Skin moisturization by hydrogenated polyisobutene— Quantitative and visual evaluation

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Synopsis

Hydrogenated polyisobutene (HP) is used in topically applied cosmetic/personal care formulations as an emollient that leaves a pleasing skin feel when applied, and rubbed in after application. This effect, although distinguishable to the user, is difficult to define and quantify. Recognizing that some of the physical properties of HP such as film formation and wear resistance may contribute, in certain mechanisms, to skin moisturization, we designed a short-term pilot study to follow changes in skin moisturization. HP's incorporation into an o/w emulsion at 8% yielded increased viscosity and reduced emulsion droplet size as compared to the emollient ester CCT (capric/caprylic triglyceride) or a control formulation. Quantitative data indicate that application of the o/w emulsion formulation containing either HP or CCT significantly elevated skin moisture content and thus reduced transepidermal water loss (TEWL) by a maximal ~33% against the control formulation within 3 h and maintained this up to 6 h. Visual observation of skin treated with the HP-containing formulation showed fine texture and clear contrast as compared to the control or the CCT formulation, confirming this effect. As a result of increased hydration, skin conductivity, as measured in terms of corneometer values, was also elevated significantly by about tenfold as early as 20 min after HP or CCT application and was maintained throughout the test period. Throughout the test period the HP formulation was 5-10%more effective than the CCT formulation both in reduction of TEWL as well as in increased skin conductivity. Thus, compared to the emollient ester (CCT), HP showed a unique capability for long-lasting effect in retaining moisture and improving skin texture.

INTRODUCTION

The upper layer of the skin, the stratum corneum (SC), holds fairly low levels of water (10-20%); some is bound and some is free to evaporate. While the interface of the SC and the live epidermis is well hydrated in normal skin, the upper layer of the skin is significantly drier because of its unique structure and exposure to ambient air (1). The gradient of water through skin layers from top to lower levels plays a role in numerous skin biochemical functions. Although moisture, like nutrition to the skin, is mainly provided by deep skin layers and the circulation, one can affect moisture retention in the skin either by covering it with a film to reduce TEWL (2) or by enhancing the capacity of the skin to hold water when humectants are applied (3). Reduction of TEWL

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is shown, in turn, to improve skin barrier function, not only in normal but also in dry or irritated skin (2,4,5).

Dry skin occurs frequently as a natural disposition in individuals and upon aging, but is also oftentimes due to irritation caused by environmental factors or disease conditions such as atopic dermatitis (6). Therefore, skin care products that enhance water retention and skin moisture become important not only for cosmetic purposes but also for treating conditions such as atopic dermatitis. Depending on the type, skin care products function not only by mechanisms in which they form an inert layer on the skin, thus preventing water loss, but also in some cases by penetration and their effect on the skin structure (7). However, the methods to study their functions are limited (8,9).

Hydrogenated polyisobutene is a non-drying oil with waterproofing properties used in moisturizers (10). Its physical structure allows water retention, making it a potential candidate for a moisturizing emollient. It is a branched-chain aliphatic hydrocarbon (Figure 1) with an average molecular weight of 370, stable over wide pH ranges and even at temperatures as high as 260°C. Despite its use as a constituent in varied proportions in commercial formulations such as moisturizers (10) and lip gloss treatments (11), information about the actual effects of HP by itself on skin is not fully understood and this is the first attempt to study its isolated functions on skin hydration. For comparison we tested another commonly used emollient ester, capric/caprylic triglyceride (CCT). CCT is used in food, cosmetic and drug delivery applications, is non-toxic, and exhibits virtually no dermal or ocular irritation (12). Use of CCT in solid nanoparticles was shown to enhance entrapment efficiency of the drug Nimodipine, and varying its proportion aided in controlled release of the drug (13). Thus, in the present study, we attempt to hypothesize the mechanism of HP as a moisturizer in comparison to the emollient ester CCT, with emphasis on its effects on TEWL, skin conductivity, and skin texture.

MATERIALS

Carbomer (Noveon Inc., Cleveland OH); triethanolamine (Ruger Chemical Co., Linden, NJ); xanthan gum (CP Kelco, Atlanta, GA); and HP, CCT, phenoxyethanol, methylparaben, butylparaben, propylparaben, isobutylparaben, and glyceryl stearate (Lipo Chemicals Inc., Paterson, NJ) were used in this study.



Figure 1. Structure of hydrogenated polyisobutene.

METHODOLOGY

PREPARATION OF SEMI-SOLID FORMULATIONS

Three similar simple o/w emulsions were compared in this study. The test formulation and control contained 8% HP and 8% CCT, while the control contained neither of the emollients. Each emulsion was prepared by simple emulsification after heating the aqueous phase and oil phase to 75° -80°C (Table I).

MICROSCOPIC OBSERVATION OF EMULSIONS

Emulsions containing HP and CCT were visualized at 400× magnification using an Olympus BX60 transmission microscope (Olympus Micro Imaging Inc., PA). Emulsion droplet sizes were compared by measuring the mean diameter of the droplets and are presented in terms of relative arbitrary units.

STUDY DESIGN

Ten healthy female panelists between the ages of 35 and 54 were enrolled, of which there were eight Caucasians, one Hispanic, and one Asian. Panelists were instructed to wash the test sites with Ivory[®] soap twice daily for three days prior to the study date. On the day of the study, panelists were required to equilibrate in a closed environment with a constant temperature of 70°F and 30% relative humidity for the duration of the study. Biophysical measurements were taken using a Corneometer (Courage-Khazaka, Cologne, Germany) and a Tewameter (Courage-Khazaka), and visual photography was performed by a Charm View video microscope (Moritex USA Inc., Natick, MA). Four test site areas of 50 cm² on the right and left volar forearms were marked (two on each arm) by using a surgical pen to designate the test sites. One of the test sites was untreated skin. An amount of

Table I Composition of Tested Formulations							
Ingredient	HP (% w/w)	CCT (% w/w)	Control (% w/w)				
Water	85.12	85.12	93.12				
Carbomer	0.11	0.11	0.11				
Triethanolamine	0.17	0.17	0.17				
Xanthan gum	0.10	0.10	0.10				
Phenoxyethanol (and) methylparaben (and) butylparaben (and) propylparaben (and) isobutylparaben	1.00	1.00	1.00				
Glyceryl stearate	2.75	2.75	2.75				
Cetyl alcohol	1.25	1.25	1.25				
PEG-40 stearate	1.00	1.00	1.00				
Cetearyl alcohol (and) polysorbate 60	0.50	0.50	0.50				
Hydrogenated polyisobutene	8.00	_	_				
Capric/caprylic triglyceride	_	8.00	_				
pH	6.56	6.54	6.60				
Viscosity in cps. (LV4@12RPM)	20,000	21,000	15,000				

0.2 ml of each test product was dispensed to each test site using a 1-ml volumetric syringe. This amount was evenly applied by a technician using a finger and rubbed until absorbed into the skin. Measurements were taken on the sites prior to product application and at intervals of 20, 60, 120, 180, and 360 minutes.

MEASUREMENT OF TRANSEPIDERMAL WATER LOSS (TEWL)

The rate of water evaporation from the skin surface was measured using a Tewameter (Courage-Khazaka). This instrument is designed to follow water evaporation from the skin by applying the principle of water diffusion in an open chamber. The density of water gradient within the skin surface is analyzed indirectly by two pairs of sensors, for temperature and relative humidity. Data measured are analyzed by a microprocessor.

MEASUREMENT OF SKIN CONDUCTANCE

Moisture content in the skin was measured using a Corneometer CM 825 (Courage-Khazaka) This instrument is designed to measure skin surface hydration via capacitance measurement of a dielectric medium. This measurement can capture minor changes in hydration levels, with relatively high reproducibility in a short measurement time of around 1 sec.

DATA COMPUTATION AND STATISTICAL ANALYSIS

Sorted data for TEWL and conductance were tabulated for each time point of application of the control emulsion, HP-containing emulsion, and CCT-containing emulsion, respectively, and the means were recorded in each case. Statistics were calculated using an analysis package provided by Microsoft Excel 2003, following the recommendations of the International Federation of the Society of Cosmetic Chemists in their monograph *Principles of Product Evaluation: Objective Sensory Methods* (14). In this approach statistical significance was evaluated using a one-tailed T-test to assess net change from the baseline. Statistical significance was defined at $p \le 0.05$ (corresponding to a 95% or greater confidence level).

EFFECT OF MOISTURIZATION ON SKIN TEXTURE

The visual effect of moisturization was observed using a Charm View video microscope (Moritex). This instrument is designed to visually magnify the skin on a video screen, allowing the monitoring of minor changes in skin texture. It is equipped with a 1/3-inch CCD color-image sensor with three polarizing filters that allow for skin texture to be observed clearly.

RESULTS

We here analyzed for the first time and compared formulations consisting of HP with CCT or a control formulation, for their physical properties and their effect on TEWL and skin conductivity as a measure of skin moisturization. The results are shown below.

EFFECT OF THE EMOLLIENTS HP AND CCT ON THE PHYSICAL PROPERTIES OF THE FORMULATIONS

Both HP and CCT in o/w emulsions at 8% increased emulsion viscosity. The emulsion structure was monitored microscopically, at $400 \times$ magnification, shown in Figure 2A. This increase may not only affect the emulsion's stability, but possibly can also contribute to the microstructure of the emulsion, and hence its film formation on the skin, and can affect interaction with the skin.

Further, we analyzed emulsion droplet size, in terms of the average diameter of the droplets. HP or CCT incorporated emulsions showed a dramatically reduced droplet size of 18.58 ± 2.02 or 26.7 + 4.05 (arbitrary units), respectively, compared to the control that exhibited 65 ± 9.56 (arbitrary units) (Figure 2B). Thus HP was much more effective than CCT in the reduction of emulsion droplet size. Depending on the substance or method of study, emulsion droplet size is shown to enhance or retard the interaction properties of emulsions with the skin. Although emulsion droplet size is cited, in some instances, to be directly correlated to skin penetration (15,16), conflicting reports exist that describe the importance of the proportion of other ingredients in the formulation (17), surface charge (18), or exposure of interactive species on emulsion droplets in affecting skin penetration and causing a decrease in TEWL, thus affecting hydration. Whatever the effect of reduced emulsion droplet size on skin penetration may be, the significant reduction of droplet size upon HP incorporation compared to the control emulsion is interesting, and additional studies on its ability to penetrate or interact with skin may reveal the intricacies of its mechanism of action.



Figure 2. (A) Visualization of o/w emulsions comparing 8% HP, 8% CCT, and control, at 400× magnification. (B) Emulsion droplet size comparison.

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QUANTIFICATION OF THE MOISTURIZING EFFECT

Measurement of transepidermal water loss (2,4,5) and of increased skin conductivity (1) are useful tools in assessing the effectiveness of moisturizers in skin hydration. Hence we further analyzed the o/w emulsions HP and CCT or a control formulation for skin moisturization using these two techniques. Data presented below include the effects of HP and CCT on reduction in TEWL (Table II; Figure 3) and skin conductance (Table III; Figure 4). Mean TEWL obtained for the untreated site at each time interval was subtracted as a correction factor from the TEWL obtained for the HP- or CCT-applied site, to derive the respective corrected means. Upon application of HP or CCT there is a gradual decrease of TEWL and an increase in skin conductance with time. A maximal decrease of TEWL by 33.36% was observed with HP treatment compared to the control at the 3-h time point. This reduction was maintained for up to 6 h. It can be clearly seen that, at all time points, both HP and CCT were significantly better than the control formulation in reducing TEWL. Furthermore, at all time points, HP demonstrated greater reduction when compared to CCT. Six hours after application, HP was significantly better (p < 0.001), exhibiting a long-lasting moisturizing effect.

Corneometer readings of the HP- or CCT-applied skin were taken as a measure of skin conductivity and were normalized against untreated skin, as for TEWL measurements. These readings increased dramatically by 45% to 50% within 20 min of CCT or HP application, respectively, compared to that with the control formulation (3.47% only). At all time points of analysis, HP performed significantly better than the control formulation (p < 0.001), whereas the difference of CCT from the control showed a significance probability value of p < 0.5. The mechanism by which both compounds contribute to the capacity of the skin to hold water may not just be related to their film-forming properties, but to their effect on the emulsion properties and the organization of water droplets in it. The

Transepidermal Water Loss Measured at Various Time Intervals After Application								
Application	Time (min)							
	20	60	120	180	360			
Untreated								
Mean	8.22	8.23	8.23	8.23	8.22			
Standard deviation	1.03	0.92	1	1.08	0.96			
HP-containing emulsion								
Mean	5.27	4.17	3.68	3.43	4.61			
Standard deviation	1.1	0.99	0.69	1.15	1.46			
% Difference from untreated	-28.32	-43.23	-49.98	-53.33	-37.26			
<i>p</i> (T <t) one-tail<="" td=""><td>1.88E-04</td><td>1.18E-06</td><td>3.21E-05</td><td>2.58E-05</td><td>1.86E-03</td></t)>	1.88E-04	1.18E-06	3.21E-05	2.58E-05	1.86E-03			
CCT-containing emulsion								
Mean	5.51	4.48	3.91	3.47	5.19			
Standard deviation	0.67	1.07	1.04	0.96	0.79			
% Difference from untreated	-24.59	-38.46	-46.46	-52.55	-29.04			
p(T < t) one-tail	2.38E-01	3.03E-01	2.70E-01	4.69E-01	1.51E-01			
Control emulsion								
Mean	7.73	7.36	6.97	6.77	7.31			
Standard deviation	1.32	1.33	1.55	1.42	1.34			
% Difference from untreated	-8.57	-12.98	-17.63	-19.97	-13.59			
<i>p</i> (T <t) one-tail<="" td=""><td>1.42E-02</td><td>2.01E-02</td><td>1.56E-02</td><td>6.28E-02</td><td>1.57E-02</td></t)>	1.42E-02	2.01E-02	1.56E-02	6.28E-02	1.57E-02			

Table II





correlation between the effect on physical properties of the emulsion that is translated to an elevation in viscosity and an effect on the skin should be studied further.

VISUAL EVALUATION OF SKIN TEXTURE

To further evaluate visual differences, skin treated with HP, CCT, or the control was visualized using a Charm View camera and photos captured both before and after the test. These show clear difference in the effects of HP and CCT when compared to the control (Figure 5). While dried pre-treated skin appears thinner, peeled off, and was therefore rough in texture, skin hydrated by application of HP or CCT exhibited a fine texture with a clear contrast between lines and planes. It is clear that HP is more effective in improving skin texture and hydration upon comparison to the control emulsion-treated site, untreated skin, or CCT-treated skin.

DISCUSSION

When designing a formulation to hydrate the skin, formulators often combine filmforming agents with humectants for possible synergistic effect. Oftentimes, the effect of the vehicle itself or other ingredients such as emollients is neglected. For example, in a study comparing different commercially available moisturizing products (1), it was demonstrated that there might not be a direct correlation between the content of the moisturizing agents and that the design of the formulation can have a key effect.

In the present study, therefore, we attempted to analyze the isolated effects of HP on skin moisturization and have compared it to the emollient ester CCT. HP causes the desired effects of decreased emulsion droplet size and increased viscosity in o/w emulsions.

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		Time (min)						
Application	20	60	120	180	360			
Untreated								
Mean	20.89	20.09	20.09	20.09	20.09			
Standard deviation	4.64	4.58	4.54	3.98	4.36			
HP-containing emulsion								
Mean	30.64	34.18	35.16	34.05	30.43			
Standard deviation	4.91	4.88	5.13	4.35	8.59			
% Difference	49.35	66.6	71.4	65.98	48.34			
from untreated								
<i>p</i> (T <t) one-tail<="" td=""><td>9.58E-05</td><td>9.35E-07</td><td>3.53E-07</td><td>5.19E-07</td><td>4.44E-04</td></t)>	9.58E-05	9.35E-07	3.53E-07	5.19E-07	4.44E-04			
CCT-containing emulsion								
Mean	30.02	32.77	34.45	32.46	29.33			
Standard deviation	5.02	5.09	5.41	6.81	6.71			
% Difference	45.35	58.62	66.76	57.13	41.98			
from untreated								
p(T < t) one-tail	3.59E+01	1.77E-01	3.74E-01	2.41E-01	3.20E-01			
Control emulsion								
Mean	20.36	20.41	20.68	21.07	20.88			
Standard deviation	4.76	4.37	4.42	4.12	4.85			
% Difference	3.47	3.71	5.1	7.09	6.11			
from untreated								
<i>p</i> (T <t) one-tail<="" td=""><td>1.86E-04</td><td>5.82E-06</td><td>2.64E-06</td><td>1.55E-06</td><td>2.15E-03</td></t)>	1.86E-04	5.82E-06	2.64E-06	1.55E-06	2.15E-03			

 Table III

 Skin Conductivity Measured at Various Time Intervals After Application



Figure 4. Percent increase in skin conductivity upon application of HP or CCT.

Moisturizers function by increasing the epicutaneous hydration that can be caused by either of two mechanisms as reviewed in reference 7: (a) by providing the skin hydration from their water phase, in which case we observe a reduction in transepidermal water loss



Figure 5. Polarized photographs taken by View Charm: baseline (upper row), untreated, versus 6-h post-treatment (lower row).

(TEWL) or (b) by increased occlusion, thereby causing a decrease in TEWL. When we measured TEWL upon application of HP, as well as of CCT, we observed that the TEWL decreased significantly, proving the effectiveness of HP and CTT in retaining skin hydration. This effect was longer-lasting in the case of HP and was maintained at a 30% lower level as compared to untreated skin for up to 6 h after application. Such reduction in TEWL has been reported previously upon application of moisturizers in several instances (2,6,5,19).

The increase in skin capacitance and conductivity upon increased hydration resulting from application of moisturizers has been studied previously (1). Humectants such as glycerin, pyrollidine carboxylic acid, or urea in o/w emulsions, in comparison to petro-leum jelly have proven to be effective in increasing skin capacitance in normal adult forearm skin (20). Matsumoto *et al.* in 2007 reported an increase in skin capacitance in infantile leg sites upon application of an o/w cream containing glycoceramide, while heparinoid-containing creams were more effective in the chest regions (3). While this variability in effectiveness with the site of application may be explained to be a result of the absorbtion of humectants by the skin, in the case of emollients like HP or CCT, due to their high molecular weight, we may speculate that the increase in capacitance is a result of the formation of an epicutaneous film rather than absorbtion. However, further studies on skin absorption and penetration will help to ascertain this hypothesis.

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