

Pemulen^{®*} TR-1 and TR-2 Polymeric Emulsifiers

Waterproof Sunscreen Emulsions Prepared with Pemulen[®] Polymers

Introduction

Lubrizon Advanced Materials, Inc. ushered in a new era of elegant, waterproof sunscreen products when it introduced a novel polymeric emulsification technology based on Pemulen[®] polymeric emulsifiers. Oil-in-water (o/w) lotions, creams and sprays of the highest aesthetic appeal can be easily prepared without heat or homogenization. In addition, these emulsions have stability and economic advantages over conventional formulations.

Theory

Like other o/w cosmetic emulsions, sunscreen lotions have traditionally been emulsified with stearate or nonionic surfactants at 2% - 6%. Inherent to surfactant emulsification of UV absorbers is the propensity for the surfactants to remove the absorbers from the skin when contacted by water. Although the vast majority of sunscreen products in the marketplace contain water-insoluble actives, the surfactants can re-emulsify the actives and cause wash-off, leaving the skin unprotected.

Formulators have countered this phenomenon by incorporating waxes or water resistant, film-forming polymers into their formulations. Such a polymer forms an effective barrier which prevents absorber wash-off, but it may produce negative aesthetic effects such as long rub-in times and a tacky or heavy feel on the skin.

Scientists at Lubrizon Advanced Materials, Inc. have discovered that sunscreen emulsions prepared with Pemulen[®] polymeric emulsifiers meet the FDA definition of "water-proof" without the use of film-forming polymers, waxes and the like. Because these emulsions contain very little or no surfactants, the water-insoluble UV absorbers remain on the skin...even after an 80 minute exposure to water. The triggered release of the oil phase upon product application ensures that the absorbers are free to spread onto the epidermis where they are immediately active.

Formulation Guidelines

A. Oil Phase Ingredients

Any of the popular oil-soluble FDA Category 1 UV absorbers are suitable as the active bases for these emulsions. Oils/esters which function as cosolvents and/or emollients are acceptable; they should not, however, possess a significant degree of surface activity or water miscibility. Low HLB surfactants (such as sorbitan oleate) may be acceptable at low levels, though they are often unnecessary. Consistent with conventional sunscreen formulations, any ingredient which may deleteriously shift the UV_{max} absorption band of the actives should be avoided.

Though not necessary for water-proofing, oil-soluble, film-forming polymers may be useful at low levels (i.e. <0.5%) to improve rub/wear resistance of a formulation. The addition of film forming polymers will also aid in formulating sunscreen products that require ultra high SPFs and longer lasting waterproofing.

B. Water Phase Ingredients

Typical water phase ingredients such as humectants, preservatives and chelating agents are fully compatible with Pemulen[®] polymeric emulsifiers and should be incorporated at typical levels. Neither surfactants nor significantly surface active materials should be used.

Though Pemulen[®] TR-1 and Pemulen TR-2 polymer emulsifiers are water phase ingredients in terms of their solubility, they may very effectively be dispersed in the oil phase. This method of incorporation, called indirect addition, calls for the polymer to be stirred into part or all of the oil phase.

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C. Preparation Procedures

Sunscreen emulsions prepared with Pemulen® polymeric emulsifiers are readily prepared without heat. Provided that the oil phase is a liquid at ambient temperature, emulsification may be conducted at this temperature. Either phase may be added to the other. When indirect (oil phase) addition of the polymeric emulsifiers is employed, allow sufficient mixing time (~1/2 hour) for the polymer to migrate from the oil and swell in the water phase before neutralizing.

Rapid propeller mixing is effective in reducing the particle size of the emulsion. Homogenization may be useful in some instances; however, it is generally not recommended as it may cause structural degradation of the polymer, resulting in emulsion viscosity variation, or even instability, if a great amount of hydraulic shear occurs.

Efficacy

An experimental sunscreen lotion (700-202-49F) utilizing Pemulen® TR-1 polymeric emulsifier was submitted to Product Safety Labs, East Brunswick, NJ for determination of its waterproofness and sun protection fact (SPF). The formulation was compared to a commercial waterproof sunscreen (SPF 15) using the procedure outlined in FDA 21 CFR Part 352, Federal Register, August 25, 1978.

The data, summarized in the table below, indicate the experimental sunscreen lotion met the standards in the FDA monograph for waterproofness and compared favorably to the commercial waterproof sunscreen. Copies of the full report are available upon request.

Summary

Greaseless, light-feeling, waterproof sunscreens are now easily obtained with polymeric emulsification. Pemulen® TR-1 and Pemulen® TR-2 polymeric emulsifiers allow for the low-energy production of extremely stable, efficacious o/w products. Prototype formulations which demonstrate the formulation versatility, the ease of production of these emulsions, and their unique aesthetic qualities on the skin are available upon request from Lubrizol Advanced Materials, Inc.

Waterproof Sun Protection Factor (SPF) Determination

Protocol: FDA 21 CFR Part 352, Federal Register, August 25, 1978
5 Subjects, Ages 18 - 57, 4 Male, 1 Female, Skin Types I and III

| | MEAN SPF VALUES | |
|---|-----------------------|---------------------------|
| | Static ⁽²⁾ | Waterproof ⁽³⁾ |
| Standard (8% HMS) 4.75 ⁽¹⁾ – Control - SPF8 | | 8.84 |
| Waterproof Sunscreen Lotion – 700-202-49F | 17.37 | 16.64 |
| Standard (8% HMS) 4.47 ⁽¹⁾ – Control - SPF8 | | 9.44 |
| Titanium Dioxide Based Waterproof Sunscreen 700-199-94B (P0030) | 12.66 | 12.66 |

(Tested formulations listed on pages 3 & 4)

(1) STD (8% HMS): Standard Homosalate; Theoretical SPF = 4

(2) Static: 0.1 grams of sunscreen preparation was applied to 50 cm² area of epidermis, 15 minutes interval prior to UV light exposure

(3) Waterproof: Repeated quantity of sunscreen preparation on equal area of epidermis as static test. 20 minutes immersion/20 minutes rest for total of 4 cycles prior to UV light exposure

Waterproof Sunscreen Lotion (SPF 8)* 700-202-49F

*Clinical testing conducted by Product Safety Labs FDA 21 CFR Part 352, Federal Register, August 25, 1978

| Ingredient / CTFA-INCI Name | Weight, % | Function | Trade Name (Supplier) |
|---|-------------|-----------------------|--|
| PART A | | | |
| Deionized Water | 72.75 | Diluent | |
| Hydroxypropyl Methylcellulose (1.0% solution) | 10.00 | Aqueous Smoothing Aid | Methocel [®] E4M (Dow Chemical) |
| Quaternium 15 | 0.15 | Preservative | Dowicil [®] 200 (Dow Chemical) |
| Disodium EDTA | 0.05 | Chelating Agent | |
| PART B | | | |
| Octyl Methoxy Cinnamate | 7.00 | UVB Absorber | |
| Octyl Salicylate | 3.00 | UVB Absorber | |
| Oxybenzone | 2.00 | UVA Absorber | |
| C12-15 Alcohols Benzoate | 4.00 | Emollient/Solvent | Finsolv [®] TN (Finetex) |
| Acrylates/C10-30 Alkyl Acrylate Crosspolymer | 0.25 | Emulsifier | Pemulen[®] TR-1 (Lubrizol Advanced Materials, Inc.) |
| Carbomer | 0.20 | Thickener | Carbopol[®] 2984 (Lubrizol Advanced Materials, Inc.)¹ |
| Methyl Paraben | 0.15 | Preservative | |
| Propyl Paraben | 0.05 | Preservative | |
| PART C | | | |
| Triethanolamine (99%) | 0.40 | Neutralizing Agent | |

¹ Lubrizol recommends the use of Carbopol[®] Ultrez[™] 10 polymer in place of Carbopol[®] 2984. Please refer to Lubrizol prototype number P0052.

Preparation Procedure:

1. Combine Part A ingredients. Mix until homogeneous.
2. Combine first four Part B ingredients in a separate vessel. Mix until oxybenzone has been dissolved. Warming will hasten dissolution.
3. Disperse last four Part B ingredients in Part B vessel. Mix to break-up lumps.
4. With vigorous agitation, add Part B to Part A. Mix for 20-40 minutes or until a smooth, non-grainy dispersion is apparent. Add Part C (triethanolamine) and mix until a smooth, lustrous product is obtained.

Titanium Dioxide Based Waterproof Sunscreen Lotion (SPF 12)*
700-199-94B
P0030

*Clinical testing conducted by Product Safety Labs FDA 21 CFR Part 352, Federal Register, August 25, 1978

| Ingredient / CTFA-INCI Name | Weight, % | Function | Trade Name (Supplier) |
|--|------------------|-------------------|--|
| PART A | | | |
| Deionized Water | 67.80 | Diluent | |
| Propylene Glycol | 5.00 | Humectant | |
| Hydroxypropyl Methycellulose | 0.10 | Spreading Aid | Bencel [®] MP943PR (Aqualon) |
| Aminoethyl Propanol | 0.25 | Neutralizer | AMP-95 [®] (ANGUS Chemical) |
| Disodium EDTA | 0.05 | Chelating Agent | |
| Diazolidinyl Urea (and) Methyl Paraben (and) Propyl Paraben | 0.30 | Preservative | Germaben [®] II-E (Sutton) |
| PART B | | | |
| C-12-15 Alcohols Benzoate | 3.00 | Emollient | Finsolv [®] TN (Finetex) |
| Butyl Stearate | 3.00 | Emollient | (Amerchol) |
| Myristyl Myristate | 4.00 | Emollient | Ceraphyl 424 (Van Dyk) |
| Sorbitan Oleate | 0.10 | P. S. Reduction | |
| Acrylates/C10-30 Alkyl Acrylate Crosspolymer | 0.20 | Emulsifier | Pemulen[®] TR-1 (Lubrizol Advanced Materials, Inc.) |
| Carbomer | 0.20 | Thickener | Carbopol[®] 2984 (Lubrizol Advanced Materials, Inc.)¹ |
| PART C | | | |
| Octyl Palmitate (and) Titanium Dioxide | 15.00 | Active | Tioveil [®] OP (Tioxide Chemicals) |
| Polyglyceryl-10 Decaoleate | 1.00 | Dispersant | Capmul [®] 10G-10-0 (Karishamns) |

¹ Lubrizol recommends the use of Carbopol[®] Ultrez[™] 10 polymer in place of Carbopol[®] 2984. Please refer to Lubrizol prototype number P0049.

Preparation Procedure:

5. Combine Part A ingredients in a vessel which will contain the entire formulation. Heat to 50°C.
6. In a separate vessel, combine Part B ingredients. Heat to 50°C.
7. Using rapid agitation, add Part B to Part A. Mix to form a smooth, viscous emulsion.
8. Using moderate agitation, slowly add Part C to the emulsion. Slowly cool lotion using continued moderate agitation.