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Natural glycol replacement for hair and skin care

Global consumer demand for natural and organic cosmetics and personal care products continues to grow at double digit rates. Cosmetic chemists are challenged to find innovative, natural alternatives to synthetic and petroleum-based chemicals that have similar or better performance. Once they have identified a new ingredient, evaluation of its safety, efficacy and performance attributes is critical prior to adoption in new formulations. Certification agencies such as ECOCERT, COSMOS, BDIH, Natrue and the Natural Products Association (NPA) have been evaluating and approving ingredients as being safe and/or natural. Products that are on the "do not use" lists from these agencies as well as information on the internet are driving various "free from" marketing claims. Paraben-free, phthalate-free and sulfate-free are some examples that you will see on the retail shelves today.

In May 2004, DuPont and Tate & Lyle formed a joint venture – DuPont Tate & Lyle Bio Products, LLC – and invested in one of the largest bio-materials processing facilities in the world at Loudon, Tennessee. The proprietary fermentation process converts glucose or corn sugar, a rapidly renewable feedstock, to 100% bio-based 1,3-propanediol. Originally intended to be an ingredient in DuPont Sorona polymer, a renewably sourced polytrimethylene terepthalate (PTT), a cosmetics grade of this material has been available since 2006 under the registered trade name, Zemea.

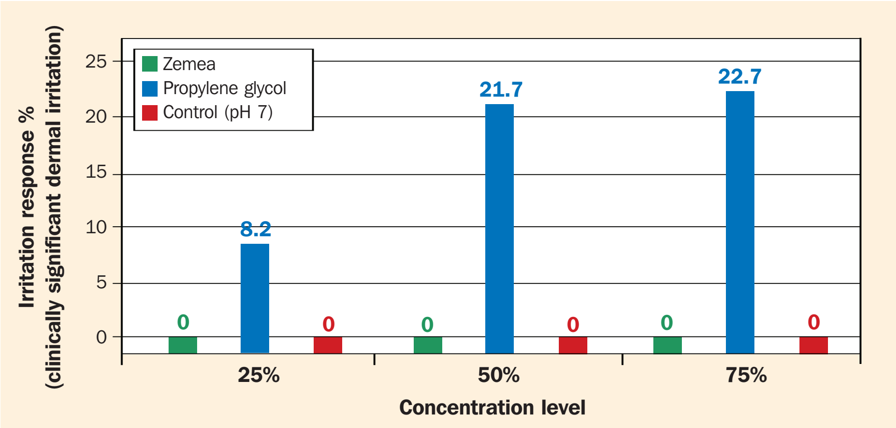

Figure 1: *Human skin patch test results (n=207). At concentrations as high as 75%, Zemea has not produced skin irritation or sensitisation reactions.*

Zemea bio-derived 1,3-propanediol (now referred to as 'the glycol replacement') can replace petroleum-based glycols such as propylene glycol (PG), butylene glycol (BG) or glycerin. It can be used as a humectant, emollient, natural solvent, viscosity enhancer, hand-feel modifier and for botanical extraction and dilution. It is also being used as a carrier for active ingredients, as an ingredient in natural preservative systems and for developing natural esters. Various technical and consumer tests have been conducted to evaluate the performance of the glycol replacement as compared to traditional glycols and glycerin. This paper will highlight the key test results.

Skin irritation and sensitisation

Two independently conducted human skin patch studies were completed using the glycol replacement. A modified Draize

Table 1: O/W skin care emulsion with 5% glycol.

INCI Name	wt%
Deionised water	61.2
EDTA	0.1
Glycol	5.0
Carbomer (2%)	10.0
Mineral Oil	10.0
Hydrogenated Polydecene	5.0
Glyceryl Stearate and PEG-100 Stearate	2.6
Stearic Acid	2.6
Cetearyl Alcohol	0.5
Dimethicone	1.0
NaOH (20%)	1.2
Preservative	1.0

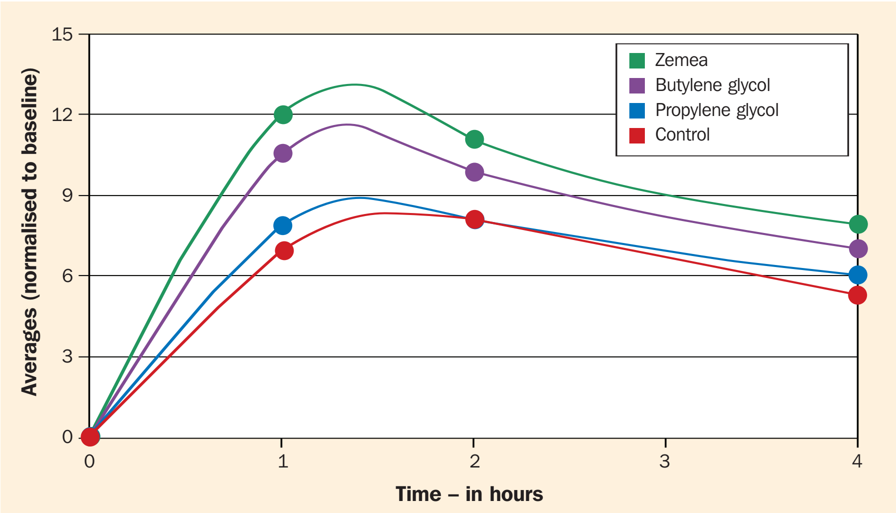

Figure 2: *Skin moisturisation averages – Zemea, PG, BG and control.*

Repeated Insult Patch Test (RIPT) method was used for the first test where solutions containing 5%, 25%, and 50% of the glycol replacement and water were applied to the skin of approximately 100 volunteers. Patches remained on the skin for 24 hours for each of nine applications in the induction phase. Following a two-week rest period, volunteers were challenged with one final application. The glycol replacement was shown not to be a skin irritant, fatiguing agent or sensitising agent in the first study.

In the second RIPT study, a single-blind comparison of the glycol replacement and PG (25%, 50%, and 75% the glycol replacement, 25%, 50%, and 75% PG) was conducted on approximately 200 volunteers. Test conditions in the second study were similar to those in the first study. In the second study, there was no clinically significant dermal irritation or allergic contact sensitisation reactions following exposure up to 75% the glycol replacement at three different pH levels. These results were in contrast to the skin irritation observed at all three PG concentrations with 22.7% of the test population indicating positive irritation results at 75% concentration (Fig. 1). The results from these human studies show that the glycol replacement has low potential to irritate and sensitise human skin.

Humectancy and moisturisation

Two independent humectancy tests were conducted on the gycol replacement versus petroleum-based glycols and glycerin. In the first study, a skin moisturisation test was conducted by Consumer Products Testing Company (Fairfield, NJ, US) on 10 female subjects, ages 46-65 years old. An oil-in-water skin care emulsion with a 5% glycol (the glycol replacement, PG, BG) plus a control was used as the test cream (Table 1). The control cream replaced the glycol with water to evaluate the relative moisturisation properties of the other ingredients. Each test cream was applied on the forearms of the volunteers. A Corneometer 825 PC (Courage & Khazaka) was used to measure skin moisturisation. The result from this test demonstrates that the glycol replacement was more efficient than BG and PG in moisturising the skin throughout the entire four hour testing period (Fig. 2).

In another study conducted by Iwase Cosfa in Japan, the initial moisturising effect of the glycol replacement was compared to glycerin in an aqueous solution. Three aqueous solutions were formulated using 10% the glycol replacement, 10% glycerin and a 5% glycol replacement/5% glycerin mixture.

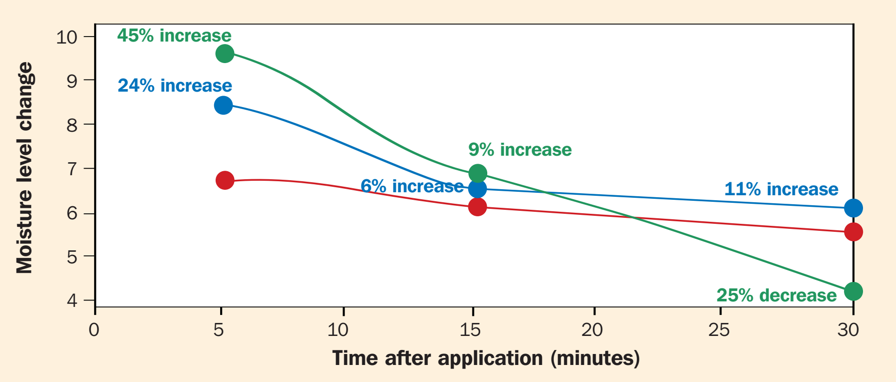

Figure 3: *Skin moisturisation performance compared to 10% glycerin.*

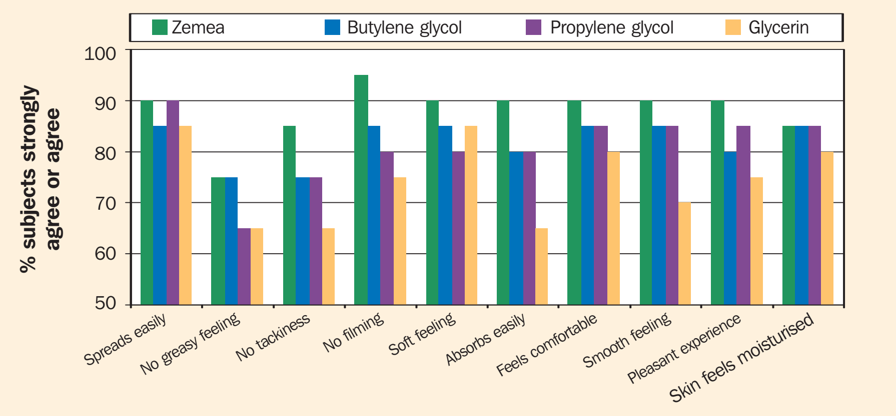

Figure 4: *Consumer skin efficacy test.*

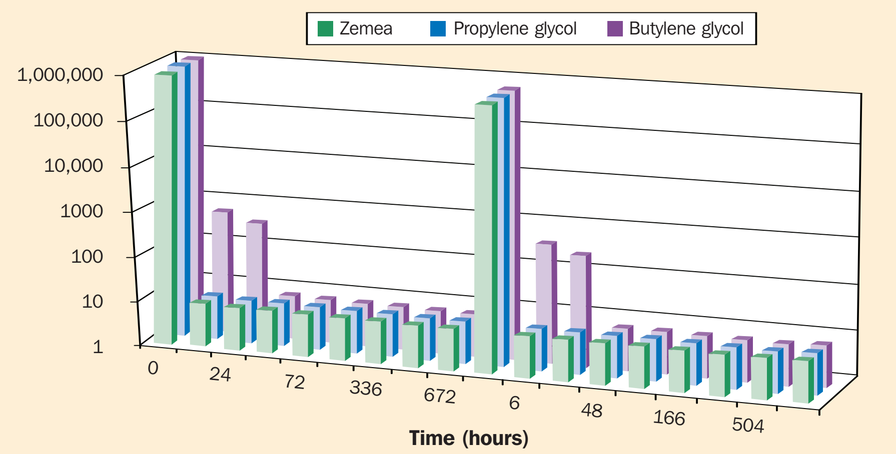

Figure 5: *CTFA challenge test: Group III moulds and yeasts.*

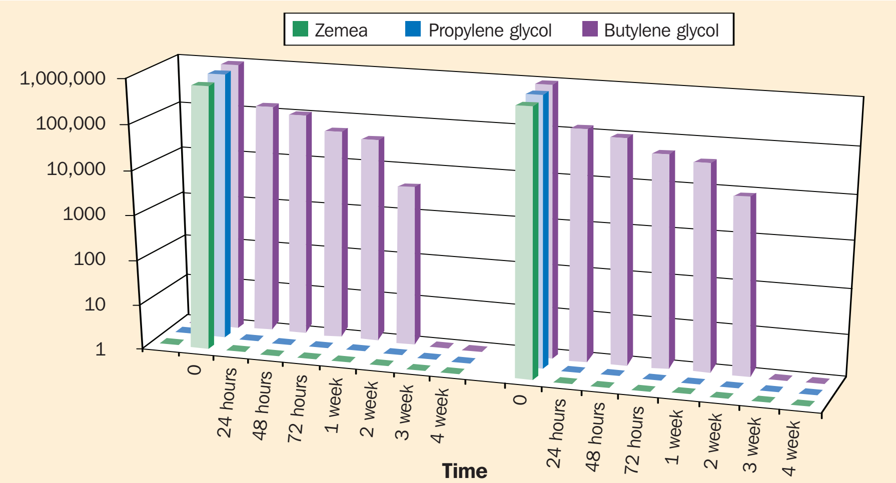

Figure 6: *CTFA challenge test: Group I bacteria.*

Each test formulation was applied to the forearms of the volunteers and moisture levels were measured by conductance using a Corneometer ASA-MI (Asahi Biomed, Yokohama, Japan). Results from this test (Fig. 3) indicate that the 10% glycol replacement solution provides better skin moisturisation during the initial application but declines over the 30 minute testing period. The solution containing 5% glycol replacement/ 5% glycerin has the best overall moisturisation effect. The glycol replacement shows a synergistic effect when formulated with glycerin that improves and extends skin moisturisation. Formulating with a glycol replacement/ glycerin mixture may reduce the tackiness effect resulting from a higher concentration of glycerin alone.

Consumer skin efficacy

A consumer testing panel consisting of 20 subjects completed a skin efficacy study using an oil-in-water lotion with a 5% glycol concentration (Table 1). The subjects tested four different formulations with a varying glycol component – the glycol replacement, propylene glycol, butylene glycol and glycerin.

This four-day conditioning and three-day product use cycle design was administered by Consumer Product Testing Company, Fairfield, NJ. This was a blind test and the formulations were randomised. The subjects completed a daily use diary and completed a questionnaire where they reported their level of agreement on a scale of 1 to 7 with 10 different statements regarding each lotion's sensory and use characteristics. Based on the top two box scores (Agree or Strongly Agree), consumers rated the lotion formulated with the glycol replacement more favourably than the other formulated lotions on almost all of the attributes (Fig. 4).

CTFA challenge tests

Neat glycol samples of the glycol replacement, propylene glycol and butylene glycol were compared using independent CTFA challenge tests for antifungal and antimicrobial properties. The testing was performed at Loricon Testing Service, Inc., Keyport, NJ. The same procedure was used for each challenge test; the samples were inoculated with approximately 6×10^6 numbers of colonies and the numbers of colonies were counted periodically. After four weeks the inoculation was repeated.

Table 2: Clear shampoo formula.

Phase	Ingredient	INCI name	% by weight
A	Deionised Water	Water (Aqua)	42.77
	NA2EDTA	Disodium EDTA	0.10
	Zemea Propane Diol	1.3 Propanediol	5.00
B	Standapol A	Ammonium Lauryl Sulfate	25.00
	Standapol ES-2	Sodium Laureth Sulfate	15.00
C	Velvetex BK-35	Cocamidopropyl Betaine	2.50
D	Monamid CMA	Cocamide MEA	2.00
	Shampoo fragrance #3599 (Belle Aire)	Fragrance	0.15
E	Glydant	DMDM Hydantoin	0.20
F	Citric Acid (20% solution) to pH 6.0-6.7	Citric Acid	0.03
G	Hest HBV Liquid		7.25

Table 3: Stages and attributes.

Application Stage	Wet Stage	Dry Stage
Ease of spreading	Ease wet detangling	Ease of dry combing
Flash foam (speed to foam/lather)	Ease wet combing	Clean feel (lack of residue/build-up)
Creaminess of lather	Clean feel (lack residue/build-up)	Conditioned feel
Foam density (small bubble size)	Moisturised/conditioned feel	Body/fullness
		Lack of static
		Shine

Table 4: US hair tress study summary results.

Stage		Zemea	PG	BG	Glycerin
Application	Ease of spreading	Best	Better	Better	Better
	Flash foam (speed to foam/lather)	Better	Best	Best	Better
	Creaminess of lather	Better	Better	Better	Best
	Foam density (small bubble size)	Better	Better	Better	Better
Wet	Ease wet detangling	Good	Moderate	Better	Good
	Ease wet combing	Best	Better	Best	Better
	Feels clean	Best	Best	Better	Better
	Feels moisturised/conditioned	Best	Good	Best	Better
Dry	Dry combing	Best	Better	Better	Better
	Feels clean	Better	Best	Better	Better
	Feels moisturised/conditioned	Best	Best	Best	Better
	Body/fullness	Best	Better	Best	Better
	Lack of static	Better	Better	Better	Better
	Shine	Better	Better	Better	Better

Antifungal

The first test evaluated the antifungal effectiveness of each glycol against Group I moulds and yeasts. The moulds and yeasts used in this testing include *Aspergillius niger, Candida albicans*, Blue/green penicillium and trichoderma.

Based on the results shown in Figure 5, it can be concluded that the glycol replacement has equal performance to PG and slightly better performance than BG after both the first and second inoculations.

Antimicrobial

The second test evaluated the antimicrobial effectiveness of each glycol against Group I, II and IV bacteria. The bacteria used in the testing include Group I: *Staphylococcus aureus, Escherichia coli, Proteus vulgaris, Enterobacter cloacae, Enterobacter gergoviae*; Group II: *Pseudomonas aeruginosa, Pseudomonas fluorescens, Psuedomonas cepacia, Flavobacterium* sp; and Group IV: Bacterial Isolates. Based on the results shown in Figure 6 it can be concluded that against Group I, the glycol replacement has equal performance to PG and significantly better performance than BG after both the first and second inoculations. The glycol replacement also showed equal performance to PG and BG against Group II and IV bacteria.

Hair care efficacy

Tress study using bleached/ damaged hair

An independent laboratory study was conducted using standard bleached (i.e. damaged) hair tresses to evaluate the efficacy performance of a glycol replacement-based clear shampoo (Table 2) compared to a similar PG and BG based formula. The evaluations were conducted by a trained laboratory panel at Bria Research Labs, Libertyville, IL.

The bleach treated hair tresses were tested and evaluated in triplicate for each stage listed in Table 3. A one cc (1 mL) amount of each shampoo was applied on a blind basis to a 2 g tress. Following treatment, each tress was rated using a 1-5 ordinal scale (1=poor, 3=moderate, 5=excellent).

Results from this study indicate that different polyols have better effects on particular attributes at different stages (Table 4). The glycol replacement exhibited excellent performance in the areas of ease of spreading in the application stage, ease of wet detangling, wet combing and moisturised/conditioned feel in the wet stage; and ease of dry combing, improved body/fullness and moisturised/conditioned feel in the dry stage.

Water retention study

A second independent laboratory study was conducted using bleached (i.e. damaged) hair tresses to evaluate the effect of glycols on the water retention of hair under extreme heat conditions. The shampoo samples were formulated by Cosmetech Laboratories, Inc., Fairfield, NJ. The evaluations were conducted by Iwase Cosfa, Tokyo, Japan.

The tresses were bleached three times, 30 minutes each, in a 31% water and 3.5% ammonium solution. Each bleached tress was immersed overnight in individual aqueous solutions containing 10% glycol (the glycol replacement, PG, BG and glycerin) plus a water only solution. The hair tresses were washed with warm water and air dried. They were stored at 25˚C, 75% relative humidity, for 24 hours. The water content for each hair tress was determined by the difference ratio of Primary (A) and Secondary (B) evaporation.

Ratio of Secondary Evaporation (%) = [(A – B)/B] x 100

(A) = weight of a 300 mg (1 cm) sample after 40 minutes at 65˚C

(B) = weight of sample (A) after 30 minutes at 180˚C

The tresses that were treated with solutions containing the glycol replacement, PG and BG all showed a higher ratio of secondary evaporation than the control (3X damaged hair) and the glycerin-treated tresses (Fig. 7). The glycol replacement tresses exhibited higher water retention under extreme heat conditions than the other glycol solutions and had similar performance to the normal (non-damaged) hair tresses.

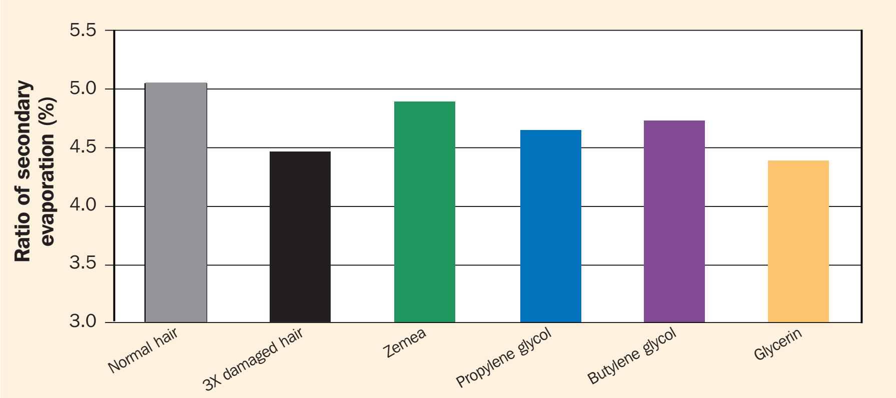

Figure 7: *Ratio of secondary evaporation.*

Environmental sustainability

Environmental sustainability is becoming more important to companies around the world. Many have corporate sustainability initiatives and personnel devoted to managing this process and are using Life Cycle Assessment (LCA) as a measurement tool for evaluating the environmental footprint of the manufacturing process of their products. Energy consumption and green house gas (CO_2) emissions are key factors in determining environmental footprint.

A cradle-to-gate LCA was conducted using design data for the glycol replacement and peer reviewed by Five Winds International. Results from this study demonstrate that the glycol replacement creates environmental benefits versus PG and PDO including significantly lower greenhouse gas emissions (42% less than PG) and lower energy consumption (38% less than PG) in its production (Fig. 8).

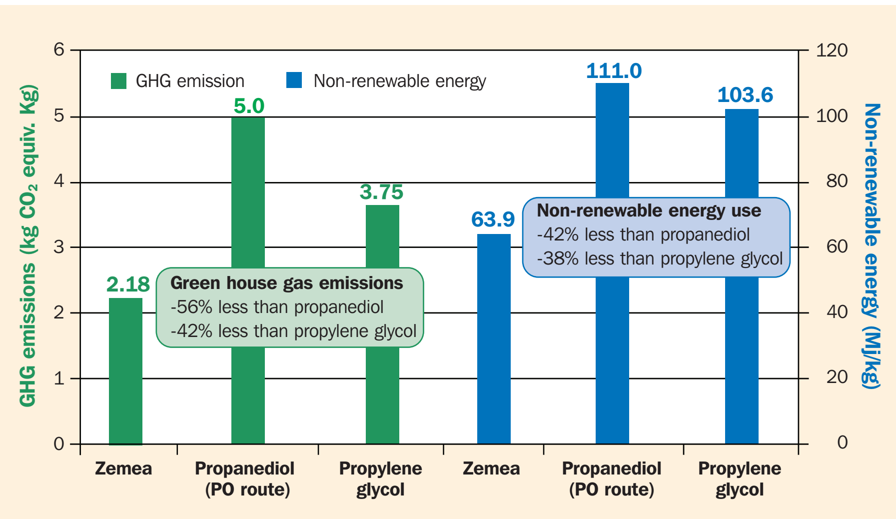

Figure 8: *Life cycle assessment.*

Conclusion

Zemea propanediol is the world's first 100% natural glycol alternative approved by ECOCERT and certified by the Natural Products Association. With its skin-friendly performance, including no irritation, enhanced moisturisation and excellent aesthetics, the product is seeing rapid adoption around the world in skin care, hair care, deodorants, fragrances, and other cosmetic and personal care products. Derived from corn sugar fermentation, Zemea can successfully replace petroleum-based glycols or glycerin in many natural and traditional personal care formulations. PC

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