

ELISABET MORAGAS*, CARMEN M. PEY, BLANCA NOGUÉS, MIQUEL PÉREZ
 *Corresponding author
 KAO CHEMICALS EUROPE, S.L.
 Puig dels Tudons, 10, 08210 Barberà del Vallès (Barcelona), Spain



Elisabet Moragas



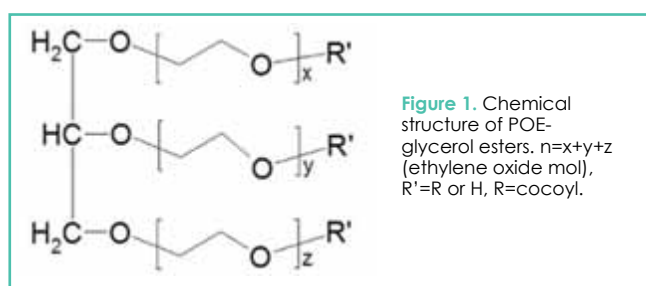
POE-glycerol esters: Application in household formulas improving CLP classification

KEYWORDS: POE-glycerol esters, hydrotropy, non-labelled, CLP, detergent, hard surface, dishwashing.

Abstract Cocoyl POE-glycerol esters from coconut oil are non-ionic surfactants that are very suitable for Home Care, especially liquid laundry detergents, neutral hard surface cleaners and hand dishwashing detergents, thanks to the unique combination of their properties: hydrotropy/thickening ability, cost/performance, mildness and safety (non-irritant to skin and eyes, non-toxic to aquatic organisms, biodegradable). New regulation 1272/2008 on classification, labelling and packaging (CLP) will call for a much stricter classification of household products than the current one. Cocoyl POE-glycerol esters have the main advantage of being fully non-labelled, and are an excellent choice when formulating household formulas because they can greatly improve their final classification.

INTRODUCTION

Non-ionic surfactants are widely used in the detergents industry for many application areas, from the cleaning of fabrics to the cleaning of hard surfaces. Within this type of surfactants, Kao Chemicals Europe produces Cocoyl polyoxyethylene glycerol esters under the trade name LEVENOL®.



Cocoyl POE-glycerol esters are 100% concentrated and colourless liquid surfactants, and are very easy to handle due to their low viscosity.

Depending on the degree of ethoxylation and esterification, several cocoyl POE-glycerol esters are available. Although they share common properties, the differences they feature cover a wide variety of applications in Home Care (1):

chemical description	trade name	main properties
Glycereth-2 Cocoate	LEVENOL® C-42T	<input type="checkbox"/> effective foam booster <input type="checkbox"/> thickener <input type="checkbox"/> high moisturizing ability
Glycereth-6 Cocoate	LEVENOL® F-200	<input type="checkbox"/> hydrotropic <input type="checkbox"/> foaming <input type="checkbox"/> most versatile of the range
Glycereth-7 Cocoate	LEVENOL® C-301	<input type="checkbox"/> balanced combination of hydrotropy and viscosity behaviour <input type="checkbox"/> foaming
Glycereth-17 Cocoate	LEVENOL® C-201	<input type="checkbox"/> outstanding solubilizing properties <input type="checkbox"/> controlled foam

Table 1. KAO's POE-glycerol esters range and their main properties.

The advantages of using this surfactant family in several household products will be discussed.

PROPERTIES AND APPLICATIONS

Product appearance and handling

Cocoyl POE-glycerol esters are transparent, homogeneous and pumpable at low temperatures thanks to their low dropping point (in some cases below 0°C). Figure 2 is an example of the better product handling. It can be seen that Glycereth-6 Cocoate at 10°C flows and is still transparent, while at the same temperature POE-7 C13/15 fatty alcohol is hazy and does not flow.

In cold areas this is a great advantage in terms of handling, cost and environmental preservation compared to typical non-ionic surfactants like POE-fatty alcohols.

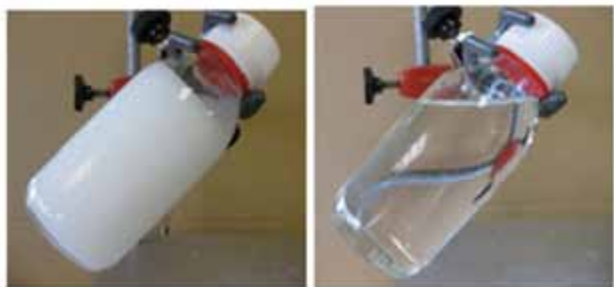


Figure 2. Product appearance at 10°C. Left: POE-fatty alcohol (POE-7 C13/15), right: LEVENOL® F-200.

Hydrotropy

The term hydrotrope refers to a compound that solubilises hydrophobic compounds in aqueous solutions. They typically have a hydrophilic part and a hydrophobic part, although this hydrophobic part is generally too small to cause spontaneous self-aggregation, therefore they do not show typical surfactant properties (2).

Cocoyl POE-glycerol esters lend hydrotropic properties to laundry and hand-dishwashing liquid formulas, with the added advantage of being surfactants and therefore having more properties than merely those of an ordinary hydrotrope. Liquid laundry detergents in developed markets are moving towards more sustainable cleaning, looking for eco-friendly products with high effectiveness (e.g. like high concentration detergents, liquid tablets, less dosage per wash, low temperature washing, less water consumption, etc.). The application properties of cocoyl POE-glycerol esters fulfil the above requirements and facilitate developments according to these trends. The effect of non-ionic surfactants (i.e. POE-fatty alcohols) on concentrated laundry detergents (40-55% active matter) lowering viscosity, improving stability and decreasing formula cloud point is known (3). Nevertheless, formulating concentrated liquid detergents usually requires the addition of hydrotropic solvents, mainly glycols, at a level that could achieve even 15% of the composition. The better hydrotropic properties of cocoyl POE-glycerol esters in comparison with typical non-ionic surfactants, especially Glycereth-6 Cocoate, allow less or even no use of additional solvents, resulting in well balanced cost-effectiveness. As an example, Figure 3 shows the appearance of a concentrated laundry detergent at 25°C depending on the non-ionic used and the % propylene glycol. Formula with LEVENOL® F-200 does not require the use of propylene glycol to be transparent, while formula with POE-fatty alcohol does.

Liquid tablets are challenging from the point of view of

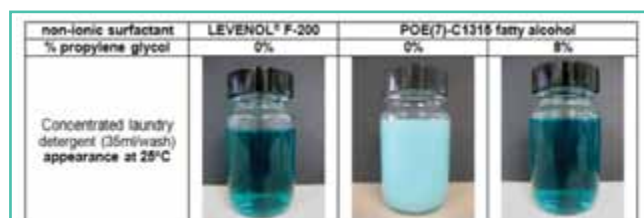


Figure 3. Example of concentrated laundry detergent formula appearance. Left: with LEVENOL® F-200 and no solvent; centre: with POE(7)-C1315 fatty alcohol and no solvent; right: with POE(7)-C1315 fatty alcohol and 8% propylene glycol. Formula composition (45% active): 15.8% non-ionic surfactant, 5.6% Sodium Cocoate, 9.0% SLES, 13.8% Na/TEA-LAS, q.s. other ingredients.

formulation with regard to obtaining a liquid product with a homogeneous and clear appearance. High amounts of surfactants (around 65%) and very low water content require the addition of a non-aqueous solvent (over 20% in many cases) to enable formulators to combine surfactants, enzymes, builders, bleaching agents and other ingredients. In comparison with typical non-ionic surfactants usually used, cocoyl POE-glycerol esters (especially Glycereth-6 Cocoate) allow liquid tablets to be formulated using glycerine (a natural and cheap solvent) instead of glycols (less ecological and more expensive). In Figure 4 it can be seen that formula with Glycereth-6 Cocoate is a transparent liquid using glycerine while formula with POE-fatty alcohol is a turbid paste using the same solvent.



Figure 4. Formula appearance at 25°C of liquid tablet formulations with glycerine. Left: with LEVENOL® F-200 (clear liquid), right: with POE-fatty alcohol (turbid paste). Formula composition (65% active): 27.3% non-ionic surfactant, 19.5% MEA-Cocoate, 7.3% SLES, 10.9% MEA-LAS, 20% glycerine, q.s. other ingredients.

The performance of POE-glycerol esters in hand-dishwashing formulas is described (4). As in the case of laundry detergents, when formulating concentrated hand-dishwashing formulas, solvents (i.e. ethanol) are used to stabilize the formulation and control viscosity. They are not cleaning aids or suds enhancers. By using Glycereth-6 Cocoate solvent content can be decreased or even avoided, while increasing the cost/performance ratio of the final product.

An example of this effect can be seen in Figure 5, where viscosity of a hand-dishwashing formula (24% total active content) is plotted against the quantity of Glycereth-6 Cocoate in the formula's active content. The formula without Glycereth-6 Cocoate has too high a viscosity for hand-dishwashing, even using 5% ethanol. When the quantity of Glycereth-6 Cocoate is increased, the ethanol content can be reduced and more controlled viscosities are obtained.

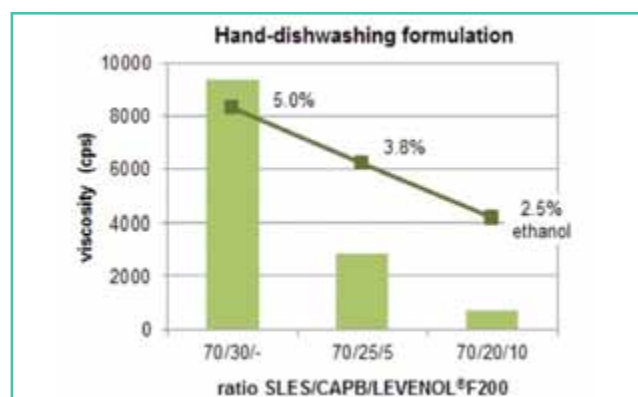
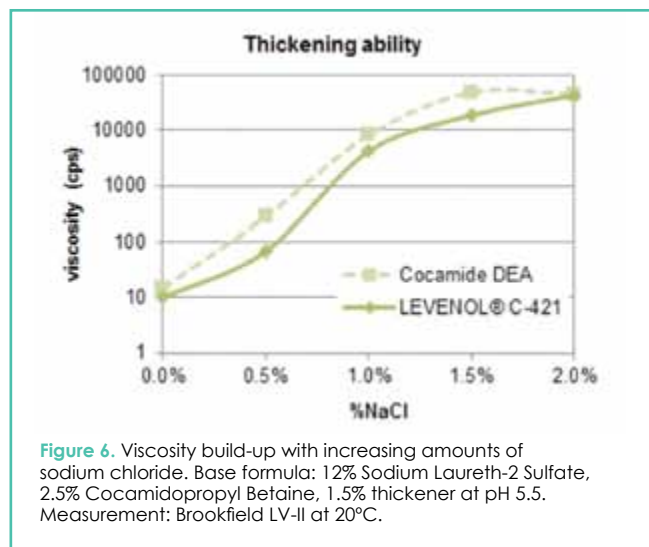


Figure 5. Viscosity of a model hand-dishwashing formula (24% active) with SLES and CAPB as main ingredients as a function of the LEVENOL® F-200 ratio and the content of ethanol added to control viscosity. Measurement: Brookfield LV-II at 20°C.

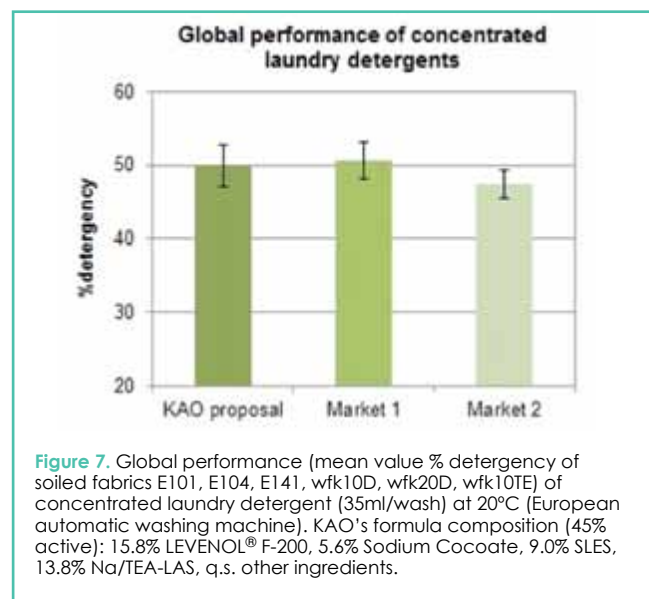
Thickening ability

As with hydrotropic ability, thickenability too can be found by choosing the correct POE-glycerol ester. For this property, Glycereth-2 Cocoate (LEVENOL® C-421) is the product to choose. Due to the increasing pressure of legislation, formulators are seeking an alternative thickener to Cocamide DEA (CDEA). Glycereth-2 Cocoate works as a CDEA replacement in liquid duty formulas, giving a similar thickening effect. Furthermore, Glycereth-2 Cocoate gives better foaming properties than CDEA in terms of quality, quantity and smoothness (5). It also has a good moisturizing effect on skin (6).



Performance

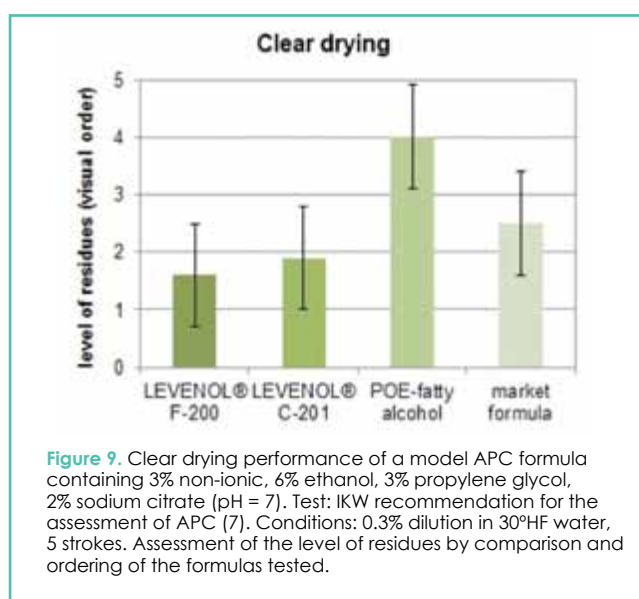
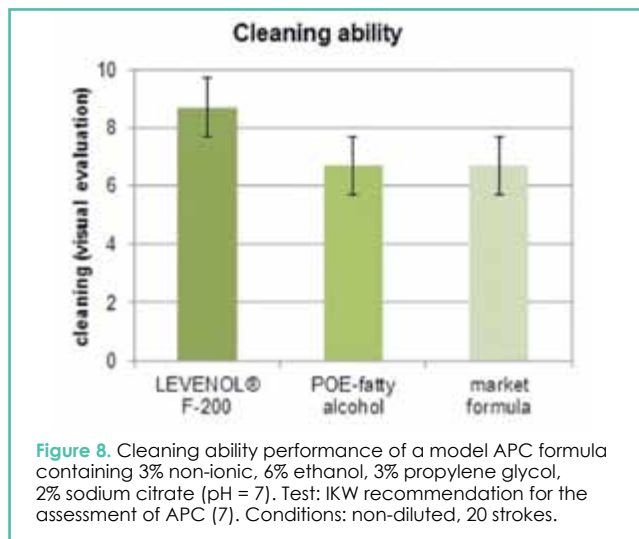
Non-ionic surfactants play an important role in the performance of both laundry detergents and hard surface cleaners. In the laundry market, consumer knowledge and awareness about carbon footprint and energy savings are increasing. This, and the fact that more delicate clothing fabrics are being used, increase the demand of good performing detergents at low temperature washing. Optimized formulations based on Glycereth-6 Cocoate



(LEVENOL® F-200) show a similar performance to that of benchmark detergents specially designed for low temperature washing, as can be seen in Figure 7 (global detergency using some typical soiled fabrics at low temperature).

In the Hard Surface Cleaners market, especially for domestic applications, there is rising concern over the danger of irritant and corrosive products. The innocuousness of cocoyl POE-glycerol esters makes them a very suitable choice as a non-ionic surfactant in Hard Surface Cleaners, in a pH range between 4 and 9.

Glycereth-17 Cocoate (LEVENOL® C-201) shows the lowest foaming profile of the cocoyl POE-glycerol esters group and is specially indicated when high amounts of perfume have to be solubilised. Glycereth-6 Cocoate (LEVENOL® F-200) is selected preferably when the overall wetting ability is important, as in neutral all-purpose cleaners. Cocoyl POE-glycerol esters perform similarly to, or even better than POE-fatty alcohols in terms of cleaning (Figure 8). The difference is more evident in the residue tests, where both cocoyl POE-glycerol esters tested outperform typical non-ionic surfactants (Figure 9) (7).



Mildness

Products that are intensively in contact with the hands, i.e. Liquid Hand Dishwashing Detergents or Hand-wash detergents, should be as mild as possible, especially in professional products with repetitive use. All cocoyl POE-glycerol esters of the range are non-irritant and reduce the irritation level of the final formulation. As seen in Figure 10, the cocoyl POE-glycerol esters give the lowest irritation potential, even when tested at higher concentration that the rest of the surfactants shown.

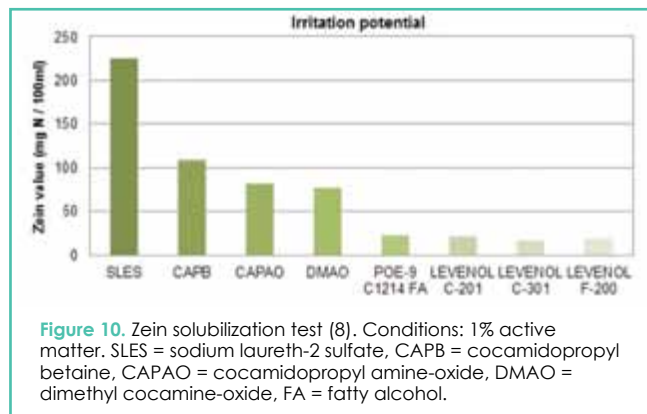


Figure 10. Zein solubilization test (8). Conditions: 1% active matter. SLES = sodium laureth-2 sulfate, CAPB = cocamidopropyl betaine, CAPAO = cocamidopropyl amine-oxide, DMAO = dimethyl cocamine-oxide, FA = fatty alcohol.

CLASSIFICATION, LABELLING AND PACKAGING (CLP)

Cocoyl POE-glycerol esters are non-irritant to skin and eyes. They are non-toxic to aquatic organisms and they are biodegradable, both aerobically and anaerobically (1). The surfactants included in the LEVENOL® range need no safety warnings or pictograms on the label, which makes them highly suitable for environmentally friendly detergents and highly appreciated when trying to formulate non-classified products. The new regulation 1272/2008 on classification, labelling and packaging, commonly known as CLP (9) (coming into force in June 2015) will imply a reclassification of mixtures according to a much stricter criteria than the current one when considering the classification of the raw material.

Mixtures can be non-labelled, irritant or corrosive, taking both dermal and ocular classifications into consideration. The biggest change in the new regulation concerns eye damage classification: more than 3% of an ingredient classified as H318 (causes serious eye damage) will result in the formula being classified as corrosive, with the corresponding corrosion pictogram on the label. Cocoyl POE-glycerol esters offer a big advantage for formulators over other common non-ionic surfactants in the market: they are totally non-labelled, therefore there is no restriction on using them in a final product. The impact on formula classification of different non-ionic surfactants can be seen in Figure 11.

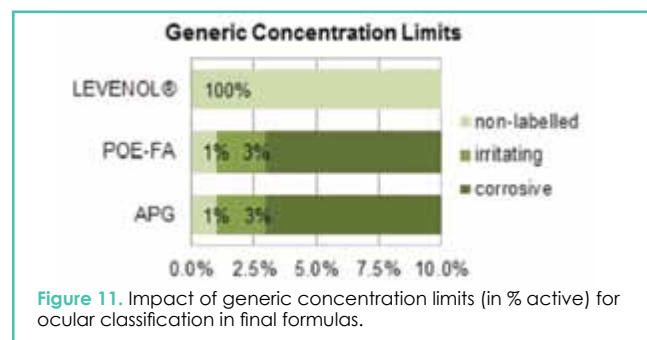


Figure 11. Impact of generic concentration limits (in % active) for ocular classification in final formulas.

Cocoyl POE-glycerol esters can improve formula classification of both hard surface cleaners and laundry detergents, which would otherwise be labelled as irritant or even corrosive, and would carry the same pictogram as more hazardous products such as bleaches or oven cleaners.

Laundry detergents

Cocoyl POE-glycerol esters are a good choice for obtaining non-labelled light-duty liquid detergents. In the case of concentrated laundry detergents, due to their high surfactant content it is a challenge to obtain a non-labelled formula. The new and stricter CLP regulation is going to make most of the Liquid Laundry Detergents classification tougher, which in many cases will result in the corrosive warning on the label. Since cocoyl POE-glycerol esters are not classified under CLP, the formulator can use them to ensure better labelling of the final detergent.

% product	light duty liquid detergent	liquid detergent	concentrated liquid detergent	liquid tablet
Deionized water	q.s.	q.s.	q.s.	q.s.
LEVENOL® C-301	11.8	-	-	-
LEVENOL® F-200	-	18.0	28.0	33.0
EMAL® 270 (Sodium Laureth Sulfate, 70%) *	4.9	7.1	14.2	14.2
BETADETH® HR (Cocamidopropyl Betaine, 30%)	1.0	-	-	-
EXCEPARL® LM-LC (Lauryl Lactate, 100%)	0.9	0.9	-	-
Potassium cocoate	2.9	-	-	-
Sodium cocoate	-	0.9	3.5	-
TEA-cocoate	-	-	3.5	-
MEA-cocoate	-	-	-	22.0
Citric acid (50%)	1.0	-	-	-
Sodium citrate dehydrate	-	3.0	5.7	-
Sodium chloride	0.9	-	-	-
Glycerine	-	-	-	28.5
other ingredients	q.s.	q.s.	q.s.	q.s.
% active matter	18%	25%	45%	66%
pH (100%)	8.2	8.1	8.1	8.1
viscosity (cps)	275	234	263	1260
dose / wash	75 ml	75 ml	35 ml	1 tablet
classification of the formula (a) using POE-glycerol esters	NL	NL	!	!
classification of the formula (b) using POE-fatty alcohols or alkyl polyglucosides	!	!	!	!

Table 2. Formulation examples and their corresponding pictogram according to CLP regulation: (a) using POE-glycerol esters, (b) using POE-fatty alcohols or alkyl polyglucosides. Other ingredients that can be included in the formulas are (a.s.): polymers, chelating agents, optical brighteners, opacifiers, enzymes, preservatives, perfumes, dyes, etc.
* EMAL® 270 has Specific Concentration Limits for the CLP ocular classification (in active: ≥ 5% H319, ≥10% H318) which is less restrictive than the Generic ones.

Neutral Hard Surface Cleaners

Cocoyl POE-glycerol esters can substitute 1 to 1 current non-ionic surfactants used in hard surface cleaners obtaining non-labelled formulas. Performance of the Table 3 formula has been shown in Figures 8 and 9.

% product	neutral HSC
Deionized water	q.s.
LEVENOL® F-200	3.0
Ethanol	6.0
Propylene glycol	3.0
Sodium citrate	2.0
Sodium hydroxide	Adjust to pH = 7
dilution	1-3 % or ready to use
classification of the formula (a) using POE-glycerol esters	NL
classification of the formula (b) using POE-fatty alcohols or alkyl polyglucosides	!

Table 3. Neutral All-Purpose Cleaner. Non-labelled formula with POE-glycerol ester (a) and corrosive formula with POE-fatty alcohol or alkyl polyglucosides (b).

CONCLUSIONS

Cocoyl POE-glycerol esters are non-labelled, non-ionic surfactants which are convenient to use in formulating household products, as they obtain a better classification of the mixture under the new CLP regulation. In laundry detergents their hydrotropic property means the detergents can be formulated without solvents, or with less of them, or with more friendly solvents like glycerine, showing good detergency washing at low temperature. In hard surface cleaning they also have the advantage of leaving less residue after the use of the cleaning formula. In hand-dishwashing they can play both the role of building up viscosity or reducing it, while improving formula mildness.

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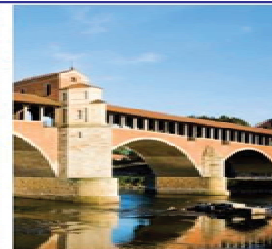
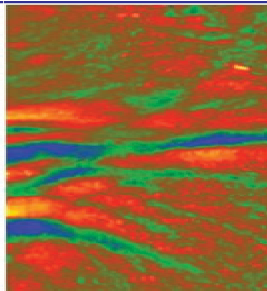
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