Crodaderms: the newest high performance emollients

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Introduction

There are probably over one thousand emollients available to the cosmetic scientist today. The actual number is very dependent on the definition of the term "emollient". The dictionary states that the term is derived from the Latin verb *emollire* meaning "to soften" and provides this definition: "that which has the power of softening and relaxing living tissue". However, many would argue that Webster did not consider the advances cosmetic science has made to instrumental methods of measurement nor the consumer use studies results that validate the benefits of emollients. It is, therefore, not easy to pose a proper definition, given that science is constantly broadening performance and consumer perceived attributes for them.

Brief history

Historical records tell us that the use of emollients quite possibly began in the days of the Egyptian Empire when the first cosmetics and personal care products were made for Cleopatra. Fragranced oils, color cosmetics and various skin care concoctions were made from animal and plant derived crushed powders, oils and greases.

Dr. Udo Hoppe[1] relays the success of lanolin, one "grease" that has survived thousands of years in one form or another. Lanolin is a refined form of wool wax harvested painlessly from shorn sheep wool. As Hoppe puts it, "Like all natural raw materials, lanolin has one big disadvantage: it has been highly contaminated by humans." As the world-renowned Dr. Albert Kligman once wrote, "The hue and cry over the high frequency of lanolin allergy is an egregious example of misplaced zeal and faulty science."[2]

The composition of naturally derived lanolin has never been completely elucidated. Consequently, it has never been successfully synthesized. The amalgam of literally hundreds of constituents that make up lanolin and contribute to its multifunctionality have been saved by proprietary refinement processes that define Croda's "medical grade" lanolin, commercially known as MEDILAN™.[3, 4] Today, lanolin is currently enjoying a rebound, especially in the pharmaceutical development arena.

Lanolin became part of a group of materials that includes petrolatum and various natural and synthetic waxes. Although they each did a marvelous job as emollients, their popularity soon gave way to mineral and vegetable oils and the fatty glycerides, primarily because these materials often had a sticky, heavy and sometimes difficult-to-formulate nature which made them unattractive to consumers who had become a more sophisticated audience.

Contemporary synthesis

The consumer's growing sophistication has driven the cosmetic industry to develop a myriad of emollients. Formulators and chemists have been driven to create even more products that succeed in overcoming the often slippery, greasy, sticky and rancid-prone tendencies of their predecessors.

A new era was born with the development of fatty esters as emollients. Esters of fatty alcohols provided a lighter but also drier skin feel that remains in demand today. Isopropyl esters became the proverbial tool for modern, elegant cosmetics and have become industrial workhorses. Even lanolin became derivatized into materials that could compete with these benchmarks.

Carson and Gallagher provide an outstanding treatise, not only on the breadth of the synthetic esters and natural derivatives that are possible but also on the kinds of physical behavioral characteristics they are likely to exhibit. The authors hint at consumer perceptions of what the various structural moieties can provide.[5] For example, modified chain alcohols, especially alkoxylates, can lower cost, modify feel characteristics and provide unique physical properties. Many of these materials have already become commercialized.[6]

Silicone manufacturers turned away from their focus on industrial sealants and adhesives to consider the role their chemistries could play in cosmetics. Once these companies achieved elegant feel characteristics, they built a real share of the emollient business worldwide. They can be credited with "staying power" because they never stopped innovating with new structural forms to target niche applications and fulfill consumer needs.

Consumer science meets chemistry

The mid-70s saw some of the first research devoted to studying the topography of the skin using a "corneal cohesograph"[7]. In 1983 two cosmetic researchers presented a paper on the effects of emollients on skin elasticity using an improved version of the cohesograph, calling it the dermal torque meter[8]. It may, at first, seem odd that consumer testing was used before instrumental analysis to fulfill expectations. Nevertheless, the industry was off on an enlightened course attempting to fulfill consumer expectations through chemical and instrumental methodologies. Today, it is apparent that both factors must be employed to succeed in the competitive marketplace. After all, cosmetic science can fail when it ignores what it is trying to capture: the consumer's desires and needs.

Today, consumer sophistication and consumer product developers have dramatically raised expectations of many functional raw materials including emollients. Most recently, economic times and business objectives further demand that we must all "do more with less". This business mindset not only applies to raw material resources but also to human resources and time. Therefore, meeting consumer and corporate demands at the same time represents a complex and even formidable, assignment.

To accomplish this, a selection process known as "cascading emollients"[9] was one suggested approach. Combined with structural functionality, this process helped formulators meet these higher demands. The concept included properly choosing two or more candidate emollients by structure and adjusting their relative ratios to meet all of the desired feel and functional properties. Obukowho and Woldin later showed that it was possible to derive multifunctionality from one properly built emollient structure. They and their colleagues have broadened our view beyond monoesters into novel ester chemistry.[10, 11]

Demand for greater functionality of all cosmetic materials will always be with us. Some even believe that cosmetic science has evolved into such an integral partnership with mankind that it now has a responsibility to it. The argument is well made in Dr. T. Ozawa's preface title in *Functional Cosmetology, Substantiation of Cosmetic Efficacy: Recent Progress and Future Promise.* It reads: "The Great Responsibility of Cosmetic Science in the 21st Century--Steady advances being made in the verification of usefulness".[12]

Crodaderms

Crodaderm S (INCI: *sucrose polysoyate*) and Crodaderm B (INCI: *sucrose polybehenate*) are two of the newest novel multi-functional high performance emollients available. As one might expect from their INCI nomenclature, these polyesters are sugar esters of fatty acids produced from naturally derived vegetable oils and sucrose feedstocks. Chemically, they consist of a sucrose backbone esterified with 6-8 fatty acid chains. Crodaderm S is a liquid derived from soybean oil fatty acids; Crodaderm B is a pastille made from a blend of C22 fatty acid chains (Behenic Acid). Crodaderms owe these features to their respective structures:

- Skin compatibility/substantivity
- Moisture retention
- Wide compatibility with oils and other non-polar materials
- Good wax solvency
- Glide enhancement for sticks
- Thickener/gellant (*Crodaderm B*)
- Viscosity enhancement/thickeners for other liquids
- Film-formation
- Non-transferability, stationary films
- Water/wear-resistance

As was discussed earlier, both physicochemical and instrumental measurements become useless without verification that they fulfill consumer needs. The properties of Crodaderms translate to these key consumer benefits:

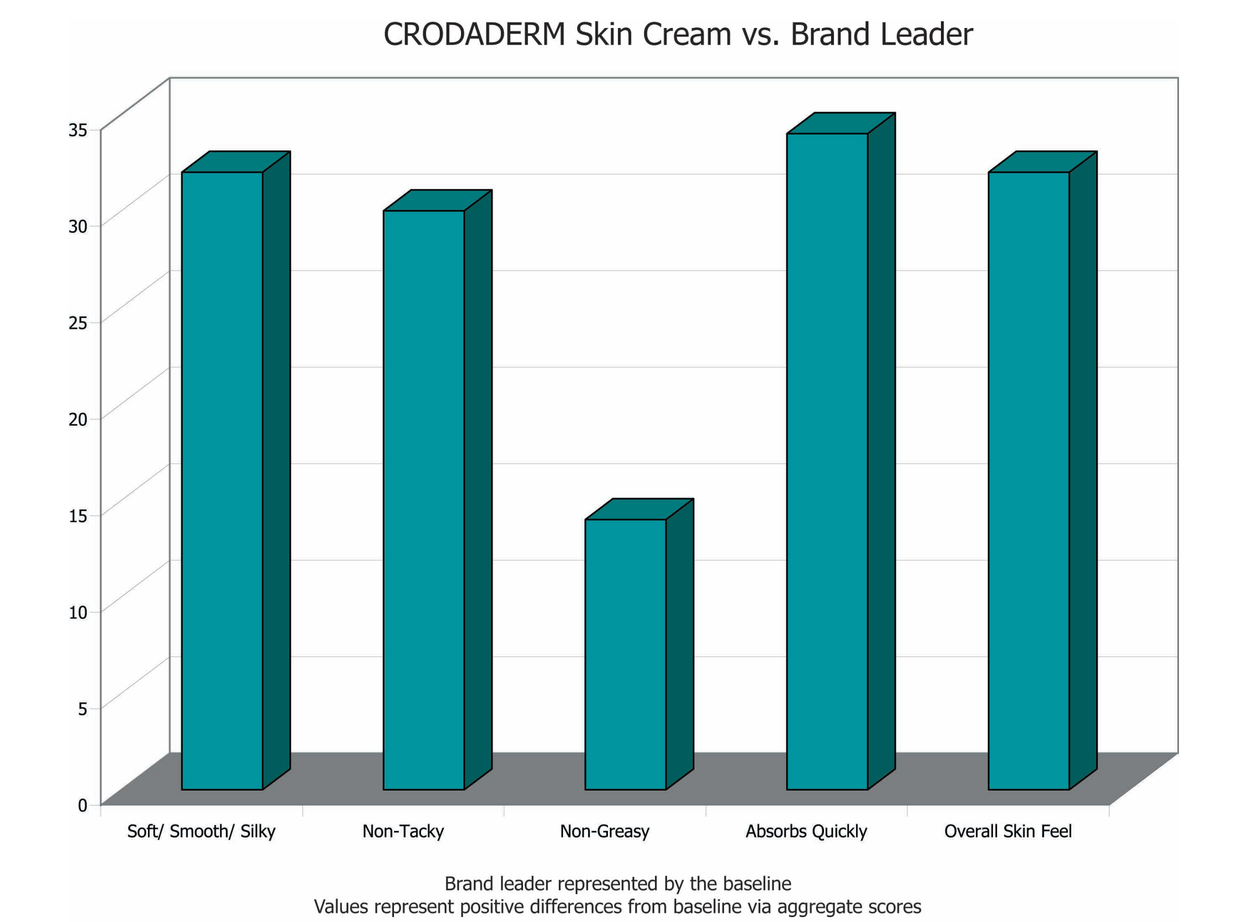
- Consumer perceived skin softness/smoothness
- Improved moisturization
- Better skin elasticity/suppleness
- Long-lasting, non-tacky after feel
- Better actives deposition
- Clean skin feel
- Protective effect on skin barrier

Crodaderm S and Crodaderm B form semi-occlusive, porous films that have the mobility to spread and provide ample coverage on the skin, yet remain stationary once applied. Because these films are highly substantive and show little, if any, migration on the skin after application, Crodaderm S and Crodaderm B tend to 'hold onto' other materials. Films such as these also promote better water retention by the skin and provide protective effects that may help improve barrier function. Thus, Crodaderm S and Crodaderm B are effective in moisturizing the skin and making it feel softer, smoother and more supple. We will now discuss some of the key benefits in more detail.

Skin Softness/Smoothness

Given the unique nature of their films, Crodaderm S and Crodaderm B offer great multifunctionality and a number of desirable performance benefits. They not only make skin feel softer and smoother but do so from a number of different systems. These two benefits were perceived by a majority of panelists during a battery of clinical studies. In consumer preference tests, a 2% Crodaderm S prototype (oil-in-water gel network emulsion) was evaluated in terms of a number of sensory parameters and found superior in providing long-lasting softness and smoothness, as compared to five other emollients in the same gel-type vehicle. In a separate but similar study using a sensory panel of 50 women, the same Crodaderm

Figure 1



S formula also outperformed a leading mass market skin cream. The results of paired comparison testing show that panelists overwhelmingly preferred the relatively simple prototype containing 2% Crodaderm, rating it considerably higher than the retail brand in nearly all categories.

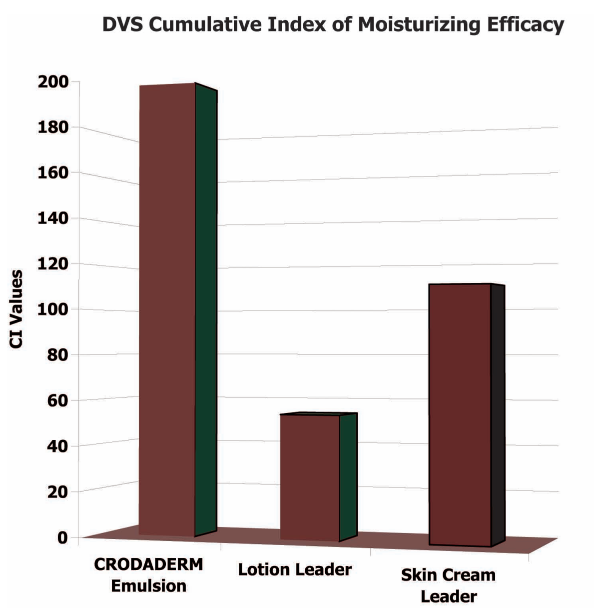
Skin moisturization

Evaluation of a material's capacity to take up and retain water is one way of screening candidates for good moisturizing performance. Dynamic Vapor Sorption is a quick *in vitro* method of monitoring the moisture absorption/desorption properties of products, as opposed to skin. Moisture uptake is determined by measuring the change in mass of test samples at intervals of increasing relative humidity (adsorption) and decreasing relative humidity (desorption) and then establishing equilibrium.

In studies using an automated DVS-1 analyzer from Surface Measurement Systems Ltd, a simple prototype oil-in-water emulsion containing 2% liquid Crodaderm had up to 4 times the moisturizing efficacy of two top skin care products. The commercial leaders are both oil-in-water types. Figure 2 shows the results.

The results of separate corneometer testing support the moisturizing effects observed in the DVS study. One test evaluated a leading U.S. day cream with 2% added Crodaderm against its leading competitor, while yet another compared a Crodaderm facial cleanser to a popular European cleansing milk. The addition of Crodaderm to the day cream beat the competitor, whereas it trailed before the addition. The cleansing milk with Crodaderm likewise demonstrated superior hydration.

Figure 2



DVS Cumulative Index (CI) = % water retained after the 90% RH stage / water release rate

Skin elasticity/suppleness

Skin hydration is closely akin to elasticity. The water content of the stratum corneum, generally thought to be about 30%, has a major impact on the skin's elastic properties. As the studies just discussed have shown, sucrose esters are extremely efficient moisturizers. Their ability to 'hold onto' other materials enables them to retain water for extended periods of time. When skin is more hydrated, it becomes more elastic, and hence, more supple. Clinical studies conducted to evaluate the effects of the Crodaderms on elasticity indicate that the products have properties that increase the suppleness of the skin. Improvements in moisturization and softness were also observed.

The Gas Bearing Electrodynamometer (GBE) is a sensitive instrument that has been used for the last 20 years or so to measure the mechanical properties of the stratum corneum.[13] The GBE operates using a mechanical gas bearing (frictionless) moving probe which is applied to the skin surface and measures the force needed to deform the skin laterally (Dynamic Spring Rate: DSR) and then computes the energy loss or total work for the skin to recover. Force is related to skin suppleness as 1/DSR and total work is the difference between the force applied and the displacement of the skin and is related to skin elasticity. The results of a GBE study using Crodaderm lotions are shown on the next page. Measurements were taken before treatment (baseline) and at set intervals after treatment and expressed in Figures 3 and 4 as differences, not absolute values. The larger the differences, the more supple and elastic the skin.

Deposition/rinse-off resistance

All compounds absorb light differently and produce a unique set of absorption bands according to their own individual chemical properties. These bands can be detected by Fourier Transform Infrared Spectroscopy (FTIR) and used to quantitatively measure deposition on a substrate. FTIR is an accepted technique used to identify the functional groups

Figure 3

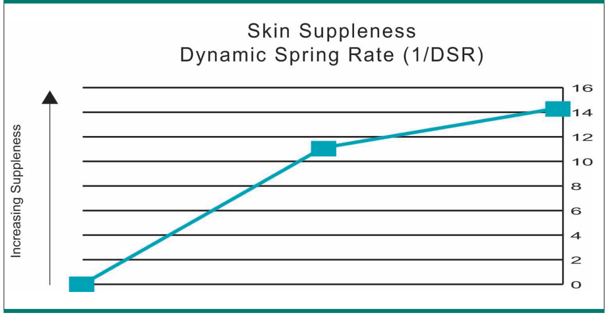
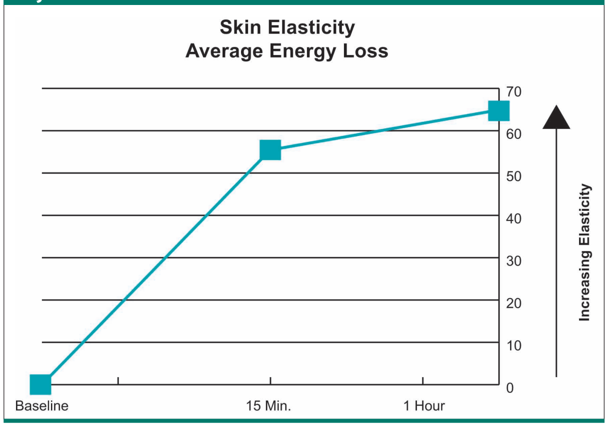


Figure 4



present in a molecule or to determine the identity of a sample material.

FTIR was used to confirm the deposition of sucrose esters of fatty acids from a rinse-off cleansing system and to evaluate their moisturizing effects on the skin, the latter of which was also established by GBE testing and discussed earlier. Because of the many fatty acid chains these sucrose esters contain, they readily absorb IR radiation in the fatty acid ester (C=O) range and are therefore easy to identify. Other components in the formula used absorb in a different range.

The study's objective was to evaluate the interaction of Crodaderm S and Crodaderm B at various levels to try to determine an optimum ratio for rinse resistance. This necessitated a test design that comprised a large number of trial samples.

Prototype cleansers of various concentrations were applied to the forearms of 16 panelists and allowed to dry for 15 minutes before rinse-off. Deposition was then measured by FTIR and compared with a calibration curve. Good correlation was observed between the calibrated data points and absorbance of the test samples (r^2=0.99).

Rather than show multiple data tables, we will summarize the results and provide some formulating tips to help enhance performance.

1. All simple cleanser prototypes containing Crodaderm provided improved deposition and rinse resistance
2. Those with higher levels of Crodaderm B gave better deposition and rinse resistance
3. The optimum cleanser formula contained a blend of Crodaderm S and B at a ratio of 2.5:1 respectively

Incorporating Crodaderms into a thixotropic emulsion allows the blend to be released onto the skin more efficiently. Such emulsions quickly break as they are applied. Skin electrolytes also assist in the destabilization of the emulsion, enabling the Crodaderm blend to be deposited more evenly over the surface. Examples of such emulsions may be found in U.S. Patent 6,117,915[14].

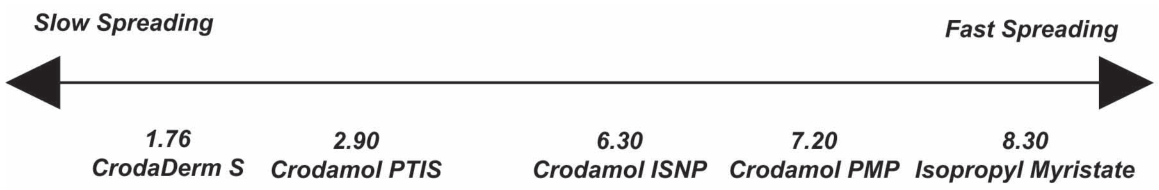
Additionally, adding the Crodaderms as a separate phase after neutralization can increase deposition efficiency; testing showed this to be as high as 50%. It is thought that the late-stage addition causes the Crodaderms to be dispersed rather than emulsified, thereby enabling them to be more quickly deposited onto the skin. Lastly, minimizing the amount of surfactant in the system can reduce the amount of Crodaderm washed off during rinsing.

Emollient skin spreading factor

Spontaneous skin spreading is the tendency of a material to spread over the skin surface without outside assistance. This phenomenon may have a direct impact on the success or failure of some finished products to perform as intended. For example, expensive active ingredients perform best when they stay where the formulator and the consumer intend them to be. An emollient carrier that spontaneously spreads quickly over the skin may also take the active away from its target. As a means of determining the spreadability of its liquid esters, Croda devised an Emollient Skin Spreading Factor (ESSF), calculated as the ratio of the final area of coverage of the ester, per unit of time, divided by the initial area over which the ester was applied.

Esters with high ESSFs spread more quickly; those with low values spread slowly or not at all. How quickly or how slowly an ester spreads affects the type of film the material

Figure 5



forms. Esters with a high molecular weight or bulky structure tend to spread more slowly. Not surprisingly, Crodaderm S has one of the lowest ESSF values we have observed. At 1.76, the ESSF for Crodaderm S is lower than that for Crodamol PTIS (Pentaerythrityl Tetraisostearate) (see Figure 5). This represents the type of spreading believed to be ideal for sunscreens, as such films deposit on the skin more evenly, stay where they are applied, and resist wash/wear-off.

Table 1 below describes the method for determining ESSF.[5]

Crodaderm B Blends

Gels of various rheology and skin feel can be made with blends of Crodaderm B and other Croda emollient esters. Blends A, B, C, D and E shown in Table 2 are prototype gels using varying ratios of Crodaderm B and Crodamol GTCC (*Caprylic/Capric Triglyceride*). These gels spread easily at all concentrations of blends tested. Blends B and C rub-in quickly on the skin but become stiffer and less lotion-like as the concentration of Crodaderm B is increased. However, they remain soft, light, and lubricous in feel. Blend D is still lubricious but acquires some waxiness. At the highest Crodaderm B level (20%), Blend E has a buttery consistency.

Gels made with Crodaderm B/Cromollient DP3A (*Di-PPG-3 Myristyl Ether Adipate*) blends, likewise stiffen with increasing levels of the sucrose ester but become more opaque as well. Gels F and G (bottom half of Table 2) appear to be optimum in that they are soft, smooth and provide a light, non-greasy feel and pleasing aesthetics.

The gelling capabilities of Crodaderm B are unique in that the ester tends to crystallize into thin platelets when cooled from a melted state. These crystallized platelets have a large surface-to-mass ratio and may help gel the oil phase of an emulsion.

A wide range of consistencies can be produced, simply by varying the level of a Crodaderm B/oil blend in a formula. In

Table 2

Crodaderm B Blends	A	B	C	D	E
CRODAMOL GTCC	95.0	92.0	90.0	85.0	80.0
Crodaderm B	5.0	8.0	10.0	15.0	20.0
Viscosity, cps*	7,400	11,600	15,000	142,600	200,000
	F	G	H	I	J
CROMOLLIENT DP3A	95.0	92.0	90.0	85.0	80.0
Crodaderm B	5.0	8.0	10.0	15.0	20.0
Viscosity, cps*	9,600	32,000	50,400	NA	NA

** Brookfield RVT, spindle TD, 10 rpm @RT*

Table 1 : Determination of the Emollient Skin Spreading Factor (liquid materials only)

1. Using a penny-sized template, draw a 2cm-diameter circle on the volar (palm side) surface of the forearm with a black fine-point pen to mark the test area.
2. Apply 5µl of test sample inside the circle using a Drummond Wiretrol tube and spread the material evenly within the circle.
3. Wait 15 minutes and then spray the test site and surrounding forearm area liberally with a 1.0% solution of FD&C Blue #1.
4. Allow the dye solution to remain on the skin for 30 seconds and then rinse off with warm (not hot) tap water.
5. Pat forearm with paper toweling (do not rub) and observe for evidence of staining. The area not stained by the blue dye indicates the area of spreading by the test sample.
6. Measure the cross-section diameter of the unstained area in two directions and use the average as the spread diameter.
7. Divide the spread diameter in half and use the radius to calculate the spread area according to the standard formula for area: $A=\pi r^2$.
8. Calculate the Skin Spreading Factor according to the following formula: $\text{Skin Spreading Factor} = \frac{\text{Spread area of test sample}}{\text{Original Area*}}$

* The original area is a constant and will always be 3.14 cm^2.

general, 2-3% of a given blend yields a soft, viscous gel that flows readily; 5-7% of the same blend will produce a gel with a petrolatum-like consistency. A firm semi-solid is obtained at higher concentrations. It is recommended that you experiment with various esters and ratios until you arrive at a blend that suits your particular application.

Summary

The cosmetic industry has not escaped the trend of mergers and acquisitions. One unfortunate consequence is that fewer people must do more with less time and money.

Raw material suppliers are trying to assist by developing multifunctional high performance products that meet consumer needs and at the same time try to meet corporate objectives.

Crodaderm S and Crodaderm B are helping to broaden the definition of the term "emollient" with performance benefits that span the functionalities of thickeners, gellants, actives deposition agents, anti-transfer agents, and protectants. These are not traditional emollient functions but are contributions well beyond what the consumer expects from an emollient. Crodaderms are functional 'tools' that can simplify the ingredient listing, shorten development time and save money. Simplicity is one key aspect to "speed to market". "Speed to market", in turn, translates to "success". Crodaderms are the newest contribution toward "…Steady advances being made in the verification of usefulness".[12]

References

(1) U. Hoppe, Introduction, The Lanolin Book, Hamburg, Germany, Biersdorf AG (1999) pp. 9-14

(2) A. Kligman, The Myth of Lanolin Allergy; Lanolin is not a contact sensitizer, The Lanolin Book, Hamburg, Germany, Biersdorf AG (1999) p. 163

(3) Croda Publication PN-72, Clinical Study to Evaluate the Suitability of the MEDILAN™ Range for Treatment of Dermatological Disorders, British J. Derm., 147 Supplement 62, 71, July 2002

(4) Croda Publication PN-71, MEDILAN™ Clinical Support Document, Feb. 10, 2003

(5) J. Carson and K.F. Gallagher, Emollient esters and oils, Conditioning Agents for Hair and Skin, New York: Marcel Dekker (1999) pp. 111-137

(6) Croda Emollient Esters for Personal Care

(7) R. Nichols and J. Marks, Novel Techniques for the Estimation of Intracorneal Cohesion In Vivo, British J. Derm. 96 (595)(1977)

(8) J. De Rigel and J.L. Leveque, Fourth International Symposium on Bioengineering and the Skin, Besancon, France, 1983

(9) B.A. Salka, Choosing Emollients, Cos. & Toil. 112(10) 101-106 (1977)

(10) P. Obukowho and B. Woldin, Selecting the Right Emollient Ester, Cos. & Toil. 116(8) (2001)

(11) U.S. Patent 5,597,555 (1997)

(12) T. Ozawa, Preface, Functional Cosmetology, Japan, Yakuji Nippo, LTD (2003) pp. 6-7

(13) D. Maes, J. Short, B.A. Turek, and J.A. Reinstein, In vivo measuring of skin softness using the Gas Bearing Electrodynamometer, Int. J. Cosmet. Sci., 5, 189-200 (1983)

(14) U.S. Patent 6,117,915 (2000)

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