Specialty Esters for Aqueous Systems

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Key words

esters, aqueous systems, humectants, emollients, viscosity builders

Abstract

A new group of branched-chain fatty acid esters is compatible with clear, fully aqueous systems. The new esters provide emollient and humectant benefits. Two also have proven viscosity-building effects comparable to the dialkanolamides, but without the safety question involving unreacted diethanolamine.

An exciting new group of specialty esters has been synthesized having the distinctive and unusual capability of being introduced into aqueous systems with either full solubility or dispersibility. Fatty acid esters have been a standard tool for the formulating chemist as emollients and moisturizers in hair and skin products. As synthetic oils, however, esters are generally lipid-soluble and incompatible in water, being introduced into aqueous systems only with the aid of emulsifiers.

The objective of our research, therefore, has been to synthesize specialty esters that are compatible with aqueous systems, or, in other words, emollients, conditioners and moisturizers that can be added to the water phase of a formulation. Additionally, by controlling the structure of the molecule we are able to utilize this innovative chemistry to produce other unexpected performance attributes such as humectancy and gelling effects in surfactant systems. These esters thus act as:

1. Oil-free emollients that rinse easily and will not leave a heavy residue.
2. Unique moisture-binding humectants.
3. Significant viscosity builders in surfactant-based systems.

Emollient and Moisturizing Properties

PEG-8 PPG-3 diisostearate: The PEG-8 PPG-3 diisostearate[a] structure in Figure 1 results, as shown, from the reaction of two moles of isostearic acid and propoxylated polyethylene glycol. The propoxylation process yields a liquid ester with water-dispersible characteristics. The relatively low degree of ethoxylation (average of 9 repeating units) produces an ester with residual emollient benefits in aqueous systems.

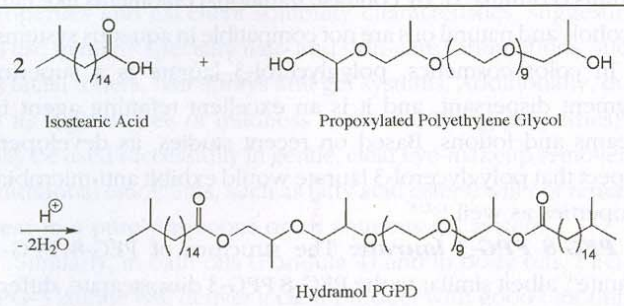

Figure 1. Chemical reaction that produces PEG-8 PPG-3 diisostearate

Having a considerable tolerance for oils and being a large, branched polymer, this ester can condition and deliver light, oil-free emolliency to hair- and skin-care formulations, especially in so-called "two in one" shampoo and body wash formulations. This is especially effective where the use of either silicones such as dimethicone and phenyl trimethicone or traditional esters like isopropyl palmitate and vegetable oils is not feasible, or where their inclusion produces build-up or over-conditioning.

The inclusion of silicones or traditional esters can also introduce a clarity problem to the formula. In contrast, the unique oil- and water-solubility parameters of PEG-8 PPG-3 diisostearate make it an excellent emulsifier and solubilizer.

In suncare products (Formula 1,next page), the use of PEG-8 PPG-3 diisostearate, by virtue of its spreading property, reduces the heavy, oily feel of the active sunscreens.

PEG-90 diisostearate: The PEG-90 diisostearate[b] is a long-chain, high-molecular-weight polymer with an average of 90 repeating units of ethoxylation. It exists as a waxy solid material. Although this polymer is not propoxylated, the high degree of ethoxylation yields an emollient ester that is completely soluble

[a]*Hydramol PGPD, Scher Chemicals Inc., Clifton, NJ, USA*

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Formula 1. SPF-15 Spray Sunscreen

A.	
Water *(aqua)* deionized	81.01 wt%
Triethanolamine, 99%	0.19
PEG-8 PPG-3 diisostearate (Hydramol PGPD, Scher)	2.00
Panthenol	0.50
Allantoin	0.20
Aloe barbadensis extract	0.05
Chamomile *(Anthemis nobilis)* extract	0.50
Disodium EDTA	0.05
Preservative	qs
B.	
Isodecyl neopentanoate (Schercemol 105, Scher)	3.00
Octyl methoxycinnamate	6.00
Octyl salicylate	4.00
Benzophenone-3	2.00
C.	
Acrylates/C10-30 alkyl acrylate crosspolymer	0.15
Sorbitan oleate	0.35
Fragrance *(parfum)*	qs
	100.00

Formula 2. Conditioning Shampoo

A.	
Water *(aqua)* deionized	47.79 wt%
Citric acid-USP (50% Soln.)	0.06
Tetrasodium EDTA	0.05
Panthenol	0.50
Sodium laureth sulfate	40.00
PEG-90 diisostearate (Hydramol PGDS, Scher)	1.00
Isostearyl ricinoleamidopropyl betainate chloride (Schercoquat RCIA, Scher)	0.60
B.	
Sodium myreth sulfate	1.50
Fragrance *(parfum)*	qs
C.	
Preservative	qs
Cocamidopropyl betaine (Schercotaine CAB, Scher)	8.50
	100.00

in water. Additionally, due to the degree of ethoxylation, water is easily bound to the molecule through the process of hydrogen bonding. Moisture is attracted and adheres to the polymer along the ethoxylated "backbone," producing a unique humectant effect when used in hair- and skin-care systems.

PEG-90 diisostearate is an excellent choice where significant solution viscosity is desired. Typical use levels are 1-2%, and resultant formulations are crystal clear in surfactant systems with excellent humectant properties due to the previously mentioned effect of hydrogen bonding of water to the highly ethoxylated polymer. Additionally, PEG-90 diisostearate can successfully gel propylene glycol and dimethicone copolyol, which may present the formulator with some very interesting options when developing novel vehicles for hair (Formula 2) and skin care.

Polyglycerol-3 laurate: The chemical structure of polyglycerol-3 laurate[c] indicates a polymer composed of three moles of glycerin to one mole of fatty acid (lauric acid). As a polymer of glycerin, this ester has superb moisturization and humectant properties. It is compatible with water-based systems so it can be used as an emollient and moisturizer in water-based hair- and skin-care formulations. In fact, polyglycerol-3 laurate contributes to the viscosity of aqueous systems and can actually form a stiff gel in water at higher concentrations, making it a candidate of choice for specialty skin-care applications, such as treatment products and serums (Formula 3). By contrast, traditional emollients like fatty alcohols and natural oils are not compatible in aqueous systems.

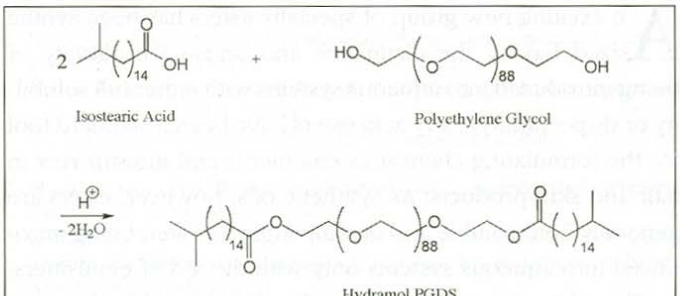

Figure 2. Chemical reaction that produces PEG-90 diisostearate

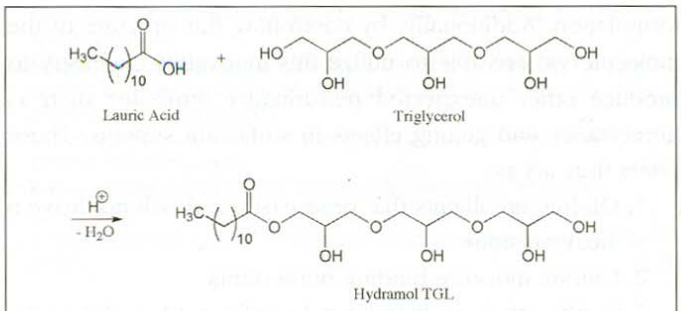

Figure 3. Chemical reaction that produces polyglycerol-3 laurate

In color cosmetics, polyglycerol-3 laurate is a superior pigment dispersant, and it is an excellent refatting agent in creams and lotions. Based on recent studies, its developers expect that polyglycerol-3 laurate would exhibit anti-microbial properties as well.[1, 2, 3]

PEG-8 PPG-3 laurate: The structure of PEG-8 PPG-3 laurate[d], albeit similar to the PEG-8 PPG-3 diisostearate, differs to the extent that one mole of alcohol reacts with one mole of

[b] *Hydramol PGDS, Scher Chemicals Inc.*
[c] *Hydramol TGL, Scher Chemicals Inc.*
[d] *Hydramol PGPL, Scher Chemicals Inc.*

Formula 3. Vitamin C Treatment Serum

A.	
Water *(aqua)* deionized	90.20 wt%
Disodium EDTA	0.05
Xanthan gum	0.30
Sodium ascorbyl phosphate	1.00
Panthenol	0.50
Sodium hyaluronate	0.50
Preservative	qs
B.	
Polyglycerol-3 laurate (Hydramol TGL, Scher)	7.00
Preservative	qs
C.	
Citric acid, 50%	0.45
	100.00

Formula 4. Silky Moisturizing Bath Oil

Safflower *(Carthamus tinctorius)* oil	69.25 wt %
PEG-8 PPG-3 laurate (Hydramol PGPL, Scher)	15.00
Decyl oleate (Schercemol DO, Scher)	5.00
Diisopropyl dimer dilinoleate (Schercemol DID, Scher)	5.00
Neopentyl glycol dicaprate (Schercemol NGDC, Scher)	5.00
DL alpha Tocopherol	0.25
Lavender *(Lavandula angustifolia)* extract	0.50
	100.00

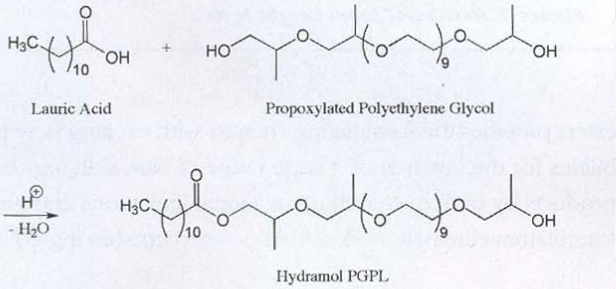

Figure 4. Chemical reaction that produces PEG-8 PPG-3 laurate

fatty acid (lauric acid) in the former, whereas one mole of alcohol reacts with two moles of fatty acid (isostearic) in the latter. By modifying the molar ratio, we can build PEG-8 PPG-3 laurate, a water-soluble compound that exhibits clarity in aqueous systems. This characteristic is especially useful where transparency is an essential attribute of a finished formulation.

PEG-8 PPG-3 laurate possesses emollient and moisturizing properties and excellent solubility characteristics, suggesting its use in many specialty hair- and skin-care formulations, such as facial toners, hair sprays and gel systems. Additionally, due to its high degree of mildness and emulsifying properties, it may be used successfully in gentle, clear eye-makeup removers. Traditional emollients, such as fatty acid esters, will not remain clear in a purely aqueous or an aqueous gel system.

Similarly, in bath oils (Formula 4) and in body oils, PEG-8 PPG-3 laurate will deliver a clear product with good blooming and spreading characteristics, being soluble in both water and vegetable oils.

Safer Viscosity Enhancers

For many years alkanolamides and, specifically, diethanolamides have been used effectively to stabilize foam and increase viscosity in surfactant-based systems, specifically for shampoos and body washes. Typically, alkanolamides have acted as adjunct thickening agents in combination with betaines, amine oxides, sultaines and other materials at use levels in the range of 1-5%.

While alkanolamides have been effective for this chosen purpose, they are not without their drawbacks. Due to their chemical makeup as condensation products of diethanolamine with fatty acids or esters, these materials usually contain a residual amount of unreacted diethanolamine. If the proposed formula will include nitrosating agents, unreacted diethanolamine is an unacceptable contaminant because it will, under those conditions, serve as a precursor in the production of nitrosamines, which have been found to be carcinogenic in animal studies.

Additionally, the National Toxicology Program (NTP) implicated cocamide DEA and lauramide DEA as carcinogens in laboratory mice. While there remains considerable controversy surrounding these studies, many formulators have been actively looking for effective alternatives to these materials pending a definitive answer on safety.

Both the PEG-8 PPG-3 diisostearate and the PEG-90 diisostearate perform as additives for increasing the viscosity of surfactant-based systems. Unlike other thickeners such as PEG-150 pentaerythrityl tetrastearate and PEG-120 methyl glycose dioleate, the branched-chain, high-molecular-weight fatty acid esters discussed here have the additional advantage of being good moisturizers. Furthermore, the liquidity of PEG-8 PPG-3 diisostearate facilitates easy handling, both in the laboratory and in production scale, and does not require heat processing and prolonged mixing.

Figures 5 and 6 demonstrate the viscosity-building characteristics of these polymers in a test formulation (Formula 5). Using PEG-8 PPG-3 diisostearate, the detergent system appeared clear at 20°C with added amounts through 7%. The

Formula 5. Basic Formula of Detergent Systems:

Sodium laureth sulfate	40.00%
Cocamidopropyl betaine	8.00
Water *(aqua)*	52.00
	100.00

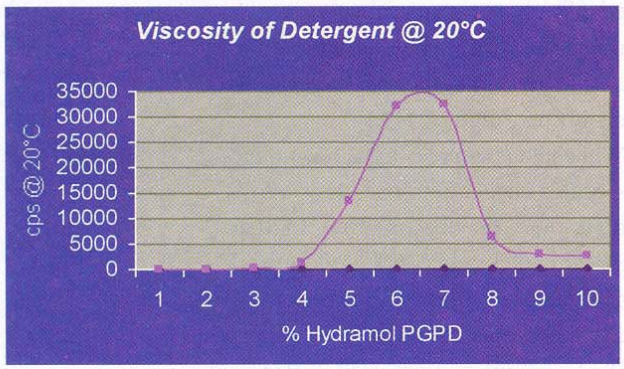

Figure 5. Viscosity increase in detergent base with increasing percentages of PEG 8 PPG-3 diisostearate

system developed a slight haze at 8% PEG-8 PPG-3 diisostearate, and was hazy at 9-10%, the highest concentrations tested. PEG-90 diisostearate systems at 20°C remained clear even with 20% in the mixture. The system's viscosity at 15 and 20% remained greater than 400,000 cps.

These polymers present excellent safety profiles and pose none of the risks or stigma of the aforementioned alkanolamides. Typical use levels in shampoo and body wash formulations range from 1 to 5% in combination with betaines, amine oxides and sultaines. Additionally, these polymeric esters do not require any neutralization or the use of electrolytes or gums to achieve their final viscosities, and the resultant flow characteristics and rheology of their use is elegant and non-pituitous. Additionally, these materials do not diminish foam height, but, in fact, have a positive effect on foam stabilization (Figure 7).

PEG-8 PPG-3 diisostearate can be used effectively to formulate elegant conditioning shampoos, body washes and facial cleansers at use levels of 3-5%. Formulation clarity is excellent with superb conditioning benefits with or without auxiliary conditioning agents such as quaternary compounds, silicones or other polymers.

Conclusion

This series of newly developed multifunctional, water-compatible polymeric

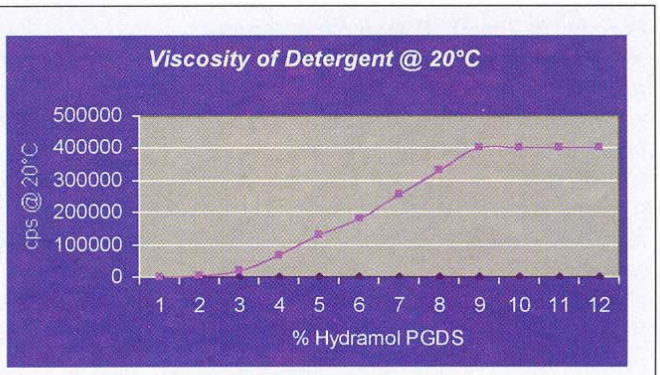

Figure 6. Viscosity increase in detergent base with increasing percentages of PEG-90 diisostearate

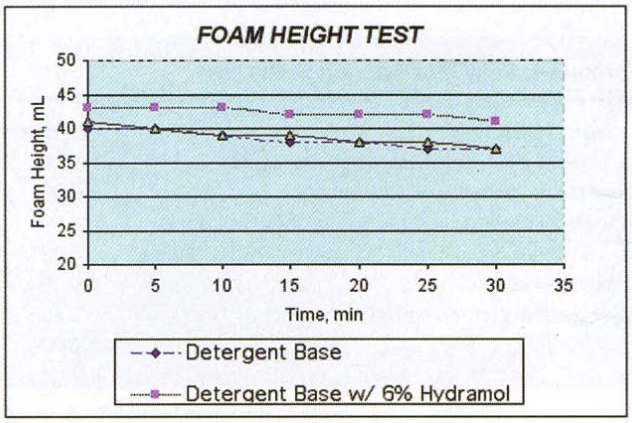

Figure 7. Results of foam height tests

esters provides the formulating chemist with exciting new possibilities for the creation of a wide range of hair, skin and beauty products by both overcoming traditional limitations and helping formulators eliminate undesirable or unacceptable ingredients.

References

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