Gelled Emollient Systems for Controlled Fragrance Release and Enhanced Product Performance

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Traditionally, emollients for cosmetic applications are used in their original form, either as a liquid such as mineral oil and isopropyl palmitate or a solid such as lanolin.

Thickened emollients are typically obtained through producing an emulsion or a microemulsion. Attempts to achieve a clear thickened anhydrous gel are normally done by using fumed silica or metal stearates. The shortcomings for these methodologies are that the emulsions must involve a water phase, and anhydrous gels based on silica or metal stearates often exhibit haziness and syneresis.

Penreco has patented a technology[1] that uses block copolymers to create clear, thermally reversible anhydrous gels for health and beauty aid applications. Clinical studies confirm that these polymeric gels[a] not only achieve good aesthetics, but also provide additional moisturizing, suspending, film-forming, controlled fragrance release and wash-off resistance benefits to the finished products in which they are used. This article discusses the ability of these gelled emollient systems to control fragrance release and to enhance the performance of skin-care products.

Block Copolymer Blends

Homopolymers and block copolymers have long been used as gelling agents for cosmetic oil systems. Polyethylene wax, for instance, has been one of the most popular gellants used in cosmetic and pharmaceutical applications.[2] Some disadvantages of polyethylene wax are difficulties in controlling the manufacturing process and syneresis problems in the finished products. In addition, gels made from polyethylene wax are not thermally reversible, which in turn can limit the options for cosmetic formulators.

Block copolymer blends dissolved in white mineral oil or similar non-polar materials (such as synthetic hydrocarbons or fatty esters) can produce heterophase, thermally reversible, crystal-clear gels that possess many desirable properties for the cosmetics and pharmaceutical industries.

The copolymers used as gellants are combinations of ethylene/propylene/styrene and butylene/ethylene/styrene copolymers. The mechanism of the gelling process is rather simple: the ethylene/propylene and butylene/ethylene elastic segments of these thermoplastic copolymers dissolve in the hydrocarbon or other non-polar base, while the styrene portions remain intact. The insoluble styrene blocks naturally gravitate toward each other and become the building blocks (domains) for a submicroscopic 3-D polymer network with molecules of enclosed oil. Figure 1 illustrates the state of a hydrocarbon gel with a mixture of diblock and triblock polymers on a molecular scale.[1]

The viscosity of the polymeric gel can be controlled via the degree of physical crosslinking of the insoluble domains.

Key words

gelled emollients, block copolymers, fragrance, controlled fragrance release, moisturization, suspensions

Abstract

Block copolymer blends dissolved in white mineral oil or similar non-polar materials can produce heterophase, thermally reversible, crystal-clear gels that possess many desirable properties for the cosmetic and pharmaceutical industries.

[a] *Offered under the Versagel brand. Versagel is a trademark of Penreco, Houston, Texas, USA.*

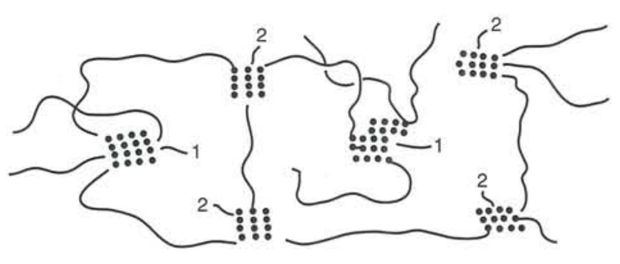


Figure 1. Hydrocarbon gel with a mixture of triblock (1) and diblock (2) polymers

The more triblock polymer in the gel, the higher the degree of crosslinking, which results in a higher viscosity for the gel. By properly balancing the ratio between triblock and diblock, one can achieve a stable gel with desirable rheological properties. Failure to achieve the proper balance between two types of polymers can often result in gels that are either too "limp" or too "rubbery." Syneresis over time also indicates the gel formula is not optimized.

The viscosity of the non-polar base has minimal impact on the viscosity of the finished gel. However, the length of the hydrocarbon chain does influence the *elasticity* of the finished gel. For instance, a mineral oil (70 SUS viscosity) may produce a nice, clear but stringy gel, while gelled isododecane has very little stringiness and can almost be scooped up from a container.

The nature of the thermoplastic block copolymers requires that preferred intermediates for gelling be non-polar hydrocarbons or fatty esters with limited carbonyl groups and relatively long mostly saturated "tails." Common esters used in cosmetic and toiletry products that fit this description and have been proven to be compatible with these block copolymers include isopropyl palmitate, C_{12-15} alkyl benzoate, ethylhexyl methoxycinnamate and other related structures.

Most natural oils and vegetable oils are composed of fatty acids and triglycerides. However, there are exceptions, such as *Simmondsia chinensis* (jojoba) seed oil. This oil is a complex mixture of long chain, unbranched esters ranging from 34 to 48 carbon atoms. The esters have little unsaturation and are very resistant to oxidation, making jojoba oil a perfect candidate for gelling with the block copolymers mentioned earlier.[3]

Table 1. Volatilities of base oils used to prepare block copolymer gels used in a fragrance release study

Block Polymer Gel	Chemical Composition	Non-volatiles (wt%)	Volatility*
Gel M	C_{13-14} isoparaffin	<20	<1
Gel L	C_{11-13} isoparaffin	<20	4
Gel G	C_{10-11} isoparaffin	<20	35

* n-butyl acetate = 100

Controlled Release for Fragrances

The essential functions of perfume are to provide a pleasant odor, to cover the base smell of a product, to give the product identity and to provide product concept support. Often times, while the attributes of a cosmetic product require time and repetitive applications to emerge, the instant gratification from a nice fragrance will help to establish a strong product image.

A perfectly perfumed product should not have an overpowering initial odor (also called top notes), but a generous smell for as long as the product remains on the substrate. In reality, the fragrance that is being incorporated into the finished cosmetic product will have to be blended with other ingredients at around 40 to 50°C, which may be detrimental to some of the fragrances. Common practice in the industry is to add fixatives, such as some high boiling point materials, to slow down the evaporation of the perfume or to "stretch" the top notes toward the end notes odor.[4]

While the primary function of gelled emollients varies from product to product, the gelled emollient will help to reduce the vapor pressure of the fragrance. In addition, since the fragrance oil is "chemically" linked to the gel network, the fragrance will have a slower and more even release through the time of exposure, as compared to the product that does not contain any polymeric gels.

We conducted an experiment to compare the release pattern among gelled materials based on base oil with different volatilities (Table 1). The results (Figure 2) illustrate the differences one would expect regarding how the top notes, middle notes and end notes would behave in the gelled environment. Gelled fragrances or fragrances in a gelled environment tend to exhibit a relatively linear-release pattern.

Another simple demonstration is to compare the evaporation rate between a water-based air freshener and an anhydrous Gel M-based air freshener (Figure 3). The gel-based air freshener gives a consistent controlled-release for volatile, versus a traditional water-based product, which presents a sharp initial discharge followed by a quick tapering off of the volatile ingredient. While this characteristic is desirable in air fresheners, cosmetic products containing gelled emollient or gelled fragrance will also benefit from it.

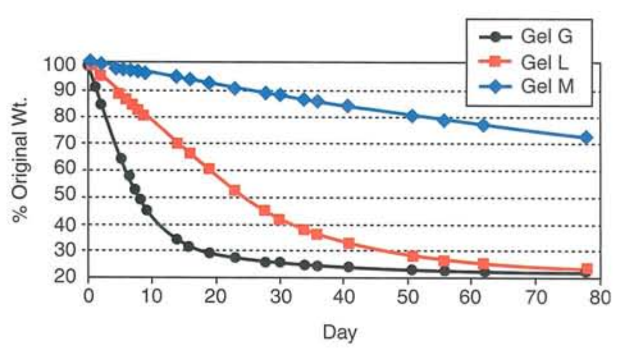


Figure 2. Fragrance release pattern of tested gelled materials

Gelled Emollients vs. Neat Emollients

"Emollient" is one of the most common words used when describing cosmetic oils and esters, and yet its definition is somewhat vague. It has been defined as a material that softens living animal tissues.[5] Essentially, an emollient is a material that is linked to smoothness, elasticity, lubrication and a healthy "gloss and glow" achieved upon application to human skin.

If water is lost more rapidly from the stratum corneum than it is received from the lower layers of the epidermis, the skin becomes dehydrated and loses its pliability. The approach to restoring water to dry skin has taken three different routes: occlusion, humectancy and restoration of deficient materials.[6] Since many of the perceptions related to emolliency are too subjective to be properly and accurately assessed at a reasonable cost, many scientists today generally rely on clinical studies such as a Transepidermal Water Loss (TEWL) test to evaluate the efficacy of selected emollients.

Currently, the technique of using an evaporimeter to measure TEWL above the stratum corneum is perhaps the most widely accepted measure of moisturization benefits.[7] The TEWL tests conducted for the following studies incorporated an evaporimeter[b] to measure TEWL on the legs of volunteers. This instrument samples the relative humidity at two points above the skin surface, allowing the rate of water loss to be calculated from the measured humidity gradient. Averages of 13 and 17 human subjects participated in the tests respectively.

The first TEWL test was conducted to compare the emolliency between gelled mineral oil and neat mineral oil (Figure 4). The results clearly indicate that the gelled mineral oil outperforms the neat mineral oil in terms of preventing water loss from the surface of the skin. This is commonly interpreted as "providing moisturization to the skin." Petrolatum is used as a positive control in this study and did confirm the fact that petrolatum is still considered to be the best occlusive agent available.

In the second TEWL test, petrolatum was used as a positive control and compared to several gelled esters. These gelled esters were evaluated by determining the percentage of reduction of water loss over their own corresponding baselines measured prior to any treatment. For instance, the C12-15 alkyl benzoate gel had an average baseline TEWL of 7.07 g/m^2/hr before any treatment was applied. One hour after the gel was applied to the subjects, the average TEWL dropped to 5.47 g/m^2/hr which represents a 22.6% improvement; while the positive control (petrolatum) logged in a 30.1% improvement. Gelled isopropyl palmitate and gelled ethylhexyl methoxycinnamate were also tested. Figure 5 indicates the outcome of the TEWL

[b] *ServoMed Evaporimeter. ServoMed is a registered trademark of Servomed, Sweden.*

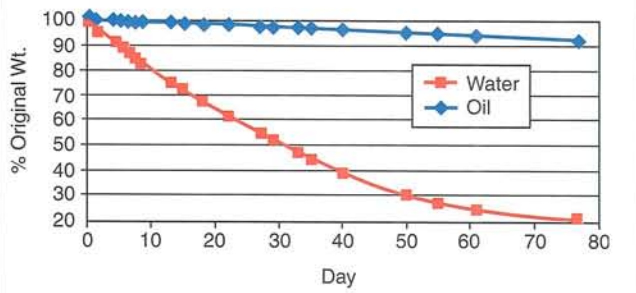


Figure 3. Evaporation rate of an air freshener based on water and an anhydrous air freshener based on Gel M

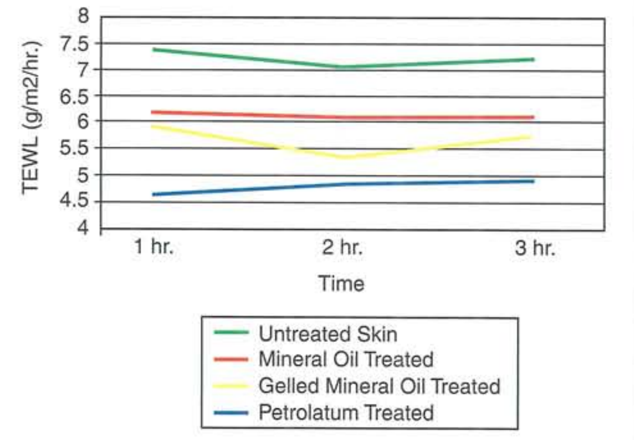


Figure 4. TEWL test for gelled mineral oil

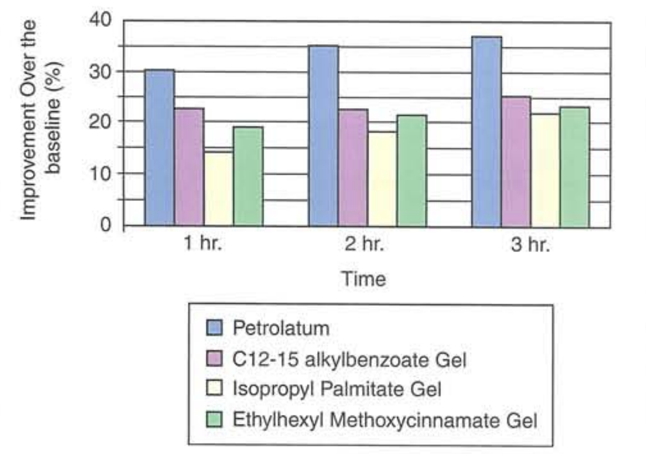


Figure 5. TEWL test for petrolatum and gelled esters

test; surprisingly, the C12-15 alkyl benzoate gel and isopropyl palmitate gel showed TEWL improvement comparable to that of petrolatum.

These test results seem to indicate that the block copolymers used to gel hydrocarbons and esters have improved the occlusivity of the corresponding neat material. It is believed that the block copolymers that are dissolved in the emollient oil are film formers and have constructed a continuous film layer on the skin when applied. The film then prevents the top layer of the stratum corneum from having an excessive loss of water. As a result, the skin remains moisturized and TEWL is reduced.

For commercial applications, the aforementioned emollients are often used in conjunction with other ingredients either in anhydrous or emulsion forms; however, the benefits of the gelled emollients should still be expected.

The film-forming characteristic of these gels is very desirable within the cosmetics industry. The benefit of employing a film-forming agent in a finished skin-care formulation is that they often enable performance claims such as "water-resistant," "transfer-resistant," "high sheen" and others.

A clinical study (FDA approved five panel pre-screen test protocol) has been conducted to evaluate the water-resistance properties of two sunscreen formulations that are identical, except that one formula contains 7.5% neat ethylhexyl methoxycinnamate and the other contains 7.5% (active) ethylhexyl methoxycinnamate gel. The test results indicated that the sunscreen product formulated with gelled ethylhexyl methoxycinnamate retained 84% of the SPF vs. 74% SPF retention for the other formulation after water immersion. While not offering water- resistance themselves, the gellants certainly have a positive impact on improving the water-resistant properties of sunscreen products.

Rheology Modifier

Thickened emollients can also be used as rheology modifiers or suspension vehicles for cosmetic products. Rheological properties of emulsions are often of major interest to personal-care formulators.

Until now, the most common chemicals used for water-phase dispersions have been carbomers and natural cellulose derivatives. Now, another option is available for the cosmetic chemist. The gelled emollients described above can be used in the oil phase of an emulsion or in anhydrous products. Generally, a skin-care emulsion that contains gelled emollients will produce a richer, more cushion type of product. Preliminary in-house experiments have indicated that the inclusion of a gelled emollient can help improve the stability of both oil-in-water and water-in-oil emulsions.

One of the gelled emollients' most intriguing properties is their ability to suspend fine particles. Using surface-treated micronized oxides like zinc oxide and titanium dioxide, gelled emollients can suspend up to 50wt% of the solids while still maintaining a stable suspension even under extreme environmental conditions. Most importantly, tests have shown that gelled emollient suspensions minimize the agglomeration and re-agglomeration of the suspended particles. This important discovery enables the formulator to achieve optimal SPF values with less physical sunscreen agents and with less of a whitening effect from the finished products.

Figures 6 and 7 are based on a 50wt% micronized and surface-treated zinc oxide suspension in gelled mineral oil. Figure 6 compares the particle size distribution between samples that were stored at room temperature and samples that had been

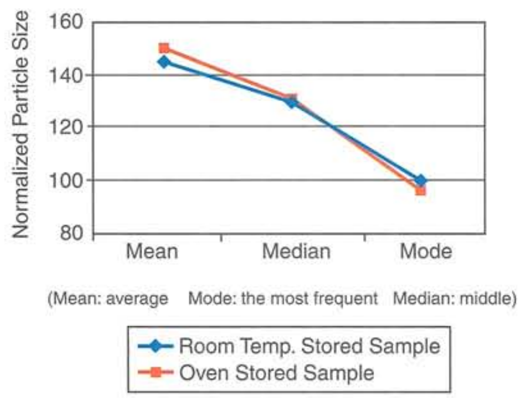
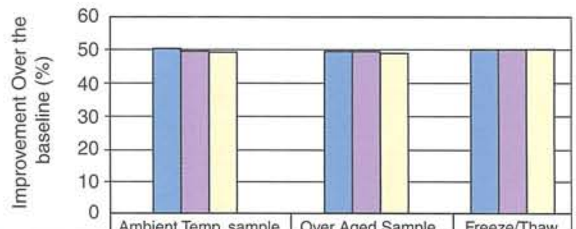


Figure 6. Particle size distribution comparisons of 50wt% micronized and surface-treated zinc oxide suspension in gelled mineral oil stored for four months under different conditions



	Ambient Temp. sample	Over Aged Sample	Freeze/Thaw
Top Layer	50.25	49.84	49.96
Middle Layer	49.93	49.8	50.27
Bottom Layer	49.82	49.47	50.27

Figure 7. Stability test comparison of 50wt% micronized and surface-treated zinc oxide suspension in gelled mineral oil stored for four months under different conditions

through 4 months accelerated aging at 52°C. Within the margin of error of the test, the results indicate that there is no significant variation of the particle sizes between two samples, which confirms the fact that no re-agglomeration has occurred.

Figure 7 illustrates the results of a stability test conducted for the same suspension product at three conditions: 4 months ambient temperature (25°C), 4 months 52°C accelerated aging, and three 24-hour freeze/thaw (–15°C/25°C) cycles. Core samples were taken from each container at different layers and then analyzed by x-ray fluorescence to detect whether any settling had occurred. As is clearly shown, samples at all conditions remained very stable, with no settling whatsoever.

With metal oxides (such as iron oxides) widely used in color cosmetic applications, incorporation of a gel in the formulation will not only reduce the particle agglomeration but also minimize the settling rate of the solids. Since some of the lighter hydrocarbon gels, such as isododecane gels or isohexadecane gels, are almost scoopable or even flowable at ambient temperature (compared to wax, which is solid), the gels make a desirable vehicle for delivering the color pigments to skin via cosmetics such as mascara, eye pencils, eyeliners or lipstick.

Formulation Guidelines

Understanding the chemical fundamentals of the thermoplastic block copolymers used in these gelled emollients is crucial to the success of personal-care product formulating.

Formula 1. Baby Oil Gel

A	Mineral (*paraffinum liquidum*) oil (and) ethylene/propylene/styrene copolymers (and) butylene/ethylene/styrene copolymer (Versagel 1600, Penreco)	44.60wt%
	Mineral (*paraffinum liquidum*) oil (Drakeol 7, Penreco)	30.00
	Isopropyl isostearate (Schercemol 318, Scher Chemicals)	10.00
	Propylene glycol isoceteth-3 acetate (Hetester PHA, Heterene Chemical)	10.00
B	Isopropyl isostearate (Schercemol 318, Scher Chemicals)	5.00
	Propylparaben	0.10
	Fragrance (*parfum*)	0.30
		100.00

Procedure: Combine gel and mineral oil and heat the mixture up to 95°C while mixing. When the mixture is uniform, lower the temperature to 75°C, then add the isopropyl isostearate and mix well. Add the rest of the ingredients except fragrance. Cool the blend to about 45°C for fragrance addition and packaging.

For anhydrous products, the gellant network can be expanded to include other anhydrous ingredients. In this case, it is very critical to heat the anhydrous gel to about 95°C before blending in other oil-soluble ingredients except fragrances. This elevated temperature enables the styrene block to disassociate or "soften." Once the styrene domain is softened, the gel network starts to open up and allows more oil (and oil-soluble) molecules to be enclosed.

Although heating to 95°C is necessary for mineral oil-based gels, any addition of polar esters and silicones will lower the critical temperature slightly. Once the critical temperature is reached, the rule of thumb has always been to add the ingredients with the least polarity to the blend first and then mix well. A stable and consistent viscosity reading is a good indication that a homogenous blend has been achieved. The baby oil gel prototype formulation shown in Formula 1 shows how an anhydrous gel product may be produced.

For emulsions, the gels should always be blended with the oil phase following the guidelines for anhydrous products. A homogeneous oil phase mixture is important to the stability of the finished emulsion.

Summary

Emollient gels based on thermoplastic block copolymers provide a different approach for many applications in the cosmetics and pharmaceutical industries. Used "as is" or formulated, the gel products' stability and suspending and film-forming capabilities make them useful for many products. The sparkling clarity of these anhydrous gels is eye-catching. The slow and steady fragrance release potential contributes to a strong product image.

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