Styrene Copolymer (and) Butylene/Ethylene/Styrene Copolymer*	3.00	--
Mineral Oil	--	3.00
C. Propylene Glycol (and) Diazolidinyl Urea (and) Methylparaben (and) Propylbaraben	1.00	1.00
	100.00%	100.00%

*Versagel™ M1600

Table 5. Makeup Foundation

INGREDIENT	WEIGHT %	
	Formula 5-1	Formula 5-2
A. Deionozed Water	46.50	46.50
Magnesium Aluminium Silicate	0.80	0.80
Xanthan gum	0.30	0.30
Nylon-12	1.20	1.20
Sodium PCA	1.00	1.00
B. Deionozed Water	10.00	10.00
Propylene Glycol	7.00	7.00
Red Iron Oxides (and) Talc	0.40	0.40
Yellow Iron Oxides	0.86	0.86
Talc	1.14	1.14
Black Iron Oxides (and) Talc	0.15	0.15
Titanium Dioxide	5.60	5.60
C. Glyceryl stearate	2.00	2.00
Stearic Acid	2.00	2.00
DEA-Cetyl Phosphate	2.00	2.00
Methylparaben (and) Butylparaben (and) Ethylparaben (and) Propylparaben	0.25	0.25
Isotearyl Neopentanoate	3.00	3.00
Isopropyl Palmitate (and) Ethylene/Propylene/Styrene Copolymer (and) Butylene/Ethylene/Styrene Copolymer*	15.00	--
Isopropyl Palmitate	--	15.00
Phenoxyethanol	0.70	0.70
Tocopheryl Acetate	0.10	0.10
	100.00%	100.00%

*Versagel™ MP750

In certain cosmetic products, increased product thickness is desired to improve coverage of the product on skin during application. For pigmented makeups, good coverage is essential for a product to be successful. Makeup foundations have been prepared using both gelled and ungelled isopropyl palmitate, as shown in Table 5. Once again, the formula containing the gelled emollient has a higher Brookfield viscosity than the one with the ungelled material (Figure 2).

of limited stability can be improved by the addition of gelled emollients, possibly to the point of becoming an acceptable product which passes required stability tests.

It is expected that this increased product stability will be seen with other gel-containing emulsions, such as those which contains solids (e.g., titanium dioxide, zinc oxide, iron oxides). Observing an improved emulsion stability from gelled emollients would not be surprising, given the viscosity increase of emulsions which utilize these ingredients.

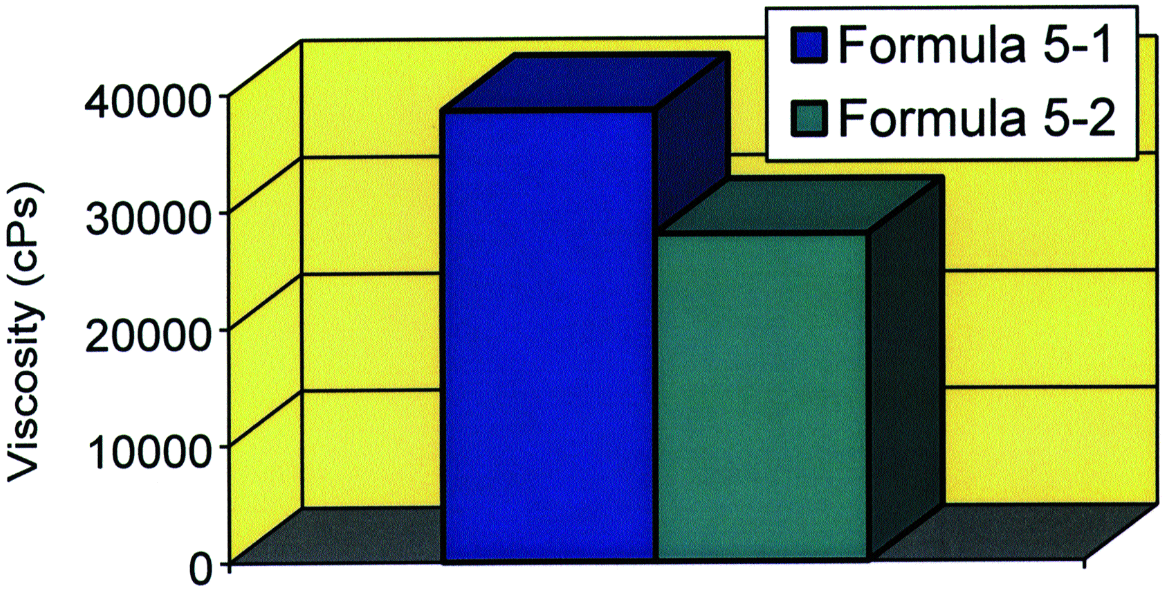

Figure 2. Makeup Foundation Viscosities

Problem: Product Instability

Product stability issues usually involve the breakdown of emulsion compositions. Schueller and Romanowski list four mechanisms of emulsion destabilization[5], each of which eventually leads to separation of the oil and water phases. Increasing the viscosity of the external phase will naturally increase product stability by reducing the likelihood of phase separation (e.g., due to coalescence)[4,6].

Just as a gelled emollient will increase an emulsion's viscosity from either the internal or external phase, it will increase product stability from either phase. Table 6 lists formulas for two high oil-phase emulsion, using hydrogenated polyisobutene in both gelled and ungelled forms. Interestingly, while Formula 6-1 was a nice white cream, Formula 6-2 would not even form an emulsion. Thus, emulsions

Problem: Poor Suspending Ability

Many types of cosmetics and toiletries contain insoluble solid materials. Such products include antiperspirants, pigmented cosmetics, and certain kinds of sunblocks. Any settling of the solid material, either during manufacture or (especially) in the hands of the consumer, can drastically affect the acceptance and performance of the cosmetic product. We have found that by using gelled emollients, the suspending ability of solid-containing cosmetics is greatly enhanced.

Tests with Versagel M200, a low viscosity, pourable mineral oil gel, have shown that this material can easily suspend 50 wt% of surface-treated zinc oxide. When the zinc oxide is blended into ungelled oil, it quickly settles to the bottom of the container.

However, a dramatic illustration of how well this gelled emollient suspends solid zinc oxide is seen when the material is tested under various temperature conditions.

In this experiment, three samples of Versagel M200 containing 50 wt% zinc oxide were analyzed by X-ray fluorescence. Test samples were removed from the top, middle, and bottom of each product and analyzed. When the zinc oxide is suspended evenly, X-ray analysis shows that the concentration of Zn in each layer is 50%. If any zinc oxide were to settle, the top layer would likely contain less zinc, while the bottom should contain more than 50% zinc.

One sample was left at room temperature, the second sample was heated in a 52°C oven for 4 months, and the third underwent one 24-hour free/thaw cycle (-20°C to 25°C).

None of the three samples showed any settling of the zinc oxide, thus attesting to this gel's unique ability to suspend very high loads of solids under extreme conditions[7]. Emulsions which contain suspended zinc oxide or other solids in combination with gelled emollients also would be expected to exhibit enhanced stability.

Product Performance – Moisturization

It is clear that gelled emollients provide increased viscosity both in anhydrous systems and in emulsions. They help stabilize emulsions and also increase the suspending ability of products which contain fine solid particles. An added benefit from the gelled emollients which has not been described is improved moisturization of the skin. Clinical studies have shown that when gelled mineral oil (Versagel M750) was compared to the ungelled oil, reduction in transepidermal water loss was 53% greater for the gelled oil than the ungelled oil[8]. Thus, using a gelled oil on skin dramatically increases its moisture content.

Conclusion

The rapid pace of technological advancements in all areas of science is changing the way we live, and the field of cosmetic science is no different.

New types of cosmetic products are constantly being developed, and new raw materials are adding to the cosmetic chemist's selection of personal care ingredients. The Versagel line of gelled emollients is one type of new raw material which can enhance current cosmetic product formulations, and also assist in the development of new cosmetics and toiletries. These ingredients are indeed multifunctional, in that they provide solutions to several formulation problems, while also adding unique benefits. In the 21st century, we will surely see even more raw materials playing multiple roles in cosmetic formulation.

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Gina Butuc was born in Romania and immigrated to the United States in 1997. She received her B.S. in Chemistry from The University of Bucharest/Romania and her M.S. in Organic Chemistry from the same university. Currently, she is a Senior Chemist at Penreco's Technology Center in The Woodlands, Texas.