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Advances in Emulsion Science For Personal Care Applications

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SUMMARY

This overview starts with an introduction summarizing the stabilization mechanisms for macroemulsions (those that are currently used in most personal care applications). These systems are thermodynamically unstable since the energy required for their formation exceeds the much smaller entropy of dispersion of the droplets in the medium. To stabilize the emulsions against flocculation and coalescence, one needs to create an energy barrier between the droplets to prevent their close approach (where the van der Waals attraction is very strong). This can be achieved by electrostatic stabilization, e.g. by the use of ionic surfactants, where the double layers prevent the close approach of the droplets. This stabilization mechanism is not ideal since the double layer repulsion is significantly reduced in the presence of electrolytes. An alternative mechanism is that of steric stabilization, whereby nonionic surfactants or polymeric surfactants may be used. These molecules consist of B chains that are strongly adsorbed (or soluble in oil) and A chains which are soluble in the medium and strongly solvated by the its molecules. Examples are given of the types of A-B, A-B-A block copolymers that can be used for stabilization of oil-in-water (O/W) or water-in-oil The stabilization mechanism by these polymeric surfactants is (W/O) emulsions. described in terms of the unfavourable mixing of the A chains, when these are in good solvent conditions, and the loss in configurational entropy on overlap of the chains.

The second part of the overview deals with the subject of microemulsions, which are thermodynamically stable systems that can be transparent or translucent (with drop sizes in the range 5 - 50 nm). These systems are produced spontaneously by mixing oil, water, surfactant and cosurfactant. The driving force for their for their spontaneous formation is the ultralow interfacial tension, in which the surface energy in expanding the interface is overcompensated by the negative entropy of dispersion of the droplets. The reason in using two surfactant molecules for reduction of interfacial tension can

be accounted for in terms of their co-adsorption at the interface. The methods that can be applied for formulation of microemulsions are briefly described. Finally, the use of polymeric surfactants for formulating microemulsions is described. This has the advantage of avoiding any skin irritation, since these polymeric surfactants cause no disruption of the stratum corneum of the skin.

The third part of this overview deals with the topic of nanoemulsions (covering the size range 50 - 200 nm) which may also appear transparent or translucent. However, these systems are not thermodynamically stable, but due to their small size they have a long term kinetic stability. This is due to the larger ratio between adsorbed layer thickness and droplet radius, when compared with the values for macroemulsions. Two main procedures could be applied for preparation of nanoemulsions, namely high pressure homogenization and application of the phase inversion temperature (PIT) principle. The droplets produced using the first technique show a narrower distribution when compared with those obtained using the PIT method. However, nanoemulsions may show growth of droplet size with time as a result of Ostwald ripening (that results from the difference in solubility between the small and large droplets). Two methods may be applied to reduce Ostwald ripening, namely incorporation of a second oil phase with very low solubility and/or incorporation of a polymeric surfactant that is strongly adsorbed at the O/W interface and has low solubility in the continuous phase.

The fourth part of the overview deals with liposomes and vesicles which are produced by dispersion of lipids followed by sonication. The principle of the critical packing parameter is applied to predict the formation of vesicles. The latter are useful delivery systems for personal care applications, since nonpolar actives may be solubilized in the hydrocarbon core of the bilayer, whereas polar and water soluble actives can be intercalated in the aqueous film between the bilayers. Liposomes and vesicles cause no skin irritation since they have similr structure to the lipid bilayer of the stratum corneum.

The last section of the overview deal with multiple emulsions which are very useful for formulation of personal care products with several active ingredients. The use of polymeric surfactants for preparation of stable multiple emulsions is described and the criteria of stability is summarized. The multiple emulsion can also be stabilized using thickeners to prevent creaming or sedimentation.

BEYOND RHEOLOGY MODIFICATION: HYDROPHILICALLY MODIFIED SILICONE ELASTOMERS PROVIDE NEW BENEFITS Michael S. Starch, Jean E. Fiori and Zuchen Lin

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Introduction:

The introduction of silicone elastomers to our industry has provided formulators with new tools for modifying the rheology and esthetic properties of silicone-based formulations. These silicone elastomers are based on crosslinked dimethicone and are typically supplied in the form of swollen gels that contain various silicone oils. One such elastomer with the INCI name Dimethicone Crosspolymer (DCP) has been shown to be useful for thickening various types of formulations, particularly anhydrous formulations, where cyclomethicone is the vehicle¹. This silicone elastomer also provides novel sensory properties that are unlike anything attainable with silicone fluids.

The addition of hydrophilic polyethylene glycol (PEG) functional groups to DCP affects both the chemical and rheological properties of the elastomer. This new class of materials, hereinafter referred to as PEG-modified DCP (PEG-DCP), has very different properties from the unmodified elastomer. The hydrophilic PEG substituents change the wetting properties of the elastomer and dramatically improve compatibility with polar ingredients². We have shown that PEG-DCP can be used as an emulsifier for oil-continuous as well as multiple emulsions.

Reduced Syneresis:

The utility of DCP and other elastomers prepared from non-polar silicones for thickening anhydrous antiperspirants is illustrated in Figure 1. This data was generated using a simple soft solid formula

composed of elastomer, antiperspirant 450,000 salt, and cyclomethicone. The solid line 400,000 with triangles shows that the viscosity of the formula increases rapidly as the 350,000 concentration of DCP is increased. The amount of syneresis for these formulas, 300,000 (dotted line) however, is relatively **A**iscosity insensitive to the DCP concentration. 250,000 When PEG-DCP is used to prepare the 200,000 formula, the viscosity is much lower, but syneresis is dramatically reduced by 150.000 increasing the elastomer concentration to 4% in the formula. These results may be 100,000 due to an associative thickening effect, whereby the PEG chains are driven to 50,000 associate in the non-polar formula 0 environment. Under shear conditions, including those used to measure formula viscosity, these 2.5 associations break down, leading to low viscosity readings. We have found that the viscosity of such formulas is highly dependent on the shear history of the sample and that stirring the sample before measuring viscosity dramatically reduces viscosity.

45 40 35 30 eresis 25 20 15 10 5 Ω 3.0 3.5 4.0 4.5 Elastomer Concentration (wt %) - Viscosity - with DOP ------ Viscosity - with PEG-DOP -o- - Syneresis with PEG-DOP - -o- - Syneresis with DOP

Compatibility with Polar Ingredients:

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Silicone elastomers such as DCP that have no polar functionality are generally incompatible with organic oils. All the exceptions we have found to this rule are low molecular weight hydrocarbon oils. When mixed with DCP that has been swollen in cyclomethicone, organic oils such as fatty esters appear to alter the gel structure of the elastomer, leading to a loss of thickening efficiency. At higher concentrations, fatty

esters can precipitate DCP, presumably due to poor solvation of elastomer. The polar functionality of the PEG-DCP elastomer increases the range of organic oils that are compatible. The data shown in Table 1 illustrates this phenomenon with tocopherol. In these experiments, DCP and PEG-DCP were pre-blended with cyclomethicone and the compatibility of these blends with tocopherol was evaluated. The tocopherol was slowly added to the elastomer blends until the mixtures became hazy, indicating incompatibility. The amount of tocopherol required to produce incompatibility was recorded as the "saturation point" for the particular elastomer blend. Two PEG-DCP elastomers with different levels of PEG substitution were tested. The data indicates that the PEG functionality is responsible for the improved compatibility with tocopherol.

Elastomer	PEG	Appearance and	Saturation
Туре	Substitution	stability of mixtures	Point (w/w)
DCP	None	hazy, separates over time	< 1 %
PEG-DCP	Low	clear, stable over time	20 %
PEG-DCP	High	clear, stable over time	28 %

Table 1: Compatibility of Silicone Elastomer / Cyclomethicone Blends with Tocopherol

Emulsification:

PEG-substituted silicones such as dimethicone copolyols are known in the industry for their ability to form water-in-oil (W/O) emulsions, where the continuous phase is composed primarily of cyclomethicone. One application for these W/O emulsions is clear antiperspirant gels, where an aqueous phase containing the antiperspirant salts is emulsified into a continuous silicone phase. We compared the emulsification performance of a widely used dimethicone copolyol with that of a PEG-DCP elastomer in a simple antiperspirant gel formulation. We found that both produced stable W/O emulsion gels, but the viscosity of the gel with PEG-DCP was significantly higher (13,000 cP for the PEG-DCP gel versus less than 6,000 cP for gel with Dimethicone copolyol), due to the thickening effect of the elastomer in the continuous phase.

In addition to simple W/O emulsions, PEG-DCP can be used to prepare multiple emulsions, including water-in-oil-in-water (W/O/W) emulsions³ and propylene glycol-in-oil-in-water emulsions⁴. In these systems, we believe the thickening effect of the silicone elastomer in the silicone oil phase helps to stabilize the initial W/O (or PG/O) emulsions and allows them to be dispersed in water without inversion. This offers the potential to formulate products with ingredients that may not be stable in conventional emulsions. Placing them in the innermost phase of a multiple emulsion could protect such ingredients from degradation.

Summary:

The development of silicone elastomers with hydrophilic functionality in the form of PEG substituents provides benefits beyond the thickening that can be achieved with non-functional silicone elastomers. We have shown that PEG-DCP, in particular, is compatible with a wider range of personal care ingredients, compared to the unmodified elastomer (DCP). When blended with cyclomethicone, PEG-DCP forms a silicone phase that can solubilize organic oil and will emulsify water to form stable W/O emulsions. The PEG-DCP provides thickening as well as emulsification, and this combination of properties allows the preparation of multiple emulsions.

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THE IMPORTANCE OF MESOMORPHIC (LAMELLAR) PHASES IN EMULSION STABILITY

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Dermatological lotions and creams are often complex multiphase emulsions with stability and physical chemical properties related to the mesomorphic phase behaviour of the emulsifiers rather than to droplet interactions described by classical emulsion theories. A knowledge of the relationship between the properties of such formulations and their microstructure is essential to optimise manufacture, provide cosmetic elegance and to control the delivery of a cosmetic agent to the skin.

In this presentation, the microstructure and properties of a range of fluid and semisolid liquid paraffin-in-water emulsions (aqueous creams) stabilised by either (i) combinations of surfactants (ionic cetrimonium bromide or nonionic ceteth 20) and pure or mixed homolog fatty alcohols or (ii) partially neutralised fatty acids will be discussed. In particular, the important relationships between emulsion microstructure, stability and rheology. The relevance of oil free ternary systems, formed by dispersing mixed emulsifiers in controlled percentages of water, to investigations into emulsion microstructure will be emphasised.

The stabilities and rheological properties of emulsions containing fatty alcohol/surfactant mixed emulsifiers (emulsifying waxes) are controlled by the swelling properties of an α -crystalline lamellar gel network formed when mixed emulsifier interacts with continuous phase water. Despite the complexity of these systems, combinations of low and high angle X-ray diffraction measurements (Daresbury Laboratory Synchrotron Radiation Source, SRS) provide direct and accurate measurements of the interlamellar water spacings (1). These spacings affect the rheological properties of the creams. The influence of batch variations of the surfactants or changes in homologue composition of the alcohol on emulsion stability and rheology can also be correlated directly to extent of swelling of the lamellar gel network.

The cationic emulsifying wax shows phenomenal swelling in water. The reflection that incorporates interlamellar water increases continuously to over 500Å at 93% water. The trend is not influenced by the method of incorporation of the components and swollen lamellar phase is also identified in the corresponding emulsion (Figure 1).



Fig. 1 Comparison of small angle X-ray diffraction patterns of cetrimonium bromide emulsion and ternary system

The extensive swelling is electrostatic in nature. The surfactant molecules interposition among the fatty alcohol molecules and electrical double layers arise from the dissociation and diffusion of counterions from the surfactant headgroups at the surface of the bilayers into the surrounding water. Electrostatic repulsion between adjacent

bilayers arise from the overlap of the electrical double layers. The thickness of the double layers is inversely proportional to the square route of the concentration of electrolyte in the surrounding water. Added salt reduces swelling between the bilayers by a non-specific compression of the double layers (Figure 2).



Fig. 2 The influence of sodium chloride on the interlamellar spacings of cationic emulsion and ternary system.

Decreases in apparent viscosities on addition of salt (from 107 mPas at zero salt to 10 mPas at 2% salt) are correlated with reductions in interlamellar swelling which result in decreases in the phase volume of the lamellar structures. On storage, creams become thicker as water layer distance increases (from ~460 Å after three weeks storage to ~600 Å after six months) probably due to surfactant rearrangement in the bilayers. High angle diffraction data confirm that the hydrocarbon bilayers are in the hexagonal α -crystalline mode of packing.

Ternary systems and creams prepared from pure alcohols, although initially semisolid, are rheologically unstable and break down on storage to form mobile crystalline fluids. A preliminary low angle X-ray study into the kinetics of structure break down shows that the swollen lamellar gel phase formed initially swells even further on storage before separating into unswollen monoclinic crystals.

The comparatively limited swelling that occurs in emulsions containing non-ionic surfactants is due to hydration of the polyoxyethylene groups (interlamellar distances of around 110Å). Initial consistency increases on storage occur as the POE groups slowly hydrate. The influence of batch variations of POE surfactant on rheological properties can be related to variations in POE chain length, for there is a linear relationship between POE chain length, interlamellar thickness and apparent viscosity.

Emulsions containing partially neutralised fatty acids show more complicated phase behaviour. Whilst swollen bilayer phases form in systems neutralised by triethanolamine, such phases are not apparent in emulsions containing sodium or potassium hydroxide as neutralising agent. The possible structures of these non-lamellar phases that also incorporate large volumes of water will be discussed.

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SELF-EMULSIFICATION OF SURFACTANT-OIL MIXTURES PRODUCED BY DIFFUSION AND CHEMICAL REACTION

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Abstract.

Drops having diameters of order 100 μ m and containing various combinations of oils, surfactants, and in some cases alcohols were injected into water or aqueous salt or buffer solutions. The resulting dynamic behavior was observed by videomicroscopy. Spontaneous emulsification yielding oil droplets a few microns in diameter was seen in a variety of systems when diffusion and/or chemical reaction caused inversion of the drop from an oil-continuous to a water-continuous phase, leading to local supersaturation in oil. Surfactants used included nonionic (C₁₂E₆), anionic (Aerosol-OT), and zwitterionic (tetradecyldimethylamine oxide). In some experiments inversion occurred because a lipophilic surfactant was converted to a hydrophilic surfactant, e.g., a double-chain phospholipid to two single-chain surfactants.

Introduction.

When emulsions are formed by mixing oil and water phases, high shear rates are typically required to generate small drops having diameters of order 1 μ m. When it is necessary or desirable to obtain small drops without high shear rates, spontaneous emulsification should be considered. Compositions of the initial oil and water phases are chosen in such a way that small droplets form spontaneously when the phases are brought into contact, i.e., no external energy of agitation is required. "Self-emulsification" refers to situations where a small amount of agitation is supplied to achieve gentle mixing. Typically the droplets form spontaneously, and mixing serves mainly to disperse them throughout a large volume and to bring together portions of the oil and water phases which were not in contact initially.

Self-emulsification of oils containing dissolved solutes is not only an intriguing phenomenon but is also of practical interest in delivery of agricultural chemicals and drugs as well as during use of cutting oils, bath oils, etc. A surfactant or a mixture of surfactants is added to the oil, so that it will emulsify spontaneously when contacted with water. The objective of our study was to gain insight into the mechanism of spontaneous emulsification, which has not been well understood, and thereby provide a basis for choosing suitable surfactant/oil mixtures.

Results.

Rang and Miller¹ used videomicroscopy to study self-emulsification of nhexadecane/ $C_{12}E_{e}/n$ -octanol drops some 100 µm in diameter injected into water. Spontaneous emulsification yielding only small oil droplets was observed when the initial ratio of alcohol to hydrocarbon was greater than that in the excess oil phase in equilibrium with a microemulsion and water at the temperature of interest, i.e., above the ratio existing at the Phase Inversion Temperature (PIT), and when surfactant concentration was sufficiently high. The mechanism of emulsification can be briefly described as follows. Initially water diffused rapidly into the oil phase, converting it to an oil-continuous microemulsion. However, as octanol diffused gradually into the aqueous phase, the ratio of alcohol to surfactant in the films covering the microemulsion droplets decreased, making them more hydrophilic and leading to an increased capability of the microemulsion to solubilize water and a decreased capability to solubilize oil. Eventually, the microemulsion was no longer able to solubilize all the oil present, and oil droplets nucleated. Moreover, the microemulsion itself inverted to become watercontinuous and miscible with water, so that the final state was oil droplets dispersed in an aqueous phase, the size distribution of the droplets depending largely on their rate of coalescence. When enough surfactant was present, coalescence was relatively slow, and the droplets remained small. No intermediate liquid crystalline phases were formed for this system. However, an intermediate lamellar phase was seen for systems where the surfactant was tetradecyldimethylamine oxide (C14DMAO). Emulsions with small oil droplets were obtained with lower surfactant concentrations in this system, apparently because the lamellar phase reduced the rate of coalescence of the droplets. Nevertheless, both the liquid crystal and the microemulsion eventually became miscible with water as they lost alcohol by diffusion into the aqueous phase.

This mechanism of emulsification may be summarized as causing the microemulsion to become supersaturated in oil by shifting it from lipophilic to hydrophilic conditions. However, achieving this behavior by diffusion of a mediumchain alcohol into the aqueous phase may not be desirable for some purposes. Later work showed that emulsification could also be produced in a similar system with octanol replaced by oleyl alcohol, which has a minimal solubility in water². In this case equilibrium phase behavior and videomicroscopy observations indicated that, when the system was near its PIT, water diffused into the oil phase, causing first transformation to the lamellar liquid crystalline phase and then nucleation of oil droplets and conversion of the liquid crystal to a water-continuous phase.

Use of ionic surfactants instead of nonionic or zwitterionic surfactants may have advantages. For instance, electrical repulsion may help stabilize the emulsion once formed. Accordingly, more recent work utilized the anionic surfactant Aerosol OT (AOT) with no alcohol and effected microemulsion inversion by a reduction in ionic strength³. This reduction was produced by a combination of water diffusion into the injected drop and AOT diffusion into the aqueous phase.

Inversion and spontaneous emulsification can also be produced by chemical reactions which convert lipophilic surfactants to more hydrophilic ones. As is well known, one such reaction is conversion of fatty acids to soaps by increasing pH. However, spontaneous emulsification produced by other reactions has been investigated recently in our laboratory, including enzymatic splitting of a double-chain.phospholipid into a lysolecithin and a fatty acid.

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CALCIOTROPIC HORMONES AND THE SKIN: A MILLENNIUM PERSPECTIVE

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It has been estimated, that within 50 years, that almost one million Americans will reach the age of 100 years. One of the major consequences of aging on the body is its effect on the skin. Retinoids have been found to be very effective in stimulating epidermal cell growth and rejuvenating the dermis to help relieve the ravages of aging on the skin. Retinoids can cause some side effects including skin irritation. There is a need to develop new safe effective approaches for maintaining skin and hair follicle health and rejuvenating skin health. It is well known that the most beneficial effect of exposure to sunlight on the skin is the production of vitamin D_3 . Vitamin D_3 is equated with bone health. However, it is now appreciated that the skin is not only the organ responsible for making vitamin D_3 but is a target tissue for activated vitamin D_3 . It is well established that once vitamin D_3 is made in the skin, it is converted in the liver to 25-hydroxyvitamin D_3 and then in the kidney to 1,25-dihydroxyvitamin D_3 (1,25(OH)₂ D_3). 1,25(OH)₂ D_3 is responsible for enhancing intestinal calcium absorption and mobilizing calcium stores from the bone to maintain physiologically acceptable blood levels of calcium for promoting metabolic functions and maximum bone health. It is now recognized that the skin also has the enzymatic machinery to make $1,25(OH)_2D$. $1,25(OH)_2D$ is a potent inhibitor of proliferation and inducer of terminal differentiation of human epidermal cells One practical advantage of this unique biologic property is that activated vitamin D compounds are effective in treating the hyperproliferative skin disorder, psoriasis. It is remarkable that although $1,25(OH)_2D_3$ is a potent inhibitor of epidermal proliferation, it does not have any adverse effects on the epidermis when topically applied for up to 10

years. It appears that this calciotropic hormone normalizes proliferative activity, and Purchased for the exclusive use of nofirst nolast (unknown) From: SCC Media Library & Resource Center (library.scconline.org) helps maintain both epidermal and dermal health. Development of vitamin D analogs for pharmaceutical and cosmetic applications for skin health holds great promise.

The skin produces the calciotropic hormone parathyroid hormone related peptide (PTHrP). Immunohistochemical localization of PTHrP in the epidermis revealed that there was a gradient of its expression with none being expressed in the basal cells and increased expression in the upper layers of the epidermis. PTHrP receptor agonists including PTH(1-34) and PTHrP(1-34) inhibit proliferation and induce terminal differentiation of cultured human keratinocytes and inhibit DNA synthesis in the epidermis of mice *in vivo*. A practical application for PTHrP agonists is for the treatment of hyperproliferative skin disorders. PTH(1-34) was formulated in a liposomal based cream and found to be effective when topically applied to patients with psoriasis.

It was reasoned that if PTHrP is the endogenous factor that down regulates epidermal proliferation, that it might be possible to block its action by using a PTHrP receptor antagonist. It is known that PTH(7-34) binds to the receptor but does not cause any biologic function thereby acting as a pure antagonist. When PTH(7-34) was co-incubated with PTH(1-34) in cultured human keratinocytes, it partially restored the normal proliferative activity of the cells. When PTH(7-34), in a liposomal cream, was topically applied to SKH-1 hairless mice, it markedly enhanced DNA synthesis in a dose dependent fashion and increased the thickness of the epidermis two to three fold. No untoward toxicity was observed in the animals that received a topical application of this antagonist for two months.

The inner root sheath keratinocytes of the hair follicle also express PTHrP. It was reasoned that if PTHrP is the endogenous factor that down regulates proliferation, that it may be responsible for regulating the hair cycle. It was predicted that if PTH (7-34) could reverse the antiproliferative activity of PTHrP in the hair follicle, that it would stimulate and maintain hair growth. Studies were conducted in C57 BL/6 mice. The topical application of PTH(7-34) that was formulated in a liposomal cream to C57 BL/6 mice that had their hair follicles in telogen state stimulated them into anagen. It was also observed that PTH(7-34) helped preserve the hair follicles in their anagen VI phase. It was also reasoned, that if PTHrP is the factor that promotes the hair cycle into telogen, that it may be possible to use topical PTH(1-34)(the PTHrP agonist) as a mechanism to inhibit hair follicle progression from telogen into anagen. When PTH(1-34) was topically applied to C57 BL/6 mice in telogen, those animals that received placebo advanced into anagen II and III while the animals receiving topical PTH(1-34) remained in telogen. Thus, PTHrP agonists may be effective in preventing or reducing the appearance of unwanted hair.

The skin is responsible for the production of two calciotropic hormones. It is now realized that these calciotropic hormones have direct actions on the skin. It is likely that of analogs of activated vitamin D, and agonist and antagonist analogs of PTHrP for skin and hair follicle growth will play an important role for the pharmaceutical and cosmetic industries in developing new skin health and skin care products for the new millennium.

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MEADOWFOAM DERIVATIVES: TECHNOLOGICALLY ADVANCED COSMETIC INGREDIENTS

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The unique chemical structure of the Meadowfoam oil triglyceride has made possible the synthesis of exciting new compounds that have special applications for cosmetics.

A series of dimethicone copolyol meadowfoam esters has been synthesized which synergistically unite the surface-active properties of silicone with the conditioning benefits of meadowfoam fatty acids. Presented as water-soluble (LIM-1), water-dispersible (LIM-3), and oil-soluble (LIM-2) forms, these esters have the remarkable ability to repair damaged hair. Experimental evidence includes x-ray microanalysis determinations to document penetration, electron micrographs to support structural repair (Fig. 1: "Cuticle Repair"), polarized light time-lapse photomicrography to substantiate restoration of functional behavior (Fig 2: "Repair and Reconstruction") and salon studies to confirm the aesthetic evaluations and conclusions. Having observed the reparative effects of dimethicone copolyol meadowfoamate with hair that had been relaxed and permanent waved, it was logical to test the ability of this special silconemeadowfoam ester to repair hair damaged by permanent oxidative hair colors. Hair swatches were dved using oxidative hair dye formulas containing from 0 to 2% dimethicone copolyol meadowfoamate. Hair fibers were pulled to the break point in a quantitative tensile testing apparatus. The average force required to break the hair increased with increasing concentrations of dimethicone copolyol meadowfoamate. The results show that the addition of this silicone ester of meadowfoam fatty acids to hair color formulations can help protect hair from the damaging effects of permanent hair color. Penetration of the LIMs into the hair fiber led to the postulate that it may well be capable of "carrying" other materials into the hair fiber. When added concomitantly with selected permanent hair colors, dimethicone copolyol meadowfoamate, at levels of 3 to 5%, demonstrated the ability to generate increased color intensity when compared to controls that did not contain the additive.

Octyldodecyl meadowfoamate (Meadowester GME) results from the esterification of the natural triglycerides of meadowfoam with a branched-chain guerbet alcohol. This ester is a high molecular weight branched compound, in the form of a clear yellow liquid, that provides appreciable user benefits in a wide variety of important personal care products. Salon evaluations demonstrate significant improvement in the quality and aesthetics of hair following treatment with conditioners containing from 2 to 5% of the ester. The ability of octyldodecyl meadowfoamate to serve as a superfatting agent is particularly important in terms of treating dry scalp since the deposition of the long-chain unsaturated fatty ester should rapidly relieve the dehydrated tissue and thereby reduce irritation to and shedding of the affected area. Quite remarkably, the meadowfoam guerbet ester demonstrates the properties of a non-occlusive moisturizer that has the ability to facilitate hydration of epidermal tissue without blocking the pores on the surface of the skin thereby allowing the skin to continue to "breathe" (Figs. 3 and 4).

Meadowestolide results from new advances in organic synthesis by which an oligomeric ester is formed from the reactive self-condensation of meadowfoam fatty acids. Molecular structure has been characterized by NMR, HPLC, and GC/mass spectroscopy. In salon evaluations, meadowestolide provided statistically significant benefits including detangling, improved combability, and measurable improvement in fiber texture. Skin hydration studies, both NOVA and TEWL, document meadowestolide as an active moisturizing agent.

Cosmetic "substantivity", or the ability to adhere to the negatively charged surface of skin and hair, results from the use of cationic quaternized meadowfoam derivatives that provide conditioning properties in a variety of personal care products. The meadowfoam quaternium, PEG-2 dimeadowfoam-amidoethylmonium methosulfate (Meadowquat HG), is a highly conditioning substantive compound that incorporates two long-chain, unsaturated fatty acid moieties in every molecule of the quat. When applied with semi-permanent hair colors at a level of 1 to 5%, PEG-2 dimeadowfoam-amidoethylmonium methosulfate provided meaningful benefits including improved pigment deposition, perceivable conditioning and greatly enhanced shine.

Meadowfoam Derivatives: Technologically Advanced Cosmetic Ingredient The Fanning Corporation Chicago, Illinois Alan Wohlman, Ph.D.

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STRUCTURE/ACTIVITY RELATIONSHIP IN COSMETIC RAW MATERIAL: TAILOR-MADE NATURAL BLENDS

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The research of new substances is often affected by industrial criteria, such as the ease of chemical synthesis, cost of basic raw materials, reproducibility and presence of impurity, as well as by the investments required by the current laws in order to ensure appropriate safety standards.

Natural resources

Industrial research has increasingly tended to develop projects, which make sensible use of the existing resources and optimize the blends of known substances of natural origin, where possible. This is due to a number of reasons, such as the uncertain prospects of animal-testing, the necessity of making considerable investments when researching new molecules, and the doubt that the proliferation of new substances is inevitably causing the research on functionality of known molecules to lose importance. These new strategies can prevent exorbitant financial costs, allow the use of easily reproducible substances at low energy cost, and create special blends whose innovation is represented by the choice and the balanced use of the molecules rather than their structure itself.

New selected blends

Many examples of this trend could be given. Our study dealt with the original blend of the Meadowfoam Seed Oil, viscous oil extracted from Limnanthes Alba seeds, and Shea Butter phospholipids, commercially named Fancol VB (INCI name: Limnanthes Alba, Butyrospermum Parkii) initially aimed at implementing the basic absorption properties of lanolin. This association brought to a special blend with new properties, with enhanced performances compared to the individual components.

We studied in detail its properties in the preparation and stabilization of emulsions and its sensorial performance in order to identify the main possible applications in cosmetics.

Main properties

From the preliminary evaluations carried out in order to check to which extent much the compounding hypothesis was confirmed, Fancol VB resulted to be an absorption base, a W/O coemulsifier and a O/W emulsions stabilizer, a good pigments wetting agent with emollient, super-fatting and make-up removing properties.

Its capability to substitute lanolin derivatives is made evident by this set of properties and has been confirmed by some experimental applications

• Natural absorption base and W/O co-emulsifier

Simple emulsions of Fancol VB (15-20-25-30-40-50-75%) with water gave decreasing viscosity at the higher water amounts, while pH was not measurable. This type of behavior is typical of W/O emulsions and very similar to what is observed with lanolin oil.

• Pigments dispersion power

Uncoated mineral pigments and organic lakes were easily dispersed into our oily blend. Powder concentrations that could be reached in order to get fluid suspensions were around 60-65 % of mineral pigments into oil, while the traditionally used castor oil, the most common dispersing agent for pigments used in make-up, may reach 40 -45 % maximum suspended powders. Moreover, lakes may be dispersed at amounts that are about the double (45-50%) of what can be obtained when dispersed in castor oil: predispersions of pigments in fluid vehicle can so be easily obtained.

• Influence on foam volume in a tensioactive blend

Considering that polarity makes molecular orientation possible and foams are stabilized by means of systems of orientated molecules, these properties was successfully exploited to achieve stable-foam products.

At 2%, foam volume and foam stability of a traditional detergent blend has increased by more than 10 %, while higher percentages did not influence the foam behavior but had noticeable effects on the skin feel of the formulations.

• Sensory characteristics

After checking the emulsifying and co-emulsifying properties, the structure of the molecules involved was considered. It was found that the loose structure of the lipids allowed the achievement of a non-tacky emollient feel as well as the lipids polarity allowed easy emulsification by polymeric emulsifiers.

The after-feel of emulsions depends also on the structure of the oils. The feel is silky when the spreading properties and the bonds of emulsified oils with surface keratin are stronger than the intermolecular attractions in the oils.

• Formulations

Moreover, the polarity of the involved molecules and the solvent power over lipids lead to alternative approach in designing new formulations for removing the make-up. These formulations act upon the proteins/waxes/horny layer bonds and do not use surfactants or emulsifiers. Examples of formulations will be given and commented during the presentation.

In conclusion, in-depth research of known substances may allow making the most of the distinctive features of their molecules, such as form, structure, polarity and its interrelations.

SURFACTIN SODIUM SALT: AN EXCELLENT BIO-SURFACTANT FOR COSMETICS

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Introduction

Surfactin, one of the most powerful surfactants, was first isolated from the culture broth of several strains of Bacillus subtilis in 1968(1) and the structure was determined (2,3,4,5). Since, many researches have been reported that such kinds of microorganisms secrete surfactin and it has good potential as a surfactant of special purposes. However, there has been little successful application to industry. The reason was that the productivity of surfactin of the microorganisms was too low to supply it to the market at a reasonable cost.

We have worked around this unique bio-surfactant for

several years, and have successfully improved the microorganism and established a production method of surfactin sodium salt with a remarkably high yield.

And we have also found its various excellent properties as a surfactant. With such a strong surface activity, we believe, it exhibits an outstanding possibility in various aspects for application to industrial use such as cosmetics, skin-care products, pharmaceuticals and general washing detergents.

In this presentation, those properties of surfactin are reported with data including emulsion stability and low skin irritation.

Experimental

Materials. Surfactin sodium salt was produced by fermentation of B. subtilis and purified in our laboratory. Human cultured model skin was purchased from Gunze. All other reagents were purchased from domestic suppliers. Male rabbits, aged 8-9weeks, were employed for primary skin irritation examination.

Surface activity. Surfactants were dissolved in water and surface activity was measured by the plate method using automatic surface activity meter CBVP-Z (Kyowa kaimen kagaku) at room temperature.

Primary skin irritation in rabbits. Surfactants were dissolved in water. Each substance was closed-patched on the skin of the rabbits for 24 hours, and the skin was observed after 24, 48, 72 hours and 4, 5, 7, 10, 14 days. The erythema and edema observed were scored by the standards of Draze's method.

Results and discussion

Structure of Surfactin molecule. The typical chemical structure of surfactin is shown in Figure 1. It has a hydrophilic peptide-ring consisted of seven amino acids. L-glutamic acid and L-aspertic acid have two carboxyl



Figure 1. A chemical structure of surfaciin



Figure 2. A comparison of the surface activity

groups that carry anionic charges. A long fatty acid residue builds up the hydrophobic domain. The chain configuration varies in length and branching. The major species has twelve outer-ring carbon atoms with branching at its end as shown in Figure 1. Our product is a mixture of sodium salts of surfactin with slightly different amino acid arrangements and fatty acid chains.

Strong surface activity. It was confirmed in our laboratory that the critical micelle concentration (CMC) of surfactin sodium salt was 3 μ M. Figure 2 shows the decrease of surface tension of various surfactant aqueous solutions. Such a low CMC of surfactin is one of the lowest values of all ever-known detergents. Compared to sodium dodecyl sulfate (SDS), CMC of surfactin is one thousand times lower than that of SDS. Generally, nonionic detergents have much lower CMC than anionic or cationic ones. It is noteworthy that Surfactin has a lower CMC than Triton X100.

High stability of surfactin emulsion. Surfactin emulsion is very stable. In this experiment, A five-milliliter of squarane was emulsified with the same volume of 0.1 % surfactant solutions using a mechanical emulsifier, and then incubated at 80°C for 60 days. The results are shown in figure 3. Only surfactin emulsion remained after such a long severe incubation. Therefore it was confirmed that surfactin emulsion was stable even at high temperature. The high stability of surfactin emulsion is quite likely owing to its large molecular size. Its molecular weight is about one thousand Dalton. Compared to other surfactants, it is relatively large. The massive molecular size contributes to stabilizing the micelle, as it requires more energy to move the arranged surfactin molecules building the micelle than other detergents.



Figure 3. Squarane emulsion at 80°C after 60 days

Low skin irritation. The primary skin irritation of

surfactin was evaluated in rabbits. Sodium lauroyl glutamate (SLG) and SDS were also evaluated as the reference substances. Each substance was closed-patched on the skin of the animals and the observed erythema and edema were scored. The degree of irritation was compared by P.I.I. (primary irritation index; a sum of scores for each substance divided by the number of animals). The results are shown in figure 4. Surfactin showed a significantly low P.I.I. It is noteworthy that no irritation was observed at all at the concentration of 2.5%, which is the expected normal concentration in cosmetics. These results indicate that surfactin is far from irritative.

Summary

Surfactin sodium salt is an anionic lipopeptide biosurfactant produced by microorganisms. It has a unique chemical structure and shows a strong surface activity. The emulsion of surfactin is very stable. It is supposed that the stability is caused by its massive structure. Furthermore, surfactin shows an extremely weak skin irritation. These properties suggest the use of surfactin suitable for cosmetics.

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Figure 4. A comparison of the primary skin irritation