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Skin Feel Agents

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INTRODUCTION

Skin feel additives are substances conferring sensorial properties to a skin care product, triggering pleasant perception during application onto the skin and after use. Effectiveness of sensory triggers is governed by their substantivity to the skin that occurs either by hydrophobic interaction, or by electrostatic interaction, or a combination of these two factors. A large variety of cosmetic ingredients function as skin feel/conditioning additives comprising lipophilic materials, silicones, water-soluble polymeric substances (including proteins) and their cationic derivatives, humectants, etc. The Cosmetic, Toiletry, and Fragrance Association (CTFA) divides skin-conditioning agents into several groups: emollients, occlusive materials, and miscellaneous substances including, among others, cationic macromolecules and various surfactants.

This chapter focuses on skin feel agents for rinse-off products and more particularly for surfactant-based skin-cleansing products: facial cleansers, soap and syndet bars, shower gels and body washes, foam baths (or bubble baths), and bath oils.

Shower gels, bars, and facial cleansers first contact the skin, before being rinsed during the cleaning process; the persistence of the conditioning agents onto the skin is crucial to ensure sensory performances otherwise they are washed off and the end benefit is not perceived by the user. For bath products intended to be heavily diluted for use, it is difficult for skin feel agents to be really effective, except perhaps in case of bath oils. Indeed, when bath oils are diluted in water, they either float at the water/air interface or lead to a coarse unstable o/w emulsion; when the body emerges from the bath, oils spontaneously stick onto the skin because of their water incompatibility, excluding them out of the "bathing liquor."

The advent of emollients in body-cleansing liquids occurred with the emergence in the early 1990s of the "body washes" referring to "2 in 1" foaming emulsions; before the development of this new product niche, cationic polymeric materials were the most used skin-conditioning agents in skin-cleansing products.

Sensorial performance profile of a body-cleansing product comes in a variety of signal attributes:

- Feeling on the skin during use: spreading of the liquid (also related to product rheology), feel of the bar (slipperiness or roughness), foam feel related to foam quality (creaminess, density);
- Skin feel during rinsing under running water: for example, slipperiness, roughness of the skin, "clean feel" (squeaky feel) left by soaps;
- Feel while drying the skin with a towel and feel on damp skin: softness, roughness, stickiness; and
- After feel and long lasting of skin sensations: smoothness, softness, moisturization, etc.

All these product attributes are governed at first by the composition of the cleansing base: the surfactant nature (amphoterics, nonionics, and anionics), their total and relative concentrations, the clinical mildness for the skin of the surfactant mixture, etc. The sensorial profile of the product can be further influenced or improved by judiciously chosen skin-conditioning agents.

Besides physical, clinical, and organoleptic characteristics of the body-cleansing product, several other imponderable parameters can act upon the skin feel performance and perception: environmental conditions, usage habits, water hardness, skin condition of the user, pilosity, etc.

Also, consumer expectations in terms of sensorial profile of a product depend on climatic (relative humidity, temperature) and socio-demographic parameters (sex, occupation, lifestyle, running water availability, etc.), skin type and concerned body part (face, whole body, etc.), product positioning (sport, moisturizing, nourishing, others), etc.

Criteria of selection and technical constraints to be taken into account when choosing skin feel agents are as follows:

- Solubility and compatibility with the surfactant system
- Sensitivity to electrolytes and pH
- Product physical form: bar, liquid
- Processability (bars) and easiness of formulation
- Sensitivity to temperature
- Impact on finished product performance profile:
  - on the foam: foam feel, volume and stability, creaminess, bubble size, texture, etc.
  - on the product rinseability
  - induction of undesirable and unexpected secondary effects on skin feel when skin is damp (e.g., stickiness)
- Impact on finished product esthetic:
  - on base odor, fragrance character, perception, and stability
  - on product clarity when relevant
  - on viscosity, rheological profile
  - on color
- Origin: animal or vegetal, natural, or synthetic
- Risk of skin sensitization
- Cost

EMOLLIENTS AND REFATTENERS

Introduction

CTFA dictionary defines *emollients* as “cosmetic ingredients which help to maintain the soft, smooth, and pliable appearance of the skin; emollients function by their ability to remain on the skin surface or in the stratum corneum to act as lubricant, to reduce flaking, and to improve the appearance of the skin.”

Emollients are also described as *refattening additives* or *refatteners* in case of bath products. The word “refattener” refers to substances improving the lipid content of the upper layers of the skin; they prevent defattening and drying out of the skin.

Several emollients showing strong lipophilic character are identified as *occlusive* ingredients; they are fatty/oily materials that remain on the skin surface and reduce transepidermal water loss. CTFA dictionary defines “occlusives” as: “cosmetic ingredients which retard the evaporation of water from the skin surface; by blocking the evaporative loss of water, occlusive materials increase the water content of the skin.”

Overall, emollients and refatteners are oils and fats derived from natural origins or obtained by chemical synthesis; they are classified as nonpolar (paraffin’s and isoparaffin’s) and polar substances (esters and triglycerides); their chemical structure influence the interaction with the skin surface and affect their sensorial properties. As a class, they comprise lipids, oils and their derivatives, fatty acid esters, lanolin derivatives, and silicones and their organo-functional derivatives.

Originally emollients were developed for use in leave-on skin care products. Formulation technology can aid the deposition of refattening additives on the skin from wash off products and avoid that they rinse off with the surfactants; nevertheless, the large dilution factor in bath products remain a significant hurdle for skin end benefit perception (except in bath oils).

Emollients and refatteners will provide after feel but will also influence skin feel during usage, foam feel, and most of the time foam quantity and quality. The more hydrophobic is the refattening additive, the more deleterious its impact on flash foam generation, foam quantity, and stability.

In other respects, the more oily/fatty the material, the better is its deposition onto the skin and its substantivity, and the easier the efficacy documentation. Proof and substantiation of claims is of more and more importance in the frame of European legislation for cosmetics and toiletries and in the context of the competitive environment.

Lipophilic Emollients and Occlusives

Occlusive materials comprise among others vegetable oils, triglycerides, mineral oil, natural or synthetic waxes, fatty acid esters, lanolin oil and its derivatives, polydimethylsiloxanes, etc. (Table 1).

They form an occlusive layer on the skin, keeping water inside the upper stratum corneum (SC) layers and consequently acting as moisturizers.

Mineral oil and vegetable oils as well as waxes generally produce heavy and greasy feeling on the skin. *Hydrophobic fatty acid esters* are an almost unlimited source of synthetic emollients and refatteners; they provide lighter and more pleasant skin feel than oils and waxes. Any fatty acid can be esterified either by ethylene glycol or propylene glycol, or

Table 1 Emollients and Refatteners

		INCI names
Fats/oils (triglycerides); hydrocarbons; waxes		Petrolatum
		Ceresin
		Mineral oil
		Wheat germ oil/wheat germ glycerides
		Almond/peach oil
		Coconut oil
		Jojoba oil
		Rape seed/olive/sesame oil
		Sunflower/corn/safflower oil
Fatty acid esters: hydrophobic emollient esters	Ethylene glycol esters	Glycol stearate, or palmitate, or oleate
	Polyethylene glycol esters	PEG-5 octanoate
		PEG-5 isononate and trideceth-9
	Propylene glycol esters	Propylene glycol myristate or laurate
	Polypropylene glycol esters	PPG-36 Oleate
	Isopropyl esters	Isopropyl myristate, or laurate, or palmitate
	Polyglyceryl esters	Polyglyceryl-10- laurate or myristate
	Alkyl esters	Octyl octanoate
		Cetearyl octanoate
		Octyl hydroxystearate
		Castoryl maleate
Fatty acid mono and diglycerides		Glyceryl oleate
		Glyceryl laurate
Ethoxylated triglycerides		PEG-6 caprylic capric triglycerides
		PEG-4 caprylic/capric glycerides
		PEG-45 palm kernel glycerides
		PEG-20 almond glycerides
		PEG-60 corn glycerides
		PEG-18 palm glycerides
		Olive oil PEG-7 esters
		Hydroxylated milk glycerides
Ethoxylated mono and diglycerides: hydrophilic emollient esters	Ethoxylated glyceryl esters	PEG-7 glyceryl cocoate
		PEG-8 glyceryl laurate
		PEG-15 glyceryl laurate
		PEG-30 glyceryl cocoate
		PEG-78 glyceryl cocoate
		PEG-20 glyceryl oleate
		PEG-82 glyceryl tallowate
		PEG-200 glyceryl tallowate

Abbreviations: INCI, International Nomenclature of Cosmetic Ingredients; PEG, polyethylene glycol.

glycerin polymers, or isopropyl alcohol, or any longer chain alcohol, etc. The feel they impart and their impact on foam is related to the fatty acid chain length; short chains (e.g., isopropyl myristate and octyl octanoate) deliver dryer feel and have lesser impact on foam than longer ones (e.g., stearates and isostearates) that are greasier and detrimental to foam quantity and stability (1).

Hydrophobic emollients are efficacious skin refatteners but not easy to incorporate in surfactant mixtures commonly used in liquid skin-cleansing products. They must be emulsified that most of the time necessitates hot process. They have a detrimental impact on foam speed, quantity, and stability. In order to circumvent this weakness of lathering capacity, manufacturers sometimes provide a mechanical foaming device with the body-cleansing product: a puff or massage flower (2).

Highly hydrophobic refattening additives are not meant for foaming preparations but rather for bath oils. Soaps and syndet bars can easily accommodate waxes and oils without impairing their basic foaming and cleaning functions. Besides beeswax, petrolatum or ceresin, lanolin and jojoba oil, cocoa butter or mineral oil are other examples of skin conditioners commonly used in bars. Paraffin wax is often used in soaps and syndets not only for the smooth feel they impart to the finished bar and the mildness they bring to the formulation but also for the role of plasticizer they play, adding firmness to the bar. Vegetal oils are included as skin nourishing/refattening agents (e.g., almond, wheat germ, olive oils).

Fatty acid mono and diglycerides (1,3) are prepared either by transesterification of triglycerides with glycerin or reaction of alkanoates with glycerin. Lipophilic character remains predominant in these esters; depending on chain length, they are soluble in surfactant solutions or they must be emulsified. Besides the improved skin feel they induce, they also reduce defatting of the skin possibly caused by surfactant-based cleansers. Monoglycerides of stearic, lauric, and palmitic acids (glyceryl mono stearate, laurate, and palmitate) are part of the composition of natural lipids of the skin. They adsorb and can be detected on skin after application through a skin-cleansing product (4).

Several mixtures of monoglycerides and mild foaming surfactants are commercially available; they claim improved foam qualities (bubble sizes, creaminess, and stability) and documentable skin-refattening properties (5,6). On top of skin feel improvement, they also reduce degreasing effect of cleansers, thanks to their lipophilic character, and improve the compatibility of the surfactants with the skin (1). An example of improvement in the skin barrier function and in skin tactile sensations has been demonstrated for glyceryl oleate in a model shower gel composition (5).

Hydrophilic Lipids

Hydrophilic lipids are (Table 1) (1) preferred for foaming skin-cleansing preparations. Ethoxylation and propoxylation make lipids more compatible with water and more easily soluble in aqueous surfactants solutions.

One has to find the right balance between ethoxylation and skin substantivity: the more the lipids are ethoxylated, the more they are soluble and the less the impact on foam but also the less their persistence on the skin, the weaker their refattening properties.

Ethoxylated glycerides are obtained either by reaction of natural triglycerides with ethylene oxide (a complex end mixture is then obtained) or by ethoxylation of monoglycerides. They are often referred to as "water soluble vegetable oils"; their solubility in water will depend on the carbon chain length of starting glycerides and on the degree of ethoxylation.

Low ethoxylates triglycerides are still enough lipophilic to provide good refattening properties, leading to very pleasant skin feel, perceivable at quite high use levels.

Ethoxylated mono and diglycerides generally associate various properties beneficial to the skin. They are more or less refattening the skin, depending on chain length and ethoxylation ratio. They act as anti-irritant or mildness additives and confer slipperiness to the foam. Depending on chain length and ethoxylation degree they are either water dispersible or soluble. Among the low ethoxylates monoglycerides, PEG-7 glyceryl cocoate is one that is mostly used. This emollient depresses skin irritation induced by anionic surfactants and shows minimum impact on lathering profile. Higher ethoxylates of longer carbon chain length (PEG-200 glyceryl tallowate) are still substantive to the skin because of their high-molecular weight; they provide a smooth feel, but because of their stronger hydrophilic character, their refatting properties are less obvious to evidence (7).

Table 2 Emollients and Refatteners

		INCI names
Lecithin		Propylene glycol (and) lecithin (and) sodium lauryl sulfate (and) disodium sulfosuccinate (and) cocamidopropyl hydroxysultaine (and) isopropyl alcohol
Lanolin and its derivatives		Lanolin oil
		Lanolin alcohol
	Ethoxylated lanolin	PEG-75 lanolin
	Ethoxylated lanolin alcohols	Laneth-16
		Laneth-25
	Propoxylated lanolin alcohols	PPG-30 lanolin alcohol ether
		PPG-12 PEG-50 lanolin
	Alkoxylated lanolin	PPG-40 PEG-60 lanolin oil

Abbreviations: INCI, International Nomenclature of Cosmetic Ingredients; PPG, polypropylene glycol; PEG, polyethylene glycol.

Ethoxylated/propoxylated fatty alcohols are useful light emollients: through an appropriate selection of optimum combination between parent alcohol chain length and propoxylation/ethoxylation degree, these emollients can be formulated up to 2% to 3% in surfactant solutions with minimum impact on foam volume.

Lanolin

Lanolin is extracted from sheep wool grease; it is a complex mixture of esters of high-molecular-weight lanolin alcohols (aliphatic alcohols, sterols, and trimethyl sterols) and of lanolin fatty acids. Free lanolin alcohols, acids, and lanolin hydrocarbons are minors. Lanolin alcohols and lanolin oil are recommended as superfatting agents in soaps. *Ethoxylation* of the hydroxyl groups *of lanolin* or of its *derivatives* leads to hydrophilic, water-soluble lanolin compounds, offering a broad range of useful emollients to the formulator (Table 2) (8,9). Some moderately to highly ethoxylated derivatives, recommended for their good emolliency and moisturization properties, are processable in liquid skin cleansers with limited impact on foam profile; as an example, *the 75 moles ethoxylated lanolin* does not depress foam and is recommended as skin conditioner in soaps, liquid body-cleansing products, and bubble baths. *Medium ethoxylates lanolin alcohols* have limited impact on foam performances of body-cleansing liquids; *lower ethoxylates* can be formulated in bars. *Propoxylated lanolin alcohols* are lipophilic emollients used in soap bars and in other cleansers on the basis of synthetic surfactants.

Alkoxylated lanolin derivatives are obtained by reaction with mixtures of propylene and ethylene oxides in various ratios; they are more soluble than ethoxylated lanolin. They serve as refattening and foam-stabilizing agents.

Esterification of *lanolin fatty acid* with isopropyl alcohol provides a range of *esters* of various molecular weights. Medium-molecular-weight esters are used as superfattening agents in soaps.

The use of animal-derived ingredients in cosmetics is regulated in Europe. Lanolin is part of those ruminant-derived ingredients considered as noninfective with regard to BSE, according to World Health Organization (WHO).

Lecithin

Lecithin (Table 2) is a natural mixture of polar and neutral lipids; the word "lecithin" is also used as the trivial name of a particular phospholipid: phosphatidylcholine.

Main vegetable sources of lecithin used in personal care products are soybean and maize; egg yolk is practically the only animal source of lecithin used in cosmetics and toiletries. The percentage of polar lipids and their fatty acid pattern are characteristic of the lecithin source.

Bare lecithin, a secondary product of soybean oil extraction, typically contains 60% to 70% polar lipids (mainly phospholipids, namely phosphatidylcholine and glycolipids), and a remaining, 25% to 35% soybean oil. This raw lecithin is further fractionated, purified, and chemically modified to allow easier processing and formulation in toiletries products. Emollient, refattening, and moisturizing properties of lecithin are guided by its content in phospholipids.

Lecithin softens, nourishes, and refattens the skin; it provides a nongreasy, long-lasting skin feel and improves foam feel and quality (creaminess, slipperiness, richness).

Ready to use mixtures of phospholipids in surfactant solutions, free of residual soybean oil, are commercially available for an easy incorporation in liquids or bars; some of these compounds allow formulation of clear products.

Silicone Derivatives

Only major materials used in body-cleansing products will be briefly discussed here (10,11).

Predominant silicones used overall in personal care products are polydimethyl siloxane also named *dimethicones*. They are not soluble in water or in surfactant solutions; their incorporation into liquid cleansers requires an emulsification process. The length of dimethylsiloxane polymer chain dictates its molecular weight and hence its viscosity. Most commonly used materials have viscosity ranging from about hundred to several thousands centistokes. High- to medium-molecular-weight dimethicones are occlusive, skin protective emollients; lower molecular weights are dryer emollients, generally preferred for use in skin cleansers. Dimethicones have detrimental effect on foam profile but are good film-forming agents, lubricant, imparting a nongreasy, nontacky, and silky feel as compared with "heavier" mineral or vegetable oils. They are used in soap bars, where they also aid mold release, and in 2-in-1 shower gels (foaming emulsion body washes). More recently, emulsions of ultra high-molecular-weight silicone were developed that are easily incorporated in aqueous systems such as body washes and facial cleansers; they impart soft residual film, moisturized skin feel even from a rinse-off product.

Polymethylcyclosiloxanes or *cyclomethicones* are tetrameric or pentameric oligomers of the same backbone as polydimethylsiloxane and show the same chemical and physical properties; they are low viscosity fluids with relatively high volatility because of their low molecular weight and the weak intermolecular attractivity. Because they are not substantive, cyclomethicones are often identified as dry emollients; they deliver light, transient, and dry skin feel during product use.

Formulation of these nonpolar insoluble silicones requests hot emulsification process (nonionic emulsifiers) and proper emulsion stabilization.

Dimethicones are modified or functionalized with other organic groups to modulate their solubility in water or in surfactant solutions (and consequently make them easier to formulate) and their skin substantivity properties. By adjusting the type and proportion of hydrophilic substituents, the resulting copolymer is soluble or dispersible in aqueous cosmetic products. The combination of the dimethicone structure with polyoxyalkylated substituents (ethylene or propylene oxide) yields *dimethicone copolyols*: copolymers more soluble in water with surface activity. They are foam boosters and stabilizers; even if they are less film forming than parent polydimethylsiloxanes, they significantly participate to skin sensations during application (use) and provide excellent smooth and silky after feel (12). They can be used to formulate clear aqueous products.

Blends of polydimethylsiloxanes with volatile and/or water-soluble derivatives are used to design a sensorial profile adapted to the finished product and its end use.

HUMECTANTS

CTFA dictionary defines humectants as "cosmetic ingredients intended to increase the water content of top layers of the skin" (Table 3).

Humectants are hygroscopic substances generally soluble in water; these "moisture attractants" maintain an aqueous film at the skin surface.

The primary humectant used in personal care products is glycerin; it tends to provide heavy and tacky feel, which can be overcome by using it in combination with other humectants such as sorbitol.

Table 3 Humectants

Humectants	INCI names
	Glycerin
	Glycereth-26 and glycereth-7
	Propylene glycol
	1,3 butylene glycol
	PEG-8 to about PEG-200
	Sorbitol
	Sorbeth-6 to sorbeth-40
	Xylitol
Ethoxylated methyl glucose	Methyl gluceth -10/methyl gluceth-20
	Amino acids
	Lactic acid/sodium lactate
	Sodium PCA
Substantive conditioning humectants	Steardimonium panthenol
	Lauryl methyl gluceth-10 hydroxypropyl dimonium chloride
	Chitosan-PCA

Abbreviations: INCI, International Nomenclature of Cosmetic Ingredients; PCA, pyrrolidone carboxylic acid; PEG, polyethylene glycol.

Less expensive than glycerin, propylene glycol is the second most widely used humectant in cosmetics and toiletries products; it reduces viscosity of surfactant solutions and tends to depress the foam.

Low-molecular-weight polyethylene glycols (PEGs from about 10–200 PEG units), amino acids, and other constituents of skin natural moisturizing factors (NMFs) such as sodium pyrrolidone carboxylic acid (PCA) and sodium lactate are also applicable for use in surfactant-based skin-cleansing products.

Humectants are not substantive to the skin, they are easily rinsed-off after cleaning; consequently, skin feel improvement is not obvious to perceive, and their efficacy in terms of skin moisturization is difficult to document.

Glycerin, propylene glycol, 1,3-butylene glycol, or sorbitol are typically used in body washes, bubbles baths, shower gels, or soaps to prevent the desiccation of the product itself and the formation of a dry layer (a skin) at the surface. They also ensure stability and clarity of liquid cleansers at cold temperatures.

Few substantive humectants can be mentioned. They are cationic in nature, which makes them adsorbing to the negatively charged skin surface. In the quaternized polyalkoxylated methyl glucose derivative (lauryl methyl gluceth-10 hydroxypropyldimonium chloride), the hydrophilic moiety delivers humectant properties; the hydrophobic chain at the cationic end of the molecule ensures both substantivity and skin conditioning.

Another example is chitosan-PCA; it is a polycationic (at acidic pH) high-molecular-weight polymer produced by deacetylation of chitin, the major constituent of invertebrate exoskeletons. Combining chitosan with PCA leads to a highly substantive, film-forming humectant material.

POLYMERS

Polymeric materials can interact both with protein of skin surface and with skin lipids. Parameters influencing the interaction between skin surface and polymers are as follows:

- The positive charge density: the more cationic the character of the polymer, the better the polymer interaction with negatively charged skin surface.
- The hydrophobicity of polymer: grafting of fatty moieties on the polymer backbone favors hydrophobic interactions with hydrophobic areas of the keratin.
- The molecular weight of the polymer: the higher the polymer size, the more its substantivity to the skin (film-forming properties). However, very low-molecular-weight polymers can easily penetrate the skin surface chinks and as such adsorb into the superficial stratum disjunctum.

- The nature of surfactants surrounding the polymer in the finished product: the polymer can interact with surfactants either through their charges or through hydrophobic interactions; also competition between polymer and surfactants for skin-anchoring sites can occur. In both cases, deposition and adsorption of polymer onto the skin surface is weakened.

Natural Polymers and Their Chemically Modified Derivatives

Proteins

Proteins differ by (*i*) the source; (*ii*) the molecular weight; (*iii*) the amino acids (AA) composition, AA side groups, and electrical charge (more of cationic or of anionic AA); and (*iv*) the chemically attached moieties (quats, fatty chains, silicone, etc.) on the peptide backbone (Table 4) (13–15).

Proteins can be from vegetable or animal origin. The use of animal-derived ingredients in cosmetics is regulated in Europe because of the emergence of BSE infection in ruminants. Hydrolyzed proteins, among other collagens, are considered as safe in cosmetics provided that the supplier implements and certifies the application of an adequate production process.

Collagen from pork or beef is still one of the most widely used *animal* proteins; "marine collagen" (fish) is used as alternative source of collagen to traditional bovine-derived materials. Milk proteins, keratin, and elastin are also considered in cosmetics and toiletries. Concerns related to BSE have initiated a shift away from animal-derived ingredients and an increased interest in plant-derived proteinic materials.

Vegetable/plant proteins are most of the time associated with significant amounts of soluble and insoluble carbohydrates because of extraction process; soluble carbohydrates confer dark color and strong odor to the raw material; in some commercial grades carbohydrates have been removed. The combination of hydrolyzed vegetable proteins and oligosaccharides produces conditioning additives with synergistic moisturizing action and

Table 4 Natural Polymers and their Chemically Modified Derivatives

		INCI names
Native proteins		
	Solubilized in anionic surfactants	Native wheat protein/lauryl ether sulfate complex
Protein hydrolyzates	Animal source	Hydrolyzed animal protein
		Hydrolyzed collagen
		Hydrolyzed milk protein
	Plant derived	Hydrolyzed vegetal protein
		Hydrolyzed wheat protein/oligosaccharide complex
		Hydrolyzed wheat protein and hydrolyzed wheat starch
		Hydrolyzed oats
		Hydrolyzed wheat gluten
Quaternized protein hydrolyzates	Animal source	Hydroxypropyl trimonium–hydrolyzed collagen
	Plant derived	Hydroxypropyl trimonium–hydrolyzed wheat protein
Fatty side chains grafted on protein backbone	Native protein	Wheat extract (and), stearic (and), sodium chloride
Quaternized fatty chains grafted	Protein hydrolyzate	Steardimonium-hydrolyzed wheat protein or collagen
		Lauryl or cocodimonium hydroxypropyl–hydrolyzed collagen
		Alkyl quaternary–hydrolyzed soya protein
Copolymers	Protein-PVP	Hydrolyzed wheat protein/polyvinyl pyrrolidone copolymer
	Protein-Silicone	Hydrolyzed wheat protein hydroxypropyl polysiloxane copolymer
	Quaternized copolymer	Hydroxypropyl trimonium–hydrolyzed wheat protein polysiloxane copolymer

Abbreviations: INCI, International Nomenclature of Cosmetic Ingredients; PVP, polyvinyl pyrrolidone.

film-forming properties. Major vegetal starting materials are wheat gluten, almond meal, rice, oat, soy, maize, etc.

Proteins are functional over a wide range of pH; nevertheless, as they are amphoteric materials, below their isoelectric point they carry a net positive charge, which makes them substantive to the negatively charged skin surface.

Film-forming properties of proteins and hydrolyzates are related to their molecular weight (the higher, the better). Overall, proteins convey smoothing and moisturizing effect, they produce soft and silky feel to the skin. They have positive effect on foam profile: they increase foam stability, creaminess, and density as well as confer slipperiness to the foam.

Proteins and hydrolyzates are also known for their ability to reduce the irritation caused by anionic surfactants and to combat skin dryness induced by detergents (16–19).

Some native proteins such as elastin, keratin, or vegetable proteins are insoluble. There exists soluble native collagen species; their use is restricted to some specialized applications. In order to make native proteins suitable for a wide range of applications, they are converted into soluble hydrolyzates by chemical or enzymatic degradation. The sizes of resulting peptides depend on the hydrolysis process used: chemical processes give rise to broader-molecular-weight distributions and enzymatic digestion to narrower ones. Besides that, native proteins solubilized in various anionic surfactants (by formation of a protein-surfactant complex), are commercially available, allowing easy formulation of these film forming, moisturizing, skin mildness additives.

A wide range of protein hydrolyzates molecular weights is available, ranging from 500,000 down to 1000 Da. Protein hydrolyzates of intermediate molecular weight (average 3000–5000 Da) are the most widely used; they are less substantive than high-molecular-weight proteins but still provide smooth skin feel, slippery feel during use, and sensation of skin hydration.

Hydrolyzates are readily soluble and compatible with all classes of surfactants.

Most of commercially available proteins and derivatives have characteristic odor and color. Furthermore, products formulated with proteins or hydrolyzates should be adequately preserved.

Chemically Modified Protein Derivatives

In order to increase interaction of proteinic material with skin surface, proteins or hydrolyzates are functionalized or chemically modified (Table 4). Protein possesses reactive side chain amino and carboxyl groups, which are sites for further modification of their intrinsic properties.

Hydrophobic interactions with the skin surface are favored and reinforced by grafting fatty carbon chains; ionic interactions are maximized by grafting cationic moieties onto the protein backbone.

Hydrolyzed protein copolymers combine substantivity and film-forming properties of parent proteins with characteristic sensorial properties of companion conditioning agents; these macromolecular proteinic complexes offer greater moisturizing and conditioning potential as compared with the individual components (20).

1. *Native proteins coupled with fatty acids* lead to macromolecular entity with dual hydrophilic/hydrophobic characteristics and physicochemical properties. Skin substantivity is guided both by the size of the starting protein and by the chain length (the hydrophobicity) of the fatty acid. The macromolecules are surface active and can be formulated in bars or liquids; they produce smooth long-lasting skin feel. Long chain fatty acid derivatives tend to decrease foam volume but confer creaminess, richness, and slipperiness to the lather.
2. *Copolymers of silicone and proteins* are obtained by covalent bonding of low-molecular-weight polydimethylsiloxanes on amino groups of (vegetable) protein hydrolyzate. They combine beneficial properties of proteins (anti-irritant effect, substantivity, film forming, soft after feel) with lubricity of silicone (21,22). Quaternized protein–silicone copolymers are also commercially available.
3. *PVP-protein copolymers*: proteinic component imparts substantivity and polyvinyl pyrrolidone (PVP) maximizes the moisture retention and film-forming properties of

the resulting copolymer. PVP/protein ratio will modulate the profile of performance on the skin and the influence on lathering characteristics of surfactant-based skin cleanser.

4. *Quaternized protein hydrolyzates*: cationic protein hydrolyzates are obtained by reaction of the primary amine sites on the protein backbone with a tertiary amine: hydroxypropyl or propyl trimethyl ammonium or alkyl trimethyl ammonium (23).

   Covalent attachment of quaternary groups strongly increases the cationic character of the protein hydrolyzate, making it further skin substantive and resistant to rinsing with water.

   Covalent attachment of fatty quaternary groups (alkyl dimethyl ammonium) on peptides greatly enhances both ionic and hydrophobic interactions with the skin. Alkyl chain can be lauryl, myristyl, and stearyl. Alkyl trimonium-hydrolyzed proteins are still water soluble and compatible with all classes of surfactants. These hydrophobically modified cationic protein hydrolyzates are highly adsorbing to skin surface at all pH levels and offer skin substantivity at minimum concentration. They impart pronounced conditioning effect; the lipophilic moieties provide emollient feel.

   Overall, quaternized versions of a protein are many times more substantive than the parent protein hydrolyzate. Quaternization of protein hydrolyzates raises their isoelectric point (IP) to pH 10 regardless of their initial IP values.

Cationic Guar Gum

Guar gum is a galactomannan polysaccharide derived from the endosperm of cyamopsis tetragonolobus seeds (Table 5).

Depolymerization of the gum by enzymatic or chemical processes allows to modulate its molecular weight and consequently to impact its solubility, thickening properties, and the transparency of the finished product. Free hydroxyl groups on the polysaccharidic backbone can participate in esterification and etherification reactions. Hydroxypropyl (HP) side groups improve guar compatibility with electrolytes. Cationic guar derivatives are obtained by reaction of HP guar with epoxypropyltrimethyl ammonium chloride; positive charge density of resulting guar hydroxypropyl trimonium chloride depends on substitution degree. Cationic guar derivatives are film forming and impart soft, smooth, and silky feel to the skin; moreover

Table 5 Natural Polymers and their Chemically Modified Derivatives

	INCI names	Comments
Cationic cellulose derivatives		
	Polyquaternium 10	Polymeric quaternary ammonium salt of HEC reacted with trimethyl ammonium-substituted epoxide
	Polyquaternium 24	Polymeric ammonium salt of HEC reacted with lauryl dimethyl ammonium-substituted epoxide; average degree of substitution=1
	Polyquaternium 67	Polymeric quaternary ammonium salt of HEC reacted with a trimethyl ammonium-substituted epoxide and a lauryl dimethyl ammonium-substituted epoxide
	PG-hydroxyethyl cellulose lauryl or coco or stearyl dimonium chloride	Average degree of substitution>1
Cationic guar derivatives		
	Guar hydroxypropyl trimonium chloride	
	Hydroxypropyl guar hydroxypropyl trimonium chloride	
Cationic phospholipid polymer	Polyquaternium 64	Cationic phospholipid polymer with phosphorylcholine moiety

Abbreviations: INCI, International Nomenclature of Cosmetic Ingredients; HEC, hydroxyethyl cellulose.

they act as anti-irritant for anionic surfactants and soaps and have positive effect on foam feel and quality (24,25).

Cationic Cellulose Derivatives

Polyquaternium 10 is a range of polymeric quaternary ammonium salts of hydroxyethyl cellulose (HEC) reacted with *trimethyl ammonium-substituted epoxide*. Polyquaternium 10 solutions are non-Newtonian and are commercially available (*i*) in several viscosity grades depending on their molecular weight (they contribute to viscosity of formulations) and (*ii*) with "high" to "moderate" cationic substitution. In vivo tests showed that these cationic cellulosic polymers protect the skin from aggression by anionic surfactants (Table 5) (26,27).

Polyquaternium 24 is a polymeric quaternary ammonium salt of HEC reacted with *lauryldimethyl ammonium-substituted epoxide*; it is a hydrophobically modified polyquaternium 10.

The degree of substitution with quaternary fatty chain is average one in polyquaternium 24; a range of alkyl dimonium hydroxypropyl oxyethyl cellulose with higher proportion of grafted cationic fatty groups (average degree of substitution is 1.2) is also commercially available.

Polyquaternium 67 is high-viscosity quaternized hydroxyethylcellulose incorporating variations in charge level and hydrophobic modification. This family of cationic cellulosic conditioning polymers combines the *trimethyl ammonium* functionality of polyquaternium 10 with various levels of *dimethyl-dodecyl-ammonium* hydrophobic functionality. Their degree of cationic substitution has been fixed at ~0.2, which corresponds to a weight-percentage nitrogen of ~1%. Low levels of hydrophobic dimethyl-dodecyl-ammonium substitution (HS=0.01) were used to impart hydrophobic character to the polyquaternium 10-type polymers. Four polymer grades are available ranging from the lowest to the higher degree of hydrophobic substitution. The whole range enables crystal clear formulations.

The presence of fatty side chains on all these quaternized cellulose ethers makes them surface active and further participates to their very high skin substantivity and film-forming properties. They impart silky smooth after feel.

These alkyl quaternary cellulose polymers are soluble in water (longer carbon chains must be slightly warmed) and compatible with a wide range of surfactants; they have favorable influence on the lathering properties providing creaminess, density, slipperiness, and stability to the foam.

Synthetic Quaternized Polymers

An array of dimethyldiallylammoniumchloride (DMDAAC)-based polymers and copolymers are commercially available. Their substantivity, film-forming properties, and resulting skin feel depend on both the molecular weight (ranging from about 400,000–7 millions) and the density of positive charges, which also dictates the compatibility of the polymer with anionic surfactants. These polymers generally make foam denser and more stable (Table 6) (28).

DMDAAC homopolymer (polyquaternium 6) carries the highest positive charge density and is not compatible with anionic surfactants.

Table 6 Synthetic Quaternized Polymers

		INCI names
Polyquaterniums		
	Polyquaternium 6	Dimethyl diallyl ammonium chloride homopolymer
	Polyquaternium 7	Acrylamide/dimethyl diallyl ammonium chloride copolymer
	Polyquaternium 11	Poly(vinylpyrrolidone/dimethylaminoethyl methacrylate)
	Polyquaternium 22	Acrylic acid/dimethyl diallyl ammonium chloride copolymer
	Polyquaternium 39	Acrylamide/acrylic acid/dimethyl diallyl ammonium chloride terpolymer
	Polyquaternium 70	Polymeric quaternary ammonium salt consisting of an ethoxylated propoxylated stearyl amine condensed with adipic and dilinoleic acid,quaternized with dimethyl sulfate

Abbreviation: INCI, International Nomenclature of Cosmetic Ingredients.

Inclusion of acrylamide into DMDAAC homopolymer decreases the positive charge density, leading to a skin-conditioning polymer more compatible with anionics (polyquaternium 7) (29,30). Polyquaternium 7 is probably one of the most widely used synthetic cationic polymer in body-cleansing products; it is highly substantive to the skin, delivering soft, silky, moisturized after feel (28).

Positive charge density is also decreased by copolymerizing DMDAAC with either acrylic acid (polyquaternium 22) or with both acrylamide and acrylic acid (polyquaternium 39). Another widely used synthetic cationic polymer in liquid skin cleansers and in bar soaps is a quaternized copolymer of PVP and dimethylaminoethyl methacrylate (DMAEM) (polyquaternium 11). This PVP copolymer is available in molecular weights ranging from 100,000 to 10,00,000.

SURFACTANTS

Benefits brought by additional skin-conditioning agents are sometimes hidden by a mild or very mild cleaning surfactant system delivering by itself very good skin feel properties; the sensorial baseline is high to start with, and the increment in performance brought by skin feel agent is leveled off, and sometimes even not perceivable (Table 7).

Table 7 Surfactants

		INCI names
Nonionics		
	Polyhydric alcohol esters	
	Sucrose esters	Sucrose laurate or cocoate
	Methyl glucose esters	PEG-120 methyl glucose dioleate
		PEG-80 methyl glucose laurate
	Glucose ethers	Alkyl polyglucosides
	Fatty acid alkanolamides	Cocodiethanolamide
Amphoterics		
	Ampholytes	Cocamidopropyl betaine
		Olivamidopropyl betaine
		Sesamidopropyl betaine
		Isostearamidopropyl betaine
		Cocamidopropyl hydroxysultaine
		Cocamidopropyldimethyl aminohydroxypropyl hydrolyzed collagen
		Dimethicone propyl PG-betaine
	Propionates	Alkylamino propionates
		Alkyliminodipropionates
	Imidazoline derivatives	Acylamphoacetate
Anionics		
	Phosphoric acid esters and salts	C9-C15 alkyl phosphate
		PPG-5 ceteth-10 phosphate
		Oleth-3 phosphate
	Acyl amino acids and salts	
	Acyl peptides	Sodium cocoyl hydrolyzed protein
		Sodium lauroyl oat amino acids
		TEA or sodium lauroyl animal collagen amino acids
	Acyl glutamates	Sodium cocoyl glutamate
	Sarcosinates	Sodium cocoyl or lauroyl sarcosinate
	Taurates	Sodium methyl cocoyl taurate
	Sulfonic acids and salts	
	Sulfosuccinates	Disodium laneth-5 sulfosuccinate
		Disodium ricinoleamido MEA-sulfosuccinate
		Disodium laureth sulfosuccinate
		Disodium PEG-8 palm glycerides sulfosuccinate
	Isethionates	Sodium cocoyl isethionate
	Carboxylates	Alkyl glucose carboxylate
		Sodium PEG-7 olive oil carboxylate

Abbreviations: INCI, International Nomenclature of Cosmetic Ingredients; PPG, polypropylene glycol; PEG, polyethylene glycol.

Table 8 Exfoliants/Scrubbing Agents

Apricot/walnut shells powder or flour
Corn cob
Jojoba beads
Polyethylene/styrene beads
Almond meal
Apricot/peach seed powder
Loofah
Maize scape powder
Kaolin

It is, however, important to notice that several mild anionic and most of the nonionic surfactants, if they provide a pleasant after feel, are characterized by a "water feel" (feel in solution) often unpleasant, with rough and drag feel sensations.

Amphoteric surfactants are amino acid derivatives, and their net charge varies with the pH in solution; at pH below the IP, they are positively charged in aqueous solution and can consequently adsorb more easily onto the skin. Alkyl chain length also significantly acts on the skin feel; some betaines based on C16/C18 cuts provide greasier refattened feel, but also have detrimental effect on foam. Polydimethylsiloxane grafted with a betaine moiety leads to an amphoteric surfactant combining substantivity, refattening properties, as well as silicone typical skin feel profile.

Some *nonionics* are used for their emollient properties and excellent after feel: sucrose and methyl glucose esters as well as sucrose ethers are mentioned as examples. Fatty acid alkanolamides are often referred to as refatteners; these are not lipids but they confer a greasy slippery feel to the foam and impart a particular after feel on the skin, which subjectively compares to refattening.

Several mild *anionic surfactants* are known to provide improved skin feel (after feel) by themselves: sarcosinate, taurate, acylglutamate, and isethionate are cited as examples. Fatty acids-protein condensate salts and also act as a conditioning aid imparting a pleasant smooth feel to the skin. The inclusion of fatty acids in soap and syndet bars contributes to enhance skin feel during and after use and produce creamier lather. Phosphoric acid fatty esters deliver soap-like skin feel: slipperiness during use and very good rinseability, leaving skin feeling "clean" and powdery like after feel.

EXFOLIATING AGENTS

Skin scrub agents or body polishers are solid materials from natural origin (clay, fine powder of seeds or shells of different vegetables) or obtained by chemical synthesis (tiny beads of styrene or polyethylene) (Table 8). When the scrub agent containing body-cleansing product is rubbed or massaged onto the skin, fine solid particles remove superficial skin horny layer by mechanical abrasion, leaving behind a fresh smooth skin surface. They are the easiest additives for the consumer to perceive. Scrubbing particles can be suspended in liquid body cleanser, thanks to structuring polymers such as xanthan gum or carraghenan, which build a viscoelastic network in the surfactant matrix. The scrubbing agent must be very carefully selected when formulating facial cleansers. Skin of the face is more sensitive or delicate than the rest of the body. For facial application, formulator should orientate his choices toward soft clays or melting jojoba beads for example.

CONCLUSIONS

The overall skin feel profile provided by a skin-cleansing product is conditioned by the huge variety of composition constituents. Many of them have been described in this chapter, but not exhaustively. Other factors can influence the sensations perceived by the consumer such as the presence of electrolytes, or of thickening polymers in the product as well as the water hardness in the user dwelling. It will be the responsibility of the formulator to consider all the potential synergisms or antagonisms in his finished product in order to deliver the desired skin feel.

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35 Silicones—A Key Ingredient in Cosmetic and Toiletry Formulations

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UNIQUE MATERIALS

Silicone is a generic name for many classes of organo-silicone polymer that consist of an inorganic siloxane (Si–O) backbone with pendant organic groups (usually methyl). It is this structure that gives silicones their unique combination of properties and, in particular, their surface properties (Fig. 1 and Table 1).

SILOXANE BACKBONE

The prime role of the siloxane backbone is to present the available methyl groups to their best advantage, and it does this by virtue of its unique flexibility. In most hydrocarbons, the bond angles are very fixed, and steric packing considerations often prevent the available methyls from adopting the lowest surface energy orientations. In silicones, the Si–O bond length is significantly longer, and the Si–O–Si bond angle is flatter than the comparable C–C and C–O bonds, resulting in a very low barrier to rotation and making the polymer chains very flexible. This flexibility makes many orientations possible and provides "free space" to accommodate different-sized substituents or to allow easy diffusion of gaseous molecules, a property useful in the formation of "breathable" films. Coupled with the low intermolecular forces between methyl groups, this flexibility also has a profound effect on the bulk as well as the surface properties of silicones, seen in the small variation of physical parameters with temperature and molecular weight, the low freezing and pour points of fluids, the low boiling points, the high compressibility, and the retention of liquid nature to unusually high molecular weights. It also makes a number of structural and compositional variations possible, resulting in many families of silicones, including linear and cyclic structures, a wide range of molecular weights, and varying degrees of branching or cross-linking.

Additionally, the siloxane bond is exceptionally strong, providing the polymer with a high degree of thermal and oxidative stability and ensuring the stability in formulation (1–3).

PENDANT ORGANIC GROUPS

The key function of the organic (methyl) groups is to provide the intrinsic surface activity of the silicones. The order of increasing surface energy for single carbon-based groups is −CF3 > −CF2– > −CH3> −CH2–. Liquid surface tension measurements show that, as expected, the order of increasing surface activity is hydrocarbon, followed by silicone, and then by fluorocarbon. Interfacial tension measurements against water, however, show the order of increasing interfacial activity to be fluorocarbon, hydrocarbon, and silicone. Silicones do not fit the simple pattern that a reduction in surface energy means an increase in hydrophobicity and interfacial tension because of their backbone flexibility, which allows them to adopt various orientations at different interfaces. The interfacial tension of silicone is also independent of chain length indicating high-molecular chain freedom. In addition, the critical surface tension of wetting values for silicones has been found to be higher than their liquid surface tension values, meaning that they are able to spread over their own absorbed film. This has an advantage as silicones achieve complete, uniform surface coverage, facilitate the efficient spreading of other materials, and result in smooth, lubricating films.

In addition, because of the organic groups the solubility parameters of silicones are significantly lower than those of water, and many organic materials make them useful in forming barriers to wash off or wear and increase the substantivity of formulations.

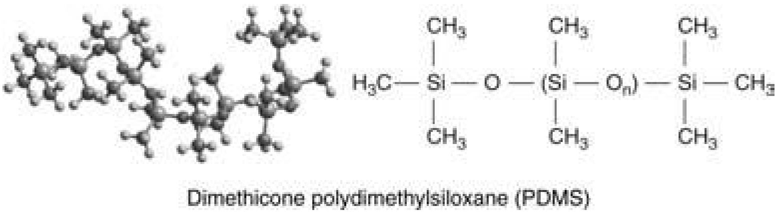

Figure 1 Unique chemical structure of silicones.

The introduction of functional groups such as phenyl, alkyl, polyether, and amino onto the backbone expands the properties and benefits of silicones further (1–3).

KEY INGREDIENTS IN THE COSMETICS AND TOILETRIES INDUSTRY

Silicones were first used in the cosmetics and toiletries industry in the 1950s, when low levels of medium-viscosity dimethicone [polydimethylsiloxane (PDMS)] were used to prevent the whitening effect, characteristic of soap-based skin lotions. It was not until the 1970s when formulators were concerned about the use of chloro fluoro carbons (CFCs) in aerosols and silicones were considered more seriously as possible ingredients for cosmetic formulations and their unique properties began to be recognized. Since then, the use of silicones has expanded rapidly to virtually all segments, and today, more than 40% of all new products being introduced into the U.S. market contain silicone, with many different types being used (4).

There are five main families of silicones that are used in the cosmetics and toiletries industry today:

1. Volatile siloxanes [cyclosiloxanes (ring structure) and low–molecular weight linear PDMSs] can be used as such or blended with each other to adjust the volatility. They are good solvents and serve as good carriers for high–molecular weight silicones that would otherwise be very difficult to handle. In addition, they have very low heat of vaporization compared with water or ethanol giving them a non-cooling feel when drying. Cyclomethicones are classified as non-VOCs (volatile organic compounds) in the United States (Fig. 2).
2. Dimethicones (PDMSs) are linear structures with molecular weight ranging from 700 to more than 100,000. The nonvolatile dimethicones exist as fluids with viscosities of 5.0 mm^2/sec up to gums. Dimethicone emulsions make handling of the higher–molecular weight fluids easier. Specialized emulsion polymer technologies allow the production of ultrahigh–molecular weight linear PDMS emulsions with an internal dynamic viscosity as high as 200 million mm^2/sec.
3. Silicone blends consist of dimethiconol or dimethicone gums or trimethylsiloxysilicates (highly cross-linked resins) dispersed in lower–molecular weight dimethicones or cyclomethicones. They have been developed to improve the ease of formulation and compatibility of high-molecular gums or resins used for their substantivity.
4. Dimethicone and vinyl dimethicone cross polymers or blends are silicone elastomers, which are cross-linked to different degrees, resulting in different product forms. They exist in powder form, pure or coated with particles (free flowing or suspended in water), or as elastomeric silicone gels that are swollen with solvent (usually volatile silicone). The introduction of different functionality into such products is also possible. They are used as rheology modifiers in skin care and antiperspirant products, providing a dry, powdery feel to formulations (5).
5. Functional silicones:
   a. Dimethicone copolyols (silicone polyethers) are fluids or waxes in which some of the methyl groups along the siloxane backbone have been replaced with

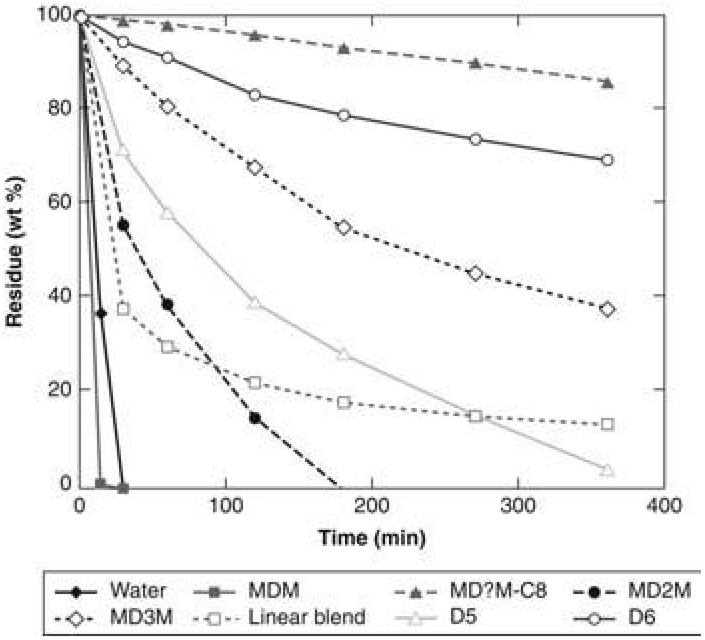

Figure 2 Comparison of volatility for volatile methylsiloxanes (0.1 g, 31°C).

polyoxyethylene or polyoxypropylene groups. The addition of polyoxyethylene substituents increases the hydrophilicity of silicones. Polyoxypropylene substituents are used to balance out this hydrophilicity by increasing the hydrophobic characteristics of the copolymer. Some of these silicone polyethers are also very good water-in-silicone emulsifiers. The addition of alkyl chains results in a material able to emulsify water into low to medium polarity oils.

Among these polyether-modified silicones, a special mention is necessary for silicone carbinol fluid (bis-hydroxyethoxypropyl dimethicone) (6), a very versatile material with good compatibility with organic materials that can act as a wetting agent to stably disperse pigments and actives, while also providing moisturization.

b. Phenyl trimethicones are fluids in which some of the methyl groups have been replaced by phenyl groups. The phenyl groups increase the refractive index and improve compatibility with organic materials.
c. Amodimethicones or trimethylsilylamodimethicones are fluids in which some of the methyl groups have been replaced by secondary and primary amine groups. The polar amine groups have a profound effect on the deposition properties of the silicone, giving it an affinity for negatively charged surfaces, such as the proteinaceous surface of the hair. Emulsions of these fluids are commonly used.
d. Alkyl dimethicones are fluids or waxes in which some of the methyl groups have been replaced by alkyl groups. This results in a family of silicone-hydrocarbon hybrids with possibilities for variations in viscosities, softening temperatures, and rheological characteristics. They have increased compatibility with organic materials.
e. Silicone acrylate copolymers (acrylates/polytrimethylsiloxymetacrylates copolymer). These film-forming copolymers can be delivered from both silicone and organic solvents and provide enhanced durability, wash off resistance, and aesthetic coupled with easy formulation for skin care and color cosmetic formulations (7)

SKIN CARE, SUN CARE, AND DECORATIVE PRODUCTS

Skin Feel/Emolliency

The main reason why the silicones are used in all types of skin care product is because of their sensory properties. Studies on the emollient properties of various materials have shown that silicones deliver greater emolliency values than many commonly used cosmetic ingredients both during and after application. They are described as smooth, velvety, and nongreasy or oily and are able to impart this feel to cosmetic and toiletry formulations, improving the negative feel associated with other ingredients (8).

Volatile silicones are used for transient effects giving slight lubricity, a light texture, fast spreading, and good distribution of the product on application, while leaving no residual effects. They are often included in formulations to remove the greasy or oily feel of hydrocarbon-based emollients and are the basis for “oil-free”-type claims (9). They are used in light products for daily use such as facial cleansers, day creams, or liquid foundations. Higher–molecular weight silicones such as dimethicone (and) dimethiconol are used to give a more lubricious, longer-lasting effect in richer, more nourishing skin treatment products such as night creams or after-sun products (10). Silicone elastomers are used to give a dry, powdery feel to skin care formulations (11). Silicones are also noncomedogenic/nonacnegenic unlike many occlusive, lipophilic fatty emollients, which can promote comedone/acne formation on the skin (12).

Substantivity (Long Lasting/Durability)

High–molecular weight dimethicone or cyclomethicone (and) dimethiconols form water-resistant films on the skin, which can help prolong the effects of skin care, sun care, or decorative products. This substantivity can be improved further by using alkyl dimethicones such as cetyl dimethicone or C30-45 alkyl methicone (Fig. 3) (13).

The use of silicones to improve the substantivity of other ingredients in cosmetic and toiletry formulations has been demonstrated in sun care products. The addition of 2.5 wt% cetyl dimethicone to an oil-in-water sunscreen formulation shows excellent in vivo resistance to wash off. The formulation has a sun protection factor (SPF) of 21.1 before immersion, which reduces to 19.2 only, after immersion for 80 minutes (14).

Volatile silicones are the basis for long-lasting/nontransfer decorative products, especially lipsticks. They are used to disperse waxes and pigments, improve application, and impart a pleasant skin feel, often replacing nonvolatile hydrocarbon oils. When they evaporate, a uniform film of waxes and pigments remains, which is resistant to transfer and wear (15).

Silicone acrylate copolymers have the ability to form non-occlusive films that resist wash off. This film-forming property is useful in sunscreens, while in lipsticks it pairs with an excellent sensory profile translating into improved nontransfer while maintaining very good wearing comfort (7).

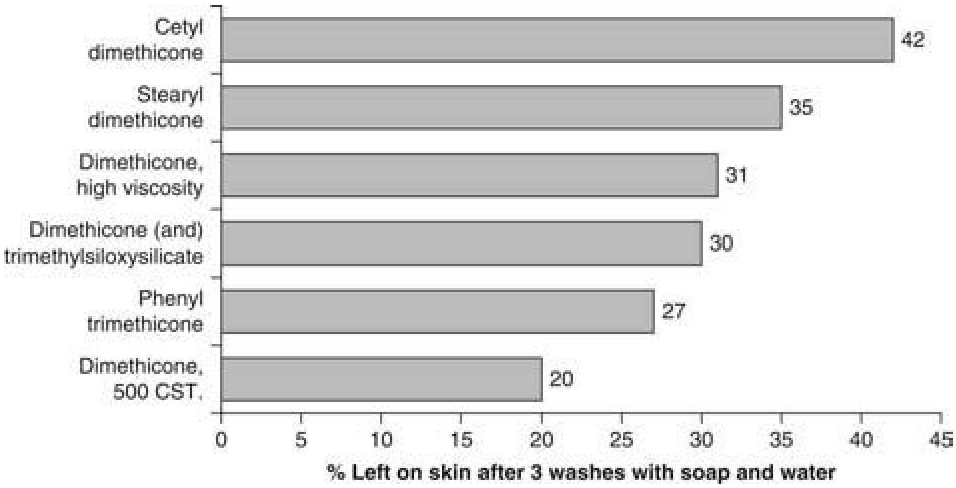

Figure 3 Substantivity of different silicones.

Table 1 Permeability of Different Materials Payne Cup Method

Material	Water vapor permeability $g/m^2/hr$
Volatile silicone	152
Sunflower oil	125
Silicone gum	121
PDMS 350 cSt	107
Mineral oil	93
C18 Alkylmethylsiloxane	37
C30 Alkylmethylsiloxane	2
Petrolatum	0

Abbreviation: PDMS, polydimethylsiloxane.

Permeability/Controlled Moisturization/Protection Against Dehydration

Because of the flexibility of the Si–O–Si backbone, the majority of silicones are permeable to water vapor, producing breathable films. This is an important parameter for cleansing products or color cosmetics to avoid clogging pores. The presence of an alkyl group in the chain, however, reduces this permeability, resulting in silicones, which can give semipermeable materials, e.g., cetyl dimethicone or occlusive material similar to petrolatum, e.g., C30-45 alkyl methicone (Table 1) (16).

Enhanced Efficacy

Apart from improving the feel and long-lasting benefits of skin care products, silicones can also enhance the efficacy of other ingredients in the formulation. Studies carried out on sun care products have shown that the alkyl methicones can enhance the SPF of products containing either organic or inorganic sunscreens. A 2% addition level of stearyl dimethicone into an oil-in-water silicone containing 11% of organic sunscreens resulted in an in vivo SPF of 49.7, an SPF/UVB ratio of 4.5, thus demonstrating high efficiency (17). For inorganic sunscreens, a 100% increase in SPF was seen with an oil-in-water system containing 2 wt% cetyl dimethicone and a 75% increase in the SPF for a water-in-oil system containing C30-45 alkyl methicone (18).

In antiaging formulations, the addition of silicone elastomer powders, at a level of 4%, has been shown to provide wrinkle-masking benefits in addition to their unique skin feel (19).

Protection

Dimethicone is listed in the FDA (food and drug administration) Monograph for Skin Protectant Drug Products for over the counter (OTC) Human Use in the United States. Because of their hydrophobicity, silicones are used in protective hand creams to provide a water-resistant barrier against waterborne contaminants. Recent studies indicate that cyclomethicone and dimethicone may also prevent irritation caused by sunscreen agents (20).

Cleansing

The excellent spreading characteristics, dry nongreasy/oily feel, and good solvency of volatile silicones make them ideal for use in skin cleansers to help lift and remove dirt without stinging. They can be used alone or in combination with ingredients such as mineral oil. Silicone emulsifiers allow low-viscosity silicone fluids to be present in the continuous phase as well as the incorporation of polar ingredients such as water and glycerin, allowing the formulation of rinseable foaming facial washes (21).

Volatile alkyl silicones (caprylyl methicone) were demonstrated to have superior cleansing properties over cyclopentasiloxane and isohexadecane, ingredients often used in biphasic makeup removers (22).

Powdered silicone elastomers have the capability of absorbing lipophilic materials such as sebum from the skin making them very useful for greasy-skin application (19).

Water-soluble dimethicone copolyols have shown benefits in foaming facial washes. They provide creamy, denser foam as well as improving the foam volume. In liquid body-cleansing products such as foam baths, shower gels, and liquid soaps, they can improve foaming and foam stabilization. They have also been recognized as additives that reduce eye and skin irritation from anionic surfactants (23).

Emulsions of ultrahigh–molecular weight linear silicones can be perceived on the skin at very low levels because of their very low sensory threshold (24).

Rheology Modification/Structural Integrity (Sticks)

As well as improving the aesthetics of formulations, silicones can also act as rheology modifiers. This is particularly applicable to water-in-oil- or water-in-silicone-type systems. One such silicone rheology modifier is the C30-45 alkyl methicone where 149% and 93% increases in emulsion viscosity have been observed for water-in-silicone and water-in-oil emulsions, respectively, with 2 wt% of the wax (11). Rheology modification using 2 to 4 wt% stearyl dimethicone is believed to be part of the reason for the success of this product in enhancing the SPF of sun care products containing organic sunscreens (17). These waxes are also used in maintaining the structural integrity of stick products, improving their feel and application. Silicone elastomers can also be used to modify the rheology of skin care and antiperspirant formulations. Such elastomers have the capacity to absorb large amounts of solvents such as cyclomethicone or low-viscosity dimethicone without exhibiting any syneresis (extraction of a liquid from a gel). It is this property, which allows them to successfully thicken formulations. The ability of elastomers to significantly modify the rheology of a formulation combined with their unique powdery feel has led to their use in antiperspirant products (5).

Formulating Flexibility

Silicones can be used in all types of skin care products ranging from simple oil-in-water gels or emulsions to water-in-silicone and water-in-oil emulsions, from crystal clear to white in color. Silicone emulsifiers increase this flexibility further. They allow silicones to be present in the continuous phase as well as allowing the incorporation of polar ingredients such as water and glycerin. Matching the refractive index of the water phase with the oil phase in such emulsions makes the formulation of clear gels possible, and adjusting the phase ratio determines the product form from lotions to gels. This technology is the basis for the clear antiperspirant gels seen on the market today. It is also possible to make nonaqueous emulsions using silicones to deliver hydrophilic ingredients or those that are sensitive to hydrolysis. In addition, the benefits of water-in-oil systems such as good sensory profiles, improved wash off resistance, and excellent moisturization have been demonstrated. Silicone emulsifiers offer versatility for low- or high-shear systems as well as cold processing, presenting new opportunities for cost-effective and highly innovative skin care and underarm products (25).

HAIR CARE PRODUCTS

Hair Conditioning/Improved Combing

Various types of silicone are used to give different degrees of hair conditioning. Dimethicone copolyols provide light conditioning due to their solubility in water and low level of substantivity. They can also help reduce eye irritation associated with shampoos and similar products that contain anionic surfactants (23). Higher–molecular weight dimethicones/dimethiconols or trimethylsilylamodimethicones/amodimethicones provide a higher level of conditioning due to their insolubility in water and greater substantivity. The latter have an affinity for negatively charged surfaces such as the proteinaceous surface of the hair that contributes to their substantivity.

Evaluation of the average detangling times of dimethiconol (gum), amodimethicone, and dimethicone (high-viscosity fluid) emulsions at a 4% level in an illustrative two-in-one shampoo formulation indicates that they all show significant improvement over the untreated control tress with the dimethiconol emulsion providing the best conditioning effect (26).

Synergistic effects have been observed between quaternary polymers commonly used in shampoos for conditioning and dimethicone copolyols (Fig. 4). Better detangling results are observed for shampoos containing dimethicone copolyol and quaternary polymers than with the quaternary polymers or dimethicone copolyols alone (27).

Similar evaluation of silicones in conditioners indicates that dimethicone emulsions provide the best conditioning effect in rinse-off products and in permanent waving products;

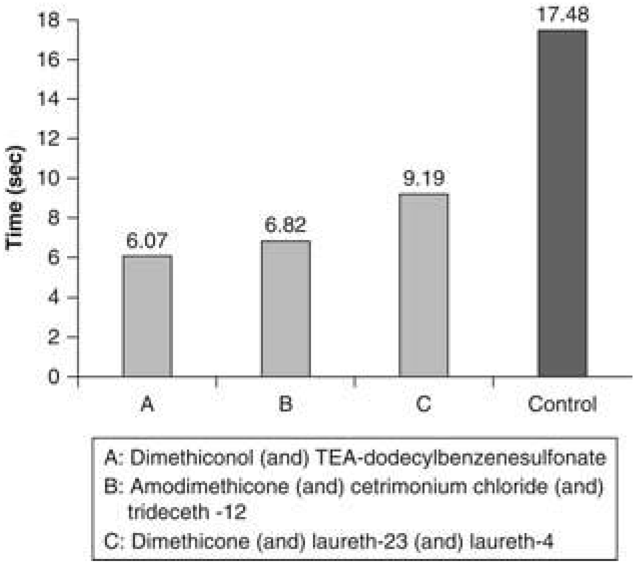

Figure 4 Hand detangling results on slightly bleached hair for diluted emulsions.

an emulsion of trimethylsilylamodimethicone significantly reduces the wet and dry combing force. Combinations of silicones such as cyclomethicone, silicone blends, and phenyl trimethicone are the basis for anhydrous leave-in conditioners, sometimes referred to as "cuticle coat" products (26).

Sensory Enhancement

As in skin care, silicones impart a soft smooth feel to the hair. Sensory evaluations of cuticle coat formulations consisting entirely of blends of silicone showed that, in addition to ease of combing, they improve spreadability, silkiness and softness, gloss, and perceived repair of split ends compared with the control (28).

Silicones as Drying Aids

Silicones such as trimethylsilylamodimethicone can help hair dry more quickly in comparison with drying aids such as stearalkonium chloride, preventing damage due to the use of hair dryers, and others (29,30).

Foam Boosting

Dimethicone copolyols can be used to boost the foaming properties of shampoos as well as provide a light conditioning effect (26).

Reduced Flyaway

Tests comparing shampoo formulations containing quaternary polymers with those with quaternary polymers and dimethicone copolyols show an improvement in static control with the addition of the silicone. Sensory evaluation has also shown a reduction of flyaway with dimethicone emulsions (26).

Improved Shine

Silicones, in particular phenyl trimethicone, are recognized for their ability to enhance hair shine and gloss along with adding softness, manageability, and smoothness to the abraded hair cuticle (26,31).

Natural-Look Fixatives

Because of their low surface tension, silicones spread easily to help fixative products distribute evenly on the surface of hair and improve their effectiveness. They are also used in conjunction with or as a replacement for organic plasticizers. Organic materials tend to be hydrophilic, which diminishes the holding power of a resin. In contrast, the hydrophobic nature of silicones helps repel water, so there is less opportunity to reduce the resin's holding properties. The use of dimethicone copolyol as a resin plasticizer can also help give hair a more natural look (26).

LONGER-LASTING PERMANENT WAVE AND COLORING PRODUCTS

Silicones, such as trimethylsilylamodimethicone, can be used to provide a more durable conditioning effect and a longer-lasting permanent wave. Pretreatments containing silicone blends help prevent hair damage during the harsh perming process. In hair color products, blends of volatile and nonvolatile silicone (cyclomethicone and trimethylsilylamodimethicone) can be used to seal the hair cuticle and hold color in. The volatile silicone evaporates, leaving behind a smooth, uniform film on the surface of the hair (32).

Amino-functional silicones can prevent degradation of the hair color due to the combination of UV exposure and washing and provide conditioning benefits such as ultra shine, improved drying time, moisturization, and a smooth and light feel without negatively impacting hair body and volume (33).

Evaluation of rinse-off conditioners indicates that silicones show excellent potential to provide color lock properties in permanent hair color products.

HAIR STRENGTHENING

Amino functional silicones leave a medium-weight film deposited primarily at the open edges of the cuticle, resulting in improved hair strength. Two possible mechanisms could explain this effect (34):

- The film may protect the hair cuticle during elongation.
- The film may assist in sealing the hair cuticle, helping prevent moisture penetration into and out the hair cortex, maintaining an optimal moisture level for hair strength.

ANTIPERSPIRANT AND DEODORANT PRODUCTS

In addition to the benefits that silicones bring to skin care products such as improved feel, delivery of actives, low residue, and formulating flexibility, the following advantages are seen in antiperspirant and deodorant formulations (35).

Anti-Whitening

Dimethicones, phenyl trimethicone or alkyl dimethicones have been shown to reduce/mask the whitening effect caused by antiperspirant salts by matching the refractive index (36).

Improved Spray Characteristics

Low levels of cyclomethicone (and) dimethiconol have been demonstrated to reduce the spray width, height, and particle size of antiperspirant pump spray and aerosol formulations, leading to a more directional spray with low mistiness and dustiness (35,37). The silicone blend may also contribute to the substantivity of the antiperspirant active and lubricate the spray valve to prevent clogging.

Non-Cooling

The heat of vaporization of volatile silicones such as cyclomethicone is much lower than that of water or ethanol meaning that much less energy is required for them to evaporate. This leads to a non-cooling effect in formulation (35).

CONCLUSION

The multifunctional benefits of silicones make them invaluable ingredients in today's cosmetic and toiletry formulations, and with the introduction of more and more new silicones, this is a trend that is expected to continue.

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Sensory Effects and Irritation: A Strong Relationship[a]

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INTRODUCTION

Most methods for testing the potential skin effects of consumer products rely on an objective evaluation of how the product affects the appearance of the skin, i.e., erythema, as scored on a predefined numerical scale. In contrast, the endpoints that consumers typically describe are subjective in nature and are an evaluation of the sensations the product causes them to experience, i.e., itchy, dry, rough, tight, etc. Even though these subjective sensory effects are the endpoints reported by the consumer and, therefore, arguably the most important, few test methods incorporate a means to leverage these endpoints.

Few reports attempt to either quantitate sensory effects or correlate sensory effects to the degree of irritation. In studies on soap and detergent bars, Simion et al. determined that test subjects differentiated between products on the basis of sensations they felt during exaggerated arm-washing applications (1). In several test methods designed to simulate normal use conditions for detergent and personal cleansing products, the perceptions of the panelists are routinely recorded during the course of the study as an additional endpoint to consider when evaluating the data (2,3). Sting tests have been used in evaluating some cosmetics and leave-on preparations (4,5).

We recently developed the behind-the-knee (BTK) test method as a means for evaluating the irritation potential of catamenial products (6–8). The BTK measures both chemical irritation and the potential for mechanical irritation due to friction. In the course of this development program, we collected subjective sensory data from our panelists in parallel with the outward signs of irritation, i.e., erythema and dryness, to determine if there may be value in attempting to quantitatively study sensory effects to learn more about the relationship between these sensations and irritant effects. We evaluated the results against the fundamental question: are differences in the irritation potential, as defined by objective scores of erythema, consistent with differences in the reported sensory effects?

Subjective sensory data on certain test products tested in the BTK were compared to several different objective endpoints: unaided visual scoring, enhanced visual scoring using polarized light, and the descriptive analysis panel (DAP).

Unaided visual scoring of erythema has been used reliably for a number of years to detect skin irritation in a wide variety of test protocols on a large number of body sites. It requires no special equipment and is easily adaptable to large-scale testing, such as the type that is required to provide safety assurance for consumer products. Trained skin graders can accurately and reproducibly score test sites for erythema and dryness (9). Several authors have demonstrated that trained graders can reliably detect evidence of irritation with equal or higher degrees of sensitivity to that of instrumental measures (10–14).

Enhanced visual scoring using polarized light has been added to existing test protocols recently in an attempt to increase the ability to differentiate between very similar products without requiring other protocol modifications. When skin reactions are scored visually, the grader is seeing a combination of endpoints: the surface changes, which provide information about the shape and texture of the skin surface, and the subsurface changes, which provide information about internal components such as erythema, pigmentation, and the vasculature (15,16). Use of polarized light sources can enable the observer to selectively examine either the surface or subsurface components. Authors have described the use of polarized light as an aid

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[a] A portion of this review appeared in Farage MA, Santana V, Henley E. 2005. Correlating sensory effects with irritation. J of Toxicol: Cutan Ocul Toxicol 2005; 24:45–52. With kind permission of Taylor and Francis Publishing Group.

in visualizing various skin conditions, including irritation, acne vulgaris, rosacea, photoaging, lentigo simplex, and basal cell carcinoma (17–20).

The DAP is used in the development of feminine care products to evaluate the intensity of six physical characteristics, including degree of plasticity, compression (loft), scratchiness, glide, cottony feel, and flexibility. We compared the results of the DAP to the results of the sensory effects analysis attempting to determine if certain physical characteristics of the products correlated to adverse sensations experienced by the BTK panelists.

The test design and conduct of the BTK studies have been described in detail by Farage et al. (6). Each study consisted of 9–22 healthy, adult volunteers (male and female) who had signed an informed consent. For each study, the protocol was approved by the test facility's institutional review board. Subjects were excluded from participation for certain skin abnormalities or health conditions that could adversely impact the test, as detailed in the prior publication.

Test materials consisted of currently marketed products and products in development for the marketplace. These included standard catamenial pads (products A, B, C, E, H, M, and N), a pantiliner (product P), a lotioned pad (product NL), intralabial pads (product IL2 and IL25), and tampons (products R and S). For application, a test material was placed horizontally and held in place behind the knee by an elastic knee band (Ace® knee bandage) of the appropriate size and removed by the panelists 30 to 60 minutes before returning to the laboratory for grading and/or reapplication of test materials. Exposures consisted of six hours per day for five consecutive days.

Visual grading of the BTK test sites was conducted by an expert grader under a 100-watt incandescent daylight blue bulb. Scoring was done using a scale of "0" to "4" previously described by Farage et al. (6). In this scale, "0" indicates no apparent cutaneous involvement and "4" is moderate to severe, spreading erythema and/or edema. The same grader was used throughout an experiment, and the grader was not aware of the treatment assignments.

Enhanced visual grading using polarized light has been described in detail by Farage (21). Grading was conducted using a polarized light visualization system (Syris v600® Visualization System, Syris Scientific, LLC, Gray, Maine, or syrisscientific.com), with separate scores recorded for parallel-polarizing illumination (surface mode) followed by cross-polarizing illumination (subsurface mode). On the basis of a communication with the manufacturer, the subsurface mode allows visualization of the site at a depth of 1 mm beneath the surface.

The mean irritation scores (unaided and enhanced visual) were compared using analysis of variance/analysis of co-variance (ANOVA/ANCOVA) or, where model assumptions failed, CMH/stratified CMH (Cochran-Mentel-Haenszel) statistical comparison.

In the BTK, panelists were asked to keep a daily diary of skin problems experienced at the test sites, as previously described (22,23). Panelists were asked if they experienced one or more of eight specific sensations, including the sample rubbing against the skin, the sample sticking to the skin, chafing, burning, itching, pain, edema, or any other discomfort. Results were evaluated for a higher occurrence of each individual skin problem with one treatment versus another using McNemar's test.

For Table 1, mean irritation scores were evaluated versus reported sensory effects using logistic regression, i.e., the presence/absence of a particular skin complaint was regressed against the specific irritation scores.

The DAP uses 15 individuals trained to evaluate six different physical characteristics of the products: degree of plasticity, scratchiness, glide and cottony feel of the top sheet, and compression and flexibility of the pad. These individuals evaluate products using their fingertips and assess the intensity of the various product characteristics on the basis of an 8-point scale, with 0 = not at all, 4 = moderate, and 8 = extreme. Results were analyzed by ANOVA, and mean differences were tested for statistical significance using Duncan multiple comparison at the 90% confidence level.

SENSORY EFFECTS AND UNAIDED VISUAL SCORES

Sensory effects have been collected and analyzed statistically in nine BTK studies containing 16 comparisons between two products or sets of test conditions. In each experiment, the reported sensory effects for the test samples were compared to determine if the results were

Table 1 Correlation of Sensory Effects with Visual Irritation Scores in Behind-the-Knee Studies

Study number	Products tested	Correlation of sensory effects with irritation scores
02017	Products N and L	Reports of burning, pain, itching, and rubbing correlate to irritation score.
03005	Products A and B under 4 different test conditions	Reports of burning, pain, sticking, and "other" correlate to irritation score.
03005-3	Products S and R under 4 different test conditions	Reports of burning, sticking, and chafing correlate to irritation scores for the w/c [a] test sites only. No correlation for d/i [b] test sites.
03005-4a	Products GT and M	Reports of burning correlate to irritation score.
03005-4b	Products GT and E	Reports of burning, pain, and sticking correlate to irritation score.
03005-4c	Products GT and H	Reports of pain, itching, rubbing, and "other" correlate to irritation score.
03005-9	Products A and B	Reports of burning, edema, and itching correlate to irritation score.
02008	Products P and IL25	Reports of burning, pain, and chafing correlate to irritation score.
02036	Product C under 2 different test conditions	Reports of burning and sticking correlate to irritation score.
02008	Products P and IL2	Reports of burning, pain, and chafing correlate to irritation score.

[a] (w/i) = wet sample on intact skin.
[b] (w/c) = wet sample on skin compromised by tape stripping. Studies were conducted as described in the legend for Table 2. For each study, the irritation scores and reported sensory effects were considered for all test sites, regardless of the products or treatments being tested. Numerical irritation scores were then evaluated versus reported sensory effects using logistic regression.

similar to those obtained when the mean irritation scores were compared. Results are summarized in Table 2. In 8 of the 16 individual product comparisons, the results are consistent (shown at the top of the Table 2). In seven of these cases, there were no differences in either the mean irritation scores or in the percentage of subjects reporting various sensory effects. In the remaining case, significant differences in the mean irritation scores appeared for at least one scoring time point, and the sample giving the higher mean score (product A) produced significantly more reports of sensory effects. In 5 of the 16 comparisons, significant differences in the mean irritation scores appeared for at least one scoring time point, and no differences appeared for the reported sensory effects. In 2 of the 16 comparisons, differences appeared in the reports of sensory effects that were not evident in the mean irritation scores. In one case, the reported sensory effects were in conflict with the mean irritation results (Table 2, study #02008, product P vs. product IL2).

Products A and B have been compared seven times in the BTK test in addition to the three comparisons shown in Table 2. In 8 of the 10 total tests (including study #03005-T9 shown in Table 2), product A was significantly more irritating than product B, on the basis of mean irritation scores with visual grading. In two comparisons (study #03005, shown in Table 2, and one other study not shown), the differences did not achieve significance.

Another analysis was conducted to determine if reports of adverse sensory effects were likely to increase as the objective score for irritation increased. In other words, if a test site is scored as a "2.0" for erythema, is it more likely that that panelist will report a sensory effect than if the site were scored as a "1.0"? Table 1 shows the results of regression analyses conducted to determine if an increase in reported sensory effects correlated to an increase in the irritation scores recorded for the eight experiments (16 comparisons) shown in Table 2. In eight experiments, reports of one or more sensory effects were correlated to the degree of irritation. In one experiment (03005-3), there was a correlation between the panelists tested under one set of experimental conditions (wet samples on compromised skin), but not under the other set of conditions (dry samples on intact skin). Burning was the effect that was most commonly correlated to higher irritation scores (in seven cases), followed by pain (in five cases).

SENSORY EFFECTS AND POLARIZED LIGHT-ENHANCED VISUAL SCORES

Two feminine protection products were evaluated in the BTK using unaided and enhanced visual grading. Scores were recorded after each product application (6-hour application

Table 2 Behind-the-Knee Studies with Comparison of Visual Mean Irritation Scores and Sensory Effects

			Results	
Study number	Samples compared		Comparison of mean irritation scores	Comparison of adverse sensory effects
Consistent results from nonaided visual scoring and sensory effects				
02017	Product N	Product NL	Not significantly different	Not significantly different
03005	Product A (d/i)	Product A (w/c)	Not significantly different	Not significantly different
03005-3	Product S (w/c)	Product R (w/c)	Not significantly different	Not significantly different
03005-3	Product S (d/i)	Product R (d/i)	Not significantly different	Not significantly different
03005-4a	Product GT	Product M	Not significantly different	Not significantly different
03005-4b	Product GT	Product E	Not significantly different	Not significantly different
03005-4c	Product GT	Product H	Not significantly different	Not significantly different
03005-9	Product A	Product B	Significantly different on days 3 and 4. Product A > product B	Percentage of subjects experiencing burning is different on all days (1–4). Product A > product B
Inconsistent results from nonaided visual scoring and sensory effects				
02008	Product P	Product IL25	Significantly different only on day 5. Product P > product IL25	Not significantly different
02036	Product C (w/i)[a]	Product C (w/c)[b]	Significantly different only on day 1. Product C (w/c) > product C (w/i)	Not significantly different
03005	Product B (d/i)[c]	Product B (w/c)	Significantly different on days 1, 3, and 5. Product B (w/c) > product B (d/i)	Not significantly different
03005-3	Product S (w/c)	Product S (d/i)	Significantly different on days 2, 3, and 5. Product S (w/c) > product S (d/i)	Not significantly different
03005-3	Product R (w/c)	Product R (d/i)	Significantly different on days 2, 3, and 5. Product R (w/c) > product R (d/i)	Not significantly different
03005	Product A (d/i)	Product B (d/i)	Not significantly different	Percentage of subjects experiencing burning is different on day 1. Product A (d/i) > product B (d/i)
03005	Product A (w/c)	Product B (w/c)	Not significantly different	Percentage of subjects experiencing pain and sticking is different on days 2 and 3, respectively. Product A (w/c) > product B (w/c)
02008	Product P	Product IL2	Significantly different only on day 1. Product IL2 > product P	Percentage of subjects experiencing itching is different on day 3. Product P > product IL2

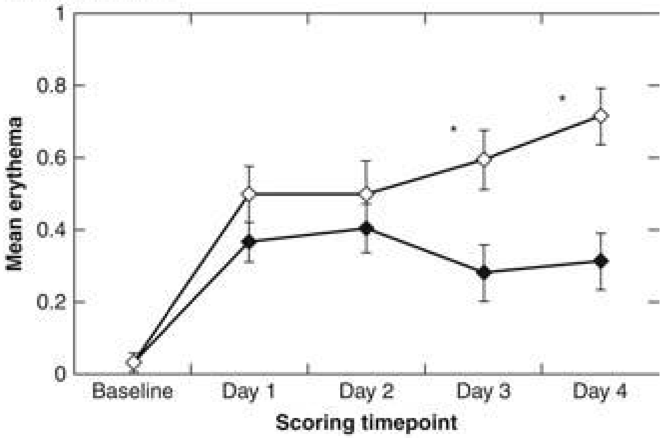
[a] (w/i), wet sample on intact skin.

[b] (w/c), wet sample on skin compromised by tape stripping.

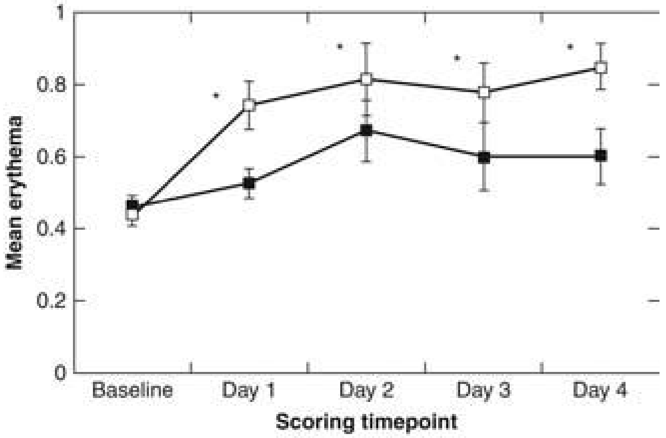
[c] (d/i), dry sample on intact skin (standard protocol).

In each study, panelists wore the test substances for 6-hr daily for 4 days in close contact with the skin behind the knee. The two test areas (left knee and right knee) were randomly assigned 1 of the 2 test materials or conditions being compared in that particular study. Test sites were scored 30–60 min after removal of each product application. The mean irritation score for each treatment at each afternoon scoring was determined. There were compared using ANOVA/ANCOVA or, where model assumptions failed, CMH/stratified CMH tests. In addition, subjects kept daily diaries of sensations associated with each test site throughout the course of treatment. Panelists were specifically asked about the sample and knee brace rubbing against the skin or sticking to the skin and about chafing, burning, itching, pain, or any other discomfort. Each individual complaint was tabulated, and the percentage of subjects who experienced that compliant was determined. The data were evaluated using McNemar's test.

(A) Visual scores



(B) Subsurface scores



(C) Surface scores

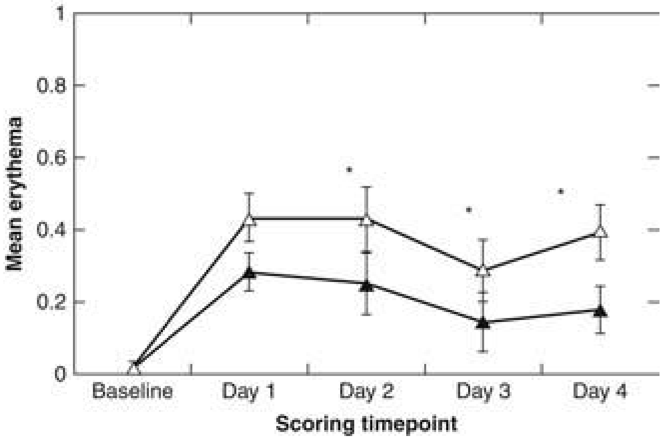


Figure 1 Standard visual and enhanced visual grading using two similar products in the BTK. Two feminine protection products (pad A and pad B) were evaluated in the BTK. Samples were applied for six hours per day for four consecutive days (14–16 panelists per group). Scoring was conducted at baseline and the morning following each patch removal (day 1–4). The graph plots mean erythema (±S.E.) at each scoring time point. Figure 1(**A**) shows visual scores; 1(**B**), subsurface scores; and 1(**C**), surface scores. Treatment comparisons were evaluated using the stratified CMH test. (*Significant difference between pad A and pad B, $p < 0.05$). Pad A = open symbols. Pad B = closed symbols. *Abbreviation*: BTK, behind the knee.

followed by 18-hour recovery period). As shown in Figure 1A, significant differences between the two products were apparent on day 3 (after three applications) using unaided visual scoring. Using polarized light-enhanced scoring, significant differences were observed after

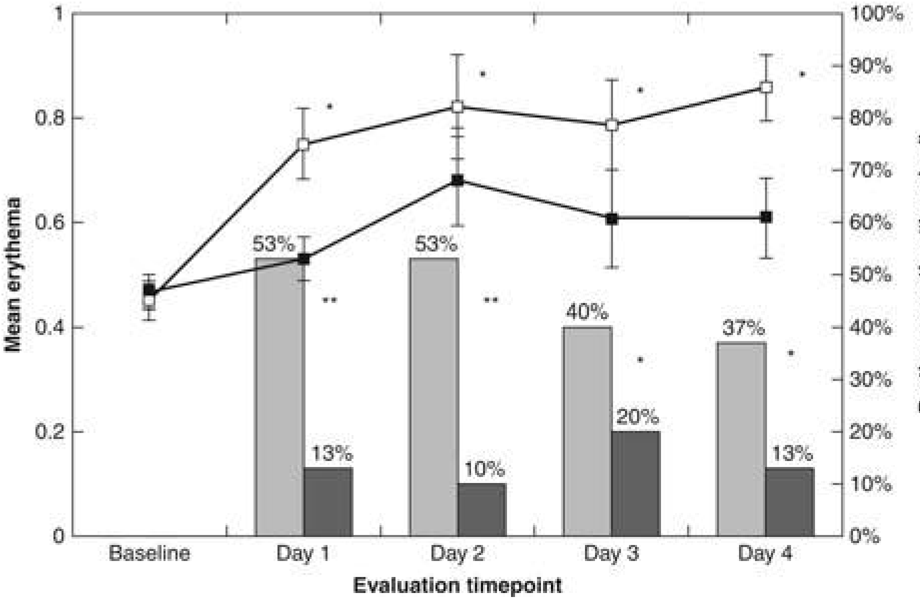


Figure 2 Reports of burning sensations in the BTK. In the BTK, each of the 30 panelists was asked to keep a daily diary of skin problems experienced at the test sites. Results were evaluated for a higher occurrence of each individual skin problem with one treatment versus another. The graph plots mean erythema (±S.E.) at each scoring time point (as shown in Fig. 1), and the portion of the subject population reporting sensations of burning at the test sites during each patch application. Treatment comparisons for the sensory effect was evaluated using McNemar's test. (**Significant difference between pad A and pad B, $p < 0.001$). (*Significant difference between pad A and pad B, $p < 0.05$). Pad A = open symbols. Pad B = closed symbols. *Abbreviation*: BTK, behind the knee.

the first and second application (for subsurface and surface scoring, Fig. 1B and 1C, respectively).

The number of panelists who experienced burning sensations at the test sites is shown in Figure 2. With every sample application, there was a significantly higher number of individuals reporting burning sensations with pad A compared with pad B. In addition, a significantly higher number of individuals reported pain with pad A during the third sample application and sensation of the sample sticking to the skin during the second and third application (data not shown).

SENSORY EFFECTS AND DESCRIPTIVE ANALYSIS PANELS

DAPs, conducted in the course of normal product development activities, evaluate certain physical characteristics of the products. Results from DAPs on products that have also been tested in the BTK are shown in Table 3. In the comparison of products A and B, product B scored lower in the negative attributes and higher in the positive attributes. Results on the comparison of products G and E were mixed, with product G scoring higher on the negative attribute of plastic feel, while product E scored higher on the negative attribute of scratchiness. Likewise, product E scored higher on the positive attribute of glide but lower on the positive attribute of cottony feel.

DISCUSSION

This study examined data collected in the course of the development and conduct of the BTK test for correlations between the objective scores of erythema and the sensory effects reported by the panelists. As shown in Table 2, in about half of the comparisons (7 of 16), the samples were not significantly different on the basis of either a difference in unaided visual scores for

Table 3 Descriptive Analysis Panel (DAP) Results for Products Tested in the BTK Test

	Mean scores			
	Product A	Product B	Product G[a]	Product E
Negative attributes:				
Plastic feel	6.8[b]	0.0	3.9[b]	0.3
Scratchiness	5.4[b]	1.5	3.5	5.6[b]
Positive attributes:				
Glide	4.8	6.7[b]	2.6	5.5[b]
Cottony feel	0.0	6.3[b]	4.2[b]	3.4

[a] Top sheet tested.

[b] Higher at the 90% confidence level.

In the DAP, individuals specifically trained to evaluate the positive and negative physical characteristics of products graded these attributes on an 8-point scale, with 0 = not at all, 4 = moderate, and 8 = extreme. Mean differences were tested for statistical significance using Duncan multiple comparison.

irritation or reported adverse sensory effects. For one sample, both the irritation scores and the sensory effects were significantly different. In 5 of the 16 comparisons, sample differences were detected in the objective scores that were not apparent in the reported sensory effects. In the remaining three sample comparisons, the reported sensory effects indicated sample differences that were either not detected in the objective scores, or in one case, were contrary to the objective scores.

In most of the studies in which sensory data were collected, the differences in mean irritation caused by the test samples were generally small, with either no significant differences or differences only at isolated time points. In the early development of the BTK, those control samples were tested that produced more pronounced differences in mean irritation, which persisted throughout the experiment. Unfortunately, sensory data were not collected at this early stage of the development of the test model. Tests on products that produce a more pronounced difference in mean irritation may improve the ability to detect product differences solely on the basis of the sensory effects and may enable more definitive conclusions about the correlation between observable irritation, as determined by objective scoring of erythema, and what the panelists feel. A logical next step is to collect and analyze sensory effects in studies where the test samples and/or test conditions would be expected to produce greater differences in the mean irritation.

Although we were not always able to reliably differentiate between the samples using solely sensory effects in these particular studies, we did observe that an increase in the irritation score is correlated with a higher percentage of panelists reporting adverse sensory effects, as shown in Table 1. This indicates that even among volunteer panelists who are not specifically trained in observing and reporting sensory effects, the increased reports of sensory effects reliably reflects an increase in irritation, as measured by objective observation. This correlation may be improved by modifying the manner in which data on sensory effects are collected. Currently, panelists are given eight different terms to describe an unpleasant sensation, including rubbing, sticking, chafing, burning, itching, pain, or "other". By providing eight different choices, and treating these as separate endpoints, we may have inadvertently designed the experiments in a way that undermines our ability to detect trends. Statistical differences for any one of the eight choices may be extremely difficult to achieve with a panel of only 15 to 18 individuals. Modifying the sensory diaries to reduce the number of choices that panelists can choose to describe any unpleasant sensation may improve our abilities to discriminate based on sensory effects.

Enhanced visual scoring enables detection of physiological changes that are not apparent using standard visual scoring, i.e., subclinical changes. Previously, we have reported that subjective consumer comments indicate that consumers can detect differences in skin effects caused by the use of two similar products. For example, consumers have consistently indicated that pad B is seen as less irritating than pad A in "real use" situations; however, most test protocols repeatedly fail to differentiate between these two products (7). Sensory effects in the BTK have been shown to be consistent with consumer comments and reliably differentiate between pad A and pad B (23). This current investigation confirms that sensory effects

Table 4 Qualitative Summary Comparison of Objective and Subjective Endpoints

Product comparisons	Comparison of mean irritation scores	Adverse sensory effects	Topsheet attributes in DAP: Negative attributes: Plastic feel	Scratchy	Positive attributes: Glide	Cottony feel
Product A vs. product B	Product A $>$ product B in 8 of 10 studies [a]	A $>$ B [b]	A $>$ B	A $>$ B	B $>$ A	B $>$ A
Product G vs. product E [c]	Product G $=$ product E in 1 study	G $=$ E	G $>$ E	E $>$ G	E $>$ G	G $>$ E

[a] Seven studies were conducted on complete products A and B, and 3 studies were conducted on the product top sheets.

[b] Sensory effects collected in one study on complete products.

[c] Top sheet for product G tested in DAP.

Mean irritation scores and adverse sensory effects data were taken from Table 2. In addition, several other studies were included in which products A and B were compared (data not shown). DAP results were taken from Table 3.

correlate with visual scoring in the BTK and confirms that sensory effects enable the differentiation between two very similar products (Figs. 1 and 2).

Unlike the BTK test, which uses healthy volunteers as panelists, the DAP is conducted using individuals who are specifically trained in detecting and grading physical attributes of products. As shown in Table 3, this trained panel was able to clearly differentiate between products A and B for four key product attributes (two positive and two negative). In contrast, products G and E produced mixed results, resulting in no clear conclusion on which product would be superior, overall.

While the endpoints in the DAP are completely different from the sensory effects reported by panelists in the BTK, the product attributes graded in the DAP are likely responsible for the adverse sensory effects the panelists reported in the BTK. This is illustrated in Table 4. This table provides a qualitative summary comparing the results on products or top sheets tested in the BTK and in the DAP. As mentioned above, in most BTK tests (8 of 10 studies), product A produced significantly higher mean irritation scores than product B. In the one BTK study where sensory effects were collected, adverse sensations were reported significantly more often with product A than product B. This is consistent with the positive and negative product attributes identified in the DAP where product A had significantly higher scores for the negative attributes and significantly lower scores for the positive attributes. When products G and E are compared in the BTK, they are similar with regard to both mean irritation scores and adverse sensory effects. Likewise, these products could not be clearly differentiated in the DAP, where each product scored higher in one of two positive attributes and in one of two negative attributes.

In future BTK studies, we plan to incorporate terms in the BTK test that are comparable to those used in the DAP. Currently, the descriptive terms are completely different for the two test methods, making it difficult to relate the results. To some degree, this is unavoidable, since the two tests are designed to measure different endpoints. However, some of the descriptors in the DAP may be meaningful for use in the BTK test. For example, a material described in the DAP as having a "plastic feel" may cause the sensation of "stickiness" or "chafing" in some individuals in the BTK. Therefore, a logical next step is to conduct a BTK test using volunteers trained for the DAP testing to determine how these individuals describe the sensations experienced in the BTK.

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37 Decorative Products

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INTRODUCTION

Makeup was created in the Middle East 5000 years ago. It was to give themselves a more attractive image, to protect their bodies from a dry and very sunny climate, and also as medical care that all the Egyptians of the Antiquity used makeup. For a long time being considered as an art, the makeup entered, with the development of the cinema and the television, in a phase or science and technique to help the esthetic preoccupations of the women. Over this century, the role of the makeup changes with the changing culture of the society. However, central themes are easily recognizable through each decade. The natural look of perfection continues in the year of today, as with the goal of restoring youth and looking younger. The cosmetics' industry has experienced some significant changes in the past five years. Marketing has evolved, the consumer has become more knowledgeable and demanding, and cosmetics themselves have become more sophisticated and innovative. Technological advances have allowed for the creation of multifunctional products that perform more than their basic role. For example, foundations with high sun protection factor (SPF) protect from ultraviolet (UV) rays, lipsticks moisturize, and mascaras lengthen, curve, and thicken. The biggest performance development in color cosmetics has been the creation of "stay-on" products, which are long lasting. These products first appeared in the foundations category, then transferred across product categories to include lipsticks, eye shadows, mascaras, and nail enamel. The concept has been extended with stay-on lipliners in addition to transfer-resistant lipsticks. All these evolutions could not have appeared without the progress of chemistry, which made pigments easier to formulate and brought polymers, which improves the sensory and physicochemical properties of makeup products. An improved incorporation of specific raw materials used in skin care products and pigments with visual effects allowed the creation of some specular effects. Makeup products contribute also in a significant way to the general health and well-being of women. They have a major role, which is to provide psychological stimulation to satisfy personal desires for self-improvement, self adornment, and good grooming for one's own sense of well-being and for the general attention or attraction of others. The "psychology of cosmetics" appears therefore as a new field concerning the characterization of the beneficial effects of cosmetic practices (1). This heightened technology of makeup products, the sensory interactions based on the skin-brain connection, and ever more stronger claims are today accompanied by the development of specific evaluation methods used to quantify these improvements and to prove the claimed efficacy.

MAKEUP FORMULATIONS

In makeup products, pigments play an essential role because they provide the chromatic modifications necessary for these qualities. Pigments used in current makeup applications can be classified as organic pigments, mineral pigments, and nacrous pigments (Table 1). Twenty years ago, the cosmetic industry introduced the treated pigments. The surface properties of pigments differ with the size and the shape of the pigment particles as produced by the various manufacturing methods. It is know that the behavior of pigments is closely related to surface properties, and can be classified into hydrophilic and lipophilic. It is very important to know these properties of powders when makeup products are formulated. Generally, pigments and substrates used (mica, talc, sericite, borum nitride, etc.) for makeup cosmetics are hydrophilic. The surface properties of these powders can be changed from hydrophilic to hydrophobic with

Table 1 Pigments Used in Current Makeup

Pigments	Description
Organic pigments	Selection of pigments for use in makeup is limited to those allowed by regulations of the Food and Drug Administration in the United States. The pigments are formed by precipitating the colorant onto a substrate, often aluminum or calcium hydroxide and thus forming an insoluble salt.
Mineral pigments	Titanium dioxide and iron oxides are the most commonly used materials
Nacrous pigments	Nacrous or pearlescent pigments are used to create frosted appearance, often with other special effects. There are 3 classes of nacrous pigments used in makeup: Natural pearl essence (for nail enamel), known as guanine (2 amino-6-hydroxy-purine), is derived from the scales of atlantic herring. It provides a soft luster. The pigment's density is lowest of the 3 types noted above, and it is therefore the easiest to suspend. Natural pearl essence exists in the form of platelets or needles. Bismuth oxychloride A commonly used synthetic nacrous pigment is bismuth oxychloride. This material's luster is more metallic than that of the other two types. The particles also have a higher density (7.7), making then much more difficult to suspend. Titanium dioxide—mica or mica coated by several different layers (silica, iron oxide, etc.). Another type of pearlescent material is mica coated with a thin layer of titanium dioxide. The interference effects change according to the thickness of the layer of titanium dioxide.

several of the aforementioned coatings depending upon the final products' function. There are many processes by which pigments may be surface treated. The most common methods used today are through chemical interactions, electron-charge reactions, mechanochemical processes, and mechanical processes. Other processes are essentially variants of these four basic methods, as witnessed by an introduction in surface treatment manufacturing called ultramicronization. Surface treatments impart easier dispersibility, better stability, and flocculation resistance to pigments. The second basic important advantage for the cosmetic chemist in using treated pigments is in development of hydrophobic systems (e.g., silicon media). Hydrophobic pigments of both types are available, including treated inorganic colors, DC colors, nylon, titanium dioxide, talc, kaolin, mica, and other minerals. These pigments, and the products made with them, show water-resistant properties, improved skin adhesion, improved color consistency, and better smooth skin feel than when uncoated materials were used in the same formulations.

Lisptick (2)

Lipsticks are mixtures of waxes, oils, and pigments in varying concentrations to yield the characteristics of the final product. Waxes will give rigidity and solidity to the stick. They can be of vegetable origin like candellila wax, which brings brightness or carnauba wax that gives hardness. They can also be of mineral origin like ozokerite wax for adhesion or of synthetic origin like polyethylene, which is compatible with silicones and avoids the exudation of oils. Usually, lipsticks contain a combination of these waxes (~20%) that are selected and blended carefully to achieve the desired melting point. Oils (40–50%) are used to give the lipstick its slippery and soft aspect when applied; for example, castor oil is used to disperse pigments and white mineral oil or oleyl alcohol is used to form a film suitable for application to the lips. Colouring agents are present between 2% and 10% and can be of several types. One mainly finds synthetic pigments, but minerals like iron oxides (red, yellow, or black) are also used to give the color and titanium dioxides bring coverage, opacity, and intensity. Pearl pigments can also be used to give color highlights. It should be noted that pigments of vegetable origin are rarely used in cosmetics because most of them are unstable to heat or light. Those of mineral origin also create a problem because they contain too many heavy metals according to the cosmetic legislation. In relation to the claims, additives can be added such as sun filters, which protect the formula or bring a sun protection index, antioxidizers, vitamins (E, C, and B5), moisturizing agents, or ceramides. A light fragrance (<1%) will be added to give the lipstick a pleasant taste on lips and mask possible smells of raw materials. Overall, a standard lipstick manufacture can be simplified in four stages: *mixing waxes, oils and extenders at high temperature; producting a concentrated dispersion of pigment (generally the pigments are grounded in an oily base* *such as castor oil); adding the colored paste at high temperature with the rest of the formula of the first stage; molding the colored paste*. The lipstick chemist must develop a formula, which has a good cosmetic feel for the range of formulated shades. Therefore, the interest for him is to estimate the influence of the pigments on the texture of the stick. From rheological studies, Tranchant and Poulin (3) showed that one can monitor the manufacturing stages. Knowing the physicochemical properties of pigments and their rheological behaviors after grinding, they demonstrated and explained the influences on the texture and the mechanical properties of the stick. One of the disadvantages of conventional lipsticks, which almost all consumers point out, is the deterioration of its fresh appearance in a short period of time. To solve this problem and improve the long-lasting properties, one of the most efficient techniques has been the use of a film-forming polymer in combination with volatile oils (cyclomethicone) (4), which are evaporated on contact with lips (no transfer effect). However, incorporation of the volatile oil into the lipstick's composition is accompanied by a loss in the application gloss over time and comfort on lips. For a very glossy lipstick, the formulation is different from that of classical and no transfer lipsticks because the level of the waxy phase goes up to about 80%. The ratio of oil to wax is higher, whereas the rate of pigments is weaker (0–5%). For matte lipsticks, we use talcs, some nylon powder, silica or polymethylmethacrylate, which give a powdered, slippery, and very soft touch.

Nail Enamel

Nail enamel constituents can be grouped in six families. Lacquer, agent for adhesion and gloss, solvents, plasticizers, pigments, and thixotropic agents, which, of course, must be compatible. The heart of the nail enamel formula is the lacquer, which may be defined as a coating that hardens and dries by evaporation of the solvent. The lacquers determine application properties, gloss, wear properties such as adhesion, flexibility and abrasion resistance, water resistance, viscosity, and suspension ability. The polymers selected must be soluble in cosmetics solvents that dry rapidly, leaving a smooth, glossy film with excellent adhesion properties and have a good pigment-wetting ability. Nitrocellulose (10–20%), a polymer obtained by nitration (12% nitrogen) of the cellulose, is the filmogenic agent currently used in nail enamel. However, used alone, it produces films, which tend to shrink and become brittle, with only moderately good adhesion to nail surface. Different modifying resins (5–10%), such as toluene sulfonamide resins, are added to improve the properties of the lacquers such as to increase wear resistance and gloss. These effects are usually adjustable by selection of an appropriate plasticizer (5–10%), a film-forming agent, which acts on the hardness of the film giving it flexibility. Indeed, nail is deformable and elastic. A film adhering to the nail surface must therefore be able to withstand any motions. Typical plasticizers used include phtalates, citrates, camphor, etc. These polymers, resins, plasticizers, and pigments are mainly dispersed in organic acetates and aromatics solvents with amount of solvents in nail enamel roughly of 70%. For formulation reasons, the ratios of solvents can be modified because the choice of solvent can affect the drying time, flow characteristics of the film, and the flexibility of the film. Note that regulations such as the "Proposition 65, California's, Safe Drinking Water and Toxic Enforcement Standard" limits use of certain solvents, such as toluene, which is considered as a reproductive toxin. Hence, most of the new formulations are without aromatic solvents. The physicochemical factors that determine the suspension stability of nail enamel are complex, such as the particle size and distribution, density differences between particles and the continuous medium, viscosity of the continuous medium, particle concentration, and particle-particle interactions. However, several authors (5–7) showed that one can predict a dispersion stability through dynamic studies of rheology, by relating directly the visco-elastic parameters (viscosity, elastic modulus, and viscous modulus) to the dispersed system structure. Thus, different formulation systems need different viscosity profiles to achieve equivalent esthetic results. Indeed, the viscosity of nail enamel has to be sufficiently high to avoid the sedimentation phenomena of pigments in the bottle, remain on the brush before the application, and facilitate precise application, but the viscosity has to be low enough for the nail enamel to be taken out of the bottle. This can be done if the viscosity is not linear. This nonlinearity is obtained by using modified clays (thixotropic agents). To prevent settling, pigments and pearlescent pigments are suspended by a rheological agent, and the organic clays are the most commomly used material. Note that smectites are the mineral group of the clays, which swell and have high cation exchange properties and can be observed as thin plates. The organic treatment of these clays consists of replacing the cations that are in the natural product (Na, Ca) by some quaternary ammonium salts. The rheological properties of the medium originate from the hydrogen bridges between the hydroxyl groups of the dispersed plates and can be summarized as undisturbed nail enamel [the plates of clay are packed and linked together by hydrogen bonds (high viscosity), when shearing, all these bonds are broken, plates are all oriented in the same direction (low viscosity), and after application, there are associations between the plates, and after application, there are associations between the plates, and thus the viscosity increases. In the early 1990s, environmental laws and regulations as well as the green movement in Europe were giving rise to new formulation and an interest in a water vehicle, because it is known that organic solvents can damage nails (e.g., moisturization and lipids].

Face Makeup

These products are used to make the skin look natural and beautiful for as long as possible; to achieve this purpose, they unify the color of the skin, improve a dull and tired complexion, give a matte finish, and mask possible imperfections like dark spots, small wrinkles, dark rings under the eyes, and the pores of the skin surface. Their application must be easy and give coverage for a natural complexion. They must have a pleasant texture, a good adhesive property, be comfortable, and have a consistent color and smooth finish. There are more and more no transfer and oil-free products. New pigments, such as pigments with an action on the light such as soft focus, photochromic (8) or auto-adaptive effects, and pigments coated with silicone or with fluoride oil giving a very specific sensory touch are also used. Foundations can contain ceramides, used to strengthen the skin barrier, moisturizing agents like glycerin and hyaluronic acid, vegetable oils, which improve the hydration and flexibility of the skin, and free radical scavengers (vitamin E) as well as UV filters (UVA-UVB) giving makeup products a sun protection index (SPF 5–30). Firming complexes to tone up and restructure the skin and seboregulating can also be added.

Face Foundations

The formulations vary according to the qualities required for the product. Foundations are available in various forms: liquids, gels, creams, solid creams, cakes (pancakes), mousse, or in sticks (pen stick). There are four basic facial foundation formulations, which are the most popular products for complexion: oil-in-water, water-in-oil, oil-free, and water-free or anhydrous forms. Oil (silicone)-in-water emulsions are better for normal- and oily-skin types, whereas water-in-oil (silicone) emulsions are better for normal- and dry-skin types. Oil-free formulations are used for women with oily complexions, and anhydrous forms are used by women with facial scarring who require camouflaging. Oil-based foundations are water-in-oil emulsions containing pigments suspended in oil, such as mineral oil. Vegetable oils (e.g., coconut and sesame) and synthetic esters (octyl palmitate and isopropyl myristate) may also be incorporated. Oil-based formulations also contain water (30–45%), siliconed tensio-actives (5%), and some specific actives (vitamins, UV filters, moisturizing agents, etc.). The water evaporation from the foundation just after application leaves the pigment in oil on the face. Water-based foundations are oil-in-water emulsions containing a small amount of oil in which pigments (10–15%) are emulsified with a relatively large quantity of water, which is the dominant substance (50–60%). Oil-free foundations contain vegetable or mineral oils, but also other oily substances, such as the silicones dimethicone or cyclomethicone, which leave the skin with a dry feeling. They come in three forms: alchohol based, glycerin based, and creams or lotions (ideal for oily or acne-prone skin). These foundations go on smoothly but dry fast, so they must be blended quickly for even coverage. Water-free or anhydrous foundations are waterproof, and high concentration of pigments can be incorporated. These several formulations and the effects of pigments can control the darkening phenomenon done from the sebum, hide the wrinkles, protect from the UV through the diffused reflection, give a smooth finish, and do a long-lasting and no transfer effect of makeup. No transfer formulations are an ingenious combination of volatile oils, which fix the pigments on the skin after evaporation giving permanent effects. The most-used ingredients in the face makeup were mica mat and micro titanium dioxide and silicon dioxide. Mica is transparent and easy to use; the titanium dioxide has good covering effects, and it is very efficient against the UV, but its touch is hard; and the silica is a multi-porous ingredient, which absorbs the oil and sebum. Nowadays, the surface treatments are wonderful techniques to give some special functionalities to the raw material pigments and sensory properties (9). The smooth feeling of a foundation mainly depends on the physical properties of the raw material pigments, such as particle size, shape, and so on. Furthermore, by adding the moisturizing and water-absorpting effect to the raw material pigments with surface treatment, the much more elegant and smooth feeling in use can be completed, and these days, polysolixane (SI) treatment is very popular for makeup products. The long-lasting effect is also a very important functionality for makeup products and especially for face makeup. A lot of women use makeup products to maintain their soft and smooth skin for a long time. For women with oily complexions, lipids secreted from skin tissue collapse the makeup finishing and the surface of the finishing skin becomes glossy, since lipid from skin tissue is miscible with pigments and binder in makeup cosmetics. This disadvantage will not be solved with SI treatment, since polysiloxane is miscible with oil. To overcome these problems of raw material pigments for cosmetics, such as poor dispersibility, high activity against skin, and collapse of makeup finishing by lipid from skin tissue, there exists a surface treatment using perfluoroalkyl phosphate (10). Fluoro-compounds are used for several kinds of fields to avoid water and oil. This treatment showed an excellent water and oil repellency and also a good dispersibility to organic and inorganic pigments, and an ability to depress the activity of ultrafine pigments. Other surface treatments can be carried out to give, for example, much more UV cut effect to pigments. Several types of organic low–molecular weight UV absorbers are commonly used, such as benzophenone and p-amino benzoic acid. It is also known that ultrafine titanium dioxides and zinc oxides absorb UV light, especially zinc oxides, which absorbs UVA and UVB both. However, it is recognized that titanium dioxide is not so stable against UV rays. To overcome the disadvantage of the photostability, new technology to coat titanium dioxide in high uniformity was explored, and a novel silica-coated titanium dioxide with broad spectrum protection against UV rays was developed (11). Other surface treatments with polymer materials were carried out to give much more UV cut effect to pigments (12). This allows the formulator to avoid the main disadvantage of physical sunscreens, namely, the visible whitening that occurs when titanium dioxide and zinc oxide are used in high concentrations to obtain a high SPF. These novel polymer surface treatments, such as organic polymers (teflon and silicones) or active ingredients (collagen, elastin, and vitamine E), give better properties of cosmetic makeups, and use of polymer or polymer matrix system are very safe compared with use of ultrafine titanium dioxides or zinc oxides.

Face Powders

Face powders provide coverage of complexion imperfections, oil control, a matte finish, and tactile smoothness to the skin. Powders give a good lasting effect to foundation makeup and possess oil-absorbing properties that are very useful for oily-skin types. Free powders are used to fix the foundation and compact powders to retouch one’s face during day. Face powder is more complicated and made by a mixture of products: Talc and serecite (to help to spread), chalk or kaolin (to give moisture-absorbing qualities), magnesium stearate (gives adherence), zinc oxide and titanium oxide (to help cover the skin thorougly), and pigments (for color). The use of mica in powder formulations improves skin feel, product application, and skin adhesion. The favourable effects are obtained with wet ground micas that have a particle size of <15 μm. Mica can also be modified by coating with inorganic or organic materials to produce another large group of fillers (spherical, special, and surface modified). Spherical fillers are widely used to improve skin feel. There are a variety of materials available, the organic types consisting mainly of polyamides, nylon spheres and inorganic types consisting mainly of silica, both as solid or hollow spheres. The improvement of skin feel is attributed to the ball bearing–like action of the spheres between other powder ingredients in the formulation and the spherical filler. When spherical materials are used, there is also an increase in the viscosity of the emulsion, allowing for a reduction of viscosity modifiers in the final formulation. Bismuth oxychloride (BiOCl), a fine white powder with a high bulk density, is well known as a pearlescent pigment, but it can also be used as a filler with no luster when in a particular crystal form. It has relatively low oil absorption characteristics and also gives rise to excellent compressibility when used in pressed powder formulations. Its hydrophobic character and good affinity with the skin also improves the skin adhesion and wear properties of powder and makeup products. However, one disadvantage of BiOCl has been a low-light stability. Nowadays, BiOCl is much more stable to UV light. Special fillers are a group of fillers that are made up of several components, which combine their individual advantages when they are processed together into a composite material. Coated mica pigments, for example, are often found as light-diffusing pigments' agents in color cosmetics, where fine particle–size micas enhance the light diffusion properties of the material coated on the surface of the mica. Mica can also be coated with very small particles of metal oxides, allowing ease of incorporation into liquid formulations. Examples of coating materials for micas are titanium dioxide (e.g., low loster pigment), barium sulfate, and BiOCl, as well as organic compounds. For surface-modified fillers, most coating materials are organic polymers (collagen, elastin, and vitamine E). Powders also contain between 10% and 20% of organic texture agents (polymers) or mineral agents (boron nitride and silica), preservatives, anti-oxidants, and perfumes (neutral or more sophisticated) can also be added there. Table 2 collects some possible raw materials for foundations and powders.

Eye Makeup

Eye makeup consists of three major categories: mascaras, eyeshadows, and eyeliners. Mascaras thicken, sheathe, separate, and lengthen eyelashes to obtain an intense look. Eyeliners help draw a precise line at the base of eyelashes, and eyeshadows bring light to the look and highlight the color of the iris.

Mascaras

Among all the makeup products, mascara formula requires a particular development. The choice of mascara depends on the type of eyelashes (short or long, stiff or curved, poor or bushy, and fair or brown) and of the required effect (lengthened, curved, and\or thicker eyelashes). Liquid mascaras are the most popular modern formulation, and they can be divided into water-based, solvent-based and water/solvent hybrid varieties. Water-based mascaras are formulated from waxes (e.g., beeswax, carnauba wax, and synthetic wax), water, pigments, which are often iron oxides, and resins dissolved in water. The water evaporates readily, creating a fast-drying product, which thickens and darkness the eyelashes. Some water-based mascaras, very rich in wax (30%), are labelled waterproof or water resistant. To color eyelashes, inorganic pigments are the most commonly used because the vast majority of mascaras are black. Note that certain pigments, like cochineal carmine, may generate some problems such as the coloration of contact lenses. The formulae also contain antioxidizers to avoid the rancid smell of fatty substances and preservatives, which protect the eye from any risk of infection. Vitamins and hydrocarbon volatile or silicon solvents can also be used to improve the performance of the makeup. Concering the solvent-based mascaras, they are formulated with petroleum distillates to which pigments (e.g., iron dioxides, ultramarine blue, etc.) and waxes (candellila wax, ozokerite, and hydrogenated castor oil) are added, making them waterproof. If it is clear that the makeup effect depends on the formula, it is also important to consider the type of brush and the diameter of the aperture of the mascara tube. Indeed, it must automatically adjust the quantity of product on the brush to avoid loads on the eyelashes during application. The packaging also must be totally airtight to avoid the degradation and oxydation of the formulation. Thus, to obtain a good application on the eyelashes, it is necessary to develop a compromise between the mascara formula viscosity and the brush type. A rheological approach can be made through the rheological characterization in situ of mascara pastes with the brushes (13). This procedure used to quantify the take up of mascara brush in the container allows to visualize the influences of the shaft, the bristle length, and the hardness and pattern on the take up, therefore to characterize the product transfer.

Eyeshadows and Eyeliners

Eyeshadows are a cosmetic designed to impart color, primarily to the upper eyelid. The formulations of eyeshadows are identical to those of compact powders for the face, but the color range is wider. Application is helped by tiny particle size, flattering the eyelid by giving a smooth rather than crepey appearance. Eyeliners are mainly liquid formulations using ultrafine pigments.

Table 2 Possible Raw Materials for Foundations and Powders

	Pigments and mineral charges				
White	Colored	Unifying charges	Mineral charges light	Silicones	Active
- Titanium dioxide - Talcs - Pearl pigments (*mica, titanium dioxide–coated mica, bismuth oxychloride*)	- Iron oxides (*Yellow, red, black*) - Ultramarine blue - Colored pigments and *pearls* (*mica + iron oxides, mica-titanium dioxides + iron oxides*)	- Nylon (*orgasol*) - Polymethylmetacrylates - Silica - Boron nitride	- Soft focus (*light diffusing*) - Photochromic - Light correcting (*auto-adaptative*)	- Dimethicone - Volatile cyclomethicone - Silicone gum blends Emulsifying - Cyclomethicone and dimethicone copolyol	- Vitamin C, A, and E. - UV filters - Enzymes - Phospholipids - Moisturizing agents (*Glycerin*)

INTERACTIONS BETWEEN SKIN AND MAKEUP PRODUCTS

Physical appearance, and more particularly physical attractiveness, is one of the most important determinants of interpersonal attraction in the early stages of many relationships (14,15), and it is obvious that the face is the part of the human body, which attracts the most attention (16,17). Thanks to makeup products, it is quite possible to bring out certain characteristics of the face or, on the contrary, to lighten them to achieve a degree of attraction for all types of face (18–20). In all cases, the perception of a makeup is an interaction between the light, the makeup product or raw-materials, which compose it, and the human skin. Two main types of interaction can be observed: visual interactions, where the optical way of light is modified by the optical properties of cosmetic ingredients and the relief of the skin surface and biophysical interactions, where the finished makeup is perturbed by the biochemical and mechanical functions of the skin surface. Concerning the visual interactions, they are mainly generated by pigments with specific effects (21): perlescents, iridescent effects (color changes according to the angle of observation), thermochromic (color changes according to the temperature), photoadaptive (preserve a radiant complexion following the lighting conditions), or soft focus effects (22–24). These soft focus pigments, mainly composed of polymers, micas, and talcs covered with rough or spherical particles of small diameters, such as silica or titanium dioxide, are used to optically reduce the appearance of wrinkles. These effects are obtained by optimizing outlines of wrinkles and reducing the difference of brightness due to diffuse reflection. Concerning the biophysical interactions, it is known that behavior of a makeup product can be modified by the biochemical and biophysical properties of the skin. For example, a woman's skin type and her facial movements throughout the day actually remove the foundation from the face. Foundation tends to shift and wear off during the day and migrate into the fine lines of the face. The outside environment such as air pollution, smoke, sun, and stress that we feel in the current world are also factors, which can disrupt the normal balance of the skin (e.g., skin discoloration or extreme dehydration) and therefore modify the behavior of makeup products. The perceptions of a makeup can create other interactions based on the relation existing between the pleasure felt after application of a makeup product and psychological and social parameters (25). These interactions are difficult to define because they often include physiological and psychological attributes. Indeed, it is difficult to quantify precisely how much pleasure a person derives from using a makeup. Overall, makeup acts and stimulates three of our senses: the touch (which encompasses all sensations from the body surface), the smell (fragrance), and the sight (the process of becoming and looking beautiful). The positive stimulation of these senses by makeup can induce sensory as well as psychological pleasure. Indeed, in a previous study whose subject was to explain the reasons that motivate women to make up, we observed clearly a high implication of psychological traits in the makeup functions (26,27). This positive stimulation can also contribute to a healthy mind and body through enhanced functioning of the body's immune system (28). An excellent article by Lévêque (29) on the relationship between appearance and health underlines the effects of makeup product on the mental health of a women who is badly affected by a serious illness or who is still in the process of creating and presenting her own image and personality. With facial makeup, women become more confident, physically attractive, enhance their well-being, and act more positively toward the external world. The implications of facial attractiveness are equally important across all of the stages of life, associated with greater or lesser sensitivities to the social interactions. For example, with changes in age, the psychological effects change (30). The young woman will use makeup to capture the eye of others and is perceived as having a more favorable personality, whereas a mature woman will use makeup rather to enhance her feelings of self-satisfaction. Beyond the simple application of colorful products on the face, makeup appears as a holistic technique that modifies not only one's appearance but also helps to cope with one's self-image, emotions, and mood.

QUANTITATIVE ASSESSMENT OF PROPERTIES OF MAKEUP PRODUCTS

Over the past few years, cosmetic research has enabled the makeup product to become a high-technology product, claiming some similar cosmetic properties to those of skin care products (hydration, protection against free radicals, etc.) as well as new physical properties (e.g., long lasting or no transfer effects). Although qualitative evaluation (mainly obtained through consumers' perception and experts' evaluation) is commonly used and remains indispensable to prove the effects of makeup products (e.g., color, comfort, or lasting effect), it is more and more necessary to associate it with instrumental data. Some may be obtained through devices already used for the evaluation of skin care products, such as the Corneometer®, which can demonstrate a moisturizing effect (31). However, the most representative effects are those, which are associated with a visual effect, which is the main property of a makeup product. Video imaging appears as a good method to prove the efficacy of makeup products. Indeed, thanks to high-resolution video cameras and sophisticated image analysis sofwares, we can visualize what the consumer perceives of the product (concerning either the whole face or smaller areas) and at the same time to associate some quantitative information. However, video imaging has its limits, and in this case, biophysical methods can be very useful to quantify certain properties.

Lip Makeup

Quantification of the Color, Brightness, and Streakiness

The color parameters can be achieved either by reflectance spectrophotometry of the optical spectrum of visible light reflected (Spectrophometer CM-508i®, CM-2002®, Konica Minolta Business Solutions Europe GmbH, Germany) or by reflectance tristimulus colorimetry (Minolta Chromameter CR-200®, CR-300®, Minolta, Osaka, Japan) following the CIE (Commission Internationale de l'Eclairage) recommendations (32). These methods give quantitative information on the color but are limited to a small analysis surface, from 7 mm^2 to a few square centimeters according to the device used. And these techniques require direct contact between the made-up skin surface and the device, which generates shrinking at every measurement and therefore modified the aspect and the long-term behavior of the product. To avoid this phenomenon, color can be evaluated by image analysis. Thanks to this technique, it is possible to study skin areas of various sizes, take measurements without any contact with the skin, and analyze the image pixel by pixel (a word invented from "picture element," which is the basic unit of programmable color), providing quantitative information according to localization. In the case of lipstick, the global color of the made-up area and the shades most represented in the global color can be quantified. Thanks to the development of specific data-processing programs (33). For example, a segmentation method by maximization of the entropy and an algorithm based on the principle of the probabilistic segmentation were used to separate the color information sent back by the skin to the makeup area. It is also possible to evaluate the streakiness, which represents the amount of lipstick in the small lines surrounding the lips, and the brightness (Fig. 1). Concerning the streakiness, the principle consists in extracting the surface of the lipstick that has migrated (lips + streakiness), smooth out the outline, and calculate the difference between that and the surface of the unsmoothed lips. All that remains is to divide the calculated surface by the perimeter of the smoothed lips to obtain a streakiness index, independent of the morphology. The brightness assessment is more complex. Indeed, the bright zones are not necessarily the part of the image where the pixels get closer to white. A darker lipstick having the same brightness surface in pixels as a clear lipstick will be perceived by the human eye as more glossy. Then, the brightness assessment is realized by calculating the difference of contrast between two adjacent pixels. From these different parameters (color, brightness, and streakiness), the long-lasting properties of a lipstick can be evaluated.

Quantification of the Moisturizing Effect

The hydration state of the skin surface is commonly evaluated by an indirect method based on the measurement of electrical conductivity (34). Various experimental instruments are commercially available such as the Corneometer (CM-820, CM-825, Courage and Khazaka, Germany) based on the measurement of the capacitance and the Nova Derm Phase Meter DPM 9003 (Nova® Technology Corporation, Portsmouth, New Hampshire, U.S.) based on the meaurement of skin impedance. Thanks to this small diameter probe (5 mm), the Nova DPM 9003 is perfectly adapted to measure the electrical properties of lip surfaces (35). However, this device requires a sufficient hydration level of lips to show differences after application of moisturizing lipstick. In all cases, the measurement protocol used to quantify the hydration

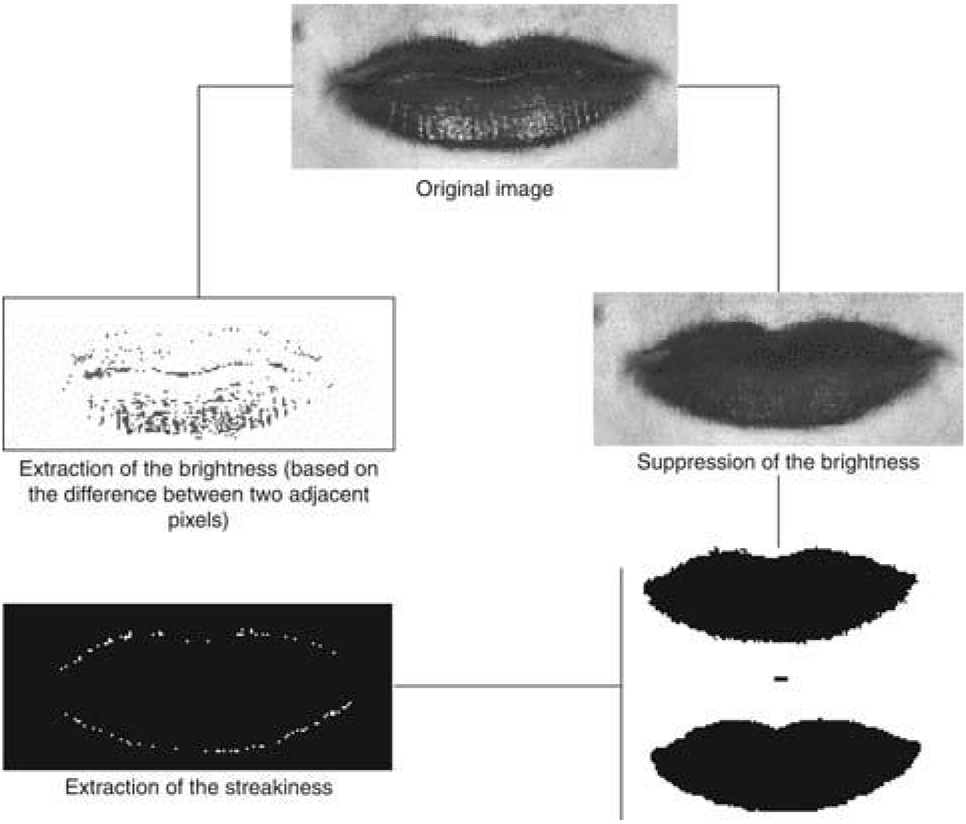


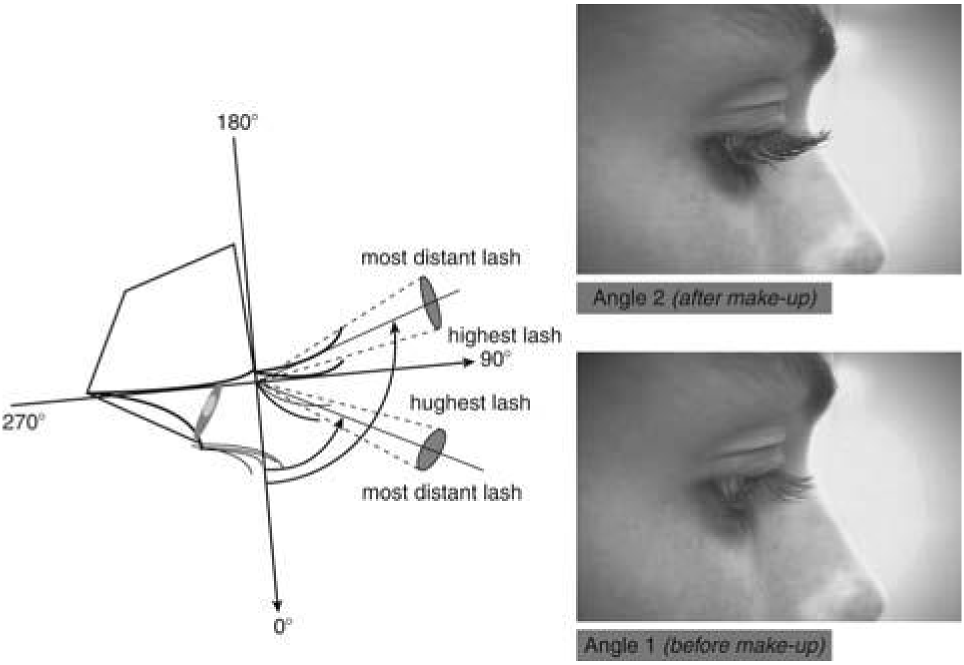
Figure 1 Extraction of the brightness and streakiness.

state of the lips is complex, especially for long-term studies and comparisons between lipsticks. Indeed, one week of "wash out" is necessary to obtain a constant physiological state of lips, and only one lipstick can be studied at the same time on the same volunteer. To screen many lipstick formulae, an original method consists in applying lipstick on the forearm zone after delipidation of the skin surface with an acetone/ether (1:1) mixture during 30 minutes (36). Once the lipstick is applied (the same quantity, which is applied on lips), it stays in contact with the skin for one day. Then, the hydration of the skin surface is measured with a Corneometer the next day after a standardized wash. The results after one week showed that a lipstick containing a glycerin/water mixture significantly increases the hydration of the skin compared with the same base of lipstick without glycerin. Note that before testing the efficacy of a moisturizing lipstick, it is recommended to check the physicochemical properties of the pigments and raw materials contained in the formulation, and more particularly those properties, which possess an electrical conductivity.

Eye Makeup

Evaluation of the Curving and Lengthening Power of a Mascara

The image analysis can also be used to evaluate the curving power of a mascara. The principle consists in visualizing the profile of the eyelashes by a video camera placed perpendicularly to the eye and calculating from the image obtained the curving power with regard to two axes situated at 90° from each other. The 0° to 180° axis corresponds to the eyelid and the 90° to 270° axis to the ciliary edge. The angles created by the highest and farthest eyelash from the eyelid are measured, and the average angle calculated. The curving power of mascara is then determined by calculating the difference between the two average angles: angle 2 (after makeup) – angle 1 (before makeup) (Fig. 2). The quantification of the lengthening power is also possible by measuring the length (in pixels) of the farthest eyelash before and after application of the mascara.



Angle 2 *(after make-up)*

Angle 1 *(before make-up)*

Figure 2 Measurement of the curving power of a mascara.

Face Makeup

Certain makeup products such as foundations and tinted day creams (which are a colored extension of skin care products) contain some raw materials in their formulation that we usually find in skin care products. Although their efficacy on the skin has already been demonstrated by several noninvasive methods, such as the measurement of epidermal capacitance, transepidermal water loss, biomechanical properties, UV protection, or free radical scavengers, their incorporation in makeup formulations can generate several problems of compatibility with pigments and some difficulties in the efficacy assessment. The best known and most difficult claims to quantify are those in relation to the lasting properties (color, degradation of the makeup surface film, migration of pigments in fine wrinkles, and modification of the shade), the intransferability on surfaces like the skin or clothes, and skin radiance.

Quantification of the No Transfer Properties of a Foundation

Foundation is considered no transfer only if it is insensitive to two types of constraints: a transfer by contact, called a “static transfer,” and a transfer by friction, called a “dynamic transfer.” To reproduce the effect observed by the consumers (e.g., transfer on the collar of blouses or pullovers), a device to simulate these two types of transfer has been developed in our laboratory. It is composed of a probe used to fix the chosen support and to control the contact pressure between the support and made-up surface, and a motorized arm allowing it to move laterally, over a known distance and at a constant speed. Once the transfer is made, the foundation print is digitalized by a color video camera. The image is then treated to extract and count the pixels associated with the colored print (Fig. 3). A foundation will be considered no transfer if no pixels are detected. For very short-term effects (e.g., 5 minutes after makeup), the no transfer properties of a foundation can be evaluated on the forearm. For long-term no transfer effects, it is better to carry out the study on the forehead because the sebaceous glands’ activity can modify the behavior of the makeup in time.

Quantification of the Long-Lasting Properties of a Foundation

The appearance of the made-up skin is dependent on many optical and physiological properties of the skin. The appearance is mainly determined by the factors of color and texture. Color perception is associated with light and the way it is reflected. The texture depends on the

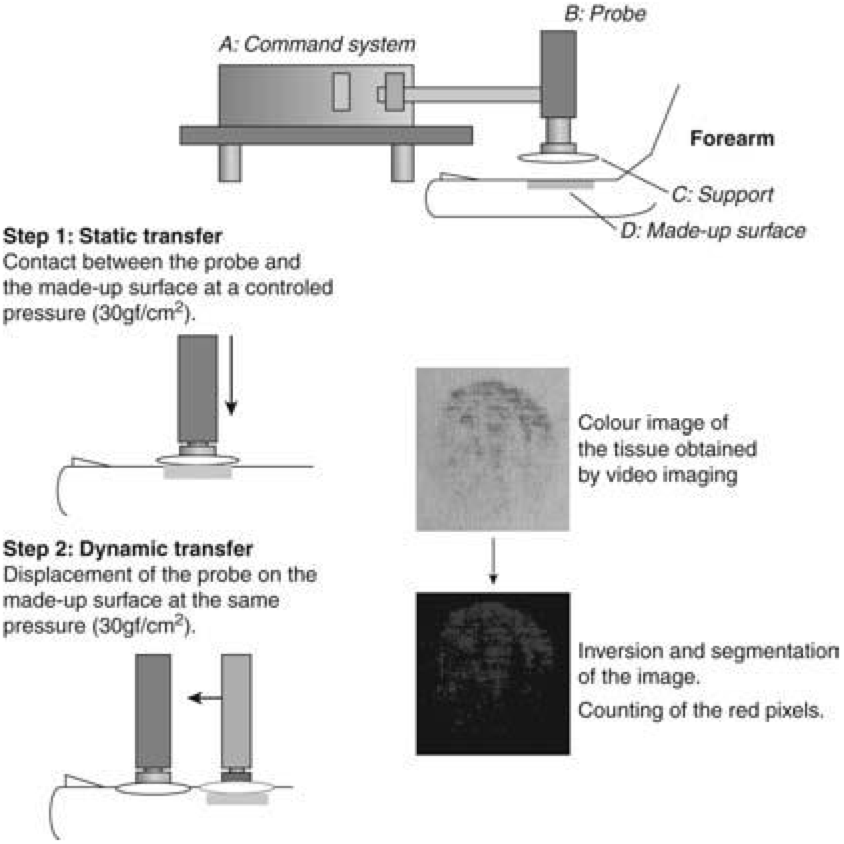


Figure 3 System allowing to simulate a static and dynamic transfer. Image analysis and extraction of pixels containing the transferred pigments.

brightness and the relief, respectively, attributable to light diffusion on the skin surface and the distribution of foundation layers. A foundation will be considered long lasting if the made-up skin preserves these properties in time. Whereas the color is the most studied and explored field, few studies have been carried out on the behavior of the skin texture in time after makeup (37–39). To follow the behavior of a makeup film, a noninvasive method based on the determination of changes in the intensity of dermis autofluorescence excited by UV irradiation (40,41) can be used. The instrumental setup for fluorescence measurements consists of a commercially available luminescence spectrometer (LS-50B Fluorescence Spectrometer®, Perkin Elmer, U.K.) equipped with flexible fiber optics surrounded by a metallic cylinder of about 1.5 cm in diameter for in vivo measurements. Skin fluorescence is induced by a radiation at 325 nm (UV light in UVB range). The excitation light was transmitted perpendicularly to the skin area and the emitted light was collected and transported at the emission slit. The emission spectra of the skin site (e.g., the forehead) present a peak at 390 nm and additional shoulder at 440 nm (42). These two wavelengths are associated with the fluorophores of the skin, such as collagen and elastin, both major compounds of human dermis, and depend on the skin's chromophores, which absorb UV radiation. The application of a makeup product creates a physical and chemical barrier between the excitation light and the skin, which decreases the skin's autofluorescence response (Fig. 4). The makeup film created by foundation layers will be considered long lasting if the emission spectrum carried out just after makeup is similar to the following ones, considering that raw materials used in formulations do not absorb UV radiation. The long-lasting effect can be studied on the first emission peak ($\lambda = 390$ nm) as well as on the second one ($\lambda = 440$ nm). The other factor, which defines the appearance of the made-up skin texture is the brightness. In relation to the degree of brightness, the skin may appear bright and healthy or dull and unhealthy. Brightness can be brought by the foundation itself or by the sebaceous gland's activity, which gives the skin an oily appearance (43). There exist a

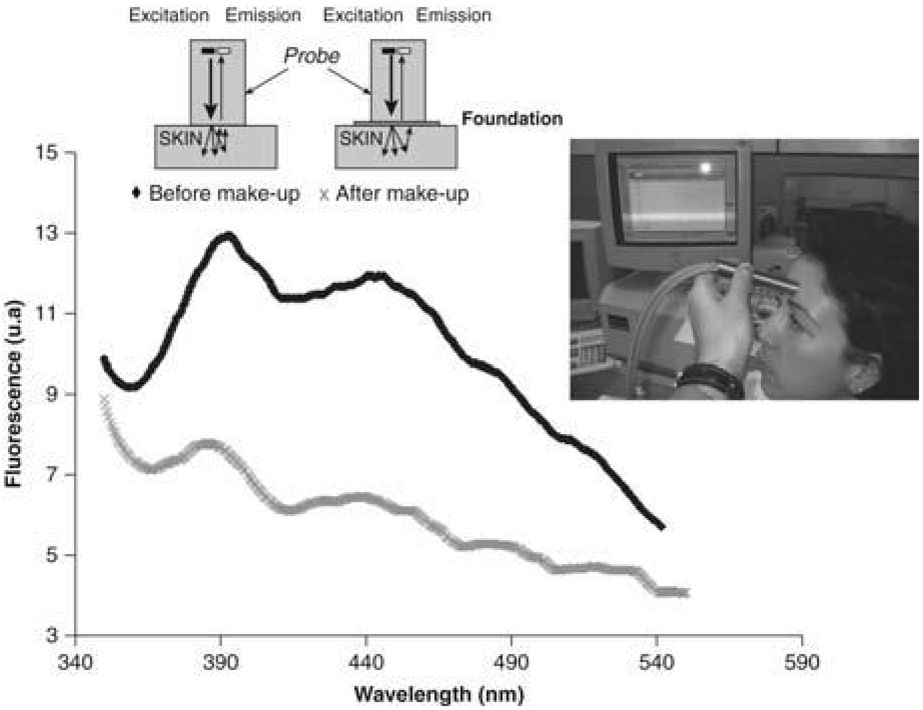


Figure 4 Measurement of the skin's autofluorescence before and after makeup. Study on forehead.

variety of established methods to estimate the oily skin (44,45). For measuring brightness, methods are mainly based on the evaluation of the intensity reflected in the specular direction, when the surface to be analyzed is illuminated by a beam of light with a fixed angle of incidence. However, these methods are not easy to use on the skin surface because they require an analysis surface as flat as possible. To avoid these constraints, brightness assessment can be performed using the same instrumental setup for in vivo fluorescence measurements. To record only reflection and eliminate fluorescence of different wavelength, the fluorescence spectrometer (LS-50B) is used and operated in the so-called synchronous mode, i.e., both monochromators (excitation and emission) are moved synchronously through the whole spectrum (250–700 nm) with a wavelength difference of zero ($\Delta\lambda = 0$ nm). Certain chromophores of the skin (melanin, etc.) and the color of makeup can influence the visible reflection spectra of human skin. For this reason, the spectral differences observed before and after makeup will be preferentially studied and compared in the UV range (250–400 nm), where the wavelength giving the maximum of difference will be extracted. As for the study of the makeup film long lasting, the matte effect will be considered long lasting if the reflectance value, recorder just after makeup, is similar to the following ones.

Quantification of Skin Radiance

There is no universal definition of the skin radiance. Each individual perceives it in a different way because it often includes physiological and psychological attributes. If there are differences in the perception of the skin radiance, dermatologists and experts in cosmetology consider that the complexion must reflect the general health of each human. The main factors that affect the skin complexion are the skin color, surface texture, luminosity, and mainly microcirculation, which gives the skin a rosy appearance. The skin radiance being a global phenomenon, it is very important to study the interaction between all these visual effects before any quantitative and qualitative interpretation. Although the qualitative evaluation (besides the consumers' perception obtained by questionnaire and experts' evaluation) (46) is commonly used and remains indispensable to prove the effects of cosmetic products used to improve the skin radiance, we are searching for more instrumental data. To approach the skin radiance in a scientific way, there are very few instrumental techniques. Color and microcirculation are the most studied and explored fields, but these methods only give quantitative information limited to a small analysis surface according to the device used. To obtain what is closer to the consumers' perception, the existing conditions of the skin radiance can be performed via pluridisciplinary approaches combining digital image analysis, consumers' perception, and experts' evaluation. From a round table meeting, several items linked to skin radiance but also taking into account emotional, psychological, and behavioral factors are defined. Then, a self-assessment questionnaire built according to the information obtained is proposed to experts to evaluate the skin radiance perceived. In parallel, facial images are carried out using a video imaging, and algorithms are required to extract skin parameters such as the brightness, the grain of the skin, skin color, and the homogeneity of the color. The comparison between image analysis and expertise allows evaluation of the degree to which each of the independent parameters contributes to the skin radiance perception, and suggests a mathematical model to quantify the global radiance phenomenon (47).

Nail Makeup

Few studies have been carried out on the behavior of nail enamel. The brightness of nail enamel can be quantified by the luminescence spectrometer (LS-50B) for in vivo measurements used in synchronous mode. However, the irregular shape of the nail requires that the diameter of the optical probe be reduced (3 mm) to adapt to the surface of the nail.

CONCLUSION

The heightened technology of makeup products (pigments, formulations, etc.), the sensory interactions based on the skin-brain connection, and more stronger claims are accompanied by the development of specific evaluation methods used to quantify these improvements and to prove the claimed efficacy. In cosmetology, the quantitative assessment of the visual effects of a makeup product becomes more and more complementary to a qualitative evaluation (questionnaires according to consumers' perception and expert evaluation). Certain quantitative studies are restricted to a small surface of measurement and require a direct contact with the skin. Video imaging appears as a method of the future to prove the efficacy of makeup products. Today, this technology allows us to study precisely the color, brightness, or streakiness of a lipstick, but also some physical properties, such as the curving and lengthening power of mascara or the no transfer properties of a foundation or a lipstick. Technological progress, combined with video imaging and data processing, allows us to imagine, in a near future, the appearance of new and more sophisticated visualization tools that will permit us to study some visual effects, which are still difficult to quantify such as certain optical effects (soft focus, photochromic effects, etc.), interactions between the product when you make up your face (distribution and migration of the pigments during the makeup process, etc.), or again, emotions generated during the makeup process. Note that biophysical methods can also be very useful when they are used differently from their main function.

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Skin Radiance Measurement

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INTRODUCTION

The term "complexion" has always attracted attention; it had to be white from the antiquity to contemporary times, and then tanned from the 1920s. Nevertheless, we are at the beginning of a new era, where a tanned complexion is no longer fashionable; a young homogeneous complexion without imperfection is now the preferred option. Today, the essential preoccupation is not so much the color of the complexion but its texture, which should evoke youth, health, and happiness (1).

The term "radiance" refers to shine and light. A vivid red is a red that shines. Radiance also defines what arouses admiration, attention, glitter, and magnificence.

In fact, the radiance/complexion is the mirror of general health, both physical and psychological. A gray skin, a "blotchy complexion" may reflect bad looks because of great fatigue, weariness, hormonal status, emotional states (sadness, stress, etc.), illness (dysfunction of vital organs such as the liver etc.), nutrition deficiency or excess, tobacco, alcohol, pollution, seasons (2–6). Inversely "peach-colored skin" reflects a smooth, pink and velvety skin, and good health. The complexion plays essential psychological and social roles (1).

Skin radiance is referred to without any precise definition and quantifiable appreciation data. All the parameters that constitute it and their relative proportions are difficult to list. The skin radiance seems to be a balanced mixture of color, itself mostly influenced by the skin microcirculation, of light reflection, and more globally of texture of the skin surface (1). Its study therefore implies the quantification of each of these components.

METHODS

When the light meets the skin surface, a small quantity [about 5% (7)] is reflected directly while the major part penetrates the different layers of the skin. The specular light gives its luminous aspect whereas the back scattered light (Fig. 1) gives the complexion (peachy-color). In other words, specular reflection (depending on the nature and state of the surface of the skin) explains the glow, absorption phenomena (depending on the skin's chromophore content) explain its hue, whereas diffusion phenomena (depending mostly on the collagen content) define its saturation.

The skin color depends mainly on the melanin as well as the hemoglobin concentrations and distributions. The melanin (brown) absorbs all wavelengths, but this absorption decreases considerably from purple to red, which makes the melanin look like a mixture of gray (global absorption) and yellow (significant absorption of blue). Hemoglobin looks red because it absorbs selectively the green and therefore retro-diffuses a light where this complementary color is missing.

The hemoglobin plays an important part in the skin radiance, which is usually perceived as "pink" skin. An indirect way to assess the radiance is consequently to study the skin microcirculation.

Assessment of Skin Microcirculation

The hemoglobin transports the oxygen inside the red globules: if there is not enough oxygen, the face will be gray and dull. If the microcirculation is effectively stimulated, the light will more easily reflect off the red blood cells at the source of the skin color.

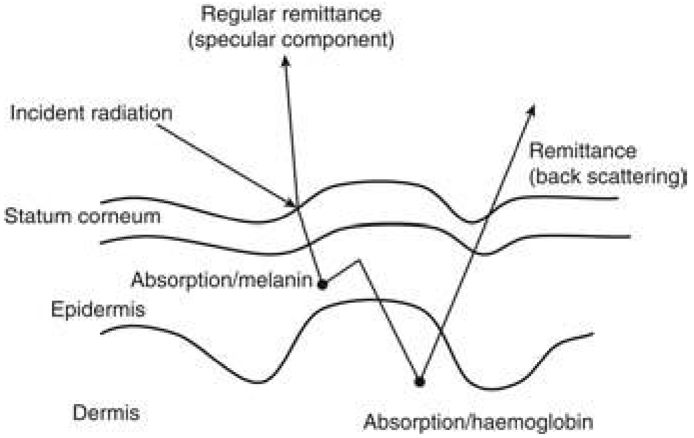

Figure 1 Optical pathways in the skin (the layer is so thin in the stratum corneum and the epidermis that its contribution to remittance other than specular is minimal over the entire visible and near infrared regions). *Source*: From Ref. 8.

The skin microcirculation is therefore an important factor of the dull complexion:

- Under stress, catecholamines are delivered in the skin, inducing vasoconstriction (and thus skin pallor) (2,9,10),
- With tiredness (lack of sleep and/or intensive activity), the body reacts by sending more blood to vital organs, and the cutaneous microcirculation is "sluggish" (6).
- With pollution and smoking, the microvessels lose their colors (grayish aspect of the skin) (4–6,11,12).
- With aging, papillar capillary loops disappear, inducing a loss in dermal nutritional vessel density and surface area for exchange (13).

Among the existing available techniques, capillaroscopy and videocapillaroscopy allow direct visualization of the capillary network in vivo. After depositing a drop of oil to enhance skin transparency, an optical magnifying system is used to visualize its vascular network. Different levels of magnification can be used to assess the surface of the microvasculature structure as well as its color (Fig. 2) (14,15).

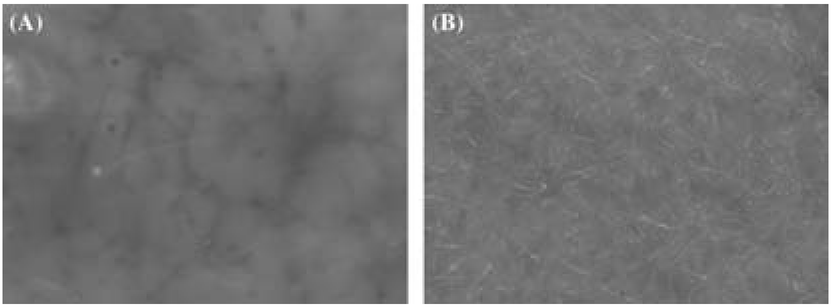

Figure 2 (**A**) ($\approx$7 mm^2) A magnification of 100× allows to quantify the vascularization network (arrows show the capillary loops and the vessels) of the skin, whereas (**B**) ($\approx$28 mm^2) a magnification of 50× allows to quantify the skin redness.

Colorimeters

The most logical way to assess skin complexion is to study its color directly. Taylor et al. described in 2006 the different techniques available (16). Among them, reflectance spectroscopy, chromameters, and narrowband reflectometers should be the most frequently used. The latter are dedicated to the assessment of erythema or pigmentation (by measuring more specifically the skin chromophores) (17,18).

The color variations of the skin surface can be measured by reflectance spectroscopy, spectrocolorimeter (CM2600D, Konica Minolta Sensing) or chromameter (CR400, Konica Minolta Sensing). These devices have sensitivities corresponding to those of the human eyes, but the measurements are performed in standardized conditions using the same light source.

The Commission Internationale de l'Eclairage (CIE) has defined the spectral characteristics of several types of typical illuminants (the D65 corresponds to average daylight and is usually used as the reference) (19).

The results are expressed in the standard L*a*b* system [CIE LAB 1976 (20)]. The L* in this space corresponds to the luminance axis (0 for the black and 100 for the white) characterizing the separation between bright and dark; a* and b* form the other two color orthogonal axes, with a* evolving from green to red (usually selected for the study of redness) and b* from blue to yellow (study of pigmentation).

The skin radiance can therefore be described by a*, which corresponds to the redness and L*, which defines the luminosity. However, additional information can be extracted, in order to qualify the skin color heterogeneity [color difference metric DeltaE (21)] and vividness [chroma = $([a^*]^2 + [b^*]^2)^{1/2}$) (19)], which are key factors in the problematics of dull complexion.

To conclude, videocapillaroscopy and colorimeters assess color hue, saturation, and heterogeneity directly or indirectly. They can be usefully combined with standardized photography, which allows to illustrate and even quantify these factors.

Photography

Once calibrated and standardized, photography offers many applications to study skin radiance/complexion. It appears more appropriate to study texture heterogeneity than glowing aspect because of the influence of the light. The image can be easily disturbed by brightness induced by the flashlight or by the environment. The nature as well as the positioning of the light source and the posture of the subject are of major importance and must be taken into consideration to avoid visual artifacts (Fig. 3).

Polarized light photography provides more information than usual in terms of heterogeneity of structure. Its principle consists in differentiating the regular reflectance (glare) from the light "back-scattered" (complexion) from within the skin. The regular reflectance contains information related to the surface relief/shininess and the other one to the color. A filter is placed in front of the camera and another one in front of the flashlight. When the orientation of the filters is perpendicular (cross polarization), the regular reflectance is blocked and only the back-scattered light from the tissues reaches the lens [revealing the complexion (skin redness or paleness, color, heterogeneity, etc.)] (Fig. 4), whereas when they are parallel (parallel polarization), only the reflected polarized light passes through the lens filter, and details of the surface are enhanced (wrinkles, shininess, scaling) (12,21–23).

Figure 3 Photography taken in an integration sphere, with a homogenous and symmetrical light.

Assessment of Skin Relief

Radiant skin is usually considered as smooth, homogeneous, without imperfections. Although innate, the microtopography of the skin is affected by the environment as well as aging, and undergoes changes in quantity, depth, and direction (24,25).

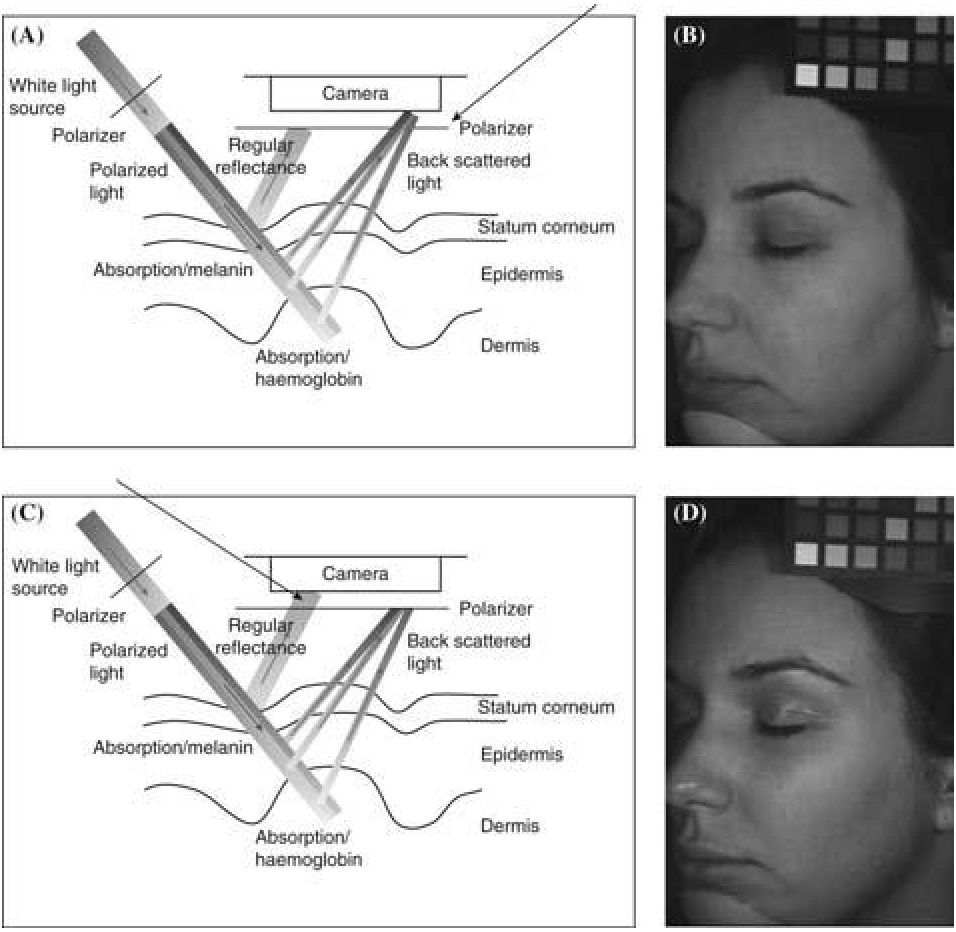

Figure 4 Simplified schema of the principle of polarized light photography. (**A**) With cross-polarization, only the back-scattered light reached the lens [revealing the complexion (photograph **B**)]. (**C**) With parallel polarization, only the reflected polarized lights pass [revealing the shininess and relief of the skin (photograph **D**)].

Profilometry (mechanical, transparency, or optical), initially developed for microtechnics, has been applied for many years to study the skin relief (26–29). From 2000, devices using fringe projections specifically dedicated to the skin have been created (DermaTop, Eotech, France and Primos, GFM, Germany). Interestingly, this in vivo technique allows to study the skin imperfections via the assessment of the volume and depth of the wrinkles and in particular the roughness and heterogeneity of the microrelief (dilated pores, comedones, fine wrinkles, etc.) (Fig. 5).

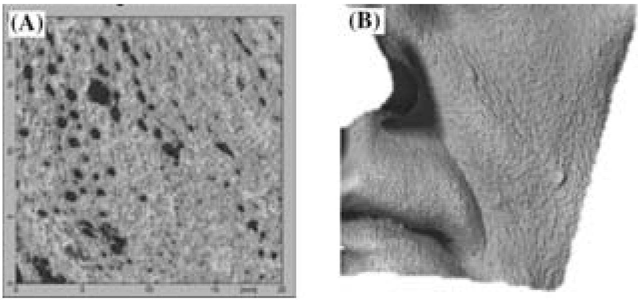

Figure 5 3-D reconstructions obtained (**A**) from the cheek (20 × 20 mm area), allowing to detect dilated pores, or (**B**) from hemi-face (60 × 80 mm area), allowing to quantify the roughness/heterogeneity of its relief.

Assessment of the Skin Ability to Reflect the Light

The relief of the skin produces different image contrasts depending on the brightness level of the surface (the same relief appears more easily in the case of a bright surface). When the skin surface is irregular, it absorbs light with difficulty and reflects it in many directions. This is particularly typical of dry and scaly skin. The assessment of the specular component provides direct information on the glare of the skin. Sandoz et al. have underlined the influence of the surface bidirectional reflection distribution function (BRDF) measurements for the visibility of the skin surface (30,31). The light intensity directed toward the observer's eye is proportional to the coefficient of reflection of the surface. The behavior of bright and matt surfaces is different since the BRDF is different for the direction of observation (Fig. 6).

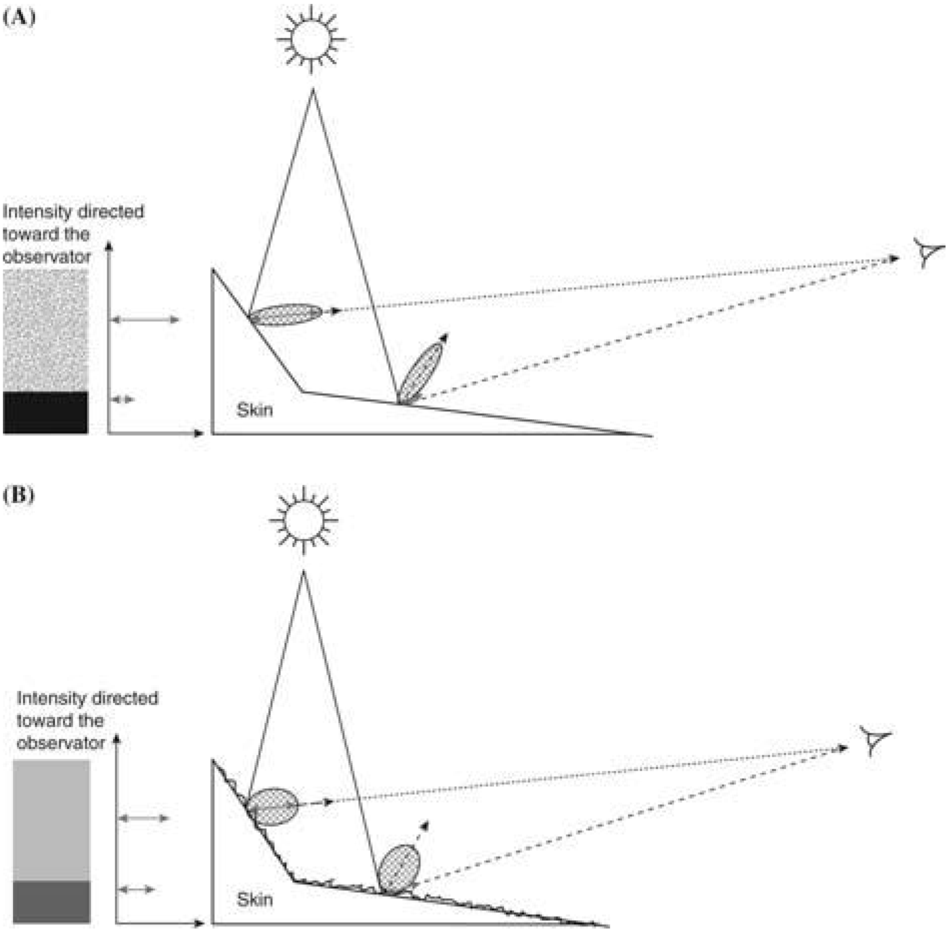

Figure 6 Simplified schema of the visibility of the skin relief: the contrast is given by the amount of light reflected in the direction of the observer. The perception of a wrinkle will be modified by the quality of the skin surface. If the skin is bright (**A**), the wrinkle will be more contrasted and more visible. If the surface is matt (**B**) it will be more blurred. ⬭, wider reflection cone ↑, specular component of the light ↔ intensity of the light perceived = simulation of the contrast of the skin perceived by the observer.

From this principle, a specific device has been developed in Besançon (31,32). Its aim is to assess the quantity of light reflected that depends on the brightness (Fig. 7). It consists of a system, which illuminates an area with white light through an objective at one end of an optic fiber. The beam is directed to the subject at a 25° angle. The light reflected is measured by inputting a profile of intensity of light for various angles values. It is generally admitted that radiant skin tends to act as a mirror, i.e., to reflect rays in a specular manner (with the same 25° angle) and dull skin tends to diffuse light more. This instrument has shown its good sensitivity and specificity to characterize the dull to glowing radiance of the skin (32). This technique allows to access to the breadth of the gaussian curve, defining the diffusion of light rays, as well as its maximal intensity, defining the skin brightness (reflection).

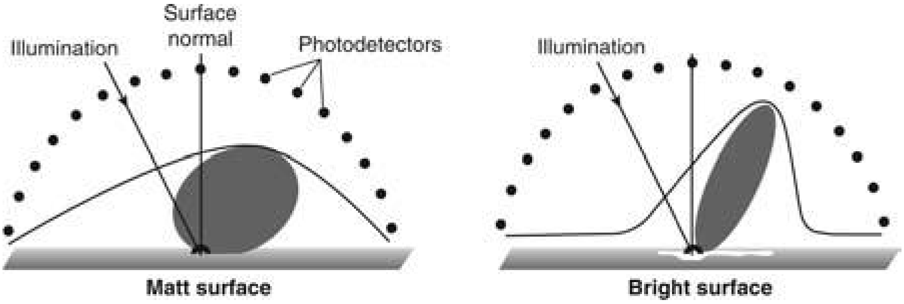

Figure 7 Principle of the instrument developed for BRDF measurement on the skin. Photodetectors distributed in the place of incidence sample the angular distribution of the reflected light. BRDF of a matt surface distributes the reflected light in a wider cone of diffusion (dull complexion). A bright surface concentrates the reflected light in a narrow cone of reflection (glowing complexion).

Gillon et al. have also developed a specific contactless device (brillanometry) (33). Its principle consists in directing a polarized light beam perpendicularly to the skin surface and to assess the reflected beam in the same direction.

The application of systems of polarization of the light currently used in photographs has given the opportunity to Bossa Nova Technologies to develop a system called SAMBA® a few years ago. It evaluates the gloss by assessing the scattering properties of the skin or the hair (34).

Finally, no instrument can quantify today the skin radiance globally, but there are devices that allow to assess its different components.

With contrast to the color, the glow remains difficult to quantify. The development of simulation systems would perhaps be one solution (35). Many terms are usually employed to characterize the skin radiance: shininess, brightness, glow, glare, gloss, etc. Shininess, brightness, and gloss refer to the reflection of light to something, and are more frequently used to characterize seborrheic skin or to assess the effect of make-up on lips. Glare seems to evoke a shine with a dazzling light, whereas the glow associates an intense color with a slight shine. The glowing aspect of the skin has, thus, to be differentiated from its brightness, which is the characteristic of greasy skin and is unaesthetic. If gloss is what women expect for their hair (34), glow is a better representation of radiant skin. All these notions show a real need to define the skin radiance more accurately.

Clinical Scoring

In 2006, Baret et al. organized a round table meeting with women (23). As a result of these exchanges, many items (including the skin grain, brightness, and color) were selected and studied in volunteers of different age groups from image analysis of video data of their face. Experts performed clinical scoring and then divided the volunteers in two groups: the young one, whose radiance was considered more dependent on skin luminosity and color (rosy color) and the old one, who was mainly characterized by irregular skin surface aspects and color variations.

These definitions corroborate the idea that radiance is multifactorial and naturally include an important subjective part.

As previously mentioned for photography, it is of great importance to perform the scoring in controlled conditions. The subjects have to be seated between "daylight" lamps and to wear white clothes as well as a white paper cap to avoid any influence from extrinsic colors, and to stay at rest in a temperature-controlled room (36).

In 2004, Musnier et al. organized a brainstorming session with several beauticians to develop a model of sensory evaluation of the skin radiance (36). One hundred volunteers were also interviewed to self-appraise their complexion. The synthesis of the data allowed to determine four skin-coloring descriptors and to construct a model "C.L.B.T.," on the basis of the visual perception of skin color (C), luminosity (L), brightness (B), and transparency (T).

CONCLUSION

Facing the increasing importance of appearance, consumers wish to reflect the image of their inner well-being represented mainly by a beautiful skin and healthy looks (34). The cosmetic industry has perfectly understood this concept and developed specific products designed to enhance the complexion, illuminate the skin, or fight off the detrimental effects of the pollution.

Several options are available to improve dull complexion. Most of the products currently on the market claim an action on the skin texture. They act either by optical effects with the help of pigments, or by a vitamin contribution to the antioxidant properties, or with exfoliating active principles that attenuate the imperfections, smooth the skin, making the complexion more glowing. Others claim an action on the microcirculation. The products often associate several of these effects.

All these data confirm that the assessment of skin radiance implies the study of the geometry of the light reflection as well as the interaction between the light (interaction with surface/glow) and the color (interaction within the skin/complexion). However, the skin relief seems to be therefore one of the key factors of the skin radiance (1).

ACKNOWLEDGMENT

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39 Tribological Studies on Skin: Measurement of the Coefficient of Friction

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INTRODUCTION

Because the skin is a surface, it is convenient to analyze and describe it in terms of its surface characteristics such as friction. Tribological studies of skin provide valuable insight into how the skin interacts with other surfaces and how it can change under various conditions, like age and health, and chemical treatments, such as lotions and moisturizers (1). Because the skin is the first-line of defense against the environment, it is repeatedly subjected to physical and chemical damage and alterations. For example, Naylor (2) showed that the moistened skin has an elevated friction response, and El-Shimi (3) demonstrated that the drier skin has a lowered friction response. Tribological studies offer convenient, noninvasive techniques to quantitatively assess skin health and hydration.

The tribological parameter generally measured is the coefficient of friction by bringing a surface into contact with the skin and moving it relative to the surface. When the two surfaces are brought in contact, the perpendicular force is defined as the normal force (N). The friction force (F_f) is the force that opposes the relative movement between the two surfaces. According to Amontons' law, the coefficient of friction (μ) is defined as the ratio of the friction force to the normal force:

$$\mu = \frac{F_f}{N}$$

Friction can be described in two different manners: the static friction coefficient (μ_s) and the dynamic or kinetic friction coefficient (μ_k). The static friction coefficient refers to the friction that builds up just before the initiation of relative movement; the dynamic or kinetic friction coefficient refers to the friction that exists as the two surfaces are moving relative to each other. Although most of the skin research has focused on the dynamic friction coefficients, with the two surfaces moving at a relative constant velocity, some work has focused on static friction coefficients.

According to Amontons' law, the dynamic friction coefficient remains unchanged regardless of the probe velocity or the applied normal load in making the measurement. Amontons' laws hold true for dry sliding contacts between solid bodies with limited elastic properties. Although Naylor (2) concluded that Amontons' law is true for skin, later studies (3–6) determined that skin deviates from Amontons' law. El-Shimi (3) and Comaish and Bottoms (4) reasoned that the increase in friction coefficient resulted from the viscoelastic nature of the skin allowing for a nonlinear deformation of the skin with reduced normal loads. Also, with the presence of liquids, as is the case for the surface of human skin, the friction coefficient can change with velocity too, because the contact moves into an elastohydrodynamic lubrication regimen.

Various experimental designs have been devised to measure the friction on skin. They focus on measuring friction by pressing a probe onto the skin with a known normal force, and then detecting the skin's frictional resistance to movement of the probe. The designs fall into two categories (Table 1):

1. A probe moved across the skin in a linear fashion.
2. A rotating probe in contact with the skin surface.

Adapted from Proceedings of the Institution of Mechanical Engineers Part J. J Eng Tribol, 2006; 220(J8): 729–737.

Table 1 Probes and Apparatus used to Measure the Dynamic or Static (When Noted) Friction Coefficient (μ) of Skin In Vivo

Author	Probe size and shape	Probe material	Motion of test apparatus	Maintenance of normal load
Naylor (2)	8 mm diameter sphere	Polyethylene	Linear, reciprocating	Static weights
El-Shimi (3)	12 mm diameter hemisphere	Stainless steel (rough), stainless steel (smooth)	Rotational	Static weights
Comaish and Bottoms (4)	15 mm diameter annular ring	Teflon, nylon, polyethylene, wool	Linear	Static weights
Koudine et al. (5)	Hemisphere lens	Glass	Linear	Static weights; balance beam
Highley et al. (7)	Disc	Nylon	Rotational	Spring load
Prall (8)	Disc	Glass	Rotational	Spring load
Cua et al. (9)	15 mm diameter disc	Teflon	Rotational	Spring load
Johnson et al. (10)	8 mm (radius of curvature) lens	Glass	Linear, reciprocating	Static weights
Asserin et al. (11)	3 mm diameter sphere	Ruby	Linear	Balloon; static weights
Elsner et al. (12)	15 mm diameter disc	Teflon	Rotational	Spring load
Sivamani et al. (6)	10 mm diameter sphere	Stainless steel	Linear	Computer controlled
Sivamani et al. (13)	13 mm diameter cylinder	Copper	Linear	Computer controlled
Egawa et al. (14)	100 mm^2 square	Piano wire	Linear	Computer controlled
Zhang and Mak (15)	Annular ring	Teflon	Rotational	Spring balance
Li et al. (16)	125 × 145 mm planar surface	Sandstone, slate, granite	Linear	Supplied by the participant
O'Meara and Smith (17) and O'Meara and Smith (18)	Cylindrical "grabrail"	Chrome, stainless steel, powder-coated steel, textured aluminum, knurled steel	Linear	Supplied by the participant

Source: From Ref. 1.

In the linear designs, the probe movement is accomplished in several ways. Comaish and Bottoms (4) utilized one of the simplest linear designs: They moved the probe across the skin by attaching it to a pan of weights by means of a pulley. More sophisticated linear designs followed the simple design used by Comaish and Bottoms (4) but provided motorized unidirectional movement of the probe or the use of a reciprocating motor to move the probe back and forth. In both designs, the motorization affords greater control in maintaining the velocity of the probe and the normal load applied to the skin. Strain gauges measure the friction force as the probe moves along the skin surface.

The second design category measures friction with a rotating wheel pressed onto the surface of the skin with a known normal force. Highley et al. (7) measured the frictional resistance by determining the angular recoil of the instrument as the wheel contacted the skin. Comaish et al. (19) developed a portable, hand held device (Newcastle Friction Meter®) that relied on a torsion spring to measure the skin's frictional resistance.

An important part of designing a friction measurement apparatus is choosing the probe size, shape, and material. Because friction is an interaction between two surfaces, the probe geometry and material will affect the values calculated for the friction coefficient of the other surface. Several shapes and material have been used as outlined in Table 1. Also, results will be more accurate when the probe's normal force is maintained at a constant value or continuously monitored; different methods have been used to maintain the normal force including spring mechanisms, static weights, or computer-controlled feedback (Table 1). Probe parameters are revisited critically later.

Previously measured values for the fiction coefficient are outlined in Table 2. Special mention should be made for friction measurements of the fingers, palms, and soles because these parts of the body are more often in contact with another surface. It may be more relevant to measure static friction coefficients at these sites, since common activities such as gripping handrails, gripping car steering wheels, or holding a cup involve the static friction coefficient more than the dynamic friction coefficient. Some authors have studied the dynamic friction coefficient of the palm (9,15), and other authors have studied the static friction coefficient of the palms and fingers (16–18). Increased sweating in the hands and feet (4) and increased roughness, because of the presence of epidermal ridges (15), may contribute to increased friction coefficients.

FACTORS

Normal Load

The control of the load is important because the friction coefficient does not adhere to Amontons' law. Wolfram provided a theoretical analysis where he shows that the dynamic friction of the skin should relate to the normal load as:

$$\mu \propto N^{-(1/3)}$$

where N is the applied load normal to the skin. Koudine et al. (5) found this dependence to hold experimentally:

$$\mu \propto N^{-0.28}$$

and this was confirmed by the analysis of Sivamani et al. (6):

$$\mu \propto N^{-0.32}$$

Hydration

Hydration is a multifaceted phenomenon influenced by intrinsic (i.e., age, anatomical site) and extrinsic (i.e., ambient humidity, chemical exposure) factors. Hydration studies have correlated increases and decreases in skin hydration with the changes in the friction coefficient. These studies reveal that drier skin has lowered friction while hydrated skin has an increased amount of friction (2–4,6–8,10,13,20–23). However, the skin response is more complex, because very wet skin also has a lowered friction coefficient much like the characteristics of dry skin (24). Most studies focus on an intermediate zone of hydration where the skin has been moistened without

Table 2 Reported Values of the Dynamic Friction Coefficient (μ) for Untreated "Normal" Skin In Vivo

Author	μ
Naylor (2)	0.5–0.6
El-Shimi (3)	0.2–0.4 (stainless steel, rough) 0.3–0.6 (stainless steel, smooth)
Comaish and Bottoms (4)	0.2 (Teflon) 0.45 (nylon) 0.3 (polyethylene) 0.4 (wool)
Koudine et al. (5)	0.24 (dorsal forearm) 0.64 (ventral forearm)
Highley et al. (7)	0.2–0.3
Prall (8)	0.4
Cua et al. (9)	0.34 (forehead) 0.26 (ventral forearm) 0.21 (palm) 0.12 (abdomen) 0.25 (upper back)
Johnson et al. (10)	0.3–0.4
Asserin et al. (11)	0.7
Elsner et al. (12)	0.48 (forearm) 0.66 (vulva)
Sivamani et al. (6)	0.33–0.55
Sivamani et al. (13)	0.45–0.65 (untreated) 0.81–1.17 (occlusion) 1.19–1.71 (petrolatum) 1.25–1.81 (glycerin)
Egawa et al. (14)	0.2–0.3
Zhang and Mak (15)	0.40–0.62 (anatomical site) 0.37–0.61 (probe material)
Li et al. (16)	2.48–3.25 (rock types) 3.00 (no chalk on hands) 2.47 (chalk on hands)
O'Meara and Smith (17)	0.78–1.39 (dry palm-no grip) 0.90–1.09 (wet palm-no grip) 0.14–0.34 (soapy palm-no grip)
O'Meara and Smith (18)	1.44–1.91 (dry palm-active grip) 1.10–1.92 (wet palm-active grip) 0.34–0.64 (soapy palm-active grip)

Authors that studied the static coefficient of friction have been noted in the Table 2, and their data for certain treatments conditions have been included.
Source: From Ref. 1.

an appreciable "slippery" layer of water on the skin. Studies investigating the hydration-induced increases in friction were varied and this possibly results from the various probes used. Although the addition of water increases the friction coefficient, this effect lasts only for minutes before the skin returns to its "normal" state (3,6,7,23). The water softens the skin and this in turn allows for greater contact area between the probe and the skin. Also, water results in adhesive forces between the water and the probe. Thus, there is more frictional resistance between the skin and the probe and results in a higher friction coefficient (20). Since the water evaporates in minutes, the skin returns to its normal state in the same time frame. For dry skin, the skin becomes less supple and the probe does not achieve as much contact area, and this allows the probe to move more easily across the skin surface. Sivamani et al. (6) showed that administering isopropyl alcohol, a dehydrating chemical, lowered the friction coefficient, and a lowered friction coefficient was also found in studies involving subjects with clinically dry skin (3,22). The agreement between the experimentally induced dry skin and clinical dry skin is expected (25).

Electrical changes in the skin have also been utilized to measure hydration. Although discussions here will focus on skin friction, a review of electrical measurements is available from Gitis and Sivamani (26). Briefly, electrical changes in the skin have been used to measure skin hydration. Skin with more hydration is more permissive of electrical flow and has a lowered resistance when compared with dry skin. Decreases in hydration have been detected with electrical measurement in clinical conditions that have a loss of hydration, like psoriasis (27) or atopic dermatitis (22).

Anatomic Region, Age, Gender, and Race

So far no significant differences have been found with regard to gender (9,13,21) or race (13,28). Age-related studies have been debatable and may depend on the anatomical site that is used for comparisons.

The friction coefficient varies with anatomical site. Cua et al. (9,21) found that friction coefficients varied from 0.12 on the abdomen to 0.34 on the forehead. They attributed this difference in the friction coefficient to differing hydration, nonapparent sweating, and sebum secretions in skin of different areas of the body. Zhang and Mak (15) found friction coefficients to differ from 0.40 on the leg to 0.62 on the palm. They too suggested that variation in hydration may be accountable for the differences among anatomical sites. Elsner et al. (12) measured the vulvar friction coefficient at 0.66, whereas the forearm friction coefficient was 0.48. Manuskiatti et al. (28) studied skin roughness and found significant differences in skin roughness at various anatomical sites. Differences in environmental influences (i.e., sun exposure) and hydration may account for this. Elsner et al. (12) showed that the more-hydrated vulvar skin had a 35% higher friction coefficient than the forearm, and this is in agreement with the hydration studies that contend that skin has an increased friction coefficient under increased hydration. Sivamani et al. (13) found the friction coefficient to differ along the volar forearm with the proximal forearm to be more hydrated and therefore have a higher friction coefficient than the distal forearm. Normally, the proximal volar forearm tends to be covered by the arm when the elbow is flexed and this can lead to less water loss and increased hydration than the distal volar forearm. However, when using an amplitude/mean measurement that serves to normalize the friction coefficient against the volar forearm "stickiness" or stick-slip friction, Sivamani et al. (13) found no differences along the volar forearm (Fig. 1). In other words, the amplitude/mean represents the ratio of the difference between the static and dynamic coefficients of friction to the dynamic coefficient of friction:

$$\frac{\text{Amplitude}}{\text{Mean}} = \frac{\mu_{\text{static}} - \mu_{\text{dynamic}}}{\mu_{\text{dynamic}}} = \frac{\mu_{\text{static}}}{\mu_{\text{dynamic}}} - 1$$

With respect to age, increased sunlight exposure can increase collagen cross-linking and therefore alter the friction properties of skin. Although studies have been conflicting,

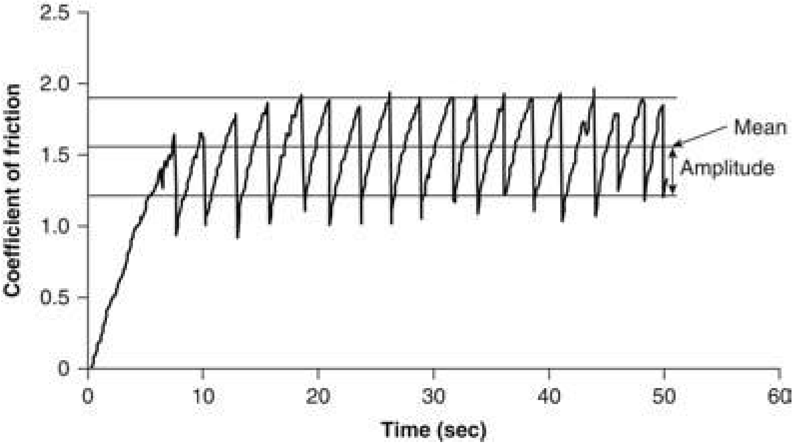

Figure 1 Calculation of the amplitude/mean measurement. The mean refers to the mean value of the measured friction coefficient as indicated on the graph. The amplitude refers to the deviation from the mean seen during the friction coefficient measurement as indicated on the graph, and is measure of the stick-slip friction along the surface. Then, the amplitude is divided by the mean to calculate the amplitude/mean. This is a measure of the skin's "stickiness." *Source*: From Ref. 13.

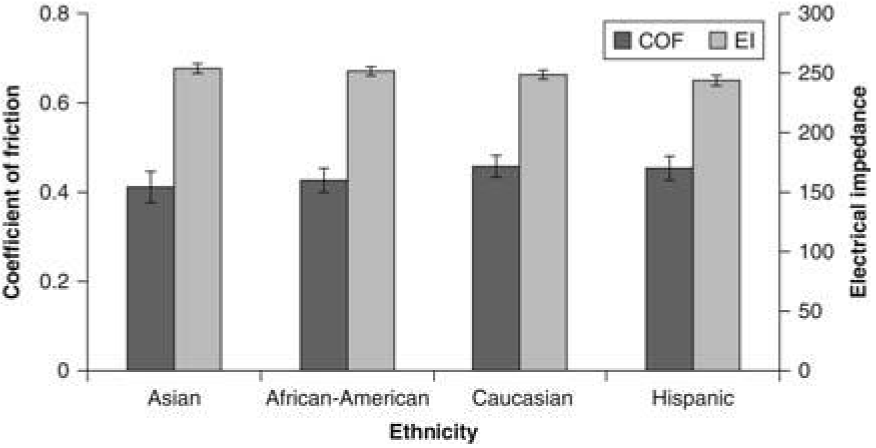

Figure 2 Coefficient of friction and electrical impedance across ethnicity. No significant differences were found among the ethnic groups. Error bars represent standard error.

recent studies have shown that the skin does not undergo age-related friction changes in areas protected from sun exposure. Cua et al. (21) found no significant age-related changes at various parts of the body, including areas that were exposed to the sun. Elsner et al. (12) conducted age-related tests and found no differences in the vulvar friction coefficient, but found a higher volar forearm friction coefficient in younger subjects. They postulate that the skin on parts of the body that become exposed to sunlight can undergo photoaging, and thus, volar forearm skin shows evidence of age-related differences, while the light-protected vulvar skin does not (12). However, Sivamani et al. (13) and Egawa et al. (14) found that the volar forearm did not change with age. This may be a reflection of variation in sun exposure among study populations.

Gender and ethnicity-related friction studies have shown no differences in the friction coefficient. Cua et al. (9,21) and Sivamani et al. (13) found no significant friction differences between the genders. Manuskiatti et al. (28) found no differences in roughness and scaliness between black and white skin; and Sivamani et al. (13) found no differences in the friction coefficient or electrical impedance among subjects of Caucasian, African-American, Asian, or Hispanic/Latino descent (Fig. 2) or in their responses to treatments (Figs. 3 and 4).

Lubricants/Emollients/Moisturizers

Much research has been devoted in determining how the application of certain ingredients influences the skin surface to appear and feel healthy, which is of interest to the cosmetic/moisturizer and lubricant industries. The studies focused on the effects of powder (3,4,16), oils (3,4,7,23), and skin creams/moisturizers (9,23). Hills et al. (29) analyzed how changes in the friction coefficient, following emollient application, differed with temperature.

Important qualitative characteristics in skin topical agents include skin smoothness, greasiness, and moisturization (20,30). Previous reports have described these subjective, qualitative descriptions in a quantitative fashion by correlating them against parameters considering the friction of the skin. Nacht et al. (23) found a linear correlation between perceived greasiness and the friction coefficient (Fig. 5). Prall (8) found a quantitative correlation for skin smoothness by taking into account the friction coefficient, skin topography, and hardness into the analysis. Sivamani et al. (13) found that an amplitude/mean measurement (Fig. 1) could be used as a marker of greasiness between different hydrative agents. When this marker is used in conjunction with electrical impedance, the quantitative effects occlusive versus directly hydrating agents could be differentiated. Occlusive agents, such as petrolatum, lowered amplitude/mean measurements and increased the electrical impedance. Directly hydrating agents, such as water or glycerin, increased amplitude/mean and increased the electrical impedance (13), and these effects are shown in Figures 3, 4, and 6. These two parameters may prove useful in studying and comparing lubricants, emollients, and moisturizers against one another.

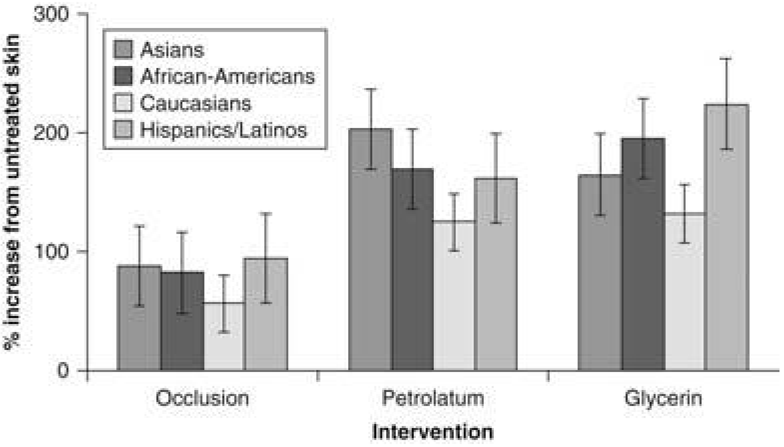

Figure 3 Coefficient of friction across ethnicity. Data represent increases in friction when compared with untreated skin of the volar forearm. No significant differences were found between the different ethnic groups. Petrolatum and glycerin increased the friction coefficient significantly more than polyvinylidene cholride (PVDC) plastic occlusion ($p < 0.01$). The increase in the friction coefficient was due to petrolatum and was not significantly different from the effect of glycerin. Error bars represent standard error. *Source*: From Ref. 13.

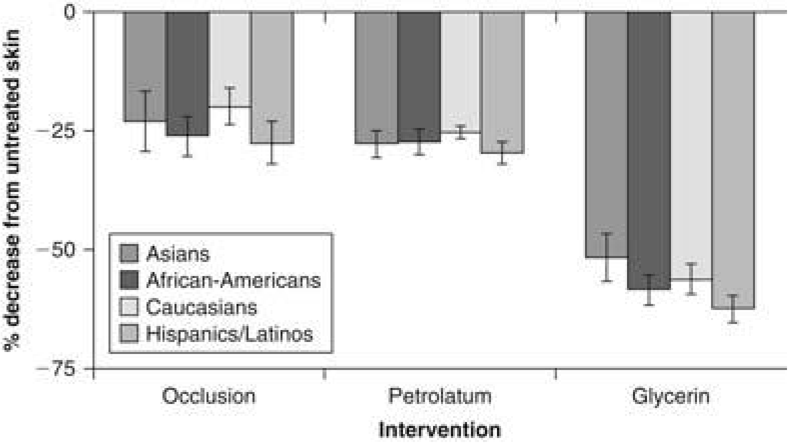

Figure 4 Change in electrical impedance across ethnicity. Data represent decreases in electrical impedance when compared with untreated skin of the volar forearm. No significant differences were found between the different ethnic groups. Glycerin lowered the electrical impedance significantly more than PVDC occlusion or petrolatum ($p < 0.01$). The decrease in the electrical impedance was due to PVDC occlusion and was not significantly different from the effect of petrolatum. Error bars represent standard error. *Source*: From Ref. 13.

Powder

El-Shimi (3) and Comaish and Bottoms (4) showed that the friction coefficient decreased after the application of powder. El-Shimi (3) found the friction coefficient to decrease by 50% after application; Comaish and Bottoms (4), in analyzing the static friction coefficient, observed an insignificant change for a wool probe and a 30% decrease in friction with a polyethylene probe. However, they also found that wetting the talc powder caused an increase in the measured friction.

Li et al. (16) also studied the effect of magnesium carbonate, or "chalk," in the static friction coefficient regimen and found that the application of chalk decreased the static friction coefficient. This contradicts with the popular use of chalk to increase friction in rock climbing. Li et al. (16) suggested that the chalk can be useful in drying the climber's hands before the climb, but suggested that all traces of the chalk be removed before the actual climb.

Figure 5 Correlation between changes in the friction coefficient and the sensory perception of greasiness. **A**, **B**, **C**, **D**, **E**, and **F** represent different creams that were applied to the skin. The reported percentage change in the friction coefficient is immediately after application, and the greasiness scores were subjective evaluations. *Source*: From Ref. 16.

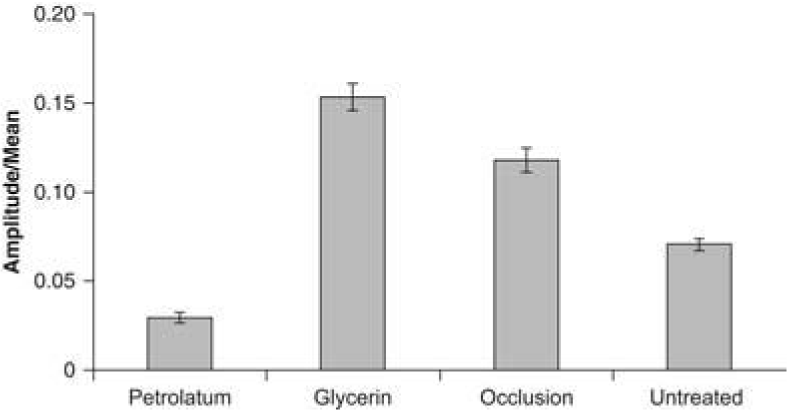

Figure 6 Amplitude/mean measurements for interventions. The application of glycerin and the PVDC occlusion increased the amplitude/mean of the volar forearm, and glycerin raised the amplitude/mean significantly more than PVDC occlusion ($p < 0.001$). Petrolatum significantly decreased the amplitude/mean, and this is quantitative evidence of petrolatum's greasiness ($p < 0.001$ when comparing petrolatum against glycerin or occlusion). Error bars represent standard error. *Source*: From Ref. 13.

Lubricant Oils

Initially the friction coefficient decreases after the application of oils and oil-based lubricants (3,7,23). Nacht et al. (23) and Highley et al. (7) also showed that after the initial decrease in friction, the oils eventually elevate the skin's friction coefficient (Fig. 7).

Emollients and Moisturizers

Prall (8) and Nacht et al. (23) found that the friction coefficient rises with the addition of emollients and creams in a similar fashion to water. However, the effects of the creams lasted for hours while the water effects lasted for about 5 to 20 minutes (6,8,23). Hills et al. (29) also studied emollients, but they examined how different emollients compared against one another and how changes in temperature changed the friction coefficient. At a higher temperature (45°C), most emollients lowered the friction coefficient to a greater degree than at a lower temperature (18°C).

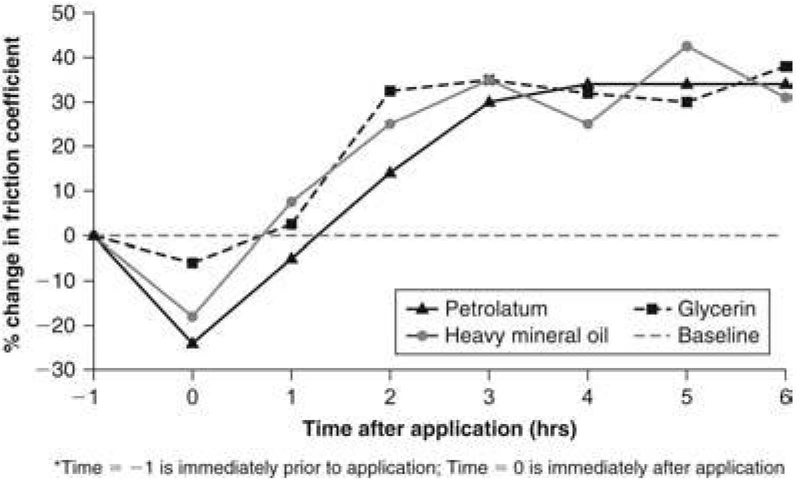

Figure 7 Effect of lubricant cosmetic ingredient on skin friction coefficient. Amount applied of each material: approx. 2mg/cm^2. Time $= -1$ is immediately prior to application; time $= 0$ is immediately after application. *Source*: From Ref. 16.

When lubricant/moisturizers are applied to the skin, the skin friction is affected in three general ways (20,23).

1. A large, immediate increase in the friction coefficient, similar to water application that follows with a slow decrease in the friction coefficient. These agents act by immediately hydrating the skin through some aqueous means to give an immediate increase in friction. In Figure 5, this is seen in creams A, B, and C.
2. An initial decrease in the friction coefficient that is followed by an overall increase in the friction coefficient. These agents are fairly greasy products (Fig. 7), and this greasiness causes the immediate decrease in the friction coefficient. The eventual rise in the friction coefficient is probably because of an occlusive effect that prevents water loss from the skin, thereby increasing the hydration of the skin. Representations of a few ingredients that elicit this response are in Figure 7 and in Figure 5 as cream F.
3. A small, immediate increase in the friction coefficient then continues to increase slowly. These agents act through a combination of mechanisms seen in the previous two cases. These lubricants/moisturizers have ingredients and agents that both hydrate through aqueous mechanisms and prevent water loss through occlusive mechanisms. Because of the presence of the these occlusive agents, which tend to be more slippery, the immediate rise in the friction coefficient is lower than in products that fall into the first category listed above. In Figure 5, this is seen in creams D and E.

Soap

O'Meara and Smith (17,18) showed that the application of soapy water to the palmar surfaces decreased the friction coefficient by 2 to 9-fold from the dry palm static friction coefficients. They also showed that textured surfaces (e.g., knurled steel) produce higher friction coefficients against soapy skin than smooth surfaces (e.g., chrome) and suggested that textured materials may be more appropriate as grabrails in showering areas (18).

Probes

As mentioned earlier, the probe geometry and material influence the measured value of the friction coefficient because friction is a probe-skin interaction phenomenon. Besides natural variations in skin, the wide range in results may be due to differences in probe movement, geometry, controlled monitoring of the normal force, and material chosen to make the friction measurement. In designing the friction measurement apparatuses, the two types of probe movements utilized were rotational probe movement and linear probe movement (Table 1). As a result, the linear probe constantly moves over "untested" skin and the rotational probe spins over "tested" skin, leading to variations in the reported values for the skin friction coefficient. Few studies have examined probe effects: El-Shimi (3) studied probe roughness, Comaish and Bottoms (4) studied probe roughness and material, Zhang and Mak (15) studied probe material, Li et al. (16) studied various rock surfaces under static friction coefficient conditions, and O'Meara and Smith (17,18) studied static friction coefficient conditions for handrails of various materials.

El-Shimi (3) and Comaish and Bottoms (4) compared probes (Tables 1 and 2) and found that smoother probes resulted in higher friction coefficient measurements. El-Shimi (3) noted that higher friction coefficient measurements were made with a smoother stainless steel probe as opposed to a roughened stainless steel probe. Comaish and Bottoms (4) found a similar result with two types of nylon probes: a sheet probe and a knitted probe. The sheet probe (the smoother of the two) gave a higher friction coefficient measurement. El-Shimi (3) postulated that the smoother probe formed more contact points with the skin and has a greater skin contact area than the rougher probe, resulting in more resistance from the skin and a larger measurement for the friction coefficient. Zhang and Mak (15) postulated that friction depends on the contribution of two actions: the "ploughing" action and the force required to overcome adhesion. Of the five probes they tested, silicone probes resulted in the highest friction measurement. They proposed that comparable probes that have higher contribution from the adhesion force, such as silicone, will have higher friction coefficients. Li et al. (16) found that sandstone produced a larger static friction coefficient than granite and slate. O'Meara and Smith (17) found in their testing of grabrail materials that smoother surfaces, like chrome or powder-coated steel, produced higher friction coefficients for dry or watery (nonsoapy) palm skin, whereas textured surfaces, like knurled steel or textured aluminum, produced higher friction coefficients against soapy palm skin.

CONCLUSION

The reviewed studies show that differences in skin, because of various factors like age and hydration, can be correlated with the friction coefficient. It can serve as a quantitative measure of how skin differs on various anatomical sites, between different clinical conditions, and how it differs under various environmental and chemical interactions. It is also a useful method for tracking mechanical changes in the skin after the application of chemicals, like skin creams or irritants and this has important implications as a quantitative measure of the cosmetic quality of skin. The design of the test apparatus is an important factor in the measurement of tribological properties, and a better appreciation of the cosmetic understanding of skin will continue to evolve with further study of skin tribology.

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40 Skin Wettability and Friction

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INTRODUCTION

> "*. . . Since many of the functional and esthetic qualities of human skin are attributed to the skin moisture balance. . .*" (1).

The skin surface is an ecosystem, stable for a given body region, within which interfacial tension and friction phenomena play a major role because of the important forces they bring into action, especially in ruling the physical interactions between hydrophilic and hydrophobic substances. Examples of these interactions are the sorption of water by stratum corneum and the spreading of water and lipidic liquids, which influences skin absorption, thermal loss, as well as transcutaneous pressure of water vapor, carbon dioxide, and oxygen. The production of a sweat/sebum emulsion as well as the behavior and effect of topical drugs or cosmetics are also under the influence of these interactions (2).

In this chapter, we first cover the human skin wettability by showing the effects of some treatments and applications on the wettability parameters. Secondly, the skin friction coefficient μ is studied in function of the surface hydrophobic/hydrophilic balance (Ho/Hi).

HUMAN SKIN WETTABILITY

The wettability—or wetting—results from the interactions between a fluid and a surface in the presence of vapor or another fluid. The wettability intervenes in many technological processes: the liquid could be a paint, a dye, an ink, water, etc. The solid could have a regular and simple surface, but could be more complex (i.e., a fiber, a porous environment, the skin, etc.).

The skin (or solids) wettability by a liquid is the fluid's aptitude to occupy a large surface. This is quantifiable by measuring the contact angle (θ) formed between these surfaces. When $\theta = 0^\circ$, the surface wets completely, while the opposite corresponds to $\theta = 180^\circ$ (dewetting), and the partial wetting refers to θ ranging between 0° and 180° (Fig. 1).

Contact Angle Measurement

The equilibrium of a liquid drop placed on a solid surface (Fig. 2) is described by Young equation (Eq. 1) (3). The general form of this equation for the solid-liquid-air system is as follows:

$$\gamma_{\mathrm{LV}}\mathrm{Cos}\theta = \gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}} - \pi_e \tag{1}$$

where γ_{LV} is the liquid-vapor surface tension, γ_{SV} is the solid-vapor energy, and γ_{SL} the solid-liquid energy; π_e (external pressure) = 0 for low-energy solids (4).

For the visualization and the measurement of the contact angle, we developed a tool especially designed for the wettability in vivo (Fig. 3). This tool is based on the use of a mirror directed at a 45° angle to the skin (profile drop method).

The advancing contact angle of test liquids, i.e., the maximum value of the contact angle when the drop is inflated without the line of contact moving, is measured on the skin surface. A drop of test liquid is deposited on the skin surface using a microsyringe and inflated up to a final drop volume of 5 μL.

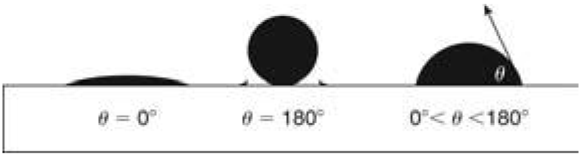

Figure 1 Solid wettability: $\theta = 0°$: total wetting, $\theta = 180°$: non wetting = dewetting, $0 < \theta < 180$: partial wetting.

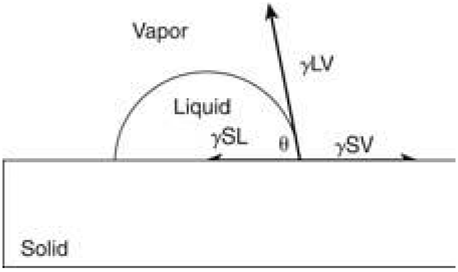

Figure 2 Equilibrium of a liquid drop on a solid surface: contact angle and surface energy.

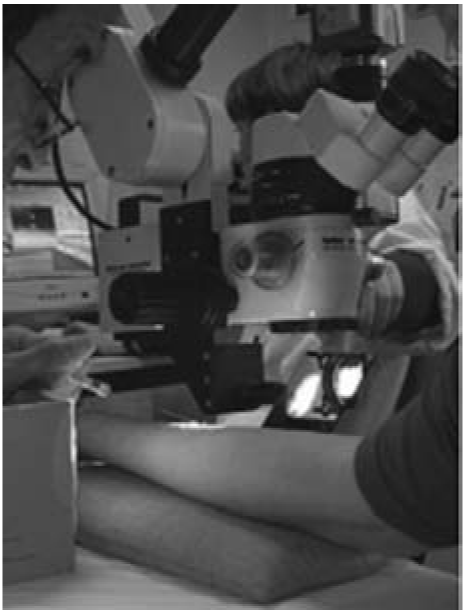

Figure 3 Contact angle visualization and measurement: tool rests on the use of a mirror directed 45° to the skin "profile drop method."

The drop's image is recorded using a video camera (CDD-Iris, Sony, France) connected to a computer and mounted on a microscope (Wild Heerbrugg M650, Switzerland), with a magnification of 16×, fitted with a slanted mirror. After visualization and storage of the drop profile, the contact angle is measured using a program that can determine θ from the tangents of both sides of the drop.

The influence of the roughness and skin temperature on the contact angle is treated in the literature (5–7). The temperature effect in the liquid in contact with the skin is minimized with the nature of the deposit (advancing contact angle) and with the very short time of deposit (15–20 seconds).

Critical Surface Tension (γ_c) and Hydrophobic/Hydrophilic Balance

Critical Surface Tension

This is the parameter that defines the capacity of a surface to be wet completely or not by a liquid. Figure 4 shows, according to Zisman's principle (8), the condition so that a liquid is spread out completely over a surface ($\gamma_{\text{liquid}} \leq \gamma_c$). γ_c is expressed according to Eq. 2.

$$\text{Cos}\theta = 1 - b(\gamma_{\text{liquid}} - \gamma_c) \tag{2}$$

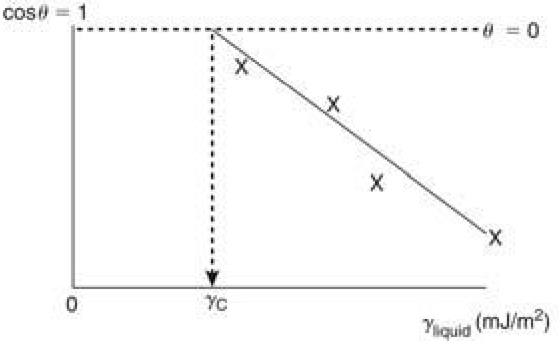

Figure 4 Critical surface tension, γ_c: total wetting condition ($\gamma_{\text{liquid}} \leq \gamma_c$).

γ_{liquid}: liquid surface tension (mJ/m^2). Note that the reduction of γ_c means the increase in the surface hydrophobia.

Hydrophobic/Hydrophilic Balance

For decades, the surface hydrophobicity has been reported to play an important role in many biological processes, such as cellular adhesion, contact inhibition, elasticity, functionality of tissue membranes, functioning of intracellular structures, and adhesion of infectious microorganisms (9).

To quantify the skin hydrophobia balance (Ho/Hi), we proposed (10) the use of the ratio γ_c/γ_{H_2O} (Eq. 3) to determine a parameter called hydrophilia (Hi). Its counterpart, hydrophobia Ho (Ho=1–Hi), characterizes the ability of the skin surface to resist wetting by water.

$$\text{Hi} = \frac{\gamma_c}{\gamma_{H_2O}} \tag{3}$$

This parameter is expressed by the ratio of its critical surface tension γ_c to the water surface tension normalized by the latter.

Surface Free Energy (SFE) (γ_s)

The γ_s of human skin is a characteristic parameter that determines most of the surface properties such as adsorption, wetting, adhesion, etc.

The γ_s of the solids cannot be directly measured because of the very weak mobility of the molecular atoms. It is necessary to resort to indirect methods such as the study of the interactions between a solid and a liquid. The γ_s is derived from measuring the contact angle of pure liquids with known surface tension parameters.

Several approaches are mentioned in the literature. The two most commonly used approaches for the skin are described below:

Geometric Mean Approach (11). The γ_s proportional to the intermolecular energy is the sum of the dispersion component γ_s^d and the polar component γ_s^p.

Acid-Base Approach (12,13). The γ_s can be expressed as the sum of Lifshitz-van der Waals γ_s^{LW} and acid-base γ_s^{AB} components: $\gamma_s = \gamma_s^{\text{LW}} + \gamma_s^{\text{AB}}$. The acid-base components can be expressed as: $\gamma_s^{\text{AB}} = 2(\gamma_s^+ \gamma_s^-)^{1/2}$, the γ_s^+ and γ_s^- components indicate, respectively, the electron-acceptor and the electron-donor components.

Data Analyses

Water Contact Angle (θ_w)

Water is an important factor for normal skin function. When the water content decreases, the skin becomes dry and itchy, and it feels uncomfortable. The degree of spreading of a water drop on the skin surface is an indication of its hydrophobic (Ho) or hydrophilic (Hi) tendency.

Water forms with the skin a semi-hydrophobic contact angle θ_w (80–91°) on the volar forearm (poor in sebum) (7,14–16). On the forehead (rich in sebum), the skin becomes less hydrophobic with $\theta_w = 57° - 73°$ (17–19).

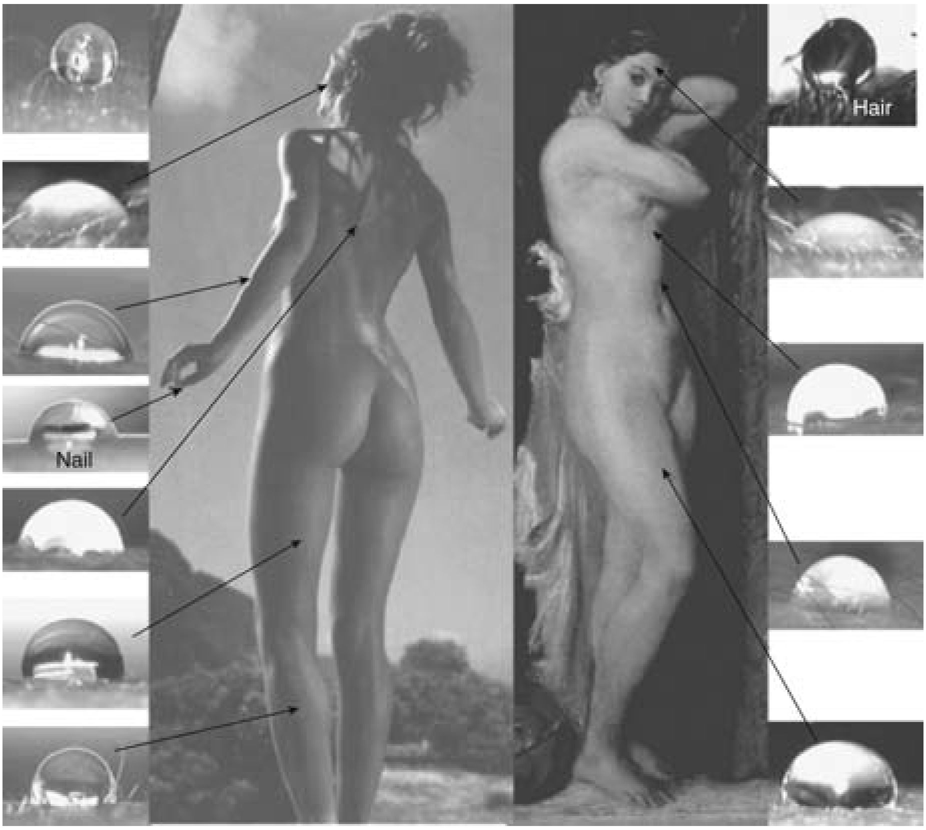

Figure 5 Human skin wettability. Effect of sebum on hydrophobic/hydrophilic balance.

Washing (soap and water) increases significantly the hydrophobicity of the skin on the forehead (+30°) (19), and degreasing (organic solvent) increases θ_w on the forearm by +10° (7,15). It is also noted that atopic skin becomes more hydrophobic with θ_w (forearm) = 102° and that θ_w (forehead) = 73° increases in dry skin (19). In contrast, the skin (volar forearm) shows a greater affinity with thermal water ($\theta_w = 70°$) (14).

Figure 5 (17) (cartography) shows that the skin is a hydrophilic surface ($\theta_w = 60–85°$) in the presence of sebum and a hydrophobic surface in its absence ($\theta_w = 91–102°$). It was shown recently (18) that the forehead skin wettability is significantly different ($p < 0.05$) between black people (Africans or Caribbeans, $\theta_w = 71°$) and mixed races (African or Caribbean, $\theta_w = 67°$) and Caucasians ($\theta_w = 67°$).

Critical Surface Tension and Hydrophobic/Hydrophilic Balance

For a liquid to be completely spread out over the skin, it is necessary that its surface tension (γ_{liquid}) is lower or equal to the skin critical surface tension, γ_c. The absence of sebum on the volar forearm leads to $\gamma_c = 26 - 30.6$ mJ/m^2 (15) (20–24), and its presence on the forehead leads to a more wettable surface, $\gamma_c = 33.2$ mJ/m^2.

The utilization of Eq. 3 shows that the skin on the volar forearm is a more hydrophobic surface with an Ho = 62% (10), and on the forehead it is a less hydrophobic surface, Ho = 54%.

Washing and degreasing significantly increase the skin hydrophobia, γ_c varies from 27.5 to 23.7 and 21.6 mJ/m^2, respectively, and therefore Ho varies from 62% to 67% and 70%. We showed that the application of cream (w/o) decreases the skin hydrophobia; the value of γ_c is 35.5 mJ/m^2 (Hi ≈ Ho ≈ 50%) (24).

Surface Free Energy of the Skin

On the volar forearm, γ_s calculated according to both approaches is approximately 38.5 mJ/m^2 (7,10), and on the forehead, γ_s ranges between 42 and 46 mJ/m^2 according to the skin type

Table 1 Human Skin Wettability

	Volar forearm		Forehead	
Parameters	No treated	Degreasing "ether"	No treated	Degreasing "ether"
θ_w	80° (14); 84° (15) 88° (7); 91° (16)	92° (15); 101° (7)	57–73° (19); 60° (17) 67–71° (18)	84° (7)
γ_c	26 (20); 26.8 (21) 27 (22); 27.5 (23,24) 30.6 (15)	21.6 (24)	33.2[a]	22.4[a]
Ho	62% (10)	70% (10)	54%	69%
γ_s	38.5 (7,10)	32.4 (7)	42–46 (19)	34.5 (7)

[a] Data unpublished.

Abbreviations: θ_w, water contact angle; Ho, surface hydrophobicity; γ_c, critical surface tension (in mJ/m^2); γ_s, surface free energy (in mJ/m^2).

(oily, normal, dry) (19). The use of the acid-bases approach shows that the forehead (sebum-rich area) has strongly monopolar basic surfaces ($\gamma_s^- = 26$ mJ/m^2), and the forearm (sebum-poor area) has weakly basic surfaces ($\gamma_s^- = 4$ mJ/m^2) (19). Washing with soap and water affects γ_s; it decreases by –10 m/Jm^2 on the volar forearm (10) and by -8 mJ/m^2 on the forehead (19). Degreasing also decreases γ_s; it varies from 42.5 to 34.5 mJ/m^2 on the forehead and from 38.5 to 32.4 mJ/m^2 on the volar forearm (7). Table 1 summarizes the previous data.

Discussion

The capacity of the skin surface lipids to increase skin wettability was ascribed to the free fatty acids and especially to those of sebum. The skin wetting by lipids was found increased with the amount of squalene and paraffin in sebum (25).

For example, if one lets a water drop (suspended on a hair: Fig. 6A) slide toward a series of droplets of natural sebum, one notes that these droplets of sebum, by difference in surface tension ($\gamma_{sebum} < \gamma_{H_2O}$), are rolled from there on water to form a kind of sebum/water emulsion. This form of emulsion (under certain temperature conditions) leads to the protection of the aqueous phase against evaporation and transepidermal water loss (TEWL). Consequently, the water in this layer is protected against the evaporation, and therefore the skin is protected from dehydration. We consider that this layer can play the role of "G*arde d'eau*" (water storage). Figure 6B shows the same experience (filmed from another angle): drop of water placed on a glass slide + drop of natural sebum.

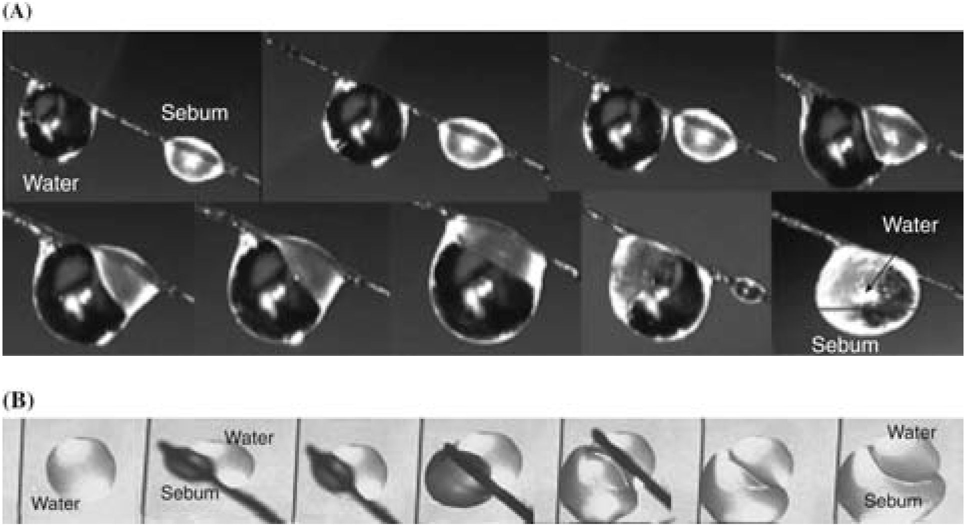

Figure 6 Spreading of sebum on water: hydrolipidic emulsion "Garde d'eau" formation. (**A**) Describes the meeting between a drop of water and a drop of sebum deposited on a hair, (**B**) described the same phenomenon, but the hair and the drops are placed on a glass side.

This emulsion form suggests that the quality of the skin hydration depends on the quality of its hydrolipidic layer/emulsion and consequently depends on a certain equilibrium between the two phases (aqueous and oily). This behaviour of sebum to wrap around the water is very important to understand the role of the hydrolipidic layer/emulsion in dry and atopic skin.

HUMAN SKIN FRICTION COEFFICIENT

The skin has three main mechanical roles: (*i*) to instantly or permanently match the changes in shape and volume of the underlying organs and the adipose tissue, (*ii*) to protect them against mechanical external aggressions, and (*iii*) to facilitate the adherence of palms and soles to the objects and ground (26).

The frictional behavior of the skin with different materials plays a critical role in the sensory perception of things that we come into contact with. The friction is extremely important in our perception of cosmetic application such as antiaging cream and moisturizers (27).

When touching an object, a contact is formed between our skin and the object. The tribological properties of such a contact influence how an object is perceived. Sensory perception is an important factor in the decision-making process of consumers (28). Even with closed eyes one can distinguish between a silk and a cotton fabric. A simple friction of the fingers brings considerable information on the rubbed skin: roughness, softness, dry/hydrated/fatty (oily) skin, hairs, etc. The friction is also very important for the clinician.

The friction coefficient is the measurement of the level of sliding between two surfaces. The initial force to start the slide is called "the dynamic friction coefficient," while the force necessary to continue this same slide is called "the kinetic friction coefficient." A high friction coefficient represents a weak slide, while a low friction coefficient indicates a large slide.

The review of the published literature on skin friction shows a wide range of measured values of μ (Table 2).

These differences indicate that the assessment of the friction coefficient of the skin is a highly complex problem. It involves skin elasticity, skin anisotropy, microtopography, anisotropy of the skin relief, nature of material employed, skin physicochemical nature, variation in testing conditions, and individual differences in measuring techniques. This last point can be divided into two types of designs for the test apparatus. One design is incorporated linear motion, wherein a probe is pressed onto the surface and dragged across the skin in a straight line. The other design is rotational and consists of a probe pressed onto and rotated against the skin surface. The friction coefficient does not vary significantly with gender but varies considerably among the anatomical regions of the body (33,35,37); the age effect was also measured (34,35,37). The friction coefficient is influenced by load (34,36,41,42); however, it is increased because of water application (36,39,43). On the other hand, the application of petrolatum and glycerine decreases the friction coefficient immediately on the forearm and on the hand and this effect lasts for at least one hour after application (42). The application of isopropyl alcohol (36) and washing with soap (44) dry the skin and decrease its friction coefficient. The finger has a friction coefficient μ ranged from 0.27 to 0.70 and varying among individuals because of different states of skin hydration (38). Recently, our group (18) showed a significant difference ($p < 0.05$) of μ measured on the forehead depending on the ethnic affiliation.

In 2004 (16), we showed the influence of the hydrophobic and hydrophilic characteristics of sliding and slider surfaces on μ. In this study, the wettability parameters for six surfaces [volar forearm, Teflon®, silicone impression material (Silflo®), vinyl polysiloxane impression material resin, steel, and glass] were measured and their influences were compared to the friction coefficient μ.

The tribometer used (Fig. 7) was developed and validated (16,34,45) to characterize the friction properties between skin in vivo and different sliding surfaces. A sliding ball of 10-mm diameter was pressed on the ventral forearm with a constant normal load (F_N) of 0.1 N and then moved at a constant velocity of 0.5 mm/sec. In order to maintain surfaces as flat as possible, a short sliding distance of 10 to 15 mm was selected.

In this study, we showed that when the skin is rubbed against a hydrophobic surface such as Teflon, the friction coefficient μ is lower than when rubbed against a hydrophilic surface such as glass or steel: hydrophobic surfaces = lowest friction coefficient.

Table 2 Human Skin Friction Coefficient (μ)

Author	Sliding material	Motion of test	μ
Comaish et al. (29)	Teflon$^{(1)}$ Nylon$^{(2)}$ Polyethylene$^{(3)}$ Wood$^{(4)}$	Linear	0.2$^{(1)}$–0.45$^{(2)}$–0.3$^{(3)}$–0.4$^{(4)}$ forearm
Kenins (30)	Different wool fabrics	Linear	0.32–0.48: dry skin 0.48–1.23: wet skin (forearm, finger)
El-Shimi (31)	Steel (rough^{a}, smooth^{b})	Rotational	0.2–0.4^{a} 0.3–0.6^{b} (volar forearm)
Highley et al. (32)	Nylon	Rotational	0.19–0.28 (volar forearm)
Cua et al. (33)	Teflon	Rotational	0.34 (forehead) 0.26 (volar forearm) 0.21 (palm), 0.12 (abdomen) 0.25 (upper back)
Asserin et al. (34)	Ruby	Linear	0.7 (volar forearm)
Elkhyat et al. (16)	Teflon$^{(1)}$ Steel$^{(2)}$ Glass$^{(3)}$	Linear	0.18$^{(1)}$–0.42$^{(2)}$–0.74$^{(3)}$ (volar forearm)
Elsner et al. (35)	Teflon	Rotational	0.48 (volar forearm) 0.66 (vulva)
Sivamani et al. (36)	Steel	Linear	0.56 (normal skin: dorsal finger) 0.50 (isopropyl alcohol exposure: dorsal finger) 0.2 (normal skin in vitro) 0.3 (water exposed skin in vitro)
Sivamani et al. (37)	Steel	Linear	0.4–0.6 (volar forearm)
Derler et al. (38)	Textile sample	Linear	0.27–0.7 (finger)
Egawa et al. (39)	Finger print		0.4 (volar forearm)
Lodén et al. (40)	Steel	Rotational	0.55 (dorsum of the hand) 1.1 (lower back) 0.65 (volar forearm) respectively in atopic skin 0.4–0.65–0.55
Fotoh et al. (18)	Steel	Linear	0.7–0.9 forehead

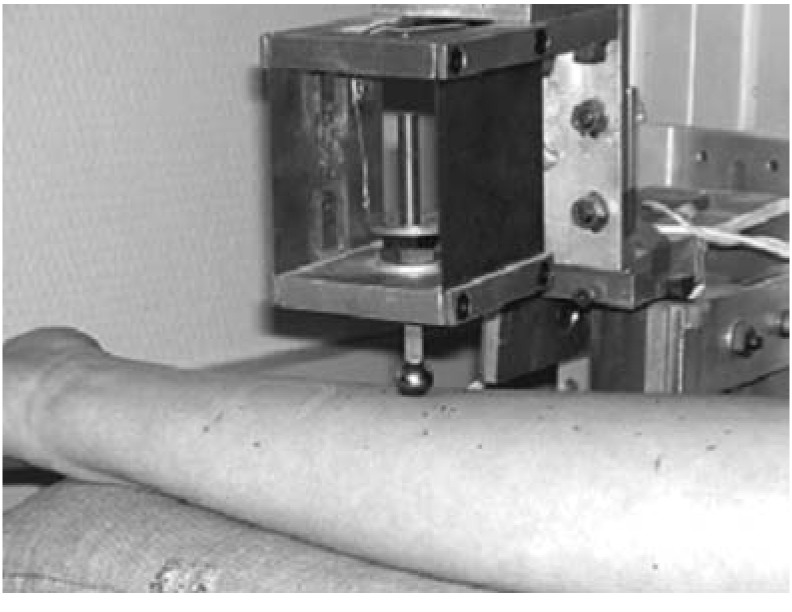

Figure 7 Linear tribometer for measuring in vivo friction coefficient.

GENERAL DISCUSSION

In this chapter, we showed that the sebum decreases the skin hydrophobia, and the wetting parameters of the surfaces in contact can play an important role in the friction phenomenon.

The largest hydrophobicity of the abdomen (Fig. 5) explains its lowest friction coefficient compared to the forehead measured by Cua et al. (33). Water application decreases the skin hydrophobia and consequently increases its friction coefficient measured by Egawa (39), Sivamani (36), and Lewis (43).

The decrease in μ after degreasing (isopropyl alcohol) (36) or after washing with soap and water (44) is quite normal; indeed these treatments increase the skin hydrophobia (Table 1), and the increased skin hydrophobia with age or in atopic skin leads to low μ reported in the literature (34,40).

The role of the surface lipids was speculated as one possible factor contributing to the frictional properties of the skin, and the correlation between μ and the skin lipid content was evaluated: Cua et al. (46) showed that the skin lipid content plays a role in the frictional properties of the skin. Moreover, in the skin, the friction resistance depends on hydrophilic and lipophilic elements present on the cutaneous surface. Fotoh et al. (18) assumed that the Ho/Hi of the cutaneous hydrolipidic film is different between the different ethnic groups studied. Black women could have a decreased skin friction coefficient as well as an increased cutaneous hydrophobicity compared with mixed race and Caucasian women.

CONCLUSION

The capacity of the skin to be wetted by water is a major parameter of the cutaneous surface ecosystem. This especially influences the equilibrium of the resident bacterial flora (either lipophilic or hydrophilic) and the possible surface colonization by pathogenic bacteria (usually hydrophilic). It also controls some functional features of the skin surface, such as triglyceride hydrolysis, skin pH, and the penetration of water into the stratum corneum, with, as major consequences, the modification of the skin mechanical behavior, permeability, and desquamation process.

We have seen that the sebum can surround water in the form of micro-emulsion to form a sort of Garde d'eau (water storage), and from this observation, we can suppose that the quality of the skin depends also on the hydrolipidic emulsion quality. This form of the hydrolipidic layer/emulsion allows the skin hydration and minimizes its TEWL.

Elias (47) noted that a significant part of the skin barrier function is provided by the stratum corneum lipids, which are suspected to play a critical role in the water-retaining properties of the stratum corneum. Grubauer (48) suggested that the TEWL serves as a signal for an increased lipid synthesis after barrier damage. Atopic skin shows an increased TEWL and indicates a defective barrier function (49,50).

The wettability and the friction coefficient of the skin provide considerable information: They can assist in the assessment of the skin nature (normal/dry/greasy skin) and its hydrolipidic layer/emulsion. They can also help to evaluate the effects of cosmetics and pharmaceuticals application in the Ho/Hi of the cutaneous surface.

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