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MORPHOLOGICAL CHANGES IN HUMAN HAIR CUTICLES UPON THE SIMULTANEOUS ACTION OF CYCLICAL MECHANICAL AND THERMAL STRESSES; THEIR RELEVANCE TO GROOMING PRACTICES

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INTRODUCTION

A hair cuticle analysis suggests that cuticle damage patterns in non-chemically treated hair can be reproduced by the appropriate application of several cyclical thermal and mechanical stresses. Common patterns of cuticle degradation such as cuticle de-cementation, cuticle lifting, shape distortion, vertical and horizontal cracks, and fine and coarse irregularities at the cuticle edges (1-3) are also shown to relate to different grooming practices.

METHODOLOGY

The cyclical strain levels used in these experiments were found to be the minimum levels necessary to reproduce the damage patterns described above. Fifty cycles of 7 % deformation under extension were applied to virgin hair fibers with a Diastron tensile tester in the automatic mode. The cyclical torsion strain levels were those resulting from imposing 20 turns per inch to the hair fiber, both, in the clockwise and counterclockwise mode for 25 times in each mode. Twenty cycles of thermal stresses consisting each in 10 seconds of dry blowing followed by 10 seconds of water immersion were applied to single fibers. A commercial blow dryer was used and it was placed 8 cm away from the fiber. In some cases the cycling experiments were carried out at three different humidities, namely: 15, 60, and 80 % RH. For abrasion studies an in-house made combing wheel was used.

RESULTS AND CONCLUSIONS

Cuticle de-cementation: Portions of lifted and de-cemented cuticles and random small horizontal cracks about 10 microns long were the result of pure cyclical extension stresses (see Fig. 1a). The cuticle lifted patterns resembled those already observed by S. B. Ruetsch et. al. (2). This type of cuticle damage was more severe at 15 % RH than at 50 % RH, and above 80 % RH no more cuticle de-cementation nor cuticle lifting was observed, only occasionally long transversal cracks were apparent. **Cuticle cracking:** Cuticle cracking was seen to take place only when any of the following cyclical stresses were applied: 1) Thermal stresses, 2) Torsion stresses at low humidities (<15 % RH), and 3) Extension stresses at humidities (<15 % RH). Thermal cyclical stresses produced multiple vertical cracks whose extension was seen to be confined to a single cuticle (see Fig. 1b) These types of cracks were only produced in new cuticles and their number diminished or vanished in severely abraded cuticles. Pure cyclical torsion stresses at low humidities were found to produce long cracks 10 to 50 microns long which appeared forming 30 to 50 degrees angles with the longitudinal axis of the hair (see Fig. 2). Cyclical extension stresses, on the other hand, resulted in small horizontal cracks 5 to 10 microns long which were randomly distributed along the fiber.

Cuticle fusion: This term is used to describe cuticle damage characterized by the loss of cuticle boundaries and cuticle structure in general, it was found after the application of cyclical torsion stresses (see Fig. 1c). **Cuticle Abrasion:** Two types of abrasion were found to take place, the first one occurred when the cuticle was still cemented and took place by the removal of fine powdery portions at the edges of the cuticle. This type of abrasion left the cuticle edges regularly spaced. The second type of cuticle abrasion took place after the cuticle had been cracked or de-cemented and was characterized by the removal of big portions of cuticle (2). Both types of abrasion have been reported in the past (2-3). **Cuticle shape distortion:** Open ripples, bulges, bumps, and crater formation were among the main forms of cuticle distortion found after cyclical stresses. The formation of open ripples by the cuticles was observed after extension cyclical stresses (see Fig. 1), while the combination of thermal and extension cycles lead to the formation of bulges, bumps, and crater formation (see Fig. 1d).

Finally, the analysis showed that hair cuticles of persons who use a blow dryer contain a great number of thermal cracks, while the hair cuticles of persons who blow dry their hair while simultaneously combing it show open cuticle ripples with thermal cracks superimposed on them. Iron curling , blow drying and combing practices were seen to result in cuticles with bumps, bulges, vertical cracks, and irregular cuticle edges.

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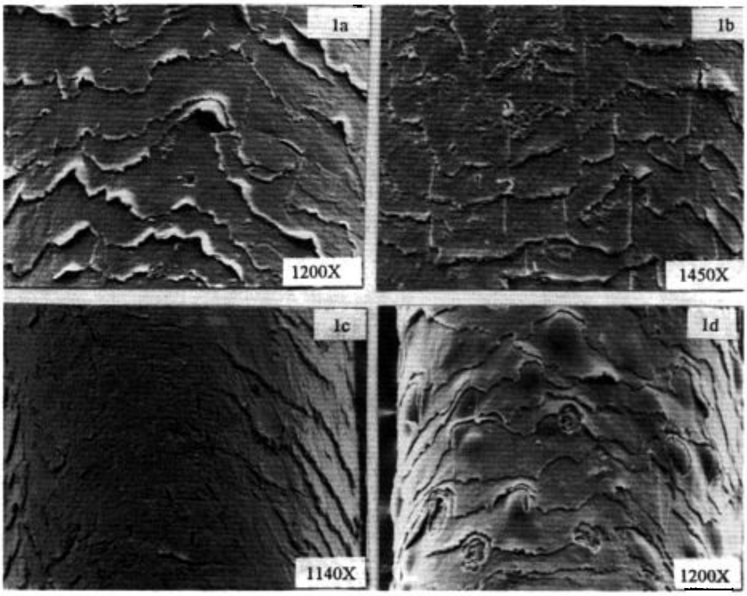

Fig.1 a-d) 1a, Cuticle de-cementation; 1b, Thermal cracks; 1c, Cuticle fusion, 1d, Cuticle bumps, bulges and crater formation.

CUTICLE REINFORCEMENT BY CATIONIC HAIR CONDITIONERS

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Introduction

In previous investigations we have studied lifting of the surface cuticle cells during extension of hair fibers which had experienced standard grooming practices, cosmetic chemical treatments, mechanical fatiguing, UV irradiation as well as combinations of these treatments. Scale lifting observed by microfluorometry during extension of the untreated hair fiber is facilitated by failure in the endocuticular domains of the surface cuticle cell. In this investigation we report on the effects of cationic conditioners of high and low molecular weight on the scale lifting behavior and on hair fiber creep.

Discussion

To study the effects of single and multiple applications of cationic conditioners on the scale lifting, we determined the changes in autofluorescence in the UV excitation beam during extension of untreated and conditioner treated hair fibers. The extension levels at which random, common and extreme scale lifting, and finally hair fiber failure occurred, were measured and plotted. Figure 1 displays the typical distribution of extensions at which the various levels of scale lifting occur in untreated hair fibers. Figure 2 shows the significantly changed distribution of extensions at which the various levels of scale lifting occur, or do not occur, in conditioner treated hair.

Fig. 1

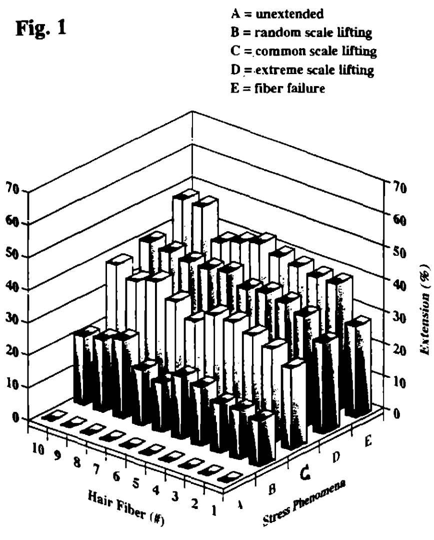
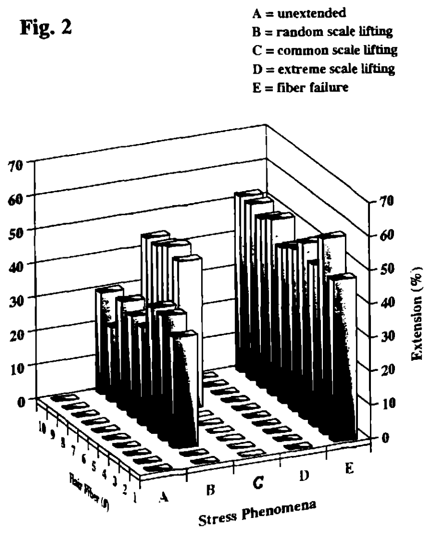


Fig. 2



Subsequent scanning electron microscopy of the extended hair fibers provided greater detail about the nature of scale lifting and the failure location.

Surface cuticle cells of untreated hair fibers tend to respond with a scale lifting mechanism to release the stress of extension. During extension, shear forces are generated between the different layers of the cuticle cell, and at high levels of extension and shearing, stress concentrations at the scale edge of the surface cuticle cell lead to failure in the easily extensible, weakly cross-linked endocuticular domains. This failure within the endocuticle results in delamination and lifting of the unextensible, highly cross-linked upper layers of the surface cuticle cell, thus producing the scale lifting phenomenon, (Figure 3).

During extension of conditioner treated hair, the high level of scale lifting, so characteristic of unaltered hair, is almost completely eliminated. Even intermediate and low levels of scale lifting occur at higher extension levels or not at all. This suggests that the conditioning compounds modify the upper cuticular layer by reinforcing the scale edges and/or the intercuticular zone.

However, when scale lifting occurs in the conditioner treated hair fiber, it involves intercellular failure in the CMC beneath the surface cuticle cell, rather than intracellular failure in the endocuticle as observed in the case of untreated hair, (Figure 4). This suggests that the conditioners modify the deformation behavior of the endocuticle which becomes reinforced and resists intracellular failure/fracture. This behavior is true also of low molecular weight quaternary compounds and may involve hydrophobic bonding of lipid chains. When scale lifting can not take place, stress is released by scale cracking. This often leads to fiber fracture and occurs only at high levels of extension. The ease of scale lifting is directly associated with the ablation of cuticle cells during grooming. ***Conditioner treatments*** which make scale lifting more difficult, ***thus provide ablation resisting properties to the cuticle and therefore are beneficial in preventing longterm grooming damage to hair fibers.***

Besides affecting scale lifting as a mechanism of stress release during extension, the conditioners also affect hair fiber creep. Multiple applications of the high molecular weight quaternized cellulose derivative significantly change the creep behavior of hair fibers in comparison to the untreated controls. This change in creep behavior suggests ***conditioner-induced improved cohesion*** within the intercellular cement and the weakly cross-linked endocuticle of at least the outer layer of the cuticular sheath, which in fine hair fibers, stops movement of the cuticle cells relative to each other, when limiting levels of shear deformation have been reached.

Our studies lead to the conclusion that at least at slow strain rates the properties of the cuticula in fine fibers can have a direct bearing in the creep deformation behavior of the cortex, contrary to generally accepted concepts.

Fig. 3

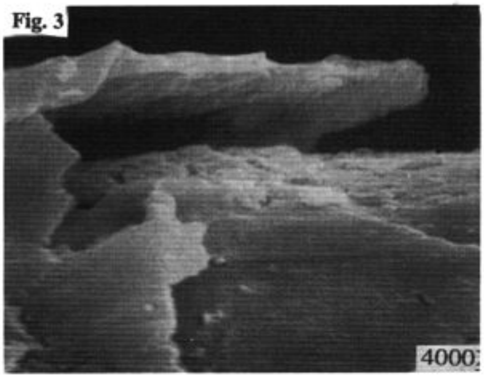
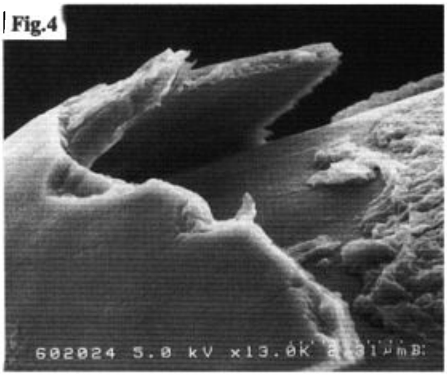


Fig.4



FORMULATING FOR MILDNESS WITH SULFOSUCCINATES

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While sulfosuccinates have been widely used for years within the personal care industry for formulating mild skin and hair cleaning products, their importance today is greater than ever.

Formulating novel products will be discussed. Synergies of sulfosuccinates with other low irritation surfactants will be shown. This will allow the formulators to achieve the performance characteristics the consumer demands while maintaining the low irritation profile required.

In addition, the general chemistry and variations of sulfosuccinates will be outlined. The main focus is to be the dermatological properties. These will be demonstrated by the comparison of in-vivo and in-vitro tests, especially the Red Blood Cell Test.

A MATHEMATICAL TREATISE OF THE PERCEIVED ATTRIBUTES AND RHEOLOGICAL PROPERTY CORRELATIONS OF THE SKIN CARE CREAMS

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INTRODUCTION

Functional properties and sensory perceptions are equally important in cosmetic product development. Determination of a universal model that can provide acceptable correlations between the physical and perceived properties of a wide range of emulsions was among ongoing interests of this group. This study seeks mathematical correlations between the rheological properties of 10, 30, 50 % O/W and 10, 30, 50 % W/O skin creams and their perceived attributes. It is continuation of the former studies that is expected to explain the functional and perceived property relationships of such products one step further.

METHODS

Preparation of Emulsions: All emulsions were perpared using castor oil (Ruger, NJ) as the oil phase, sorbitan stearate (ICI, NJ) and ceteareth-6 & stearyl alcohol (BASF, NJ) as surfactants. The oil phase and water containing 5.0% (w/w) surfactant were heated up to 72° C and mixed together using a Ross Mixer ME 100 LC (Charles Ross & Son Co, NY) at 5,000 rpm for 10 minutes. O/W and W/O emulsions containing 10, 30 and 50% w/w dispersed phase were prepared and characterized. All emulsions were in the cream form and had similar appearences.

Determination of Perceived Attributes: Twelwe untrained oriental female adults with healthy skin, whose ages ranged from 24 to 32 years participated in these studies. Emulsions prepared were placed in identical containers and presented to the panel for evaluation. The panel members were asked to rank the **pick-up** (firmness, stickiness, peaking and cohesiveness), **rub-out** (wetness, thickness, absorbency, amount of residue and spreadability), **after-feel** (stickiness, gloss and slipperiness) and **over-all** properties (liking, absorbency and softness) from 1 (the worst) to 9 (the best) according to ASTM Committee E-18 Guidelines for the Descriptive Analysis of Skin Feel. The means and standard deviations of each attribute was calculated.

Determination of Rheological Properties: After determination of the optimum stress-sweep range which was within 0.05 -100 Pascals, the rheological properties of the emulsions were measured with a CVO 50 Bholin Instruments Rheometer, software version 4.5, at 25^0 C by using a 1 mm gap width. The rheological components measured were the phase angle, elastic (G') and viscous (G") moduli, complex viscosity and strain.

Correlation Studies: Among the rheological components measured, the loss tangent (G'/G" * 100) was found to be the most represantative parameter to describe the flow properties of the creams. They were tabulated from the data obtained and correlated to the sensory attributes by using linear (Y=AX+B), logarithmic (Y=A+B*Ln(X)), exponential (Y=A*Exp(B*X)) and power ($Y=AX^B$), equations, where X was either the oil concentration or the loss tangent, Y was the perceived attribute and A and B were the regression constants. The probable fits were postulated and their resulting correlation coefficients (r^2), were used to compare the goodness of fit. The data were fitted to the models by using Hewlett Packard 48G software. Additionally, a linear three-dimensional model which incorporated the weight fraction of oil, perceived attribute, and the loss tangent was tested by the use of Maple version 4.0 software and resulting correlation coefficients were also obtained in order to compare its fit .

RESULTS AND DISCUSSION

All creams were in the form of singular emulsions. As shown in Table 1, the two dimensional models showed scattered correlations with only occasionally acceptable fits. Whereas, the three dimensional model, Z=Co+AX+BX, where Z was G'/G"*100, X was the weight fraction of oil , Y was the perceived attribute and C_0, A and B were the regression constants, presented their relationship with most acceptable accuracy,Table II. In this model the correlation coefficients of 0.993 to 0.936 (eigt cases) demonstrate an excellent, and 0.768 to 0.738 (four cases) good correlations. Coefficients that change between 0.600 to 0.256 (three cases) are the measure of poor fit,(Table II).

Among all the models tested, the three dimensional linear model was the most satisfying to describe the relationship between the perceived attributes, the weight fractions and the rheological properties of the emulsions.

Table I: Linear, Logarithmic, Exponential and Power Fits of Perceived Attributes and Complex Viscosity

	Model Tested							
Attribute	Linear		Logarithmic		Exponential		Power	
	A	**B**	**A**	**B**	**A**	**B**	**A**	**B**
Firmness	0.75	-0.52	0.76	-0.49	0.79	-0.58	0.83	-0.57
Stickness	0.64	-0.69	0.61	-0.72	0.49	-0.81	0.46	-0.81
Peaking	-0.33	-0.34	-0.42	-0.34	-0.22	0.20	-0.31	0.24
Cohesivenes	0.15	-0.54	0.17	-0.64	0.26	-0.20	0.26	-0.29
Wetness	-0.81	-0.18	-0.80	-0.14	-0.76	0.46	-0.72	0.48
Thickness	0.89	-0.19	0.88	-0.14	0.89	-0.63	0.92	-0.56
Absorbency	-0.67	-0.38	-0.66	-0.40	-0.62	0.26	-0.62	0.24
Amount of Residue	0.90	-0.12	0.91	-0.06	0.85	-0.66	0.91	-0.57
Spreadability	-0.90	-0.14	-0.90	-0.12	-0.92	0.42	-0.89	0.47
Stickiness	0.94	-0.04	0.93	0.06	0.91	-0.59	0.94	-0.32
Gloss	0.93	-0.03	0.94	0.02	0.85	-0.62	0.90	-0.57
Slipperiness	-0.70	-0.29	-0.70	-0.29	-0.76	0.27	-0.71	0.29
Liking	-0.75	0.04	-0.75	0.11	-0.73	0.53	-0.69	0.60
Absorbency	-0.83	-0.14	-0.82	-0.11	-0.83	0.43	-0.80	0.48
Softness	-0.88	-0.13	-0.87	-0.10	-0.88	0.45	-0.84	0.49

A: r^2 of perceived attribute vs. oil percentage, B: r^2 of perceived attribute vs. rheological property (Tan(y)*100).

Table II: Three Dimensional Fit of Perceived Attributes and Complex Viscosity

Attribute	**Correlation coefficient (r^2)**
Wetness	0.993
Overall Softness	0.978
Amount of residue	0.962
Gloss	0.962
Spreadability	0.958
Stickiness	0.950
Overall Absorbency	0.936
Overall Liking	0.936
Slipperiness	0.768
Thickness	0.756
Absorbency	0.745
Stickiness	0.738
Peaking	0.600
Firmness	0.388
Cohesiveness	0.256

NEWLY DEVELOPED EMULSIFICATION TECHNOLOGY FOR USE IN HIGHLY EFFICIENT COSMETIC AND SUNSCREEN FORMULATIONS; RHEOLOGICAL, MICROSCOPIC AND SUN PROTECTION EFFICIENCY CHARACTERIZATION

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INTRODUCTION:

The aim of the present work was to develop a highly efficient emulsification technology.
The technology describes several emulsifying systems for Oil in Water emulsions. The systems are comprised of a non-conventional rheology modifier/emulsifier, in combination with a low HLB emulsifier and/or a polymer. The rheology modifier/emulsifier also works as a suspending agent by itself
The technology is useful in skin care products and sun care products, including creams and lotions for sensitive skin and water resistant SPF sunscreens.

CONCLUSIONS:

The advantages of the technology are summarized by the following key findings:

1. The emulsifying system, comprised of 2% of the rheology modifier/emulsifier and 1% of a low HLB emulsifier (such as Glycerol Monostearate), is very versatile rendering stable emulsions with various oils and active ingredients over a wide range of HLB's (from 5 to 12).
2. The emulsifying system, comprised of 2% of the rheology modifier/emulsifier and 1% of a low HLB emulsifier, is very efficient yielding stable oil in water emulsions with total oils emulsified ranging from 7.5% to 45%.
3. The emulsification technology improves the delivery of cosmetically active ingredients, such as sunscreens, silicones, moisturizers and vitamins, resulting in highly efficient formulations.
4. The emulsifying system has a synergistic effect with physical sunscreens and/or water soluble sunscreens in combination with organic sunscreens.
5. The emulsions developed based on this technology are extremely mild and have intrinsic water resistant characteristics, two attributes stemming from the presence of the rheology modifier/emulsifier.

RESULTS AND DISCUSSION:

CHARACTERIZATION OF THE RHEOLOGY MODIFIER/EMULSIFIER BASED TECHNOLOGY

The rheology modifier, the key component of the technology, is the sodium salt of stearyl amidobenzoic acid. Its anionic nature renders activity at the oil/water interface* and its unique rheological profile (Fig.1) renders thixotropy and shear thinning characteristics to the emulsions employing it (Fig.2), eliminating the need for hydrocolloid thickeners.

Fig. 1

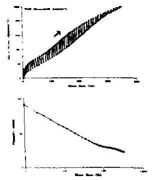


Fig. 2

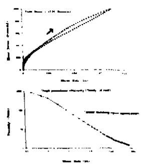
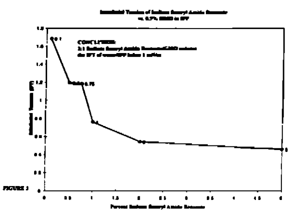


Figure 1: Rheological profile of stearyl amidobenzoic acid sodium salt (slurry in water).
Figure 2: Rheological profile of O/W emulsion.

Interfacial Tension Measurements recorded on Spinning Drop Tensiometer identified the optimum ratio of the components of the emulsifying system as 2:1, when the sodium salt of stearyl amidobenzoic acid is paired with a low HLB emulsifier. Figure 3 illustrates the interfacial tension reduction recorded for different concentrations of the sodium salt of stearyl amidobenzoic acid at the water/Isopropyl Palmitate interface vs. 0.5% low HLB emulsifier (Glycerol Monooleate). A ratio of 2:1 of the components of the emulsifying system reduces the IFT of water/IPP below 1 mN/m.



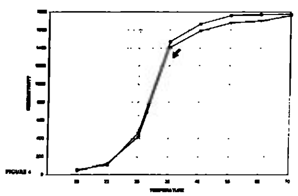


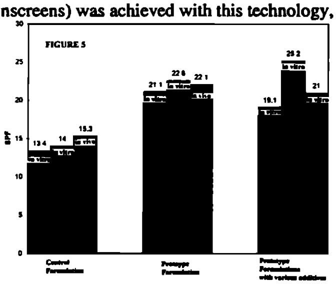
Figure 3: Interfacial Tension Measurements.
Figure 4: Conductivity measurements vs. temperature during the cooling phase of the emulsification process.

The newly developed emulsification technology works differently than a soap-based system: the rheology modifier/emulsifier dissolves @80°C to form a lamellar liquid crystalline phase; during cool down, a phase transition occurs between 35-45°C, as indicated by the change in conductivity in Figure 4, and the emulsion "sets". The phase change yields a network that provides rigidity at the oil/water interface, preventing coalescence*.

EMULSIFICATION TECHNOLOGY

Prototype formulations based on the newly developed technology will be provided to demonstrate important attributes such as efficiency, versatility and skin aesthetics.

Some in-vivo evaluations, such as irritation test results, SPF static and waterproof will also be presented in correlation with in vitro work in support of the superior mildness and SPF efficiency of the emulsions employing the newly developed emulsification systems. The key findings are that the emulsifying system has a synergistic effect with physical sunscreens and water soluble sunscreens in combination with organic sunscreens. An SPF enhancement up to 40% (vs.conventional emulsions employing the same level of sunscreens) was achieved with this technology, as illustrated in Figure 5*.



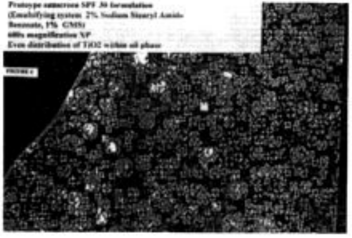


Figure 5: SPF enhanced emulsions vs. conventional emulsions employing the same level of sunscreens
Figure 6: Microscopic evaluation of sunscreen emulsion.

Figure 6 illustrates the ability of the technology to evenly distribute the physical sunscreens in combination with organic sunscreens in the continuous film resulting in an SPF over 30. Most importantly, the visual consumer signal is positive because no whitening effect upon rub in is noticeable. Possible explanations for the mechanism of emulsification will be presented based on rheological and microscopic evaluation of the emulsions.

*Note: Due to lack of space, only a few results are illustrated. More results will be shown in the presentation.

RHEOLOGY MODIFICATION OF HYDROGEN PEROXIDE-BASED APPLICATIONS USING A CROSS-LINKED POLYACRYLIC ACID POLYMER

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Introduction:

Hydrogen peroxide has been widely used as an oxidizer and bleach in hair care applications since the 1940s. Hydrogen peroxide is one of the most important ingredients in almost all hair color and permanent wave products on the market today. It is also used frequently in a variety of topical and oral care applications. As environmental regulations and consumer trends make the use of chlorine bleach less acceptable in detergent and household products, "oxygen" bleach will be used more widely. The focus of thickening hydrogen peroxide in this paper will be for the applications of hair bleach and two-part permanent hair color.

Hydrogen peroxide, by nature of its reactive chemistry, is difficult to stabilize in many applications. There are many commonly-used ingredients that are incompatible with hydrogen peroxide. Careful selection of formula ingredients, thickeners, stabilizers, as well as the proper order of addition, pH, and processing equipment are all essential to ensure acceptable long-term physical and chemical stability of a finished product. Thus, achieving both the desired viscosity and appropriate rheological properties can be a challenging task in peroxide-based formulations. Although cross-linked polyacrylic acid polymers are currently being used in some hydrogen peroxide-containing personal care and topical pharmaceutical applications, no systematic studies have been done to evaluate different cross-linked acrylic acid polymers for specific hydrogen peroxide applications and the optimum conditions to achieve acceptable long-term stability. Recent systematic experiments have demonstrated that excellent long-term stability of hydrogen peroxide-based gels, thickened with cross-linked polyacrylic acid polymers, can be achieved.

A fundamental study of the stability of hydrogen peroxide-based gels, thickened using cross-linked polyacrylic acid polymers, will be presented. The study evaluates different types of cross-linked polyacrylic acid polymers (as well as an associative acrylic polymer), several commercial sources of hydrogen peroxide, varying hydrogen peroxide concentrations, and the effect of pH. Viscosity results from some of the combinations of these variables will be presented. The effect of accelerated aging on percent active peroxide and viscosity of the thickened peroxide gels will also be discussed.

Materials and Methods:

Experiments:

Study I: Two separate studies of thickening hydrogen peroxide with cross-linked polyacrylic acid have been performed. The first study evaluated a single source of hydrogen peroxide (peroxide "D") and a single cross-linked polyacrylic acid polymer (Polymer A, fig. 1). Gels were made at four peroxide concentrations (3, 6, 9, 12 $\%_{wt}$) and three pH values (3.5, 4.0, 4.5). These low pH values were selected because of the inherent instability of hydrogen peroxide at neutral or high pH. Ammonium hydroxide was used to adjust the pH of the gels.

Study II: After learning a great deal from the first study, a second study was initiated. The second study focused on peroxide and pH values appropriate for two-part hair dye applications. Most of the discussion of this presentation will focus on the second study. Four cross-linked acrylic acid polymers, as well as a liquid acrylic associative polymer, were evaluated in the second study. Several commercial sources of hydrogen peroxide were used in the study at a concentration of 6.0 $\%_{wt}$. The gels were made at three pH values: 2.7 (no neutralizer), 3.6, and 4.0. As before, ammonium hydroxide was used to adjust the pH of the gels.

Thickening Polymers:

The polymers used in the study will be referred to as Polymer A, B, C, D, and E (fig. 1). All polymers were used at 1.0 $\%_{wt}$ active solids level in the peroxide gels in both studies.

Hydrogen Peroxide:

Four types of commercially available hydrogen peroxide were evaluated in the two studies: Peroxide A and C are standard personal care grades, peroxide B and D are specially stabilized grades. They will be referred to in this study as Peroxide A, B, C, and D.

Formula and Procedure:

A standard 6 $\%_{wt}$ active hydrogen peroxide gel formula and preparation procedure were used for both studies. Samples were made in plastic beakers and mixed with plastic stirrers. The test formula was made in the following order and consisted of the following: Deionized water 87.0 %, polymer 1.0 %, hydrogen peroxide (50%) 12.0%, ammonium hydroxide (29.9 %) q.s. to desired pH (by weight).

Accelerated Aging of Samples:

Triplicate samples of the peroxide gels were placed on stability at room temperature and at 45° C in opaque polyethylene containers. Samples were tested at intervals of 1, 2, 4, 8, and 12 weeks. Samples were evaluated for the following properties: pH, viscosity (Teflon coated spindles were used), % active peroxide, and appearance. The active peroxide was determined using the USP monograph assay for hydrogen peroxide (potassium permanganate titration). The peroxide gel samples were also tested for peroxide stability using an industry accepted peroxide "boil test".

Application Testing of Samples:

1. High pH Viscosity Response: To test the high pH thickening efficiency of the peroxide gel samples, 5% $_{wt}$, ammonium hydroxide was added to each sample to achieve a pH of 10.0. The pH, viscosity, and appearance of each sample was recorded after 3 minutes.

2. Two-Part Mock Hair Color Formula: In order to test if the hydrogen peroxide gels would respond appropriately in two-part permanent hair color applications, a "mock" formula test was performed on each sample. The test was as follows: Equal portions of Part B was added to Part A and mixed. The polymer concentration in the final mixture was 0.5% $_{wt}$. The appearance, pH, and viscosity measurements were recorded after mixing at 3 minutes.

Formula: Part A: Hydrogen Peroxide (6 % $_{wt}$) Gel Phase (1 % $_{wt}$ polymer)
Part B: High pH phase (8 % $_{wt}$ ammonium hydroxide)

3. Commercial Hair Dye: In order to test if the peroxide gel samples would thicken in an actual two-part hair dye application, five commercial permanent hair dyes were purchased. The "peroxide developer sample" made with Polymer D (pH 2.7) was selected to mix with the color phase of each commercial hair dye sample because of the data obtained from the previous two experiments.

Results:

Accelerated Stability Testing Results:

1. Study I: The hydrogen peroxide stability in the gel samples after 24 weeks of accelerated stability at 45° C showed no loss of hydrogen peroxide over time, except when a high level of hydrogen peroxide (12.0 % $_{wt}$) and a high pH (4.5) was combined, where only about 4 % loss occurred (data will be shown in presentation). The viscosity was also very stable in most samples until week 16, when some viscosity loss occurred. This viscosity loss only occurred in samples with a high level of peroxide (12.0 % $_{wt}$) and/or a high pH (4.5).

2. Study II: The initial viscosity of the peroxide gels made in this experiment (as seen in fig. 2) is directly related to pH. Gels made with the cross-linked acrylic acid polymers have a low viscosity at a pH of 2.7 and a hazy appearance. Gels made at pHs of 3.6 and 4.0 are a very viscous clear gel while the associative thickener (polymer E) did not thicken at any pH (see fig. 2). At the current writing of this article, we have completed 8 weeks of accelerated stability at 45° C of the peroxide gel samples. The accelerated stability of the hydrogen peroxide samples shows no loss of hydrogen peroxide (see fig. 3). The viscosity results of the gel samples made with peroxide "A" shows no loss of viscosity at a pH of 2.7, but do show some viscosity loss at pH values of 3.6 and 4.0 after 8 weeks of accelerated stability (see fig. 4 & 5).

Application Testing Results:

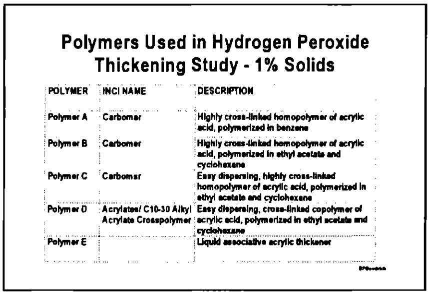
1. High pH Viscosity Response: Appearance, viscosity, and pH values were recorded after the addition of 5 % $_{wt}$ ammonium hydroxide to the peroxide gel samples. The pH for all samples was 10.0 +/- 0.1. The viscosity of the neutralized cross-linked acrylic acid gels ranged from 1,000 - 18,500 cP (measured after 3 minutes), while the gels made with a liquid acrylic associative polymer only attained viscosities of 55 - 1070 cP. Samples made with Polymer D resulted in the highest viscosities (see fig. 6). The neutralized gels appeared hazy except those made with Polymer D, which were very clear.

2. Two-Part Mock Hair Color Formula: Part A and Part B were mixed together as described above. The pH of all samples resulted in 9.9 +/- 0.1. The viscosity of the cross-linked acrylic acid neutralized gels ranged from 85 - 6,200 cP (measured after 3 minutes), while the gels made with a liquid acrylic associative polymer only attained viscosities of 10 - 25 cP. Samples made with Polymer D again resulted in the highest viscosities and best clarity.

3. Commercial Hair Dye: Five dark brown commercial permanent hair dyes were mixed according to their directions. The dye phase from each of these commercial hair dyes was also mixed at a 50/50 ratio with the "peroxide developer sample" made with Polymer D (pH 2.7). Viscosity and pH of the dye mixtures were all measured after 3 minutes. The pH values of the standard and test sample mixtures were very similar. The "Polymer D developer" produced much higher viscosities compared to that of the standard in most hair colors that were tested. For example, the viscosity of the hair dye "A" mixture was 1,230 cP (standard) and 7,470 cP (Polymer D developer).

Conclusions:

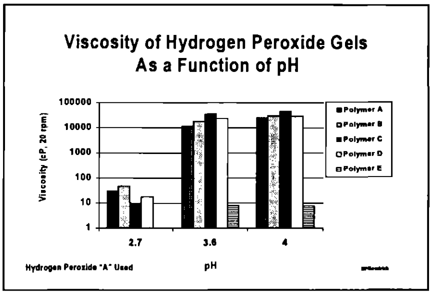
From the results of this study, it has been demonstrated that cross-linked acrylic acid polymers are very stable in peroxide containing systems and are an ideal thickener for two-part permanent hair dye applications. In particular, we recommend Polymer D, which is an easy dispersing acrylic acid copolymer, because of its efficient viscosity building characteristics and clarity when exposed to high pH environments. Polymer D has a very low dispersion viscosity at low pH (2.7), which is ideal for a low viscosity peroxide developer phase, but can also make a stable viscous gel at a pH of 3.6, which is ideal for a hair bleach gel application. Polymer D is an excellent choice to thicken peroxide-containing systems with or without surfactants, unlike the associative thickener studied here that may only thicken at a very high polymer concentration or in combination with other surfactants. In addition, cross-linked acrylic acid polymers offer the following advantages: capability to buffer pH, vertical cling (no-drip rheology), shear-thinning properties, and no odor.



Polymers Used in Hydrogen Peroxide Thickening Study - 1% Solids

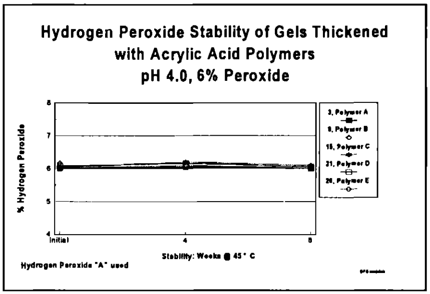
POLYMER	INCI NAME	DESCRIPTION
Polymer A	Carbomer	Highly cross-linked homopolymer of acrylic acid, polymerized in benzene
Polymer B	Carbomer	Highly cross-linked homopolymer of acrylic acid, polymerized in ethyl acetate and cyclohexane
Polymer C	Carbomer	Easy dispersing, highly cross-linked homopolymer of acrylic acid, polymerized in ethyl acetate and cyclohexane
Polymer D	Acrylates/ C10-30 Alkyl Acrylate Crosspolymer	Easy dispersing, cross-linked copolymer of acrylic acid, polymerized in ethyl acetate and cyclohexane
Polymer E		Liquid associative acrylic thickener

Fig. 1



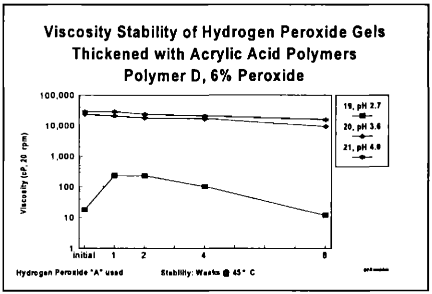
Viscosity of Hydrogen Peroxide Gels As a Function of pH

Fig. 2



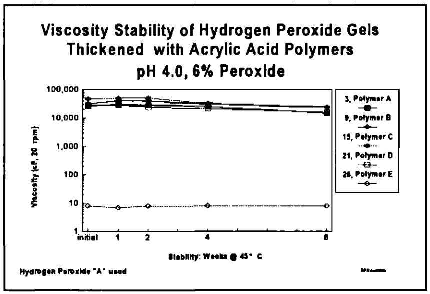
Hydrogen Peroxide Stability of Gels Thickened with Acrylic Acid Polymers pH 4.0, 6% Peroxide

Fig. 3



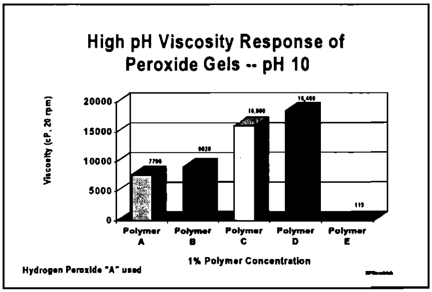
Viscosity Stability of Hydrogen Peroxide Gels Thickened with Acrylic Acid Polymers Polymer D, 6% Peroxide

Fig. 4



Viscosity Stability of Hydrogen Peroxide Gels Thickened with Acrylic Acid Polymers pH 4.0, 6% Peroxide

Fig. 5



High pH Viscosity Response of Peroxide Gels -- pH 10

Fig. 6

EVALUATION AND TREATMENT OF SENSITIVE SKIN
A MULTI-FACETED APPROACH

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Esteè Lauder Laboratories, Melville, NY 11747

Introduction:

Users of cosmetic products, often perceive their skin to be "sensitive", as they experience transient adverse reactions such as itching, burning, redness, and in some cases edema. Although some of these adverse effects do not qualify as sensitive skin reactions, we believe it is necessary to understand the etiology of these cutaneous responses, in order to develop products which not only will be milder, but in addition will reduce the reactivity of the real "sensitive skin".
To be able to create such technology, it is necessary to understand the mechanisms of the processes leading to skin sensitivity, and to develop the methodologies which will allow the accurate measurement of the factors involved in the development of a cutaneous reaction.

Skin sensitivity can be evaluated on the basis of three different parameters:
Skin permeability which is controlled by the barrier function of the Stratum Corneum, skin immune reactivity which dictates what type of reaction is going to take place (irritant or allergic), and skin neuro-sensory response.
We propose to first review the correlation between these three factors and the development of sensitive skin. We then will review the most recent technologies available to control these factors in order to reduce significantly the reactivity of the skin to the environment.

The etiology of sensitive skin:

One of the most important cause of a cutaneous reaction, is certainly the disruption of the skin's barrier function. Even if this factor alone cannot account for all the different aspects of sensitive skin, it remains certainly one of the most common factor leading to the development of chronic, sensitive skin.

To evaluate such correlation, we measured the Trans Epidermal Water Loss on the facial cheek area of a group of individuals with sensitive skin, after removal of successive layers of the stratum Corneum using adhesive tape. The results clearly showed that it took significantly less strips to destroy the barrier function of the individuals with sensitive skin compared to a group with normal skin.

Similarly, measurements of the skin reactivity (blood flow), clearly separate the sensitive from the non-sensitive populations, showing a clearly distinct reaction to an irritant between the two groups.
Additional measurements done in-vivo after application of Methyl nicotinate on the skin, showed a significant increase in the release of two key inflammatory mediators, Arachidonic acid and Prostaglandin E2, providing some additional insight on the possible mechanism behind the previously observed increase in blood flow.
Similar conclusions were obtained as far as the neuro-sensory response is concerned as the group with sensitive skin experienced a stronger stinging reaction to lactic acid than the population with normal skin.

Treatment of sensitive skin:

The diversity of the causes of a skin reaction makes the treatment of sensitive skin a fairly complex matter. It is obvious, that an efficient therapy should include various technologies which will simultaneously improve the skin's barrier function, reduce the reactivity of the skin's immune system, and finally modulate the neuro-sensory response of the skin.

We intend to review in the first place, some of the technologies which strengthen the barrier function of the Stratum Corneum, resulting in a significant reduction of the skin reactivity. We will then present the different aspects of the modulation of various inflammatory mediators such as PLA2, PGE2, IL1, TNFalpha, as well as the impact of the control of leukocyte adhesions to endothelial cells. We will describe the role played by anti-oxidants in reducing the impact of lipid peroxidation on the cascade of inflammatory reactions. We will finally present some interesting technologies aimed at the control of phosphodiesterase to increase cAMP levels in monocytes.
To conclude this review, we will look at the correlation between each of these variables and the clinical signs of skin sensitivity. We will review the effect of various anti-inflammatories, phodiesterase inhibitors, adhesion inhibitors, and anti-oxidants on the clinical manifestation of sensitive skin.

Conclusion:

Due to the complexity of the sensitive skin reactions , it becomes obvious that only a multi-faceted therapy will be able to control this condition.
The understanding of the etiology of sensitive skin, as well as the development of cosmetic products based on the technologies described in this review, allows us not only to provide relief to those consumers experiencing regularly sensitive skin reactions, but in addition, to create products which are perfectly compatible with a large variety of skin conditions.

EXPLORING THE RELATIONSHIP BETWEEN FACIAL SEBUM LEVEL AND MOISTURE CONTENT

Louis B. Fisher Ph.D.
Mary Kay Holding Corporation

A common perception is that a direct relationship exists between sebum and moisture content, implying that sebum may somehow moisturize the skin, maybe by preventing water loss. To test the accuracy of this concept, a group of 60 women was studied aged from 20 to 60. They were asked to cleanse their faces using their normal procedure prior to coming to the laboratory, but apply no other product, including moisturizers, facial makeup, sunscreens, etc. Two to three hours after cleansing, individuals were equilibrated to 20°C and 40% RH for 15 minutes. Four sites (forehead, cheeks, jawline and chin) on the face were evaluated for moisture (Novameter^{TM}) and oil levels (Sebumeter^{R}). A notation was also made of the person's opinion as to their own skin type, showing a distribution of 35 people with normal to oily skin; 12 with normal to dry skin; 6 with normal skin and 7 with oily/dry combination skin.

Combining data from all individuals resulted in remarkably little variation being seen across the face in terms of moisture (120.05 ± 5.9), although there was some suggestion of a t-zone distribution, particularly in certain individuals. In contrast, a clear-cut t-zone distribution resulting in a large variation across the face was seen for sebum values (65.7 ± 44.4). It was also apparent that the moisture level found in the different groups was very similar (fig.'s 1-4). In other words the individual's perception of dryness did not seem to be reflected by differences in instrumental measurements.

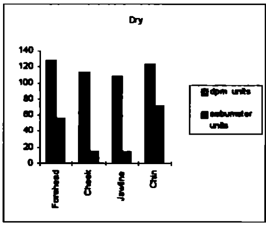

Fig. 1

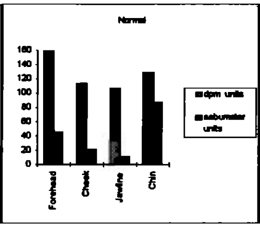

Fig. 2

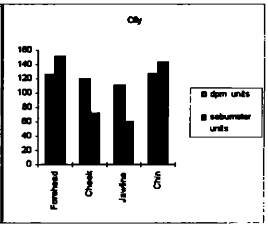

Fig. 3

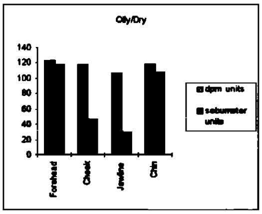

Fig. 4

This supports a similar conclusion made by Laufer & Dikstein (1). The levels of sebum on the other hand, although they were similar between the dry and normal groups, showed a considerably higher level in the oily group. The sebum level of the combination skin group was intermediate between the dry/normal and oily groups.

In a further study, 20 women selected at random, were asked to apply a light moisturizer to just one side of the face following baseline measurements of sebum and moisture from both sides of the face. Two and six hours later (i.e. 4 and 8 hours after cleansing) panelists returned to the laboratory and following equilibration, sebum and moisture measurements were repeated. On the side of the face without moisturizer, the skin moisture level stayed relatively constant. On the other hand, the skin surface sebum level increased somewhat during the day (fig. 5-7) at all sites measured. The t-zone pattern remained throughout the study with the forehead and chin levels being higher than those for the cheek and jawline. It was also noted, on an individual basis, that the perception of oiliness or dryness was not related to the actual level of sebum detected instrumentally. Indeed some subjects in the oily groups had sebum levels no higher than some subjects claiming to have dry skin. Apparently a high oil level for one person would not be excessive for someone else. This might explain a certain degree of incorrect selection by consumers, when faced with an unfamiliar product.

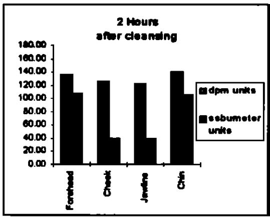

Fig. 5

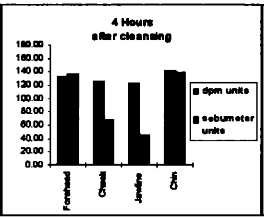

Fig. 6

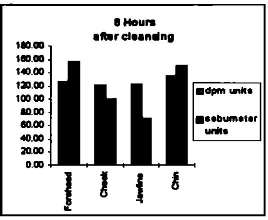

Fig. 7

Application of a light moisturizer in the morning increased the average moisture level 2 hours later by 31% (fig.'s 8-9). Some of this increase in moisturization occurred at all facial sites. After a further 4 hours this moisture level had decreased somewhat, but was still 14% above the baseline levels (fig. 10). However, as with the untreated side, the sebum levels continued to increase throughout the day. These data suggest that the moisturizer effect is independent of the level of sebum.

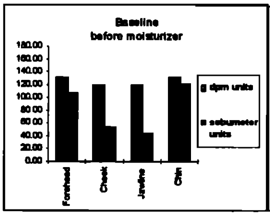

Fig 8

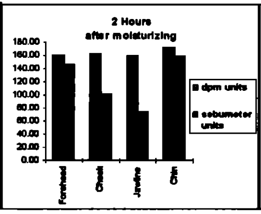

Fig 9

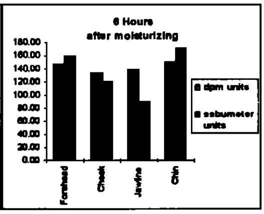

Fig 10

It is concluded that the perception of skin type is due more to variation in surface oil than a variation in moisture level. In addition, the lack of correlation between moisture and sebum levels suggest that sebum may not be serving as a defense against skin dehydration; and a high level of sebum does not influence the effect of a light moisturizer. These results also suggest that individual perception of skin type may not always result in correct product usage.

1. Laufer A. & Dikstein, S., *Cosmetics & Toiletries*, **111,** 91-98, *1996*

MODULATION OF INFLAMMATORY REACTION IN THE SKIN: A NEW APPROACH IN THE TREATMENT OF PREMATURE AGING

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Abstract:

The human skin is permanently challenged by prooxidative events generated exogeneously by the environment (UV light, smoke), and endogenously by the reaction of the skin's own immune reaction: inflammatory reactions. A significant amount of research has been done over the past years, showing the interest of an anti-oxidant therapy to control the pace of the premature aging process. However, very little work has been done so far to evaluate the activity a topical treatment containing anti-inflammatory compounds in protecting the skin from the damages resulting from the over reaction of the immune system. We propose to review the role played by the inflammatory reactions in the development of the premature aging process, and then to present the available technologies which allows to reduce significantly the progress of inflammatory reactions in the skin.

Introduction:
The human skin is constantly exposed to environmental insults that challenge it's integrity and function. These insults are in themselves damaging to the skin structure but they also precipitate the immensely complex inflammatory reaction that also if in excess will degrade and atrophy the tissue. Contributing to this wasting induced by the insult is the poor repair function observed in chronically aged skin that limits the replacement of extracellular matrix and cells. We theorize that the struggle between anabolic and catabolic forces will shift with increasing age and result in a more catabolic nature. Therefore the tissue will degrade both from external and internal drives. The cosmetic appearance of aging skin is due to these forces.

Methods:
Antioxidant ability was measured using a liposome oxidation method. Liposomes composed of phosphatidylcholine are irradiated with UVB or UVA light from Philips FS40 bulbs. In vitro Assays: Arachidonic acid release was monitored by prelabeling for 24 hours followed washing free unincorporated label. After UV irradiation samples of media are counted in scintillation counter.
Interleukin-1alpha and TNF-alpha release are measured using commercial available ELISA kits on supernatants from culture media. Collagenase activity was measured using N-2,4 dinitrophenyl-pro-leu-gly-leu-trp-ala-D-ard-amide. This substrate is converted to a fluorescent product which is measured at 360 nm after excitation with 280 nm (1). Elastase activity was measured using the fluorescent substrate N-methyoxysuccinyl-ala-ala-pro-val-amido-4-methyl coumarin (2). Human leukocyte elastase (Sigma Co.) was used in reaction. Enzyme reaction was monitor using fluorescent excitation at 370 nm and emission at 470 nm.

Results: UV irradiation of both human skin and artificial skin grown in the lab demonstrated increased levels of lipid peroxidized. Figure 1 shows that 100 mJ/cm2 of UVB increased the amounts of TBA reactive material (lipid peroxides) over time in human skin models. This increased lipid peroxidation was reduced if skin models were pre- and post- UVB treated with antioxidant mixture of 1% vitamin E and 1% vitamin C.

Figure # 1

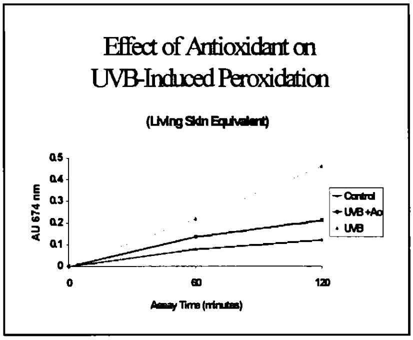
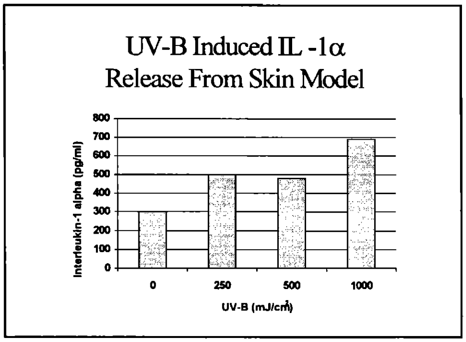
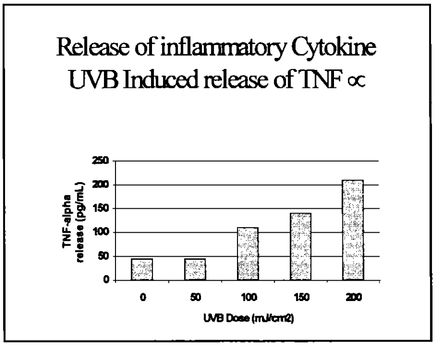


Figure # 2



Human skin has been observed to release interleukin-1 alpha after being irradiated with UV light (3). We have observed similar release of interleukin-1alpha from skin models after UVB irradiation (figure # 2). 250 mJ/cm, 500 mJ/cm2 and 1000 mJ/cm2 increased the media levels of interleukin-1 alpha from 300 pg/ml to 500 pg/ml 475 pg/ml and 675 pg/ml, respectively.



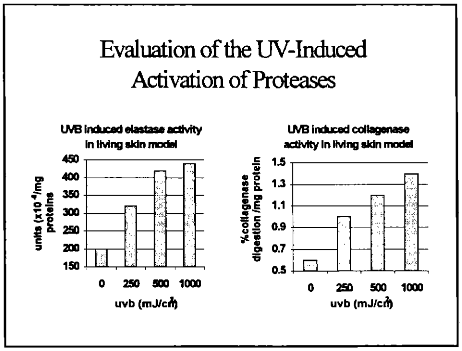


Figure # 3 Figure # 4

Tumor necrosis factor alpha (TNF alpha) has also been shown to be released from human skin (4). We observed release from skin models in culture after treatment with UVB doses of 0 - 200 mJ/cm2 (figure # 3). Both interleukin-1 alpha and TNF alpha have catabolic functions in that they cause the degradation of various tissues and extracellular matrix (5).

We observed that UVB increase the enzymatic activity for collagenase and elastase in extracts from human skin models (Figure #4). UVB doses of 250 mJ/cm2, 500 mJ/cm2 and 1000 mJ/cm2 in collagenase activity between 1.5 - 2 fold over unirradiated controls. Elastase activity was increased by 2 fold at the highest doses of UVB.

Conclusion:

The inflammatory response of human skin to various environmental insults, such as UV light or cigarette smoke, results in the release of messengers with detrimental effects. Interleukin-1 and TNF alpha are well know to increase the catabolic metabolism of a tissue. These inflammatory cytokines will contribute to the degradation and atrophy characteristic of photoaged skin. In addition, UV and environmental pollutants activity the catalytic enzymes ,collagenase and elastase, that will directly cause atrophy and tissue degradation of exposed skin. Therefore a successful cosmetic intervention for photoaging or premature aging must address this catabolic pathway at multilevels to suppress the detrimental effects. The treatment cosmetic design should incorporate the benefits of antioxidants, protease inhibitors, and inflammatory cytokine release inhibitors.

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SKIN-MOISTURIZING EFFECT OF POLYOLS AND THEIR ABSORPTION INTO HUMAN STRATUM CORNEUM

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Introduction

Lack of water in stratum corneum results in dry and scaly skin. Humectants in skin-care cosmetics play an important role in the moisturizing of stratum corneum. It is well known that glycerol has excellent skin-improving effects as a humectant. Bissett and McBride demonstrated the skin-conditioning effects of glycerol on human and pig skin.[1)] Batt et al. reported on the skin improving benefits of glycerol.[2)] Rowlings et al. suggested the important role of glycerol for enhancing desmosome degradation of stratum corneum.[3)] However, systematic investigation on the distribution of glycerol in stratum corneum and its skin-moisturizing effect had not been conducted. In this work, we investigated (1)the adsorption of polyols in stratum corneum and (2) its skin-moisturizing mechanism.

Experimental

Materials:

Glycerol, 1,3-butylene glycol, dipropylene glycol, erythritol and diglycerin were selected as a model of humectant of polyol and purchased from Tokyo Chemical Industry (Tokyo, Japan).

Evaluation of skin-moisturizing effect:

Healthy male volunteers were selected for this study. In each individual, 3 or 4 sites of the forearm skin were treated with polyol aqueous solutions. The skin-moisturizing effect was evaluated by skin surface conductance, measured with a high-frequency impedance meter, SKIKON-200 (IBS, Hamamatsu, Japan). These measurements were performed at 23°C and 50% RH. In order to avoid the influence of residual humectant, perspiration, and sebum, the skin surface was washed with water and soap 30 min before the measurements.

Penetration study of humectants into stratum corneum:

Repeated tape-strippings were carried out on the skin treated with polyol aqueous solutions. The weight of collected stratum corneum was estimated from measurement of weight of a sheet of adhesive tape before and after the tape-stripping. The humectant was extracted with methanol from stratum corneum on the tape and analyzed by gas-chromatography.

Hygroscopicity of polyols:

Water content of the humectant at various relative humidity was measured with Karl Fischer's method.

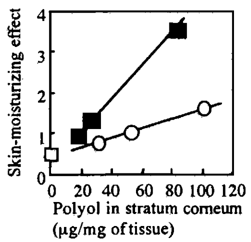

Fig. 1 The relationship between skin-moisturizing effect and absorbed polyol The closed square (■) represents glycerol; the open circle (○), dipropylene glycol; the open square (□), untreated control. Skin-moisturizing effect (y-axis) was evaluated from following equation.

$$\text{Skin-moisturizing effect} = \frac{\text{Skin surface conductance after application}}{\text{Skin surface conductance before application}}$$

The lines were regression line, which was caluclated from data points.

Results and Discussion

In vivo skin-moisturizing effect and amount of polyol absorbed in stratum corneum:

Fig. 1 shows the relationship between skin-moisturizing effect of glycerol or dipropylene glycol and its amount of humectant in stratum corneum for. The skin-moisturizing effect increased linearly with the amount of absorbed humectant in stratum corneum in both cases. If the delivered amount of both humectants in stratum corneum was the same, the skin-moisturizing effect of dipropylene glycol was smaller than that of glycerol. The result shows that the moisturizing effect depend on the hygroscopicies of humectants. These results suggested that skin-moisturizing effect was due to the amount of polyols in stratum corneum and its hygroscopicity.

Time dependence of concentration profile of polyol in stratum corneum:

In the case of one time application with 50% glycerol and dipropylene glycol aqueous solutions by a glass tube(3.2 cm inner diameter) for 30 min to the skin, skin-moisturizing effect of glycerol was comparable to that of dipropylene glycol 30 min after the application. Although the effect of dipropylene glycol decreased with time, no remarkable decrease of the effect of glycerol was observed. In order to clarify this difference, we investigated the time dependence of concentration profile of polyol in stratum corneum the changes in concentration profile of polyols with time. Fig. 2 demonstrates the polyol concentration profile across the stratum corneum at 0, 1, and 6 h after the application. The x-axis, which indicates the integrated weight of stratum corneum obtained by tape-stripping, corresponds to the depth of horny layer. Amount of absorbed dipropylene glycol at various depth of stratum corneum immediately after application was greater than that of glycerol, but decreased rapidly with time. However, the amount of glycerol absorbed at various depth of stratum corneum showed no change with time. These results indicate that decrease in skin-moisturizing effect of dipropylene glycol with time is due to its disappearance from stratum corneum.

Accumulation of humectant in stratum corneum:

After the application twice a day for 10 days by the above method, the concentration profile of dipropylene glycol in stratum corneum and the skin-moisturizing effect had no remarkable change. On the other hand, glycerol was accumulated in stratum corneum upon the continuation of use for 10 days with showing its skin-moisturizing effect.

When 20 mL of 10 % glycerol aqueous solution was applied twice daily for 10 days to 20 cm^2 forearm skin and then stopped to apply, glycerol concentration profile in stratum corneum and skin-moisturizing effect were investigated. Maximum concentration of glycerol in stratum corneum was approximately 20-30% of weight of stratum corneum, and skin-moisturizing effect corresponded to the amount of absorbed glycerol in stratum corneum.

Conclusion

These results suggested that (1) the skin-moisturizing effect depends on the amount of absorbed humectant and their physico-chemical property in stratum corneum and (2) the excellent skin-moisturizing effect of glycerol is due to the high accumulation of glycerol in stratum corneum.

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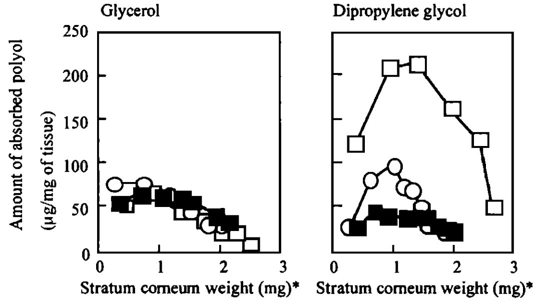

Fig. 2 Concentration profile of polyol in stratum corneum at 0, 1, and 6 h after application The open square (□) represents the amount of polyol in stratum corneum immediately after application; the open circle (O), that after 1 h; the closed square (■), that after 6 h. The asterisk (*) indicate the integrated weight of stratum corneum obtained by tape-stripping and correspond to the depth of horny layer.

MEASUREMENT TECHNIQUES LEADING TO IMPROVED ON-HAIR PERFORMANCE OF LOW VOC HAIR SPRAYS

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INTRODUCTION

The California Air Resource Board (CARB) and other State agencies are moving to reduce the volatile organic compound (VOC) emissions generated by cosmetic and household products, in order to improve air quality. As the VOC content of hairspray formulations in the U.S. are lowered from ~95% in the early 1990's to 55% VOC by June 1, 1999, a great effort has been undertaken by formulators and raw material suppliers to maintain the proper performance properties[1]. The most cost effective low VOC formulations involve the replacement of organic solvents with water. Unfortunately, water has a deleterious effect on just about every property that is critical to hairspray performance[2-4]. Optimization of low VOC formulations requires a detailed knowledge of the correlation between the formulation physical properties and the on-hair performance properties.

In this presentation, the relationship between fundamental physical / surface chemistry with hairspray performance will be discussed. Objective testing methods will be used to demonstrate the importance of physical properties such as wetting, viscosity, dynamic surface tension, pH, and polymer composition on performance properties such as spray aesthetics, drying time, hold, stiffness, and corrosion.

RESULTS AND DISCUSSION

WETTING:

For a hairspray to perform optimally the formulation must coat adjacent hairs and create a bond, which results in the properties of hold and stiffness. The length, continuity, adhesion and toughness of this bond contributes to the effectiveness of the formulation. Anhydrous hairsprays of the past had excellent wetting, with a contact angle between the formulation and hair that approached 0°. As the water content is increased, to attain low VOC formulations, the contact angle increases and wetting along the hair is hindered. In order to maximize performance, contact angle must be minimized.

Capillary wicking is another wetting mechanism for the formation of hair/polymer bonds. This phenomenon is also maximized by low viscosity and contact angle. Wicking was measured by plotting weight gain of a hair bundle, in contact with a hairspray formulation, over time. In high water, low VOC systems dioctylsulfosuccinate resulted in large increases in wicking rates.

***VISCOSITY*:**

High viscosity will impede the sprayability , flow out and film formation of a formulation on hair. Unfortunately for the formulator and ultimately, the consumer, high water 55% VOC systems tend to result in the highest viscosity compared to higher VOC and alcohol-free systems. Lower molecular weight polymers are usually employed to counter this problem. However, these polymers tend to result in more brittle films and less hold compared to their higher molecular weight analogues. The use of additives and well designed blends of polymers have proven to be effective in approaching an optimum system.

DYNAMIC SURFACE TENSION:

Dynamic surface tension reduction is critical in achieving acceptable spray aesthetics. Although surface tension is mainly influenced by the solvent system (ie: amount of water in the formulation), additives can be employed that minimize the problem. The surface tension reducing agent must be able to migrate extremely quickly to the air / liquid interface in order to be effective. The Kruss BP2 bubble tensiometer was used to demonstrate that cyclomethicone is a superior additive to address this problem.

pH:

The formulation pH and ionicity greatly affects the corrosivity of dimethyl ether / water systems toward tin plated steel cans. Polymer systems below a pH of 7.5 are more corrosive than those above that pH. Polymer composition and neutralization were examined relative to corrosion potential.

POLYMER COMPOSITION:

Polymer composition, molecular weight, neutralization and Tg were examined for their effect on solution surface tension and viscosity, film toughness, and on-hair stiffness. The use of inorganic neutralization agents and polymer molecular weight had the largest impact on stiffness. Polymer molecular weight and composition had the largest effect on polymer toughness and viscosity. The hair fixative polymer identified by the INCI name of Acrylates Copolymer (butyl acrylate/methyl methacrylate/methacrylic acid) was used as the control in these experiments.

CONCLUSIONS:

For the hair spray formulators in and the suppliers to the hairspray industry, it is obvious that in order to achieve water-containing hair sprays having performance which approaches that to which the consumer is accustomed, a thorough understanding of the physical and chemical mechanism of hair spray effectiveness is required. These studies have taken into account all aspects of the hair spray system. This understanding has being obtained through the development of new and applied analytical techniques and fundamental studies. Preliminary results have given indications of how to approach these difficult formulation problems.

In order to optimize the performance of water-containing low VOC hair sprays; the number, strength and length of the polymer bond between hair fibers must be maximized. One method to achieve this was to maximize the flow of the formula once sprayed onto the hair. It has been shown that flow can be increased by reducing the viscosity and contact angle of theformulation liquid on hair.

Polymer composition is an extremely important parameter in achieving the optimum system the polymer predominantly controls the spray aesthetics, stiffness, long term holding power, feel characteristics, and corrosivity. Several additives were identified which also aid in optimizing the desired performance.

The ideal high water low VOC hairspray systems must be built from the ground up taking advantage of the newest technology in all formulation aspects. Polymer, solvent, propellant, additive, and delivery system must be optimized interdependently to achieve a hairspray which will satisfy a discerning consumer.

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CHARACTERIZATION OF ANTIPERSPIRANT ACTIVES USING SIZE EXCLUSION CHROMATOGRAPHY AND LIGHT SCATTERING DETECTION

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Introduction

Size Exclusion Chromatography (SEC) has been successfully applied to characterization of antiperspirant actives in terms of their polymer distributions (1). This information was crucial for fully understanding the chemistry of antiperspirant actives with subsequent development of high performance (enhanced efficacy) actives which were synthesized and manufactured to contain particular polymer distributions which enhanced clinical performance (2, 3, 4). Not withstanding the success of SEC it still remains difficult to obtain accurate absolute molecular weight data from SEC analysis due to the lack of satisfactory "marker" compounds necessary to accurately calibrate SEC columns for the type of polymer species present in antiperspirant actives (highly charged cationic polymers). Since light scattering has been used to obtain molecular weights of polymers in solution, the idea was to combine SEC with light scattering detection to determine on-line molecular weights of the separated polymer species present in antiperspirant actives.

Methods

On-line determination of molecular weights of aluminum polymers present in aluminum chlorohydrate (ACH) actives were obtained by separating the aluminum polymers on a Sephadex G-25 (S) column followed by light scattering detection (measuring the scattering intensities) of the separated polymers using the Dawn DSP Multi-angle Laser Light Scattering Photometer (Wyatt Technology) followed by refractive index (RI) detection of the eluent stream exiting from the Dawn Photometer. Molecular weights are calculated from the scattering intensities and RI responses using the Wyatt Technology Astra program.

dn/dc values (change of refractive index versus change of concentration) of the aluminum polymers being evaluated are required for the molecular weight calculations. In the case of antiperspirant actives it is virtually impossible to isolate and measure dn/dc values for each individual polymer present in the active. Therefore, dn/dc values for the bulk solution of active is used for each of the aluminum polymers. This approximation will perturb the resultant molecular weight value of each polymer, the degree of which is dependent upon the difference between the bulk dn/dc value and the "true" dn/dc value of the individual polymer. Bulk dn/dc values were determined in separate experiments using an Optilab 903 Refractometer which is specially designed for such measurements.

Operation and calibration of the Dawn Photometer was checked by determining the molecular weight of a pullenen standard. For this work a value of 47,000 daltons was obtained which is within 2.5% of the stated value of 45,800 daltons.

Results and Discussion

Figures 1 and 2 show aluminum polymer distributions for a standard ACH active (Summit ACH-323) using light scattering and RI detection, respectively. Both profiles are similar with four distinct aluminum polymers observed. This is typical for ACH characterization using Sephadex G-25 (S) columns. The similarity in relative peak heights for both profiles indicates that the molecular weight range between peak 1 polymer and peak 4 polymer is not very large since scattering intensities are strongly dependent on molecular weight.

Table 1 summarizes SEC-light scattering results for ACH-323. Also included are literature values of molecular weight ranges for the aluminum polymers compiled from a variety of experimental techniques (5).

TABLE 1
SEC-Light Scattering Characterization of Summit ACH-323

Peak	Literature MW Ranges	MW From SEC-Light Scattering
1	5,000 - 8,000	7,600
2	3,000 - 4,000	6,000
3	1,500 - 3,000	5,000
4	500 - 1,500	2,100

As seen in Table 1 molecular weights obtained from SEC-Light Scattering are somewhat higher than the estimated literature ranges except for the peak 1 polymer which falls within the range. These differences may be due to individual dn/dc values differing from the bulk value used in the molecular weight calculations, the small scattering intensities for the aluminum polymers which can impact accuracy and the uncertainty of the literature values themselves. Further work is in progress to address the above issues.

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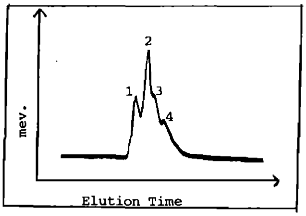

Figure 1. Aluminum polymer distributions for ACH-323 using light scattering detection.

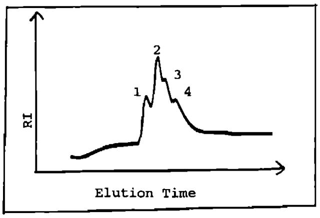

Figure 2. Aluminum polymer distributions for ACH-323 using RI detection.

RAPID PREDICTION OF EMULSION STABILITY

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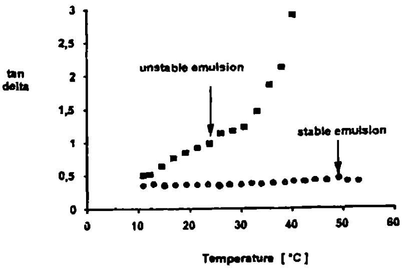
Introduction

The prevalent method for testing the physical stability of cosmetic emulsions is storage at temperature. A disadvantage of this method is the long time interval between production of the sample and the observation of any visible phase separation that would indicate instability. This time interval stretches to several weeks. Methods employing rheological or conductivity measurements can predict physical stability within 6 or 48 hours respectively after sample production, and with 100% reliability. Such methods thus offer the potential to greatly accelerate this part of the formulation development process.

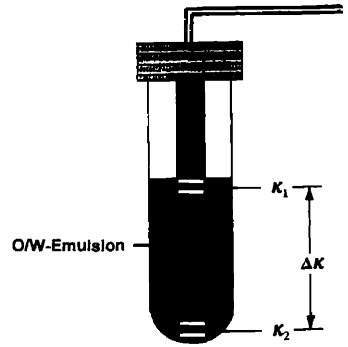
Rheological Methods

Physical instabilities such as creaming or coalescence are caused by flow phenomena in emulsions. Droplets which are unable to move through the continuous phase cannot flow together or move to the top or bottom of a container through the operation of Stokes' Law. The viscosity described by Stokes' Law is the "zero shear viscosity", i.e. the viscosity of an emulsion in the state where no structure breakdown has taken place.
To be stable, oil-in-water emulsions need to display an infinite zero shear viscosity, i.e. to display a yield stress. At very low shear rates, they behave more like an elastic solid than a viscous liquid. The forces applied to the continuous phase by the discontinuous phase due to gravity/buoyancy must be below the system yield stress. The yield stress is due to structure set up in the continuous phase by rheology modifiers or liquid crystalline gel networks.

A cone-and-plate rheometer can be used in oscillation mode to extract the magnitude of the elastic forces operating within the emulsion G' (i.e. the extent to which the emulsion is behaving like a solid), and the magnitude of the viscous forces within the emulsion G" (i.e. the extent to which the emulsion is behaving like a Newtonian liquid). These two parameters can be measured across a range of temperatures. Essentially an oil-in-water emulsion will be stable so long as, at very low shear rates, the viscous forces are less than the elastic forces, i.e. the ratio G"/G', also known as tan delta, is less than 1. The temperature at which tan delta climbs above 1 is the temperature at which phase separation will inevitably occur with time.



Determination of stability by rheological assessment



Measurement system to determine conductivity in oil-in-water emulsions

Conductivity Methods

If phase separation is occurring in an emulsion, differences in conductivity between the bottom and the top of the body of the emulsion will be detectable considerably in advance of any visual signs of phase separation. This method is applicable to both oil-in-water and water-in-oil systems.

Experiments

The above principles have been exhaustively tested on a large number of systems. However, we show some exemplary data below to illustrate the principles in operation. An oil-in-water formulation was stabilized by gradually increasing the concentration of a carbomer in the aqueous phase. For each sample, stability was assessed by:

- observation of phase separation after storage for 6 weeks at temperature
- measurement of tan delta between 0 and 60°C 4 hours after emulsion preparation
- observation of the difference in conductivity between top and bottom of the emulsion while cycling between 0 and 60°C over a 24 hour period starting 24 hours after emulsion preparation.

INCI Name	wt%
Glyceryl stearate (and) PEG-100 stearate	2.00
Caprylic/capric triglyceride	8.00
Mineral oil	4.00
Carbomer	0.05, 0.10, 0.20
Glycerin	5.00
Phenoxyethanol	0.50
Purified Water	q.s.
	100.00

0.05% Carbomer	25 deg C	40 deg C	50 deg C
Water Separation	15% vol	40% vol	60% vol
Oil Separation	no	no	no
Tan Delta	1.5	2.9	3.2
Difference in Conductivity	0.6	0.6	0.63

0.10% Carbomer	25 deg C	40 deg C	50 deg C
Water Separation	no	no	4% vol
Oil Separation	no	no	no
Tan Delta	0.35	0.58	2.2
Difference in Conductivity	0	0	0.26

0.20% Carbomer	25 deg C	40 deg C	50 deg C
Water Separation	no	no	no
Oil Separation	no	no	no
Tan Delta	0.31	0.38	0.52
Difference in Conductivity	0	0	0

TESTING SKIN CARE AND COSMETIC PRODUCTS AT HIGH RESOLUTION TO ESTABLISH COMFORT

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Introduction:

In recent years the consumer has come to expect complete comfort from skin care and cosmetic products. Gone are the days when any degree of stinging or irritation are tolerated. In order to meet this challenge, testing far beyond traditional patch tests have been developed. Traditional patch testing, such as the cumulative irritancy test, was adequate in the past but now since the standard of comfort is higher and the products are better, more rigorous tests are required to uncover even the smallest potential for irritancy. This new generation of high resolution irritancy testing involves challenging the skin, either physically or chemically before or after a product use period. By either abrogating the barrier or pre-activating the skin's immune machinery, it is possible to evaluate the potential for irritancy or discomfort at a more sensitive level.

Methods:

Tests for irritancy at higher resolution involve several different paradigms: In one instance, panelist are asked to use the product for a defined period. At the end of the use period, the skin is challenged, either physically or chemically to determine the integrity of the stratum corneum barrier. The physical challenge involves using tape stripping to determine the resistance of the barrier with respect to transepidermal water loss.

The chemical challenge involves application of an irritant and recording the neurosensory and erythemic responses. Validation of the methods was achieved by evaluating agents known to damage the barrier and create irritancy. Significant correlation was observed between panelist perception objectively measured endpoints.

Another paradigm involves damaging the barrier or activating the immune system and then applying the test agent under a variety of conditions including a semi-occlusive patch. In one approach, barrier damage is achieved by creating a scratch with a needle or tape stripping to a pre-determined degree of T.EW.L.. In the latter case, both reduction in the rate of barrier repair as well the degree of erythema generated are direct indications of the potential for irritation by the test agent.

In both cases, resolution of lower level irritants is easily achieved due to the ability of the agent or entire formula to enter into the viable epidermis. In another approach, immune system activation is achieved by pre-treating with a defined minor irritant.

Results:

In the results presented below a traditional oil in water emulsion is compared with saline in three different measures. With traditional test methods, the oil in water emulsion is indistinguishable from saline. In the more sensitive tests, these two materials are resolved.

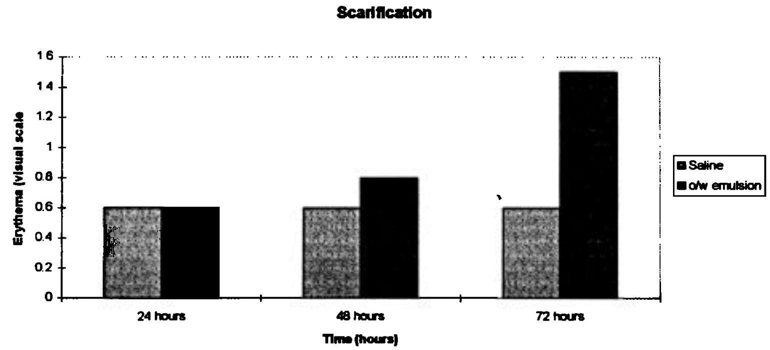
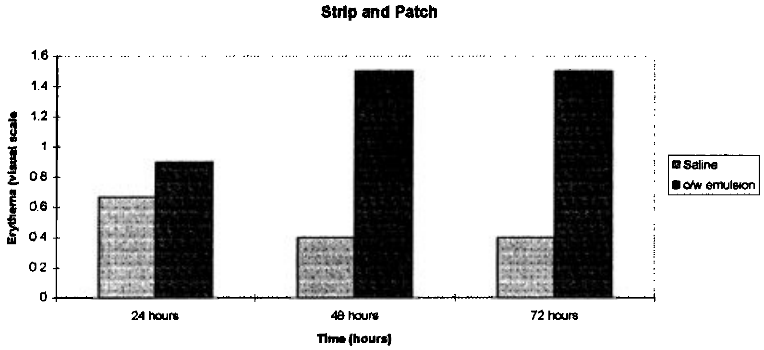


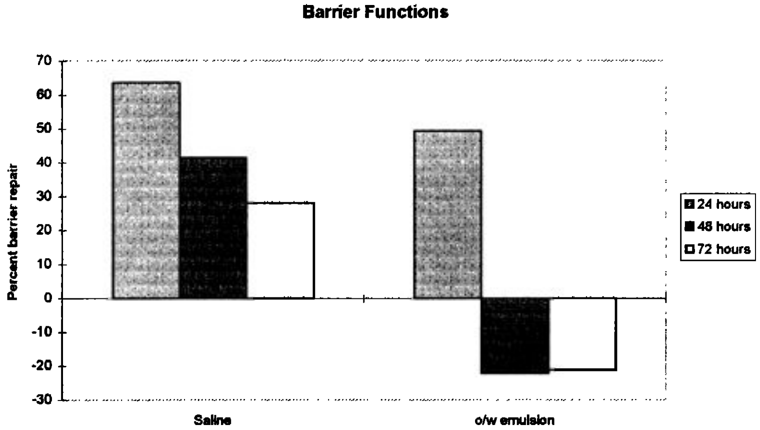
Figure 1 illustrates the results of application of the test material to lightly scarified skin. In this procedure a small gauge needle is drawn across the

Conclusion:

This more rigorous approach to testing for product comfort has proven to be highly effective and necessary for identifying consumer products that may not be satisfactory by today's extremely stringent level of acceptance. It is a reliable way to help assure consumer satisfaction with greater certainty.

skin surface to break the barrier. the surface is then treated with the test material in a semi-occluded patch and evaluated every 24 hours for a total of 72 hours.





Figures 2 and 3 demonstrate the effect of the same two materials when applied to skin that was tape stripped until the rate of transepidermal water loss reached approximately 18g/msq/hr. In this case the degree of redness is slightly increased and the rate of barrier repair is decreased due to the presence of the emulsion.

SUBSTANTIATION OF CONDITIONING CLAIMS

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Conditioning claims are made for a variety of hair products, including shampoos, conditioners, hair color products, and perms and relaxers. Claims can concern many hair attributes, and may include statements of conditioning, combing, feel, softness, shine, or resistance to damage and reduction of split ends. Substantiation of claims is specific to the claim and the product. The purpose of this paper is to review types of claims, and to provide specific examples of claims and appropriate substantiation methods.

Claims substantiation is done by finished goods companies to satisfy the legal requirement that all claims must be true and accurate. The practical purpose of substantiation is two-fold: 1) substantiation supports the products, when questioned, and 2) the outcomes of testing can assist in product development. Substantiation may be demanded by several sources, including television networks, the National Advertising Division of the Council of Better Business Bureaus (NAD), competitors, State Attorneys General, and magazines.

There are three general types of claims, two of which need substantiation. Puffery claims are either statements of opinion ("I love this shampoo"), or other statements that can't be proven, such as "We feel....". Statements about products that have a basis, however, must be substantiated. Of these, express claims are what we will concentrate on, such as "hair feels soft", " gives excellent wet combing" and "does not build up". Comparative claims also come under this group, as in "best wet combing".

Substantiation of express claims may include performance evaluations of the marketed product, made by the consumer goods company or outside labs, coupled with supplier's performance evaluations for their active materials. Objective measurements should be included, and these may be obtained through laboratory instruments or expert evaluators. Subjective measurements are the third means of substantiation, and include consumer evaluations.

At their best, claims substantiation studies are double-blind performance evaluations of the final product, they are randomized, and statistical differences are derived at the 95% confidence interval. Studies are specific, and custom-designed to address the product claims. Typically, a package of studies is assembled for a product and its attributes.

For example, performance characteristics were evaluated for conditioning polymers in shampoo formulas. These prototype shampoos were studied for efficacy and statistical differences. The performance of the polymers and delivery systems were evaluated through the objective means of : instrumental combing, dye assays for deposition and build-up, Scanning Electron Microscopy (SEM), and clinical evaluations of expert evaluators, and subjective panel evaluations.

Typical hair conditioning claims for conditioning shampoos will be discussed as examples of express claims, and studies of prototype shampoos will be given as examples of substantiation methods.

Claim 1: Excellent conditioning, or excellent wet combing.

Substantiation methods: 1) Instrumental combing, and 2) Salon test.

1) Instrumental combing An instrumental combing test was done, comparing two shampoo formulas, containing 10% SLES-EO2, plus 0.3% Guar Hydroxypropyltrimonium Chloride, (Formula A) or 0.3% Polyquaternium-10 (Formula B). Bleached hair swatches were evaluated wet with a Dia-Stron tensile tester before and after the shampoo treatments. Eight swatches were included in each set, and they were combed five times each, for a total of 40 combings on each treatment group, before and after the randomized treatments. At the 95% confidence level, Formula A significantly reduced the combing energy compared to Formula B, as seen in Figure 1. Therefore Formula A can carry a claim of excellent conditioning, if Formula B is a known conditioning shampoo in the market.

2) Salon test A randomized, double-blind half-head salon test compared two conditioning shampoo formulas. Both shampoos contained 12 % active SLES, plus Formula E contained 0.5% Guar Hydroxypropyltrimonium Chloride, and Formula G contained 0.5% Polyquaternium-10. Each formula had 120 evaluations by one expert evaluator, who blindly rated the half-heads on a scale of 1(excellent) to 5 (poor). The results for wet combing, wet hair feel, dry combing, and dry hair feel are shown in Table 1, where statistics at the 95% confidence interval showed Formula E to be superior to Formula G.

Table 1. Salon test results, for conditioning and wet combing.

Attribute	Shampoo E	Shampoo G
Wet Combing	2.7*	3.5
Wet Hair Feel	2.7*	3.3
Dry Combing	2.0*	2.3
Dry Hair Feel	2.0*	2.4

- Significantly different, better in each attribute.

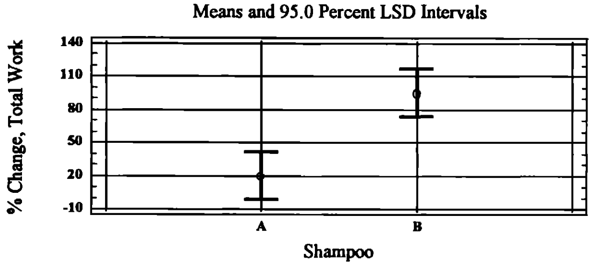

Figure 1. Instrumental wet combing results for Shampoos A and B, showing Shampoo A to be superior.

Claim 2: Makes hair soft.

Substantiation methods: 1)Salon test, and 2)Panel evaluation.

1) Salon test An expert evaluator blindly evaluated 120 half-heads treated with two conditioning shampoos. The shampoos were formulated with 14% SLES, with 0.3% active Hydroxypropyl Guar Hydroxypropyltrimonium Chloride (Formula P) or 0.3% active Polyquaternium-11 (Formula Q). The softness of the dry hair was rated on a scale of 1(excellent) to 5 (poor). In this randomized, double blind experiment, differences between the formulas were found at the 95% confidence interval, as shown in Table 2. Shampoo P was superior, and carries the claim, "Makes hair soft."

Table 2. Salon test results, for hair softness.

Attribute	Shampoo P	Shampoo Q
Softness	2.3 *	3.0

* Significantly different, better in this attribute.

2) **Panel evaluation** A double-blind panel evaluation was conducted where treated hair swatches were evaluated by 25 panelists. This subjective evaluation was conducted with a control shampoo (no active, 10% SLES-EO2) (Shampoo L), and a shampoo with 0.3% active Hydroxypropyl Guar Hydroxypropyltrimonium Chloride in this base (Shampoo J). As seen in Figure 2, Shampoo J, with the active material, made hair softer than Shampoo L, showing the contribution of the guar to hair softness.

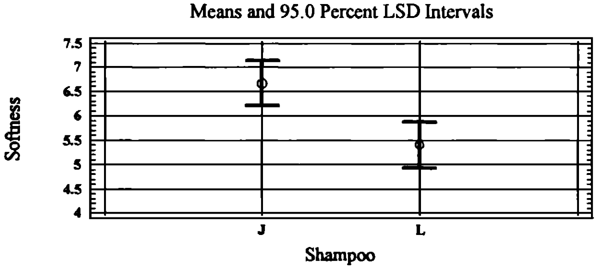

Figure 2. Softness panel ratings for Shampoos J and L, showing Shampoo J to be superior.

NEW APPROACHES IN EVALUATION OF MOSQUITO REPELLENTS

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Personal Repellents applied topically to the skin evaporate to form a vapor barrier above the skin that breaks the seeking-feeding approach of the female mosquito, thereby repelling the mosquito from the skin. Topical mosquito repellents have traditionally been evaluated by application to the skin, followed by exposure to mosquitoes over a period of hours. New approaches in evaluation of novel repellent formulations include in vitro assessment of repellent volatility and simultaneous measurement of evaporation and penetration of repellent from skin in vitro using a variation on skin permeation cells. Results from these studies have identified differences in repellency and attractancy among people and also groups of human skin emanations that repel and attract mosquitoes. Several combinations of these naturally occurring skin emanations have demonstrated repellency comparable to the most common repellent compound, N,N-diethyl-m-toluamide.