Chapter Six

Protective Creams and Hand Cleansers

Introduction

One of the main functions of skin is to protect the body from the hazards of its environment—to keep dirt out and water in. During its long evolution, however, the developing skin tissue probably never encountered the chemical and physical hazards to which modern technology gives rise in the home and the workplace; consequently this same technology has had to provide some extra protection to prevent the skin itself from becoming damaged.

The chemicals that are in everyday use and are capable of inflicting damage on unprotected skin are far too numerous to allow a definitive list to be drawn up, but include domestic materials such as detergents, floor and metal polishes, bleaches, oven cleaners, paints and varnishes. Industrial hazards include acids, alkalis, organic solvents, resins, dyestuffs, weedkillers, insecticides, lubricants and many more.

The obvious and complete way to afford protection against such a vast array of potential irritants is the use of protective clothing made of suitable material—particularly the wearing of gloves. However, such clothing may be deemed uncomfortable, unglamorous and restrictive for constant use, even in the workplace. Thus the way is open for the cosmetic formulator to provide skin protective products of a more subtle nature, allowing the hands and body to be used naturally and unencumbered while still affording a sufficient degree of protection. The influence of comfort and aesthetic appeal in determining the extent to which protective skin products are used should not be underestimated. Experience has shown that workers will not apply an unattractive product, no matter how effective it may be.

For convenience, the types of hazard from which the skin is to be protected can be placed in a number of categories—for example, the following:

(1) Dry solids, dust and dirt.
(2) Aqueous solutions or suspensions.
(3) Non-aqueous materials, including oils, fats and solvents.
(4) Emulsions.
(5) Physical hazards, such as heat, cold, UV radiation and abrasion.

It seems unlikely that any one product would effectively protect the wearer against such a range of hazards: some degree of product specialization is

therefore to be expected (although 'all-purpose' barrier creams have been marketed).

The damage caused by topically applied materials can be thought of either as direct damage to the skin surface (as with strong acids, alkalis, oxidizing agents, abrasives) or as physiological damage (as with the absorption of hormones and other chemicals interfering with normal metabolism or with primary irritants and sensitizers and allergenic agents).

The aim of the formulator should be to develop a product which, besides forming a continuous, impervious, flexible barrier to the appropriate hazard, is easy to apply and to remove when required, is of pleasing consistency, odour and appearance, and is itself non-irritating.

Barrier Materials—Protective Creams and Gels

Of all the barrier materials available for use in protective creams and gels, those giving protection against waterborne hazards are the most numerous. There are many hydrophobic substances that can be spread upon the skin in a continuous film to form a water-repellent occlusive film. These include petrolatum, paraffin, waxes, vegetable oils, lanolin, silicones and occlusive esters. Additionally other water-repellent materials can be included which are not themselves capable of forming a continuous film, but which are capable of modifying the film-forming agent to improve its aesthetic or functional qualities; these include alumina, zinc oxide, zinc stearate, talc, titanium dioxide, kaolin and stearic acid. Oil-repellent films can be formed from water-swellable polymers such as alginates, cellulose derivatives, bentonites and natural clays. Combined water-repellent and oil-repellent materials can form the basis of a general purpose barrier cream.

Example Formulae—Creams and Lotions

Example 1 is an unsophisticated cream utilizing the barrier properties of lanolin, petrolatum and kaolin. It also contains a small amount of sodium stearate to facilitate easy wash-off. Such a cream might best be used to protect the skin against dust and dry powders.

	(1) *per cent*
Stearic acid	6·00
Cetyl alcohol	3·00
Lanolin	3·00
Petrolatum	2·00
Sodium hydroxide	0·65
Water	67·35
Kaolin	18·00
Colour, preservative, perfume	*q.s.*

Examples 2 and 3 are water-in-oil emulsions using nonionic emulsifiers which are thickened by the presence of stearic acid. Example 2 utilizes the barrier properties of silicone oil whereas example 3 illustrates use of the water-repellent properties of zinc stearate together with a film-forming material, methylcellulose. The presence of sorbitol in each case prevents 'rolling' on application and

provides an additional emollient effect. (Example 2 can be used as an aerosol if packaged in a nitrogen-pressurized container.)

Protective hand creams	(2) *per cent*	(3) *per cent*
Stearic acid	20·00	15·00
Dimethicone	5·00	—
Zinc stearate	—	5·00
Isopropyl myristate	2·00	—
Sorbitan stearate	1·50	1·50
Polysorbate 60	3·50	2·00
Sorbitol	20·00	6·00
Methylcellulose (4% aqueous)	—	25·00
Water	48·00	45·50
Perfume, colour, preservative	*q.s.*	*q.s.*

Examples 4 and 5 also utilize the barrier properties of silicones; the emulsifier system consists of a mixture of polyethylene glycol esters of cetyl alcohol and the viscosity is controlled by the presence of another film-forming agent, Carbomer 934 (neutralized with triethanolamine).

Protective hand lotion	(4) *per cent*	(5) *per cent*
Dimethicone	10·0	10·0
Ceteth-2	2·6	4·0
Ceteth-10	4·9	—
Ceteth-20	—	3·6
Triethanolamine	0·2	0·2
Carbomer 934	0·2	0·2
Water	82·1	82·0
Perfume, colour, preservative	*q.s.*	*q.s.*

Example 6 is a more complex oil-in-water protective hand lotion utilizing lanolin as well as silicone and a magnesium aluminium silicate film as barrier material.

Protective lotion	(6) *per cent*
DEA-oleth-3 phosphate	2·0
Cetyl alcohol	0·5
Lanolin	0·5
Dimethicone	2·0
Isopropyl myristate	2·0
Stearic acid	3·0
Triethanolamine	0·5
Propylene glycol	5·0
Magnesium aluminium silicate	0·5
Water	84·0
Perfume, colour, preservative	*q.s.*

Procedure: Disperse the magnesium aluminium silicate as a 20 per cent dispersion in some of the water before adding it to the emulsified product at 60°C.

A simpler cream containing silicone, mineral oil and sodium magnesium sulphate is represented by example 7.

Barrier cream	(7) *per cent*
Dimethicone	19·0
Mineral oil	19·0
Glyceryl oleate	2·0
Sodium magnesium silicate	2·0
Water	58·0
Colour, preservative, perfume	*q.s.*

Film-forming materials such as cellulose ethers, PVP and silicates have been shown to present some barrier properties, although they may be adversely affected by water and are thus more appropriate for protection against organic solvents and other non-aqueous irritants. In formulations containing these materials, protection against waterborne irritants can be given, as has been demonstrated, by water-repellent constituents. There have been attempts, however, to utilize film-forming materials of a type completely impervious to and unaffected by water. A method of using such polymeric films is to apply the material in a water-soluble form and then to convert it, *in situ*, into an insoluble analogue. The use, for example, of acid polymers that are soluble as alkaline salts but insoluble in the free acid form could be considered. If the substance were to be presented as an ammonium salt, for example, the volatile alkaline end of the molecule would detach itself leaving the polymer behind in the free acid form. Similarly, soluble sodium salts of certain film-formers (for example, alginates) can be converted into an insoluble form by the subsequent application of calcium or other suitable ions.[1]

Non-aqueous Barrier Products

Some formulators have proposed that protection against water-soluble irritants can best be given by film-forming materials applied from a non-aqueous medium. The use of nitrocellulose films (in conjunction with silicones) has, for example, been patented.[2] Similarly, compositions containing fluorocarbon polymers[3] and acrylates of acrylamides and other polymers have been advocated from time to time. Such compositions have two disadvantages, however. Firstly, the solvents that may be required in the formulation to dissolve or disperse these polymers may themselves be irritant or harmful to skin or unpleasant to use. Secondly, such impervious films may seriously impair the normal functioning of the skin surface, particularly the transport of water across the epidermis, leading to maceration. Moreover, the eventual removal of such films may require the application of further solvents which may irritate or damage the skin.

Perhaps the most widely used non-aqueous protective product of all is the zinc and castor oil ointment which has been smeared onto the more vulnerable skin surfaces of countless babies and young children. Less sticky, anhydrous, modern equivalents are given in the chapter on baby products—these are based upon the protective action of zinc oxide, silica and paraffin hydrocarbons. The following anhydrous formulation is suggested as protection against flash burns.[4]

Protective base	(8)
	per cent
Dimethicone	50·0
Titanium dioxide	30·0
Magnesium stearate	18·0
Iron oxide	2·0

A much more pleasant and sophisticated product is the gelled oil formulation given in example 9.[5]

Protective gel	(9)
	per cent
Lanolin oil	12·00
PEG-75 Lanolin wax	2·50
Mineral oil	50·48
Olive oil BP	20·00
Sorbitan oleate	5·00
BHT	0·02
Silica	10·00

Barrier Properties of Cationic Polymers

More recently, it has become possible to show that certain water-soluble cationic resins seem to be able to afford protection to the skin against irritants and allergens and to reduce the damage done to the barrier function of skin caused by prolonged exposure to water. It is claimed that the measure of protection given by such polymers is greater than might be expected from the simple mechanical barrier of uncharged polymer films.[6] Evidence is offered that such polymers may penetrate into the stratum corneum by reason of their cationic charge, thus modifying the bulk and surface properties of the stratum corneum so as to decrease its sensitivity to soaps and detergents, to alkalis present in depilatory creams and to certain allergens.[7–11] Example 10 illustrates the use of such a polymer in a protective hand lotion.[12]

Protective hand lotion	(10)
	per cent
Mineral oil	2·40
Isopropyl myristate	2·40
Stearic acid	2·90
Lanolin	0·50
Cetyl alcohol	0·40
Glyceryl stearate	1·00
Triethanolamine	0·95
Propylene glycol	4·80
Quaternium-19	0·20
Water	84·45
Colour, perfume, preservative	*q.s.*

Testing of Protective Preparations

Although laboratory screening tests to determine the relative efficacy of protective creams have been described, none of them in its present form presents a real criterion by which the behaviour of the protective cream in use

can actually be predicted, though some of them give some useful indications, particularly in the negative aspect, in that they can help to eliminate preparations which are obviously unsuitable, before the selected preparations are submitted to actual practical user trials.

In opening a paper on occupational dermatitis, which concerns itself among other things with test methods for assessing barrier substances, Porter[13] called attention to the deficiencies in the test methods so far proposed.

Perhaps the simplest of the tests carried out is that in which a film of the barrier or protective cream is applied to a series of clean glass microscope slides which, after being allowed to dry for a prescribed period, are immersed in various solvents (such as water, alcohol, acetone, and various oils and other substances) against which the resistance of the product is to be assessed. The slide may be subjected to standardized conditions of agitation, and the integrity of the barrier film after such treatment examined, preferably against a control preparation which has been found to be of promise.

In another test the preparation is applied to a porous supporting membrane (which can be filter or other paper, animal skin or other desired substance) and after drying, various solutions—the resistance of the barrier preparation to which it is desired to determine—are applied. The length of time which the test solution takes to penetrate the membrane containing the protective film is taken as a measure of the resistance of the preparation to that solution. Various modifications of this procedure, in which the pH of the test solution is made to change the colour of an indicator solution spotted on the reverse side of the membrane, in which the penetration of the aqueous phase renders a suitable indicator fluorescent under ultraviolet light, or in which the test solution merely contains a soluble dye which, on penetration, stains the far side of the membrane, have been employed. One of the main difficulties has been to obtain the protective substance on the test membrane in a layer of standardized thickness and area.

In order to overcome this difficulty, Schwartz, Mason and Albritton[14] controlled the thickness of the film by placing it on the test paper by means of a specially shaped sheet of metal of standardized thickness which, after filling with the preparation to be tested, was subjected to a pressure of 5000 psi (35 MPa) by which the thickness of the film of protective cream became that of the standard metal shim.

An apparatus for measuring the permeability of films of barriers cream was devised by Marriott and Sadler[15] in which the passage of the test solution through the barrier could be measured by reading the meniscus from time to time in a glass tube of fine bore, graduated in hundredths of a millilitre.

All the above tests, while they may have value as sorting tests in that they serve to reject those creams which are unsatisfactory, omit to take into account the flexibility of the barrier film, and also its resistance under conditions of use where conditions of high humidity or electrolyte content may be encountered on one side of the film only.

Porter[13] proposed the use of a technique based on that used for testing the water-penetration of leather, which flexes a film of cream held on the filter paper folded in a boat-shape and containing a liquid against which the cream's performance is to be judged.

When it comes to the final choice between a number of different experimental samples, all of which have shown promise in laboratory tests, the choice must be based on practical trials.

It has been found in practice that by applying the protective preparation to the hands, allowing to dry, flexing the fingers and then immersing the hands in various solutions (against which it is desired to determine the resistance of the product, such solutions being highly coloured with an innocuous but soluble dye) a good idea of both the flexibility and general behaviour of the preparations in use may be obtained. It is of interest to note that in the experiments carried out by Schwartz, Mason and Albritton, mentioned above, anhydrous lanolin and petroleum jelly fell in the same class as the best commercial protectives, not only against alkali and acid, as might have been expected, but also against oil. It was also noteworthy that a far higher proportion of the preparations, stated by their manufacturers to be protective against oils or solvents, actually fell into this category under laboratory tests than those which claimed to be protective against water.

Barrier creams will usually remain effective for at least 4 hours, and they are usually applied twice a day. However, when dealing with particularly corrosive substances or whenever the cream is likely to be rubbed off more regularly, more frequent applications of the barrier cream are indicated in order to provide full protection for the hands.

All protective creams should be properly labelled, and the substances against which protection will be conferred should be clearly indicated, so that the user may avoid contact with irritants against which a particular cream will not protect him.

Hand Cleansers

Skin cleansers of various types are now considered to be a valuable part of the skin care regime along with toners and moisturizers. Such cleansers, however, are formulated to remove everyday grime, secretions and make-up and they may not be equally effective against the heavy stains, greases, resins, adhesives, oils, paint, tar, and dyestuffs with which the skin (particularly the hands) may get covered in the modern home, garage or workplace. Heavy-duty cleansers offer the possibility of removing many of these problem contaminants with little risk of permanent damage to the skin.

Historically, the first heavy-duty skin cleaners other than soap and water were sulphonated oils—these being particularly valuable in the removal of oils and solvents where the habitual and frequent use of soap had caused skin irritation. Sulphonated oils, however, have now been largely superseded by the so-called waterless hand cleansers. The term 'waterless' is misleading because many of them contain water in the formulation, and 'waterless' refers to the fact that they can be used without the use of *additional* water (although a final rinse-off in water is often recommended by the manufacturer).

Waterless hand cleansers can be formulated as pastes, creams, gels, lotions or clear liquid and consist of a cleansing agent, a thickener, an emulsifier and (usually) water

Since most of the contaminants with which heavy-duty cleansers have to deal are not water-soluble, the cleansing agents most commonly employed in these products are aliphatic solvents, these being reasonably effective, cheap, innocuous and readily available. Thus the majority of examples given below contain odourless kerosene, mineral spirits or mineral oils.

Any agent which will thicken either the water phase or oil phase of the product may be used as a thickener. In the examples given, use is made of magnesium aluminium silicate (example 17), sodium magnesium silicate (example 16) a methyl vinyl ether–maleic anhydride copolymer (example 18) and methylcellulose (example 17). The soap or nonionic detergents which are often used for emulsification and for their detergent action also cause thickening by the formation of a gel. Ancillary emulsifiers may also be employed to increase the cleansing power of the product (as with the amphoteric in example 12, the sulphonate in example 13 and the cocamide in example 11).

The soaps used as emulsifiers to produce gels may be the sodium, triethanolamide or monoethanolamide salts of stearic or oleic acids or a mixture of both.

Emollients are added to improve the application properties and to prevent the defatting of the skin. The choice of emollient is wide: in the following formulae, lanolin (example 11), ethoxylated lanolin (example 12), myristyl myristate (example 19) and propylene glycol (example 14) have been used.

Waterless hand gels	(11) *per cent*	(12) *per cent*
Deodorized kerosene	35·00	25·00
Lanolin	10·00	—
Cocamide DEA	4·00	—
Stearic acid	2·43	6·00
Oleic acid	3·64	8·00
Sodium hydroxide	0·38	0·80
Amphoteric-2	—	2·00
PEG-75 Lanolin	—	0·50
Water	44·55	57·70
Perfume, colour, preservative	*q.s.*	*q.s.*

Waterless hand gel	(13) *per cent*
Deodorized kerosene	20·00
Alkylaryl sulphonate (amine neutralized)	5·00
Cocamide DEA	2·00
Oleic acid	8·00
Monoethanolamide (20%)	8·00
Water	57·00
Perfume, colour, preservative	*q.s.*

Waterless hand cleansers	(14) *per cent*	(15) *per cent*
Deodorized kerosene	20·00	55·00
Mineral oil	20·00	—
Glyceryl stearate	3·00	—

Waterless hand cleansers (cont.)

	per cent	*per cent*
Stearic acid	5·00	—
Oleic acid	—	4·50
Stearamide-MEA stearate	—	6·00
Propylene glycol	5·00	—
Triethanolamine	1·50	1·50
PEG-8 Cocoate	—	3·00
Water	45·50	30·00
Perfume, colour, preservative	*q.s.*	*q.s.*

Skin cleansing gel	(16)
	per cent
Mineral oil	15·50
Stearic acid	4·40
Triclosan	0·10
Sodium magnesium silicate	2·00
Triethanolamine	1·60
Water	76·40
Perfume, colour, preservative	*q.s.*

Example 16 illustrates the possibility of using antiseptic agents (such as triclosan) and other additives to provide additional benefits to the product. If the product is designed to remove particularly tenacious grime (such as the ink from carbon paper or typewriter ribbons) the formulator may choose to include a mild abrasive such as finely ground pumice. Such a product would not be recommended, however, for use on sensitive skin.

Example 17 is soapless, utilizing nonionic emulsifiers to produce a cream. Such a formulation might be favoured by users who find that alkaline products are irritating to their skin. Example 18 is a much milder form of cleanser in simple liquid form:

Waterless hand cleansing cream	(17)
	per cent
Magnesium aluminium silicate	2·50
Sorbitan stearate	2·00
Polysorbate 60	8·00
Deodorized kerosene	35·00
Methylcellulose	0·50
Water	52·00
Perfume, colour, preservative	*q.s.*

Liquid hand cleanser	(18)
	per cent
PVM/MA polymer	0·40
PEG-6-32	5·00
Octoxynol-9	5·00
Water	89·60
Potassium hydroxide	to pH 7
Perfume, colour, preservative	*q.s.*

The final example is somewhat unusual since it comprises a base which may be turned into a number of different products of varying consistency by the addition of solvent together with variable amounts of oleic acid:

Waterless hand cleanser (19)

A Base (smooth paste)

	per cent
Cocamidopropylamine oxide	18·00
Cocamide DEA	38·00
Dioctyl sulphosuccinate	15·00
Myristyl myristate	15·00
Oleic acid	14·00

Mix until smooth at 45°–55°C.

B Finished products

	Gel *per cent*	Cream *per cent*	Lotion *per cent*
Base	15·00	13·90	12·95
Odourless kerosene	30·00	27·70	25·90
Oleic acid	1·50	1·40	1·40
Water	53·50	57·00	59·75
Perfume, colour, preservative	*q.s.*	*q.s.*	*q.s.*

Procedure: Heat and stir all the ingredients except the water until clear at 55°–65°C. Add water slowly at 55°C with high-speed stirring until the product is homogeneous and smooth.

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Bath Preparations

The bath products market has undergone considerable change in recent years in terms both of volume and of the range of products available. In particular, bath salts, tablets and crystals, which previously dominated the market, are now much less popular and have been replaced to a large extent by bubble bath products. The range of bath preparations nowadays includes bath oils, shower gels, after-bath body lotions and the even newer hydroalcoholic products sometimes referred to as bath satins.

FOAM BATHS

Introduction

Foam baths are undoubtedly the most popular bath preparations currently on the market and they have enjoyed a very healthy growth in recent years. Generally, they are available in liquid, gel and powder forms. Body cleansing, the primary function of a bath, is performed very well by a bubble bath, which in addition offers the opportunity to apply many desirable health and beauty ingredients to the skin, although not necessarily so efficiently as when these aids are used individually. Functioning as a body cleanser, a bubble bath soaks off and suspends dirt, grime and body oils and prevents the formation of the 'bath-tub ring' that usually results from the use of soap. In this respect a bubble bath is superior to the traditional soap and water bath. Additionally, a well formulated bubble bath will condition the skin, deodorize, perfume the body and the bathroom, stimulate the senses, yet promote relaxation.

A good foam bath should exhibit the following characteristics:

(1) It should provide copious foam at minimal detergent concentration.
(2) The foam should be stable, particularly in the presence of soap and soil and within wide limits of temperature. Simultaneous attributes of stable foam and ready removal from the bath are unattainable in practice and a compromise must be aimed at to provide reasonable but not excessive foam stability. By delaying the use of soap it is, of course, possible to prevent premature breakdown of the foam, thereby satisfying the aesthetic requirements of the bather and facilitating the subsequent removal of the dirty water from the bath.
(3) It should prevent bath-tub ring formation.
(4) It must be non-irritant to the eyes, skin and mucous membranes. Bubble baths have been claimed to produce symptoms of irritation in the lower urinary tract and it is essential to check the irritation potential of all these products before marketing.

(5) It should have adequate detergent power so that it will cleanse the body efficiently. In order to counteract any excessive harshness to the skin it is advisable to include a low level of skin emollient.

Formulation of Foam Baths

As already mentioned, foam baths are available in several physical forms and clearly the choice of raw materials is highly dependent on the final product form. Before discussing the product types in detail, it is of interest to examine the raw materials available.

Foaming Agents

Obviously, the foaming agent is the most important ingredient in all foaming bath products and great care should be taken in its selection. When selecting a surfactant it is important to bear in mind the properties that good foam baths should exhibit. Of the many surfactants currently available, anionics are the most widely used; both nonionics and amphoterics are also of considerable interest. Cationics, however, because of their incompatibility with soaps and other anionics and their much greater eye irritancy, are seldom if ever used in bubble bath formulations.

Among the most popular anionic surfactants used are the sodium, ammonium and alkanolamine salts of fatty alcohol sulphates, fatty alcohol ether sulphates and (sometimes) alkyl benzene sulphonates. Soaps are not suitable surfactants for use in foam baths, since in hard water calcium and magnesium soaps precipitate as a dirty hard scum.

The fatty alcohol sulphates, principally the lauryl sulphates, were the first anionics of any importance to be used as the primary foaming agents in bubble baths. Although they give less flash foam than the even more widely used fatty alcohol ether sulphates, their foam is often judged to be much creamier; this attribute, together with relatively low irritation potential, gentle 'feel' on the skin and inhibition of bath-tub ring formation, has contributed to the widespread use of lauryl sulphates. The versatility of the various salts available offers formulators great freedom in creating products in many forms. Highly concentrated sodium lauryl sulphate, for example, can be dry blended into powder products. Sodium lauryl sulphate, however, is not particularly recommended for liquid products because of its relative insolubility and hence high cloud point values—for instance, a 30 per cent solution of sodium lauryl sulphate has a cloud point of about 20°C. Ammonium lauryl sulphate is considered by some to be the best foamer and cleanser and it has the advantage over the sodium salt of being less prone to hydrolysis at low pH values. One problem, however, is that the pH must be kept acidic in order to prevent the release of ammonia. The various alkanolamine lauryl sulphates, by virtue of their greater solubility and lower viscosity, permit the formulation of more highly concentrated liquid products but tend to produce less foam.

Perhaps the most popular surfactants used in foam baths are the fatty alcohol ether sulphates, especially the sodium salts and, in particular, those based on lauryl–myristyl alcohols and containing 2–3 moles of ethylene oxide per mole of the alkyl ether sulphate. Copious foaming independent of water hardness,

reasonable foam stability in the presence of soap, fragrances, oil additives and body debris, together with good skin compatibility, make these materials an obvious choice for bath products. A high degree of proficiency as a lime soap dispersant prevents bath-tub ring even in very hard water. Other advantages of these surfactants are good colour, which permits the use of very delicate pastel colours if required, a good viscosity response to electrolyte and unusual solubilizing powers for perfumes.

Primarily for reasons of cost, alkyl benzene sulphonates (mainly branched-chain dodecyl benzene sulphonates) soon found their way from household detergent uses into toiletry items such as bubble baths. Of all the synthetic surfactants, the sodium alkyl benzene sulphonates are probably the most suitable for spray drying and until recently most of the commercial products on the market in bead form consisted of this material and various salt builders and extenders. When biodegradability considerations became critical, the importance of linear alkyl benzene sulphonates grew. However, in 1970 an increasing number of complaints involving irritation and infection, mainly in young girls, were reported by the US Food and Drug Administration. Linear alkyl benzene sulphonates were suspected and, in order to avoid threatened regulatory actions,[1] the use of both the sodium salt in powder bubble baths and the more soluble triethanolamine salt in liquid foam baths declined.

Other anionic surfactants worthy of mention are the alpha-olefin sulphonates, lauryl sulphoacetates, the half ester sulphosuccinates and the paraffin sulphonates.

The alpha-olefin sulphonates are commercially attractive and have been used as alternatives to linear alkyl benzene sulphonates in powder foam baths. Their toxicological properties, however, have yet to be clarified, while in liquid products viscosity regulation with electrolytes is said to be a problem.

Lauryl sulphoacetates are sometimes used in high-priced powder or granular bubble baths but limited solubility has greatly restricted their use in liquid products.

The sulphosuccinates, particularly the monoesters such as the di-sodium lauryl alcohol polyglycol ether sulphosuccinate, Rewopol SBFA30, are considered to be very mild detergents with good foaming properties and free from any tendency to irritate the skin and mucous membranes. Furthermore, they are also claimed to increase the tolerance of the skin to other detergents such as fatty alcohol ether sulphates and alkyl benzene sulphonates.

The paraffin sulphonates produced by the sulphoxidation of *n*-paraffins are relatively cheap and, therefore, are of undoubted interest. In particular, the secondary alkane sulphonates known commercially as Hostapur SAS are interesting. This material, in addition to being biodegradable and exhibiting good physiological properties, is also a good foamer with high solubility in water. The use of Hostapur SAS on its own, however, normally results in excessive degreasing of the skin and moreover the finished product is difficult to thicken. When it is combined with other surfactants such as alkyl ether sulphates, these problems can be overcome.

Nonionics do not foam particularly well and consequently these surfactants are not used as primary foamers. Instead, the nonionic components of bubble baths are used to stabilize foam, to enhance the viscosity of the product, or to

solubilize skin care ingredients and fragrances. Among the nonionic surfactants used in bubble baths, the alkanolamides and amine oxides are possibly the most widely used; in addition, ethoxylated derivatives such as ethoxylated fatty alcohols, ethoxylated fatty acids, alkyl phenol ethoxylates, ethoxylated alkanolamides, ethoxylated propylene oxide condensates (Pluronics) and ethoxylated sorbitan fatty acid condensates are occasionally employed.

The alkanolamides comprise a very broad class of surfactants and there are many types commercially available. They are derived by condensing various cuts of fatty acids *ex*-coconut oil with alkanolamines. The diethanolamides tend to be used in liquid foam baths because of their greater water solubility. Both the Kritchevsky amides (2 moles of diethanolamine reacted with 1 mole of fatty acid) and the super amides (1 mole of diethanolamine reacted with 1 mole of fatty acid methyl ester) perform well in this application and are hard to surpass in terms of economy for foam boosting, foam stabilization and viscosity building in conventional foam baths based on alkyl sulphate and alkyl ether sulphate. The water-insoluble monoethanolamides and isopropanolamides tend to be used mainly in dry products. The fatty acid portions of these amides are generally 12 to 18 carbons in length, with the purest C-12 fatty acid amide usually giving the greatest foam stability and compatibility with soap. The level of alkanolamide used will vary depending on which primary detergent is used, but is usually less than 3–4 per cent. The presence of high levels of an emollient, perfume or pearlescing agent may occasionally necessitate increasing this level.

The ethoxylated alkanolamides contribute to the overall formulation in much the same way as the alkanolamides but are more soluble as expected and in most cases do not thicken the finished product to the same extent.

Amine oxides are claimed to have superior foam boosting properties to alkanolamides but this is open to question. Perhaps the most widely used is the C-12 dimethylamine oxide, since cloud point problems can be experienced with the C-14 dimethylamine oxide.

The ethoxylated nonionics previously mentioned tend to be used as emulsifiers, solubilizers and emollients, rather than foam boosters. The Pluronic block polymers, for example, have been recommended as useful perfume solubilizers. Water-soluble gums have been claimed to act as foam stabilizers when used at low concentrations and they are believed to act by supporting the walls of foam bubbles and thereby increasing their resistance to collapse.

Amphoteric surfactants whose charge can vary according to the pH of the system appear to be one of the faster growing speciality surfactant groups. Much interest has recently been focussed on the alkyl imidazoline betaines and, in particular, two alternative coconut imidazoline betaines, Empigen CDR10 and Empigen CDR30, manufactured by Albright and Wilson. These two materials are very similar but differ considerably in their effect on viscosity. Both products are claimed to exhibit outstanding mildness and, in addition, excellent foaming properties comparable to those of conventional anionic surfactants; the foam stability is also said to be good, even in the presence of soil and soap. Nevertheless, for improved cleaning, viscosity control and cost performance it is recommended that these materials be combined with conventional anionic surfactants. Other amphoterics that have been used in foam baths are the alkyl amido betaines, which are claimed to be good foam producers in addition to

having foam stabilizing properties. In particular, these materials are claimed to be exceptionally good at promoting foam stability in the presence of oil and sebum. They are available commercially from a number of sources, for example Tego-Betaine L7 *ex* Goldschmidt, Steinapon AM-B13 *ex* Rewo and Empigen BT *ex* Albright and Wilson. The alkyl dimethyl betaines, for example Empigen BB *ex* Albright and Wilson, on the other hand, tend to be used only as foam stabilizers.

Emollients

In an attempt to overcome any possible harsh effects of foam baths on the skin, special ingredients known as emollients are often added to the formulation to help achieve and maintain a healthy and attractive skin. The value of many of these conditioners has been challenged but they continue to be used with apparent success. Although it has been argued that the bather stays in the bath for too short a time to receive any real benefit, equally strong opinions have been expressed that, even in this short time, the skin absorbs active substances. Many such ingredients are available. The following list, though not exhaustive, gives some of the most popular in common use: branched chain esters, for example isopropyl myristate; decyl oleate; ethoxylated partial glyceride fatty acid esters (Softigen 767); protein derivatives; lanolin derivatives; and fatty alcohol ethoxylates; etc. Polymer JR from Union Carbide, which is a cationic cellulose ether derivative, has been recommended for use in foam baths and, because of its cationic nature, is said to be more substantive to skin than many other emollients.

Two further interesting and relatively new materials are Aethoxal and Cetiol HE *ex* Henkel. In addition to emolliency, these oils exhibit mild surface activity and do not interfere with the foaming of other surfactants. Both are more soluble in cold water than in hot and consequently when they are added to warm bath water an instant bloom occurs.

It is worth while to remember that careful formulation is necessary when using some of these ingredients in order to prevent foam loss and to protect against product instability.

Perfumes

There is no question that the perfume used in a foam bath is extremely important: it is perhaps equal in importance to the foaming agent. Most of the larger companies marketing foam baths spend a great deal of time and money in selecting the perfumes for their products. A good perfume must, of course, convey the marketing image of the brand and it should also fulfil the following requirements:

(1) It should be acceptable when sniffed in the bottle.
(2) In use it should be fresh and have sufficient volatility to give a strong impact.
(3) It should linger on the skin to give a feeling of freshness and wellbeing.
(4) It must have an acceptable shelf life in the product.

The level of perfume used will vary between 1 and 5 per cent, depending on the cost limitations. The nature of the perfume ingredients may require the use

of additional solubilizers; the most commonly used are nonionics such as ethoxylated fatty alcohols, ethoxylated fatty acid esters, ethoxylated sorbitan fatty acid esters and ethoxylated propylene oxide condensates (for example, Pluronics). A recent interesting publication by Blakeway *et al.*[2] on perfume stabilization merits attention.

Because of their complex nature, perfumes often cause problems of product instability. They not only affect odour stability, but can cause discoloration, upset preservation systems and cause instability in clear, opacified and emulsion products. The need to test the shelf life of all new products adequately cannot be overstressed. The ingredients used in perfumes should also be adequately safety tested before use.

Herbal extracts, while not strictly to be classed as perfumery ingredients, are used in bath preparations, usually to help convey the brand image and to justify therapeutic claims with respect to minor skin disorders. Herbal extracts of most living plants can be obtained if required, but their medicinal nature is open to speculation.

Viscosity Controllers

The problem of achieving the required viscosity of liquid products is not simple since this depends on many factors such as the choice and level of surfactant and foam booster. Even certain perfumes have been found to have significant effect on viscosity. Generally, inorganic salts such as sodium and potassium chloride are used to thicken the product where possible, whereas alcohol, hexylene glycol, propylene glycol and polyethylene glycols are used to lower the viscosity. Certain thickening problems, however, can only be solved by the use of natural gums such as tragacanth and gum acacia, or synthetic gums such as methyl cellulose and hydroxyethyl cellulose.

Colour

Colour of foam baths is clearly important in marketing and care should be taken to select colours that are stable in the chosen product. Obviously, if the products are marketed in clear bottles adequate light testing should be carried out. Interesting colour effects in the bath can be achieved by the use of indicator colours and fluorescein. Before finally selecting a colour system the legislative requirements of the country in which the products are to be sold should be carefully checked.

Preservatives

Except in the case of dry bubble bath preparations and those with a very high detergent concentration, foam baths should contain an adequate amount of preservative to prevent attack by moulds and bacteria, particularly the Pseudomonas species. Bacterial attack can produce opacity in products that are intended to be clear, separation in emulsified and pearlescent products and can cause changes in both perfume and colour system. Prevention is a matter of selecting a suitable preservative in accordance with the legislative requirements in the country of sale. Suitable preservatives include ethanol; methyl, propyl and butyl hydroxy benzoate; phenylmercuric nitrate; formaldehyde; Bronopol; and

many others. The best preservative for a particular foam bath can only be determined by properly designed microbiological testing. Good housekeeping in the manufacturing unit is, however, just as important as choice of preservative if product contamination is to be avoided.

Opacifying Agents

When an opaque liquid foam bath is required, an opacifier is needed. The following are the most commonly used: higher alcohols such as stearyl or cetyl alcohols; ethylene glycol mono- and distearates; glyceryl and propylene glycol stearates and palmitates; and the magnesium, calcium and zinc salts of stearic acid.

Clearly, viscosity is an important factor in the stability of such systems but also the manufacturing technique used is vitally important in achieving maximum stability. Ideally, when using the opacifiers mentioned above, all the ingredients (except perfume) should be heated to 65°–70°C and allowed to cool slowly to ambient temperature with gentle mixing, when the pearl will develop. Rapid cooling will produce less pearly products that may be unstable. It is possible, however, to obtain blended opacifier–detergent concentrates of some of these opacifiers which eliminate the need to heat the batch. Other opacifiers, for example polymeric materials such as the Antara range *ex* GAF and the Morton Williams E Series opacifiers, can also be incorporated without heat, but these tend to be less pearly in appearance.

Types of Product

Liquids

Liquids can be further divided into clear, translucent, opaque, pearlescent and multi-layer products. The formulation possibilities for a medium-priced clear liquid foam bath are endless; a typical and very simple product formulation would be as follows:

	(1)
	per cent
Sodium lauryl ether sulphate (28% active)	50
Coconut diethanolamide	3
Perfume	1–2
Citric acid	*q.s.* to pH 7
Colour, preservative, emollients, solubilizer	*q.s.*
Sodium chloride	*q.s.* to required viscosity
Water	to 100

More expensive but milder formulations can be achieved by replacing part of the sodium lauryl ether sulphate by a coconut imidazoline betaine, for example Empigen CDR10 (Albright and Wilson), or the disodium salt of lauryl alcohol polyglycol ether sulphosuccinate (Rewopol SBFA30—Rewo). In addition, an alkyl amido betaine, for example Empigen BT (Albright and Wilson), could be introduced to improve foam stability, particularly in the presence of soap:

	(2) *per cent*	(3) *per cent*
Sodium lauryl ether sulphate (28% active)	25	30
Empigen CDR10	25	—
Rewopol SBFA30	—	40
Empigen BT	4	—
Coconut diethanolamide	—	3
Perfume	1–2	1–2
Citric acid	*q.s.* to pH 7	*q.s.* to pH 7
Colour, preservative, emollients	*q.s.*	*q.s.*
Sodium chloride		*q.s.* to required viscosity
Water	to 100	100

Translucent and pearlescent products can be created by the addition of insoluble stearates, as already discussed. These are readily available from all major surfactant manufacturers and the depth of opacity is governed by the level of incorporation, which is usually between 1 and 5 per cent. Opaque non-pearlescent products are achieved by the use of polymeric materials such as Antara 430 (GAF).

Multi-layer products can be achieved and a typical formulation taken from a British Patent[3] is as follows:

	(4) *per cent*
Sodium lauryl ether sulphate (28%)	50·0
Coconut diethanolamide	9·0
Hexylene glycol	14·0
Neutral monoethanolamine citrate	13·0
Citric acid	3·0
Perfume, colour, preservative, water	to 100·0

Gels

Basically gels are very similar to liquid products, except that they have a much higher viscosity. This is achieved by increasing the level of detergent, foam stabilizer or electrolyte content, depending on the particular formulation. Shower gels may also be considered here since they are virtually identical in formulation to the highly viscous liquid bath products; however, because they are sold for direct application to the body they must be very mild, and it is usual to adopt for shower gels the types of formulation, already mentioned, that have a milder action on the skin and eyes.

Dry Bubble Baths

Dry bubble baths, of considerably less importance than liquid bubble baths, are nevertheless worthy of discussion. Basically they consist of a mixture of one or more foaming agents, fillers and water softeners to add bulk or act as carriers, perfume, colour and free-flow agents.

The major surfactant ingredients are usually dry products, sometimes fortified with liquid surfactants, for example sodium lauryl ether sulphate, to give good

flash foam. The principal surfactants employed in the past were linear alkyl benzene sulphonates; because of sporadic incidents of alleged urinary tract irritation, these tend to have been replaced by alpha-olefin sulphonates. Other surfactants that have been used include sodium lauryl sulphate, sodium lauryl sulphoacetate and isethionate derivatives.

Inorganic fillers such as sodium chloride and sodium sulphate are often used in the more inexpensive products. These can, however, be replaced by functional fillers which, in addition to acting as fillers, also have water-softening properties. These include sodium hexametaphosphate, sodium sesquicarbonate and tetrasodium pyrophosphate. One of the main problems in formulating a powdered bubble bath is to keep it free flowing and prevent it from caking. This can be achieved by adding tricalcium phosphate, calcium silicate or sodium silica aluminate. Bentonite or starch is usually employed to absorb the perfume, in order to disperse it throughout the product, while colour is usually incorporated by premixing with one of the fillers. Example formulations are as follows:

	(5) *per cent*
Alpha-olefin sulphonate (40% active spray-dried beads)	20
Lauric isopropanolamide	3
Sodium sesquicarbonate (low density)	60
Sodium chloride	14
Perfume	3
Colour	*q.s.*

	(6) *per cent*
Sodium lauryl sulphate	30
Sodium lauryl sulphoacetate	10
Lauric isopropanolamide	3
Sodium sesquicarbonate (low density)	50
Calcium silicate	4
Perfume	3
Colour	*q.s.*

Product Assessment

Complete assessment of foam bath products is difficult, since interpretation of the initial and residual feel on skin, efficacy of special ingredients, fragrance and the amount and texture of foam is subjective and requires large consumer panels to get significant results. It is normal, therefore, to limit laboratory testing to the assessment of foam volume and stability in the presence of, perhaps, soil and soap. This is not unreasonable, since foaming power is probably the single most important property as far as the consumer is concerned. A convenient technique for measuring foam is detailed in a paper by Beh and James.[4] Using a relatively simple method, it was demonstrated that the addition of a small quantity of calcium ions actually increased foam volume, although in the presence of soap foam stability was worse when calcium ions were present. It was also demonstrated that the effect of calcium ions could be destroyed by the incorporation of

EDTA. A number of foam stabilizers were also examined and from this study an alkylamido betaine was shown to be the best stabilizing agent against soap, with the N-alkyldimethyl betaine second. Some apparently anomalous results in this paper highlight the importance of carrying out foaming measurements on all finished products in order to detect the possible inclusion of foam destabilizers.

BATH SALTS

Bath salts, also known as bath crystals, were among the first bath additives to be used but today they form a relatively unimportant part of the total bath market. They consist of soluble inorganic salts attractively perfumed and coloured and they are designed to give fragrance, colour and, in most cases, water-softening properties to the bath. Some are effervescent in action while others include oily additives for emolliency. Fragrance is unquestionably the most important property of bath salts and this should be refreshing and relaxing, with sufficient strength to pervade the bathing area.

Size, colour and attractiveness of the crystals are clearly also important; in addition the crystals must be free flowing and easily dispersed and must dissolve rapidly in the bath water. Low alkalinity and mildness to the skin are also very important and, whether water-softening or not, bath salts should never be deleterious to soap lather or detergency—nor should they contribute to a bath-tub ring.

Ingredients and Formulation

Salts

Sodium sesquicarbonate ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$), which is a mixed salt, is probably the most popular material used in the preparation of bath salts. It is available in uniformly sized, elongated, attractive translucent crystals which are extremely stable, non-caking and free-flowing. It dissolves rapidly and completely in water, is easy to colour and perfume, is an excellent water softener and is quite mild to the skin, having a pH value of about 9·8 for a 1 per cent solution.

Other carbonates that have been used are sodium carbonate decahydrate, $Na_2CO_3 \cdot 10H_2O$, and the monohydrate, $Na_2CO_3 \cdot H_2O$. The decahydrate, otherwise known as washing soda, is a good water softener and consists of large attractive crystals that are readily soluble in warm water. Unfortunately, it has several serious disadvantages including a low melting point of 35°C, at which temperature it dissolves in its own water of crystallization. This clearly precludes its use in hot climates. Even under ordinary storage conditions it tends to effloresce to become powdery and unsightly, although this can be overcome by coating the crystals with a film of humectant such as glycerin. It is also more highly alkaline than the sesquicarbonate. The monohydrate is the most stable form of sodium carbonate and is available in attractive crystal agglomerates with excellent stability. Its main disadvantages are its slow rate of dissolution and the fact that it is more alkaline than the sesquicarbonate.

Phosphates are often included in bath salts to improve the water-softening properties, the most commonly used being sodium hexametaphosphate

(Calgon), tetrasodium pyrophosphate and sodium tripolyphosphate. Trisodium phosphate is a good water softener but because of its highly alkaline nature it cannot be used without buffering. However, it can be used in combination with either sodium sesquicarbonate or borax, both of which buffer it quite effectively.

Borax ($Na_2B_4O_7 \cdot 10H_2O$) is less alkaline than the carbonates and possesses a mild detergent action, although it is less effective as a water softener than the carbonates and is slow to dissolve.

Rock salt, NaCl, is used in bath salts of the type that provide fragrance only; it is very stable and its large crystals are attractive and easily coloured. It is of course non-alkaline and mild to the skin. Its disadvantage are that it has no water-softening properties and, if used in quantity, it tends to interfere with soap lathering; furthermore, the large crystals do not dissolve easily.

For effervescent systems, sodium bicarbonate and tartaric or citric acid are included.

Fragrance

Instability of fragrance can be a problem in bath salts, since in these products the perfume is distributed in a thin film on the surface of an inorganic salt which can be quite alkaline. Consequently, the perfume must have good fixative properties in addition to adequate stability to alkalis, light and oxidation. Oil-absorbing powders such as calcium silicate or fumed silica are sometimes used to aid deposition, retention and stability of the fragrance and they may also improve the flow characteristics of the product.

Colour

As with fragrance, the choice of colour is limited by stability to both alkalis and light. Colour stability may also be affected by perfume. Insoluble colours have been recommended because of their better stability to alkalis and light. These are best dispersed at a concentration of about 1 per cent in a suitable medium such as a glycol or liquid nonionic surfactant.

Example Formulations

Bath salts—fragrance only	(7)
	per cent
Sodium chloride	95–99
Perfume	1–5
Colour	*q.s.*

Water-softening bath salts	(8)
	per cent
Sodium sesquicarbonate	95–99
Perfume	1–5
Colour	*q.s.*

Effervescent bath salts	(9)
	per cent
Sodium sesquicarbonate	25
Sodium bicarbonate	50
Tartaric acid	20
Perfume, colour	5

The manufacture of bath salts is a straightforward process and can be carried out in most types of dry powder blender. Colouring is done either by spraying with colour solution, mixing and drying or by immersing the salts in the colour solution, followed by drying. Colour solutions should be hydroalcoholic or, if possible, alcoholic. Alcohol, in addition to reducing the drying time, helps to prevent solution of the bath salts. Fragrance is added either by spraying an alcoholic solution or by dispersing the perfume in the colour solution. Perfume can also be mixed with oil-absorbent powders. Clearly, in colouring effervescent salts no water can be used.

Bath Cubes and Tablets

Bath cubes and tablets employ the same materials as bath salts, but in powder form. The powdered bath salts are first granulated with starch and a small amount of alcohol-soluble gum binder is normally added. The granules are then compressed into tablets or cubes. Prior to compressing, a suitable disintegrating material such as sodium lauryl sulphate or starch should be included to aid the dissolving process in the bath.

BATH OILS

Introduction

The primary function of a bath is to cleanse the body. It is essential, therefore, to point out straightaway that the function of bath oils is not one of cleansing but of skin lubrication; in addition, they are sometimes used to impart fragrance to the body.

The oil bath has emerged as the simplest and most effective method of lubrication for generalized skin dryness. Dry skin affects both young and old and, in its mildest form, appears as a slight roughening and scaling of the skin. Severe dryness can result in disturbing itching and both the incidence and severity of itching becomes progressively worse as the individual becomes older. With age, atrophic changes in the cutaneous and subcutaneous layers cause thinning of the skin and, because the sweat and sebaceous glands slow down, the skin surface becomes dry, flaky and tends to form fissures more easily. This is a result of the horny layer losing water to the environment more rapidly than it is receiving moisture from the lower epidermal and dermal layers. In the winter months, particularly in heated homes where the relative humidity falls as low as 10 per cent, skin dryness can be considerably exacerbated. Clinical efforts to overcome skin dryness are based on the concept that a surface oil or lipid film on the skin retards water loss through evaporation—hence the importance of oil baths in combating dry skin.

A number of workers have carried out investigations aiming to quantify the adsorption of different oils by skin. Taylor[5,6] made one of the first objective attempts to quantify oil deposition onto skin, using the technique of arm immersion in a bath of oil. He concluded that products based on mineral oil adhere to skin better than vegetable oil formulations. Further, an oilated oatmeal preparation (colloidal oatmeal combined with mineral oil and lanolin) was found to be adsorbed very poorly by the skin, the likely explanation for this

being that oatmeal is a better adsorptive substrate for oils than is the skin. Taylor also observed that adsorption increased as the temperature of the bath was raised and as the concentration of oil increased. Soaking for longer than 20 minutes, however, did not cause a significant increase in oil adsorption. Knox and Ogiva,[7] employing a modification of the Taylor technique but using ground stratum corneum, obtained results in close agreement with those reported by Taylor. The incorporation of surfactants into bath oils may, of course, be expected to change the adsorption characteristics and this has in fact been shown by Knox and Ogiva.[8]

Bath oils can be classified into four main categories: floating or spreading bath oils which are water-immiscible; a dispersible or blooming type which turns milky on addition to water; a soluble type which forms a clear dispersion in water; and a foaming type similar to the foam bath.

Floating or Spreading Oils

Floating or spreading bath oils are hydrophobic in nature. By virtue of their lower specific gravity they float on top of the bath water, covering the bather's skin with an oily film on emergence from the water. In addition to providing the bather with a luxurious emollient coat, this type of product is ideal for augmenting the aesthetic nature of the bath by providing a pleasant fragrance to the bathroom, since the oil layer on top of the hot bath water allows the fragrance to distil readily into the atmosphere. One problem with this type of product is the occurrence of an unsightly 'ring' around the bath caused by the oil deposit. This deposit is compounded by a soap scum if the bather also uses a true soap in conjunction with hard water. Furthermore, since oils are natural foam depressants, the floating oil layer is likely to impede the lathering performance of the soap. Ideally, a floating bath oil should fully cover the surface of the water and be deposited on the skin in a very thin film, covering as much of the skin surface as possible. A lubricating bath oil should not be deposited in a heavy greasy layer, which is unattractive to the user, nor should it leave in the bath a heavy oily film that is difficult to remove.

In order to formulate a spreading oil system it is necessary to understand the physicochemical principles involved. If a drop of bath oil is placed on the surface of water in which it is insoluble it will either spread into a film or remain as a lens-like blob. Clearly, for use as a bath oil a non-spreading oil would be unsatisfactory since it would provide only a patchy deposit on the skin. Whether the drop spreads or remains intact depends on a balance of two surface forces. The first force is the work of cohesion, W_c, which is that component of surface free energy that causes any drop of liquid to take on the shape of minimal surface area. The second force is the work of adhesion, W_a, and this is the component of surface free energy that maximizes the interface between two immiscible liquids. The difference between these two forces, known as the spreading coefficient, S, determines whether the drop spreads or not. This relationship can be expressed as follows:

$$S = W_a - W_c = \gamma_w - \gamma_o - \gamma_{ow}$$

where γ_w is the surface tension of the aqueous phase, γ_o is the surface tension of

the oil phase and γ_{ow} is the interfacial tension between the two phases. The derivation of this equation can be obtained from any standard textbook on physical chemistry, or by reference to a specific article on floating bath oils by Becher and Courtney.[9]

This equation predicts that spreading will occur when $S>0$ and non-spreading when $S<0$. Table 7.1 lists some typical spreading coefficients for oils commonly used in bath products, based on the surface tension value for water of 72 dyn cm^{-1} at 25 °C. From these data it is obvious that only the light mineral oil will not spread on water. Spreading, however, can be achieved by the addition of a suitable surfactant, of which the effect on the surface tension of the oil is usually small compared with the dramatic reduction in the interfacial tension between the oil and the water. In fact, with a high-performance surfactant such as polyoxyethylene polyol fatty acid ester (Arlatone T), the interfacial tension of mineral oil–water can be reduced almost to zero with the addition of 1 per cent, and this results in a spreading coefficient of approximately +40, which is optimum.

A high positive spreading coefficient is desirable from several considerations. Firstly, the area covered by the oil is proportional to the spreading coefficient. Secondly, a rapidly spreading oil is important for aesthetic reasons because it is more appealing to the user, and since the velocity of spreading is directly proportional to the spreading coefficient divided by the viscosity of the liquid on which it is spread, the merits of a high spreading coefficient are obvious. The tendency for spreading coefficients to decrease with increasing temperature is noteworthy, since in some cases a reversal from spreading to non-spreading can occur with a temperature change of about 20°C. It is important, therefore, to measure the performance at bath water temperatures (40°–50°C). This can be done relatively easily by the following simple method; a pan about 25×25 cm is filled with water at 50°C and dusted with starch; a small measured quantity of oil is then dropped into the centre; the oil will move the starch away from the centre to the edge of the pan, showing both the spread and velocity of spread quite clearly.

Although it has been shown that the HLB value (hydrophilic–lipophilic balance) of the surfactant is directly related to the spreading coefficient (that is, spreading coefficient increases in magnitude with increasing HLB value), the surfactant with the highest HLB is not necessarily the best choice. Clearly, for an acceptable product the surfactant must be soluble in the oil and in the case of high HLB surfactants this might not be the case. As already mentioned,

Table 7.1 Spreading Coefficients at 25°C

Oil	Surface tension, γ_o (dyn cm^{-1})	Interfacial tension, γ_{ow} (dyn cm^{-1})	Spreading coefficient, S (dyn cm^{-1})
Hexadecyl alcohol	28·6	22·6	20·8
Hexadecyl stearate	30·6	23·2	18·2
Isopropyl myristate	29·1	25·2	17·7
Light mineral oil	29·0	50·6	−7·6

Arlatone T, which has an HLB of 9·0, has been found to give both good solubility and spreadability in many systems.

Possibly the most widely used oil in such formulae is mineral oil, because of its economy, safety, availability and, of course, emolliency. It is often used, however, in association with isopropyl myristate, which helps to overcome the greasiness of mineral oil and is a much better perfume solubilizer. Many other emollients have been used and these include vegetable oils such as olive oil, cottonseed oil, peanut oil, safflower and castor oil, etc. Lanolin and lanolin derivatives, as well as fatty acids, fatty alcohols and their esters, have also been used to give better emollient effects such as better skin feel. One of the newer emollients is a fatty acid propoxylate (Arlamol E) and this is said to be particularly suitable for bath oils because of its distinctive feel on the skin and its exceptional solvency for perfumes. Indeed it is claimed to be more efficient than isopropyl myristate for carrying perfume into mineral oil.

Perfume is obviously an important ingredient and its level of incorporation is very much dependent on the cost requirements. Other ingredients sometimes included are antioxidants, colours and sunscreens.

Manufacture of these products is relatively straightforward and usually involves simple mixing. Sometimes filtration or even chilling before filtering is necessary in order to produce a perfectly clear product.

Typical formulae for floating bath oils are given in examples 10 and 11.

	(10) *per cent*
Arlamol E	49
Arlatone T	1
Light mineral oil	45
Perfume	5

	(11) *per cent*
Light mineral oil	46
Isopropyl myristate	48
Arlatone T	1
Perfume	5

Dispersible or Blooming Oils.

Dispersible bath oils consist of emollient oils and perfume oils and contain a surfactant selected to emulsify the oils in the water instead of making them spread on the surface. When poured into the bath water they bloom into a milky cloud. They are sometimes preferred to the floating type because the oils are dispersed uniformly throughout the bath water, providing thorough contact with the body during the bath. When properly formulated they leave very little oily stickness or ring in the tub after the water is drained. The emollient oils used tend to be similar to the ones used in floating bath oils, with perfume levels between 5 and 10 per cent.

One of the most commonly employed surfactants in the formulation of blooming bath oils is Brij 93 (polyoxyethylene (2) oleyl ether). It has a low HLB (4·9) which is indicative of its good solubility in oil; however, it is

sufficiently hydrophilic to disperse the oils in bath water. Since it is nonionic, it is effective in either hard or soft water.

A typical formula for a dispersible bath oil would be as follows.

	(12) *per cent*
Mineral oil	65
Isopropyl myristate	20
Brij 93	10
Perfume	5

Mineral oil is used as the principal emollient because of its low cost. Isopropyl myristate also adds to the emolliency and helps to dissolve the perfume oils. The amount of Brij 93 will vary with the emulsion requirements of the emollient and perfume selected. For example, the bloom can be increased by reducing the isopropyl myristate and increasing the mineral oil, or by increasing the Brij 93 content.

Soluble Oils

Soluble bath oils contain large quantities of surfactants to solubilize the high-fragance oil concentrations and to dissolve or disperse these oils readily in the bath water. They leave no residue in the bath and have no emollient effect on the skin. Soluble bath oils are either anhydrous concentrates consisting of perfume and surfactant or solubilized products consisting of perfume, surfactant and water. They contain between 5 and 20 per cent perfume oil, which can usually be solubilized quite readily by means of a hydrophilic surfactant. Tween and Brij surfactants in the HLB range of 12 to 18 are widely used in perfume oil solubilization and a typical formulation is shown in example 13.

	(13) *per cent*
Perfume	5
Tween 20	5–25
Preservative	*q.s.*
Water	to 100

The quantity of Tween 20 (polyoxyethylene sorbitan monolaurate) is clearly dependent on the type of perfume used. A higher-viscosity product can be achieved by the use of Tween 80 (polyoxyethylene sorbitan mono oleate).

Foaming Oils

Foaming bath oils can be considered either as bubble baths with high fragrance levels or as soluble bath oils with foaming agents and stabilizers added. These products provide both fragrance and foaming action and also serve to eliminate the bath-tub ring. Like the soluble bath oils they generally have no emolliency properties. The foaming agents and stabilizers discussed under foam baths are used, while Tween 20 is often used to solubilize the fragrance in the foaming bath oil. Thickeners such as carboxymethyl cellulose, methyl cellulose

and other gums are commonly added, as are sometimes sequestrants. A typical formulation is shown in example 14.

	(14) *per cent*
Perfume	5
Tween 20	20
Sodium lauryl ether sulphate (28% active)	40
Coconut diethanolamide	2
Preservative	*q.s.*
Water	to 100

Very occasionally emollient oils are included in these products at significant levels but most of these have such a foam-depressing action that the final product can barely be considered to be a foam bath.

AFTER-BATH PRODUCTS

After-bath products include body or dusting powders and the various lotions for use after a bath or shower.

Body or Dusting Powders

Body or dusting powders are also known as body talcs or talcum powders and have a wide appeal because of the smooth feeling and cooling effect which they impart while they temporarily absorb moisture. The cooling effect is due to the extra heat loss from the large surface area of the talc particles.

Talc is the major ingredient in these formulations, which should have good slip characteristics, covering power, body adhesion and absorbency. The slip and texture properties are essentially based on the talc. It is essential, therefore, that grit-free, alkali-free high quality cosmetic talc is used. Talc should, of course, be free of bacteria and sterilized grades should always be used. In order to improve adhesion properties, metallic stearates such as zinc or magnesium stearate and kaolin are incorporated, while magnesium carbonate, starch, kaolin and precipitated chalk all improve absorbency. Zinc and titanium oxides at low levels along with earth colours can be incorporated for tinting purposes when required. Perfume oils are easily incorporated and should be sufficiently powerful to cover the base odour yet not interfere with other perfumes that may be used. Other ingredients sometimes included are boric acid to act as a skin buffering agent and fumed silica to give a powder of lower density.

A typical formulation is as follows:

	(15) *per cent*
Talc	75
Kaolin	10
Fumed silica	2
Magnesium carbonate	6
Zinc stearate	6
Perfume	1

After-bath Emollients

After-bath emollients or moisturizers are applied to the body with the object of replacing natural skin liquids removed during bathing. Their function, therefore, is to prevent the occurrence of dry skin. Basically four product types exist: anhydrous oil-based systems; oil-in-water emulsions; water-in-oil emulsions; and hydroalcoholic emulsions. Because of their greasy nature, anhydrous oil-based systems and water-in-oil emulsions are far less popular than the other two types and will not be considered further. Oil-in-water emulsions are perhaps most widely used since there are almost limitless opportunities in the design and formulation of these systems. Generally, they are sold in lotion form and are usually formulated to give good 'rub-in' and feel properties. The formulation possibilities are too extensive to be covered here and are discussed in Chapter 4.

The hydroalcoholic emulsions, sometimes referred to as bath satins, are worthy of mention in greater detail since they are quite a recent development. These products act in a similar way to any other emollient skin product in that they deposit a film of oil on the skin in order to reduce the rate of water loss. In addition, however, 'bath satins' give a cooling effect as the alcohol evaporates from the skin.

Basically these systems consist of an emollient oil emulsified in an aqueous alcoholic base. In order to produce a stable system, however, it is essential to include a sufficient quantity of an alcohol-compatible gum such as Carbopol or Klucel. A typical outline formulation is shown below.

	(16)
	per cent
Crodafos N-3 acid	0·5
Emollient oil	5·0
Carbopol 941	0·4
Denatured ethanol (95%)	40·0
Triethanolamine	*q.s.* to pH 6·5
Perfume	1–5
EDTA	*q.s.*
Water	to 100·0

Such a product could be made without heat by hydrating the Carbopol in the water with efficient mechanical agitation, followed by the addition of a mixture of emollient oil, perfume and Crodafos. Finally, the emulsion is completed by the addition of the alcohol in which the triethanolamine has been dissolved. EDTA or other suitable sequestrant is included to stabilize the Carbopol gel, since metal ions can depolymerize Carbopol and this can lead to loss in viscosity and hence emulsion instability.

Increased emolliency can be achieved by raising the level of emollient oil. This will produce a more opaque product and may destabilize the emulsion unless the levels of emulsifier and gelling agent are increased at the same time. Increasing the level of alcohol serves to provide greater perfume lift and quicker drying but produces a thinner, less opaque and sometimes a more unstable emulsion. Alcohol concentrations greater than about 50 per cent should be avoided since they tend to be unstable owing to coagulation of the Carbopol.

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Chapter Eight

Skin Products for Babies

Introduction

During the first few years of life, the skin of the child undergoes extensive change and development—this is particularly so during the very earliest weeks after birth. It follows, therefore, that the skin of the young child differs from that of the adult and from that of the older child. It has been shown, for example, that the very young skin is very thin,[1] less cornified, less hairy and contains a relatively high proportion of water in comparison with the adult. Sebaceous glands are not only present in the newborn skin, but begin to function very early.[2] Apparently, however, transepidermal water loss at this time is lower than for adults (at least for some body areas).[3]

It is known that during the first few weeks of life the infant has very little capacity of its own to resist infection, its immunological protection being derived largely from antibodies passed on by the mother. It has often been argued that at this early stage the child is particularly susceptible to skin irritation and infection and that, being comparatively thin, the skin should be more permeable to topically applied agents. While it is certainly true that skin irritation and infection are not uncommon in very young children, the extent to which these are the result of the skin's special susceptibility due to its structure and how much the result, on the other hand, of the unique environment into which certain areas of the skin are placed, is debatable. Certainly, it has been shown that the skin surface of most babies at birth is far from sterile.[4]

Typically, the skin of babies and very young Caucasian children is pink, very soft and smooth to the touch.

Skin Problems in Babies

In spite of its histological differences from adult skin, the skin of young children is not exempt from the general rules governing skin care which apply universally. If exposed to excessive sunlight or very drying conditions, if subjected to abrasion and if allowed to accumulate grime and secretions, the very young skin reacts in the same way as adult skin and may become damaged. In addition, however, there is a hazard which applies exclusively to the very young and which becomes manifest most frequently as 'nappy' or 'diaper' rash. This condition arises because of the combination of close confining clothes and the uncontrolled urination and defaecation performed by the child at this age. As its name implies, nappy rash appears between and around the buttocks and groin, the area in which the excretions are contained by the close-fitting nappy, thus providing a damp and warm nutritive environment for the proliferation of

bacteria. The metabolites of these (particularly of *Brevibacterium ammoniagenes*, which feeds on urea with the production of ammonia) combined with the abrasive nature of the nappy lead to the irritation and reddening of the skin which typifies nappy rash. If allowed to proceed to a severe form, nappy rash can result in an ulcerative condition with secondary eruptions being infected with pyrogenic organisms and causing extreme discomfort. *Candida albicans* is a frequent secondary invader and was isolated from 41 per cent of all napkins by one group of workers.[5] There is no doubt that badly laundered and inadequately rinsed napkins are a contributory cause to nappy rash if they are left with a rough, alkaline surface.

The infant skin is also susceptible to other forms of rash, notably infantile eczema (the origins of which remain somewhat controversial, but which may be related to diet) and impetigo neonatorum. These are clinical conditions, however, requiring medication which is not the province of cosmetic science.

It seems probable that most skin problems in babies stem from the tendency to wrap them up in tightly-fitting garments, thus providing a warm, stagnant environment for the growth of bacteria. Nappy rash is unknown in countries where infants are allowed to lie naked.

Functional Requirements of Baby Products

It follows from the foregoing considerations that, from the functional point of view, baby skin care products need to protect the skin from a hostile environment, to cleanse the skin thoroughly from sebum, grime and excreta and to keep the skin surface as dry as possible.

While there is no shortage of expert opinion on the best methods of cleansing baby skin, many of the views expressed are contradictory and confusing. The product types available are precisely the same as for cleansing products designed for older skins, namely soap and water, oils, emulsions and surfactant-containing gels. All these types are represented in the market although gels are relatively rare at the time of writing. In view of the association of nappy rash with bacterial growth, many formulators have been tempted to include a germicide in their products, the most frequently encountered examples being quaternary ammonium compounds such as cetyl trimethyl ammonium bromide, alkyldimethyl benzyl ammonium chloride, cetyl pyridinium chloride and benzethonium chloride. There appears to be no substantial evidence, however, that the incorporation of such active ingredients is of great benefit in the prevention of nappy rash. A more rational approach would seem to be to provide products which clean effectively and to treat skin infections of any kind with topical, pharmaceutical preparations (which are not themselves the province of the cosmetic chemist).

Most baby skins come into contact with soap and water within a few days of birth and subsequently at bath times thereafter. Although there is no evidence that ordinary soap has a bad effect on the baby, most baby soaps are white and free from perfume. An alternative not readily available in every country at the time of writing is the neutral or slightly acidic detergent bar.

Cleansing creams are not popular among baby products. This is perhaps due to the need to clean between the folds of baby fat for which a more liquid

product is desirable. There is some evidence that oils and greasy materials can, by occluding the skin surface, predispose infants to prickly heat.[6,7] Thus, for cleansing purposes, lotions seem to be preferred. As with most baby products, these are only lightly perfumed or are not perfumed at all in deference to the potentially irritating effect of some perfume constituents.[8]

In view of the previously noted controversy over the use of occlusive oils on baby skin, it seems surprising that baby oils remain a popular product type. They represent a very convenient and relatively inexpensive method of cleansing the nappy area, and the residual layer which remains on the skin undoubtedly affords some protection to it from nappy contents. While baby oils composed of vegetable oils, lanolin derivatives, higher alcohols and esters have been cited, the most popular brands consist almost entirely of high purity mineral oil with, perhaps, a trace of perfume and solubilizer.

The protection which the baby skin requires has traditionally been given by zinc and castor oil creams or ointment. Zinc oxide is thought to have mildly antiseptic, astringent and anti-inflammatory properties; this accounts for its use in protective products, usually in the concentration range 2–10 per cent. Other raw materials frequently used to give a protective, occlusive barrier include petrolatum, castor oil, beeswax, lanolin, silicone oil and polyethylene wax. These may be used as anhydrous preparations or as the oil phase of protective baby creams. Inorganic salts of stearic acid and oleic acid are used to improve the water-repellent effect of creams while stabilizing the emulsion.

Baby powder is another traditional and valuable toiletry product. Its main function is to provide a dry and lubricated surface to skin that has been cleaned and protected with oils or lotions. The main constituent of baby powder is talc, but since this lacks the absorbency of other powders it is often blended with such materials as kaolin, hydrated aluminium silicate, magnesium and calcium carbonates, starches and pyrogenic silica. The grades of materials used are naturally important—particularly talc, which should be the very purest available and devoid of any fibrous materials. The adhesive power of baby powders as well as their water repellency can be improved by the incorporation of aluminium, zinc and magnesium stearates; cetyl and stearyl alcohols and zinc oxide perform a similar function.

One of the main problems associated with the use of talc is its susceptibility to contamination by micro-organisms. Various methods are available for the sterilization of talc, some being more suitable and successful than others.[9] Ethylene oxide treatment may leave irritating residues, while heat treatment is not always sufficient to sterilize the material completely.

The use of boric acid and borates in baby powders as a mild antiseptic and as a neutralizing buffer, although once popular, has now largely ceased because of the potentially toxic nature of these substances.[10,11]

Safety of Baby Products

The lack of resistance to bacterial attack in very young babies, together with the differences in histological appearance from that of the adult which baby skin exhibits, has already been discussed. Naturally, it is extremely important to ensure that all baby products are free from bacteria when sold and that they

contain adequate preservative systems to prevent accidental contamination during use; such principles should apply equally to all cosmetic and toiletry products.

As the baby grows, however, there is an additional danger to which he is exposed and of which baby product formulators would do well to take note: namely, the possibility of poisoning from the ingestion of the contents of bottles and jars. The mouth is probably the most sensitive area of the body and the young child uses it to explore his environment. Moreover, liquids in bottles are associated with good things to drink. Cases of poisoning of very young children by ingestion of toiletry products are fortunately rare but, nevertheless, the major manufacturers of baby products report that they are frequently contacted by worried medical practitioners in search of reassurance about the contents of a product which has been swallowed in quantity by a lively youngster.

For this reason, if no other, it seems sensible to restrict the use of active constituents such as germicides to a minimum, since these can be potentially toxic to a baby. The other important safety aspect in protection against misuse of baby products concerns their packaging, in particular the ease with which the pack may be opened and the size of the contents available for the baby to eat or drink. While such matters are not normally in the hands of formulators to control, it is well that they should themselves be aware of the contribution to safety which such considerations may make.

The logical conclusions to be drawn from these considerations is that the raw materials used in baby products should, wherever possible, be chosen for their low toxicity as well as their non-irritating character when applied topically.

Example Formulations

The first two formulae for baby creams and lotions illustrate the use of a comparatively new type of mild, non-toxic emulsifier based on sucrose esters of palmitic and stearic acids.[12] These materials, which are known by their trade name 'Crodestas', are admixtures of mono-, di- and tri-esters giving a range of HLB values.[13] Example 1 is a lotion and example 2 a cream.

	(1) *per cent*	(2) *per cent*
Mineral oil	25·00	35·00
Cetearyl alcohol	—	0·50
Petrolatum	—	4·20
Lanolin alcohol	—	1·25
Crodesta F70	3·00	—
Crodesta F160	0·50	—
Crodesta F110	—	3·00
Hydroxyethylcellulose	0·20	—
Water	71·30	55·05
Glycerin	—	1·00
Perfume, preservative	*q.s.*	*q.s.*

More traditional baby creams and lotions are based upon the triethanolamine stearate (anionic) emulsifier system, of which there are many examples, examples 3 and 4 being fairly representative.

	(3) *per cent*	(4) *per cent*
Mineral oil	26·00	15·00
Lanolin	1·04	5·00
Stearic acid	0·94	2·00
Triethanolamine	0·52	1·00
Water	69·68	52·00
Stearyl alcohol	0·94	—
Cetyl alcohol	0·52	—
Sodium alginate	0·36	—
Isopropyl palmitate	—	2·00
Beeswax	—	8·00
Propylene glycol	—	5·00
PEG-400 stearate	—	10·00
Perfume, preservative	*q.s.*	*q.s.*

Examples 5–7 illustrate the use of some of the nonionic emulsifiers based upon sorbitol in baby creams and lotions.

	(5) *per cent*
Cetearyl alcohol	1·00
Mineral oil	4·00
Polysorbate 60	1·70
Sorbitan isostearate	1·00
Glyceryl stearate	1·00
Liquid lanolin	0·25
Water	83·35
Hydroxyethylcellulose	0·20
Glycerin	7·50
Perfume, preservative	*q.s.*

	(6) *per cent*
Mineral oil	35·50
Lanolin	1·00
Cetyl alcohol	1·00
Sorbitan oleate	2·10
Polysorbate 80	4·90
Dimethicone	5·00
Water	50·50
Perfume, preservative	*q.s.*

	(7) *per cent*
Petrolatum	20·00
Sorbitan isostearate	2·10
Microcrystalline wax	3·34
Mineral oil	10·55
Glycerin	3·14
Water	60·87
Perfume, preservative	*q.s.*

Examples 5 and 6 are of oil-in-water creams, whereas example 7 is water-in-oil. The last cream formula (example 8) illustrates the use of polyoxyethylene sorbitan lanolin derivatives, which are also thought to be fairly mild.

	(8) *per cent*
Mineral oil	15·00
Stearic acid	15·00
Beeswax	2·00
Lanolin	1·00
PEG-20 sorbitan lanolate	5·00
PEG-40 sorbitan lanolate	1·00
Sorbitol	10·00
Water	51·00
Perfume, preservative	*q.s.*

In view of its potentially irritating nature, the use of lanolin itself in baby products should be carefully considered. No doubt new information on the safety of this otherwise valuable raw material will be produced from time to time over the next few years and the cosmetic formulator will be well advised to study it.

In the transition from emulsions to baby oils, the use of anhydrous ointments (of which the zinc and castor oil cream in the *British Pharmacopoeia* is an example) should be considered. The following formulation is a little less sticky and more pleasant to use than zinc and castor oil, while still affording excellent barrier protection against excreta.[13]

	(9) *per cent*
Mineral oil	83·50
Acetylated lanolin alcohol	1·50
Silica	5·00
Zinc oxide	10·00

Procedure: Disperse the silica into the hot mineral oil/acetylated lanolin alcohol. Add the zinc oxide last and subject the whole to shear in a mill or by using a high speed rotor/stator device.

Baby oils are composed predominantly of a very pure grade of mineral oil. Small amounts of fatty acid esters, vegetable oils, lanolin derivatives and other compatible materials should be included only after careful consideration of safety and irritation potential.

Baby powders function, as has been noted, to lubricate, dry and perhaps to impart a slight perfume to the skin. The following formulae illustrate how the absorbency and adhesiveness of talc can be improved by the blending-in of other materials.

	(10) *per cent*	(11) *per cent*	(12) *per cent*	(13) *per cent*
Sterilized talc	80·00	74·00	95·00	90·50
Magnesium stearate	10·00	4·00	—	2·50
Calcium carbonate	10·00	—	—	—
Kaolin	—	20·00	—	5·00
Glyceryl stearate	—	1·00	—	—
Cetyl alcohol	—	1·00	—	—
Starch	—	—	5·00	—
Zinc oxide	—	—	—	2·00
Perfume	*q.s.*	*q.s.*	*q.s.*	*q.s.*

Cleansing of Nappies (Diapers)

Although nappies are not, strictly speaking, skin products for babies, or even cosmetics in the broad definition of the word, the cleansing of nappies plays such an important part in the care of baby skin that a short note on the subject here is appropriate.

The obvious requirement is for cleanliness, softness and sterility without the deposition of any potentially irritating residues. Most popular at present are the 'nappy soak' products which are dissolved or diluted in water to provide a cleansing/sterilizing medium in which the dirty nappies are merely allowed to soak for a few hours. This has obvious advantages for a busy mother. Formulae are based upon the bleaching and sterilizing properties of chlorine and hydrogen peroxide (the former being somewhat quicker-acting but potentially more irritating if traces are left behind). Liquid products may utilize hypochlorite but the more common powder formulae make use of chlorine or peroxide release agents. The following illustrative example employs sodium perborate in a powdered detergent base:

	(14) *per cent*
Sodium tripolyphosphate	30·00
Sodium carbonate	10·00
Sodium dodecylbenzene sulphonate (80%)	6·00
Sodium perborate tetrahydrate	20·00
Sodium sulphate	33·90
Optical brightener	0·10
Perfume	*q.s.*

After soaking, the nappies may be softened, if necessary, with a cationic clothes softener and—most important—thoroughly rinsed.

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Chapter Nine

Skin Products for Young People

Introduction

In the majority of the population, skin first comes into contact with cosmetic or toiletry products during the first few weeks of life. At this stage, there are few benefits which such products can provide other than those of cleaning and protecting the skin from its watery environment. During the early years, the skin of most children is healthy, soft, free from spots and blemishes (provided they enjoy a sensible diet) and requires little care other than regular cleansing. At the onset of puberty, however, the skin becomes susceptible to a range of problems, most of which can be attributed to over-activity of the oil-producing sebaceous glands. More than one survey among groups of adolescents in the age-range 12–18 years has indicated that the incidence of excessive spots, pimples, blackheads, acne and related conditions is greater than 50 per cent of the population.[1] Not surprisingly, therefore, the majority of skin products purchased by young people in this age group are concerned with the treatment, prevention or camouflage of blemishes or of oily skin. Additionally, there are other skin products bought and used by teenagers but which have the same composition as those sold on the general market, with perhaps a difference in presentation. These are dealt with in the appropriate chapters elsewhere in this book.

Adolescent Skin Problems

The sebaceous glands together with the muscular, nervous and vascular systems which are associated with them are collectively known as the pilosebaceous apparatus. It has long been realized that the pilosebaceous apparatus is largely under the control of endogenous hormones which are present in unusually high concentration in the blood during adolescence and puberty. The corresponding increase in activity of the sebaceous glands themselves gives rise to the production of excessive amounts of sebum. In itself, this causes an unpleasant oiliness of the skin, giving it a patchy, shiny appearance and (in girls) making it difficult or impossible to apply make-up to the affected areas. Unfortunately the condition is made worse by a simultaneous increase in the rate of keratinization of the skin's horny layer (the stratum corneum). In some young people, strips of dead keratinized cells can be removed from the face by simply rubbing with the fore-finger and this, naturally, adds to the problems of applying anything to the skin surface. Even more significantly, however, the horny cells lining the sebaceous follicles also proliferate; they become tightly-packed and can form an occlusive plug or comedone. This physical barrier, coupled with the increased production of sebum, leads to a rapid accumulation of back pressure and the

stagnant sebum forms an ideal medium for the proliferation of bacteria (mainly *Staphylococcus aureus*, *Staphylococcus albus* and *Corynebacterium acnes*). When the plugged follicle eventually ruptures and allows the discharge of its contents, these will include the breakdown products of bacterial metabolism (including such irritants as fatty acids), causing local swelling and inflammation. Even then there remains the possibility that the exposed follicle cells will darken from the deposition of pigment from damaged cells in the deeper layers, giving rise to 'blackheads'. (Blackheads, it should be noted, are *not* due to the accumulation of dirt or debris.)

Products for Oily Skins

There is no topically active substance yet known capable of inhibiting local sebum production. The main treatment for oily skins therefore consists of careful and regular cleansing to prevent the accumulation of oil on the surface, the use of absorbent materials to soak up excessive oil and the application of products (particularly liquid foundations) capable of drying to a matt, non-shiny finish.

Frequent and adequate cleansing of the skin—particularly the face, neck, chest and back—is of paramount importance in the control of oily skin and the complications which often arise from it. Emulsion cleansers would not seem to be the best choice since they must, perforce, lay down additional oil on the skin surface. Oil-in-water emulsions with a low oil content are, nevertheless, marketed for the adolescent age group and, provided that the last traces of emulsion are removed by the subsequent use of astringent tonic or toner, such products may be satisfactorily used. A more traditional soap-and-water regime is very effective in the removal of surface oil and, although many experts believe that the prolonged use of anything as alkaline as soap can cause damage to the skin, there is no cheaper method of cleansing. As an alternative to soap, several varieties of detergent bar (of slightly acid pH) are now becoming available in soap-bar form.[2] Perhaps the most logical approach to the cleansing of oily skin is the simple aqueous solution of surfactant (which, for variety, may be gelled with a conventional organic gelling agent). Such cleansing products, containing no oils or harsh, alkaline materials, provide efficient cleansing power without exacerbating the oily condition of the skin. Additionally, they may be enhanced by the inclusion of ethanol as an astringent and a germicide to aid the control of acne-producing bacteria on the skin (this latter principle can also be applied to many of the other adolescent cleansing products already discussed). Two examples of the general principle:

	(1)
	per cent
Triclosan	3·00
Menthol	10·00
DEA-oleth-3 phosphate	2·50
Hydroxypropylcellulose	2·50
Amphoteric-1	5·00
Water	37·00
Ethanol (96%)	40·00

	(2) *per cent*
Phenoxyisopropanol	2·00
Sodium laureth sulphate	5·20
Propylene glycol	8·00
Quaternium-15	0·20
Hydroxyethylcellulose	1·00
Water	83·60
Perfume, colour	*q.s.*

Ranges of germicides, surfactants and gelling agents are available for substitution into the above formulae at the discretion of the formulator.

A second approach to the problem of oily skin consists in the development of products leaving a matt layer on the skin surface in order to combat shine or to absorb the excess oil. The most common approach is the incorporation into the product of pyrogenic silica which has the dual properties of oil absorbency and matt appearance.[3] The silica may be incorporated into the oil phase of an emulsion or, alternatively, applied as a gel or solution from aqueous or aqueous–alcoholic suspension. Other non-irritating powders may be used for a similar purpose, including polyethylene, talc and bentonite.[4]

Specific Treatments for Acne

In spite of much research, modern treatments for acne consist of containment until the condition clears up of its own accord. Successful treatment, limited though it may sometimes be, tends to be time-consuming and repetitive.[5] However, two lines of approach are simultaneously available. The first of these involves the use of 'peeling agents' for the rapid and effective removal of keratinized squamous cells of the horny layer which, if allowed to accumulate at the skin surface, make the formation of a comedone much more likely. Secondly, very thorough cleansing of the affected parts of the skin—particularly with some of the germicidal cleansing products already referred to—will help to keep the proliferation of the acne bacilli under control.

Among the 'peeling agents' commonly used are resorcinol, sulphur and benzoyl peroxide and these (particularly the latter) have been shown to be valuable in this limited role. Salicylic acid is sometimes incorporated, probably in an attempt to reduce the irritant effect of benzoyl peroxide. Guanidine and its compounds have also been used for the same purpose[6] although the extent of the irritation caused by the peroxide appears to depend on formulation variables, particle size and on the quality of the raw material itself.[7] A selection of published 'peeling' creams and lotions is given below. The formulator should avoid the use of organic amines and inorganic hydroxides since, like most organic peroxides, benzoyl peroxide decomposes in alkaline solution to give hydrogen peroxide.

Medicated vanishing cream	(3) per cent
Laneth-10	2·00
Lanolin alcohol	0·50

Medicated vanishing cream (cont.)

	per cent
Cetyl alcohol	5·50
Polawax	6·00
Myristyl myristate	2·00
Benzoyl peroxide	2·00
Resorcinol mono-acetate	0·20
Magnesium aluminium silicate	4·00
Methylparaben	0·20
Sulphur	1·40
Perfume	*q.s.*
Water	76·20

Procedure:
Dissolve the benzoyl peroxide in the propylene glycol and then add the rest of the oil phase ingredients. Add the magnesium aluminium silicate to the water at 75°C and disperse under shear, add the sulphur and methylparaben and shear again to disperse. Combine the phases and emulsify at 70°C, adding the perfume at 50°C.

Peeling lotion (4)

	per cent
Resorcinol	3·50
Salicylic acid	2·00
Alcohol	17·00
Rose water	77·50

Acne cream (5)

		per cent
A	Cetearyl alcohol	1·50
	Ceteareth-20	1·00
	Diisopropyl adipate	1·50
	Water	73·20
B	Cellulose	2·80
C	Benzoyl peroxide	5·00
	PEG-4000	5·00
	Water	10·00

Procedure:
Grind phase C together in a colloid mill. Add B to A and mix at 75°C. Add C at 40°C.

Some modern vehicles for benzoyl peroxide involve the use of gels.[8] The precise mode of action of benzoyl peroxide in aiding the removal of inflamed and superficial layers of skin does not seem to be known. Other oxygen-potentiating compositions have also been patented, however, notably one based upon N-acetyl-*dl*-methionine complexed with quaternary ammonium salts.[9] It is known that the primary acne-producing bacteria are anaerobic and cannot proliferate in the presence of oxygen.

Much interest is now being shown in vitamin A acid (retinoic acid or Tretinoin) in the control of acne. Vitamin A has long been known to influence

the cells of the horny layer. Retinoic acid appears to stimulate epithelial growth so that a less adherent horny layer is formed. It may be applied directly to affected areas as a 0·025 per cent alcoholic solution or gel. Such formulations may be improved by the addition of antibiotics.[10] Antibiotics alone are not very effective for topical application, but there seems to be a complementary action between certain of them and retinoic acid, the latter helping to reduce the early aggregation of horny cells and the former inhibiting secondary infection. Tetracycline is an example of an antibiotic that can function in this way. It is also known that zinc is involved in the metabolism of vitamin A and some people with particularly severe acne improve as the result of being fed zinc sulphate. Other patents mention the use of retinoic acid in combination with lactic acid esters[11] and of desmethyl vinyl derivatives of retinoic acid.[12]

Further patents describing topical treatments for acne will no doubt continue to appear, although the nature of some of these will undoubtedly confer the status of pharmaceutical preparations on any products containing them. Much research is now needed into the problem of prevention rather than cure. There is evidence that some cosmetic ingredients can actually worsen or potentiate acne, thus giving rise to the term 'comedogenic'. Some clinical work seems to indicate that these raw materials tend to have a comedogenic effect on susceptible skins no matter what type of formulation they appear in.[13–16] Such research is still regarded as somewhat controversial but will undoubtedly continue and may prove a valuable aid to the cosmetic scientist interested in formulating products for the adolescent skin.

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Chapter Ten

Antiperspirants and Deodorants

Introduction

If a vote were taken to select the one cosmetic product that best illustrates the versatility of packaging, the deodorant/antiperspirant would likely be the unanimous winner,[1] for there is probably no other product that is sold in at least eight different kinds of package. Each was developed to meet a specific marketing and convenience need and each has inherent advantages and disadvantages.

Deodorants/antiperspirants are commonly packaged in:

Stick—solid	Pump sprays
Pads	Squeeze bottles
Dabber units	Creams
Aerosols	Stick—creams
Roll-ons	

With the confusion about the use and purpose of antiperspirant and deodorant products it is helpful to distinguish between the purposes they are intended to serve.

Antiperspirants are designed primarily to reduce (axillary) wetness. In the USA they are classified legally as drugs because their mode of action affects a body function, namely, eccrine sweating. Deodorants (except soaps) are designed to reduce axillary odour. Since this is considered a non-therapeutic purpose and a function of the body is not considered to be altered, they are classed as cosmetics.

Despite the avalanche of topical antiperspirants which has descended upon the consumer, and despite the implications of the advertising claims, there is not a single topical agent available today that eliminates axillary sweating in the hidrotic individual.[2]

Perspiration and its Control

The odour in the human skin is produced from the secretions of sebaceous and sweat glands.[3] Sebaceous glands are found with every hair, on the red surface of lips, in the nostrils, in the papillae, on the anus, and on the foreskin and labia minora.

The sebum secreted by these glands is made mainly of cholesterol and its esters, palmitic and stearic acid and their esters, and various other substances

whose nature is not fully understood. Sebum is generally oily and may solidify on the skin surface. Pure sebum is not a critical factor in skin odour. The known constituents are odourless:[4] generally they are substances whose molecular weights are higher than those of odorous compounds.

To assess properly and to understand the action of deodorants and antiperspirants, a review of the physiology of sweating is essential.

Perspiration assists in the regulation of body temperature by dispelling heat through evaporation of moisture from the surface of the skin. It also functions in other capacities such as by eliminating lactic acid which is formed during muscular exercise and by protecting the skin from dryness.

It has been estimated that there are about 2 380 000 sweat glands distributed over the body surface. These sweat glands are of two types: the eccrine glands and the apocrine glands. The eccrine glands or small coil glands are the true sweat glands that occur over almost all of the body surface. They originate in the deeper layers of the dermis or in the subdermis and open via a thin duct directly on to the skin. The apocrine glands or large coil glands are those glands which are associated with sexual development, being post-pubertal in occurrence. They occur in relatively small numbers and are found in such areas as axillae, around the nipples, on the abdomen and in the pubic region.

Although the axilla is virtually an apocrine organ, the profuse flow of sweat we term hyperhidrosis is the result of intense activity of the eccrine rather than the apocrine sweat glands in this area. Numbering about 25 000 in each axillary vault, these eccrine glands can secrete large quantities of sweat. In hyperhidrotic individuals, each armpit may produce upwards of 12 grammes per hour. It is this heavy local outpouring which is so injurious to the affected individual's composure and clothes.

Laboratory studies indicate that both eccrine and apocrine sweat are sterile and odourless at the time of discharge.[5] The odour is produced later through the action of bacteria on primarily the apocrine sweat, which is rich in organic material and is an ideal substrate for bacterial growth. The far more abundant eccrine sweat is a highly dilute aqueous solution and has been shown to be much less important as a source of axillary odour.[6] However, the moisture from eccrine glands probably promotes odour production indirectly in two important ways: (i) the small amount of sticky, oily material from the axillary apocrine glands is dispersed over a wider surface; (ii) the moisture in the warm axillary vault completes an ideal environment for the rapid growth and proliferation of the resident bacteria feeding on this organic material. Axillary hair also has been found to promote the development of odour. It is thought that axillary hair acts as a collecting site for apocrine sweat and increases the surface area available for bacterial proliferation.

Decomposition of the sudoriferous and sebaceous gland secretions by the skin microflora and likewise decomposition of proteins on the surface of the skin give rise to numerous odorous substances often of strong smell. This is the mixture which produces the natural odour of human skin.[7] In it are the lower fatty acids (C_4–C_{10}) and macrocyclic systems, steroids, lactones, etc. Although these have no smell of their own, they serve to fix the odour potential. The basic skin odour of *Homo sapiens* is also dependent on the individual or group, from the combined action of food last eaten and physical and psychological conditions.

The actual odour of the human being is the sum of the natural and acquired odour: two women may smell differently although they are identically dressed, washed and perfumed. Human beings find it very difficult to recognize this difference, but a dog has no difficulty in such detection. Body odour is thus a completely individual property of a human being just like fingerprints or the characteristic sound of the voice. The intensity of body odour differs from person to person, depending upon personal circumstances, environment, social and psychological conditions.

From these findings these are several obvious ways to reduce or control axillary odour: (a) reduce apocrine sweating in the axillae; (b) remove the secretions from both types of sweat glands as quickly as practicable; (c) impede bacterial growth; (d) absorb body odours.

Many workers have taken it for granted that human emanations contain pheromones,[8] which have sexually pleasing, winsome effects and reflect the psychological state of the individuals. Good human odour can, therefore, be of great importance.

Antiperspirants act by limiting the magnitude of sweat gland secretion delivered to the skin surface. Consequently, the mechanism of action may involve a decrease in sweat production at the glandular level, formation of a blockage or plug in the sweat duct, alteration of the sweat duct permeability to fluids (as in a perforated water hose), or any one of several other theories involving concepts such as electrophysiological potential along the sweat duct. The many theories presented to explain the action of antiperspirants can be found in several papers and review articles.[9–11]

Despite the preponderance of mechanistic theories, the detailed mechanism of axillary anhidrosis is relatively unknown.

Papa and Kligman[12] have produced histological evidence with human subjects that aluminium chloride alters the physiological state of sweat ducts. Methylene blue iontophoretic sweat pore patterns suggested increased permeability of the sweat duct to water while adhesive tape stripping of the stratum corneum did not abolish the anhidrotic state produced. Both sets of data suggest that poral closure or obstruction (plug formation) does not occur when anhidrosis is produced by aluminium chloride. Furthermore Lansdown[13] has produced evidence that high concentrations of aluminium chloride result in epidermal damage in mammalian skin and, in addition, decompose phospholipids. On the other hand, Papa and Kligman have also reported that known protein precipitants, such as formaldehyde, produce superficial obstructions in the eccrine duct. Anhidrosis produced by several known protein precipitants was abolished by stripping of the stratum corneum.[14]

Partial or complete anhidrosis produced by anticholinergic drugs does not proceed via a mechanism involving such anatomical and histological factors. Several authors have reported that various drugs exhibiting anticholinergic activity suppress the secretion of sweat by direct action on the secretory process of the sweat gland.[9,15] Such drugs appear to inhibit the action of acetylcholine in stimulating the product of perspiration.

The vehicle from which anticholinergic drugs are delivered plays a significant role in influencing efficacy, as these compounds must penetrate the stratum corneum and epidermis in order to reach the active site.[15,16]

The modern story of topical antiperspirants for the axilla began with Stillians's observation in 1916 that a 25 per cent solution of aluminium chloride hexahydrate in distilled water, dabbed gently on the armpit every second or third day, will reduce excessive sweating.[17]

To date, the most detailed comprehensive review of the subject of antiperspirants is that of Fiedler[18] which contains 411 references. It is interesting to note today that Stillians's formulation of 1916 remains one of the most effective antiperspirants in use. It is not toxic and it is not allergenic. Nonetheless, it enjoys only a limited sale today because (a) it is irritating to the skin of some users and (b) its high acidity is damaging to clothing. One of the first major developmental changes occurred in the 1940s when it was found that a less acidic complex salt of aluminium—aluminium chlorhydroxide—could be substituted for aluminium chloride. This reduced irritation to the skin and markedly lessened the damage to clothing. Unfortunately it also reduced the antiperspirant effect.

Antiperspirant Ingredients

Several metal salts have astringent properties including those of aluminium, zirconium, zinc, iron, chromium, lead, mercury and several rarer metals.[19] Various attempts have been made to find the most effective antiperspirants from the salts of these metals. Obviously many had to be discarded straight away on grounds of toxicity, and the field has been narrowed to mainly aluminium and zirconium.

Zirconium

In 1955 sodium zirconyl lactate was used in deodorant sticks containing an alcoholic soap gel. In 1956 cases of granulomatous eruptions in the axillae of users of these products had been reported.[20]

Despite this, a whole series of patents was published over the period 1955 to 1961[21–24] covering the antiperspirant use of zirconium salts, sometimes in combination with aluminium compounds and/or buffers such as urea or glycine.

The next major effort started in 1968 with a Bristol-Myers patent[25] zirconium-based complex which was claimed to be both effective as an antiperspirant and also non-irritant. Several other patents followed and a number of aerosol antiperspirants containing zirconium complexes were introduced in USA from 1972 to 1975. These were claimed to be much more efficient antiperspirants than the aluminium compounds being used in commercial antiperspirants.

In 1973 Gillette withdrew their aerosol zirconium-based products because of 'mild inflammatory reactions in monkeys'.

In 1975 the US Food and Drug Administration was reported to be looking at a possible ban for zirconium-based aerosol antiperspirants, following suggestions of long-term hazards with such products. In 1977 the official FDA ban came, by which time no products were left on sale.[26] The FDA stated that there was no reason to ban zirconium-containing antiperspirants directly applied to the skin and aluminium–zirconium complexes are in Category I ('safe and effective) for non-aerosol application at concentrations 20 per cent or less (on an anhydrous basis).

In 1978 three of the top four US roll-ons contained zirconium salts.[27]

Aluminium

Observed differences in the antiperspirant behaviour of aluminium chlorhydroxide and aluminium chloride have been attributed to differences in their interaction with skin.[28] The literature contains many references to methods for measuring the interactions of exogenous materials with skin. The electrical properties of skin have been used successfully as a means by which to describe this effect and it was thought appropriate to investigate this approach with respect to aluminium salts. Instrumentation and techniques for measuring the electrical impedance of excised epidermal membrane were developed. The effects of two aluminium salt antiperspirants on the impedance of guinea pig stratum corneum were measured. Aluminium chlorhydroxide reduced the impedance five times more than aluminium chloride. The results are in agreement with reported skin sorption behaviour for these salts and with their antiperspirant activities *in vivo*. The hypothesis that antiperspirancy is based, in part, on antiperspirant–skin interaction is supported by this study.

On 10 October 1978 the US Food and Drug Administration published the recommendations of the Advisory Review Panel on Over-the-Counter (OTC) Antiperspirant Drug Products as a proposed rule and expressed serious concern about the possible consequences of the inadvertent long-term inhalation of aerosolized antiperspirants. Aluminium-containing aerosol preparations have been placed in Category III by the OTC Panel (that is, insufficient available data to permit final classification at this time).[29]

While the nature of aluminium in many respects differs markedly from that of zirconium, particularly with its lack of potential antigenicity, its implication in possible granuloma formation under various conditions does not appear to be as clearly distinguishable.

Active Ingredients

The OTC Panel has developed a comprehensive and rigorous set of guidelines which is intended to serve as the standard protocol to be employed in chronic animal inhalation studies, designed to bring successfully-tested products into Category I classification (safe and effective).

Based upon the apparent awareness of the commercial availability of controlled-particle-size bulk aluminium antiperspirant powders intended for 'powder-in-oil' aerosol suspension use, the OTC Panel[30] has recommended that all marketed suspension-type aerosol systems in the USA should be formulated so that not less than 90 per cent of emitted particles are greater than 10 μm in diameter. Since the nose is considered to be the primary filter, there is virtually complete retention of particles in excess of 10 μm. Almost 50 per cent of 5 μm particles are retained, while almost all 1–2 μm particles penetrate beyond the nose. In general, particles below 5 μm are respirable and will penetrate into the lung.

Rubino *et al.*[31] describe the development of a controlled-particle aluminium chlorhydrate in which a minimum of 95 per cent of weight of the particles possess diameters of 10 μm larger.

Table 10.1 sets out the OTC Panel's categories of active ingredients.

Table 10.1 Categories of Active Ingredients—US FDA OTC Antiperspirant Review Panel
I = Permitted. II = Prohibited. III = Temporarily permitted.

Ingredient	Non-spray	Spray
Aluminium bromohydrate*	II (S,E)†	II (S,E)
Aluminium chlorhydrates	I	III (S)
Aluminium chloride (15% or less aqueous solutions)	I	III (S)
Aluminium chloride (alcoholic solutions)	II (S)	II (S)
Aluminium sulphate	III (S,E)	III (S,E)
Aluminium zirconium chlorhydrates	I	II (S)
Buffered aluminium sulphate	I	III (S)
Potassium aluminium sulphate	III (S,E)	III (S,E)
Sodium aluminium chlorhydroxy lactate	III (E)	III (S,E)

* This ingredient has never been marketed in the USA for a material extent or material time and, therefore, cannot receive general recognition of safety and effectiveness.
† (S) refers to safety considerations; (E) refers to effectiveness considerations.

Category I Ingredients

1. Aluminium chlorhydrates at concentrations of 25 per cent or less, calculated on an anhydrous basis, in topical (non-aerosol) formulations for underarm use only.
2. Aluminium zirconium chlorhydrates at concentrations of 20 per cent or less, calculated on an anhydrous basis, in topical (non-aerosol) formulations for underarm use only.
3. Aluminium chloride in 15 per cent concentration or less, calculated on the basis of the hexahydrate form, in aqueous solution and for topical (non-aerosol) formulations for underarm use only. Alcoholic solutions are Category II because of excessive irritation noted in submitted data.
4. Buffered aluminium sulphate as an 8 per cent concentration of aluminium sulphate plus 8 per cent sodium aluminium lactate for topical (non-aerosol) formulations for underarm use only.

Category III Ingredients

1. All Category I ingredients described above except for zirconium salts, when used in aerosol formulations. The reason for this is the lack of sufficient evidence for long-term inhalation safety data.
2. Sodium aluminium chlorhydroxy lactate. The Panel concluded that this ingredient is safe, but lacked sufficient evidence of efficacy to permit final classification at this time. Evidence of efficacy is required as for all other antiperspirants.
3. Aluminium sulphate. The Panel found that this ingredient lacked sufficient evidence for safety unless its acidity is first reduced with sodium aluminium lactate. Also, its efficacy data was deemed insufficient due to lack of human test data.
4. Potassium aluminium sulphate (potassium alum). This ingredient was placed in Category III due to insufficient evidence for both safety and efficacy.

Antiperspirant compositions employing a starch-coated aluminium derivative as the active agent from the subject of two patents issued to L'Oreal.[32,33] The active agent described in one of the patents comprises microcrystals of a derivative of aluminium coated with degraded starch which gels in water at a temperature lower than 100°C so as to provide an atomizable gel with a starch concentration ranging between 5 to 30 per cent by weight. The starch coating is to prevent the aluminium compound reacting with perfumes and to reduce irritation to users with sensitive skins.

It is claimed that all these disadvantages can be avoided by using particles of a hygroscopic aluminium compound which are coated with a polymer that will

dissolve in water at human body temperature sufficiently rapidly to permit quick release on contact with perspiration.

The second L'Oreal patent also employs a starch-coated aluminium compound but this time it is aimed at producing a delayed antiperspirant activity.

It is claimed that conventional micronized antiperspirant derivatives of aluminium dissolve immediately on contact with perspiration, resulting in antiperspirant activity of only a short duration; by the use of a coated antiperspirant agent, the active material is progressively released during contact with perspiration and hence is active over a longer period of time.

Unilever published a patent in 1977[34] describing the use of moisture-absorbent organic polymers for absorbing superficial skin moisture. They can be applied in the form of an aerosol spray and include certain polysaccharides, polypeptides, vinyl carboxy polymers and copolymers. The preferred polymers are characterized by their ability to absorb an amount of moisture which is greater than their own weight and up to ten times their own weight after deposition of the composition on to the skin.

Evaluation of Antiperspirants

Efficacy of Antiperspirants

Since a product with a sweat reduction of 20 per cent promises only a barely perceptible antiperspirant effect, antiperspirants that achieve less than 20 per cent effectiveness in hotroom tests are probably worthless in terms of consumer benefit. The OTC Antiperspirant Review Panel[35] in the USA has proposed a statistical criterion that provides a reasonable assurance that only antiperspirant products that are likely to give 20 per cent sweat reduction in at least half of the subjects will be marketed.

The range of effectiveness (average percentage sweat reduction) in laboratory hotroom tests of OTC antiperspirants submitted to the Antiperspirant Review Panel is given in Table 10.2. One general conclusion that appears valid is that antiperspirants in aerosol form are generally not as effective as the other dosage forms.

Table 10.2 Range of Average Sweat Reduction—US FDA OTC Antiperspirant Review Panel

Dosage form	Average reduction (%)
Aerosols	20–33
Creams	35–47
Roll-ons	14–70
Lotions	28–62
Liquids	15–54
Sticks	35–40

Many factors influence antiperspirant activity.[36] A minor variation in formula composition is one of the most critical and is one which is occasionally not recognized. A formula additive may seriously inhibit antiperspirant activity or, in certain circumstances, may definitely enhance activity. Additives that reduce formula irritancy without adversely affecting antiperspirant activity are in this latter class.

There is marked variation of response between subjects. For example, unformulated aluminium chloride reduces sweating of some subjects by 40–50 per cent but increases that of others by a similar amount. Subjects showing marked increases in sweating (properspirant activity) will usually show visible axillary irritation. Majors and Wild[36] have also observed, however, many instances of samples that were effective on most subjects but exhibited no antiperspirant effect—or even showed properspirant activity—on some subjects, with no visual evidence of axillary irritation. This would indicate that there is some factor other than inactivation of antiperspirant activity by formula components which results in certain subjects' specificity of decreased individual efficacy.

The efficacy of an antiperspirant is best defined as the percentage reduction in the rate of sweating in the axilla that may be achieved after a realistic application or series of applications of the test product. The preferred methods for the determination of efficacy are gravimetry or the use of electronic hygrometers.

Gravimetric Method.[36] Panellists are required to abstain from the use of all antiperspirant materials for at least one week prior to initiation of the study. Sweat collections are carried out in controlled temperature rooms at 100 ± 2°F and about 35 per cent relative humidity. Sweat collections are made during two successive 20-minute periods using tared absorbent pads. These collections are preceded by a 40-minute conditioning period in the hot room during which the panellists hold unweighed pads in their axillae. A ratio of sweat produced by the left and right axillae is determined in the series of controlled collections. The effect of antiperspirant materials on the perspiration rate of each individual is determined by comparing the post-treatment ratio with the subject's average control ratio. For each individual the percentage change is calculated as

$$\text{reduction (\%) in sweat rate} = \frac{\text{post-treatment ratio}}{\text{average control ratio}} \times 100$$

Hygrometry. The most accurate methods available are those using electronic hygrometers. A cup is attached to the skin and the water from the enclosed area is evaporated by a constant stream of dry gas. The water content of this gas stream is monitored and the sweat rate is calculated.

Because the cell used to cover the skin is not very large and only encloses a small area in the axilla, the positioning of this probe is critical. Unless the cells are replaced in exactly the same position for each experimental session the difference in sweating of the different sites can be larger than any changes induced by the use of the antiperspirant products.

The forearm is probably a more suitable application site because (a) the even distribution of glands means that the positioning of the cell on the skin is not so critical and (b) the reflexes affecting sweating unilaterally are not so pronounced in the forearms or can be avoided completely by using two sites on the same forearm.

Mechanism of Deodorants and Deodorant Ingredients

Since axillary odour is largely produced by the action of bacteria on nutrients present in apocrine secretion, any compound which inhibits the growth of those micro-organisms found in the axillae will, in theory, exhibit deodorant properties. Antibacterial agents reported in the literature or employed by cosmetic and toiletry manufacturers include quaternary ammonium compounds such as benzethonium chloride (di-isobutyl phenoxyethoxy-ethyl dimethyl benzyl ammonium chloride monohydrate), cationic compounds such as chlorhexidine acetate (1,6-di-(N-*p*-chlorophenyldiguanido)hexane acetate and triclosan (2,4,4'-trichloro-2'-hydroxydiphenyl ether).

Before World War II cresols were the most popular bacteriostats. However, their objectionable odour limited their application. In 1941 researchers at Givaudan Corporation discovered that a halogenated bisphenol, hexachlorophene, exhibited bacteriostatic qualities when incorporated in soap. In mid-1971 the FDA issued a report that brain lesions in test animals could be produced by feeding high dosages of hexachlorophene (HCP). The FDA took its final position on hexachlorophene on 22 September 1972. This ruling completely banned the use of hexachlorophene in all non-prescription products. The major impact of this ruling was felt by Armour-Dial, the manufacturer of 'Dial' soap. Armour-Dial announced immediately that within one week it would change the 'Dial' soap formulation from 0·75 per cent HCP plus 0·75 per cent trichlorocarbanilide (TCC) to 1·5 per cent TCC alone.

A UK patent[37] relates to extended efficacy in use of hexamethylenetetramine which was previously utilized as a urinary antiseptic. An example of a deodorant composition is as follows:

	(1) *per cent*
Hexamethylenetetramine	14–20
Zinc oxide	16–23
Starch	16–23
Petroleum jelly	38–43
Perfume	0·5–1·2

The effectiveness of this deodorant is said not to decrease within 7–15 days.

The use of sodium bicarbonate (baking soda) as a deodorant has been known for many years.[38] Sodium bicarbonate is an acid salt which can act chemically as either a mild alkali or a mild acid. Underarm odours are largely caused by volatile acidic compounds which are absorbed by baking soda to form stable odourless salts. In 1975 aerosol products appeared in the USA containing baking

soda and a patent specification was issued by Colgate-Palmolive[39] on aerosol compositions containing this material.

Metallic salts of ricinoleic acid,[40] particularly those of zinc and of the elements close to zinc in the periodic table, show a marked reactivity toward low molecular organic compounds with functional groups containing amino nitrogen and mercapto sulphur. This results in a deodorizing effect which can be intensified by adding small quantities of other derivatives of polyhydroxy fatty acids or resinic acids. A sensorial test does not reveal to any degree this deodorizing effect in the case of allied derivatives of other fatty acids.

L'Oreal published a patent[41] on deodorant compositions based on vegetable extracts, and after extensive investigations located the desired activity in the *Ungulina* species of fungus of the *Polyporaceae* family. The invention provides a composition suitable for application to the human body which comprises an extract from at least one fungus of the *Ungulina* species, a compatible vehicle and a perfume, the extract containing argariac acid. *Ungulina officinalis* is a parasitic wood-infesting fungus of larch trees, found mainly in alpine regions of Russia and Siberia.

Kabara[42] describes structure–function relationships of surfactants as antimicrobial agents. Nonionic surfactants, which in the past were considered not to have antimicrobial activity, were shown to be active when the monoesters were formed from lauric acid.

Ethyl alcohol, used as a vehicle in deodorant products, is also an active antibacterial agent.[43]

The antimicrobial properties of essential oils have been known for half a century. An extensive review and bibliography of the publications in this field up to 1955 was published by Cade.[44] These studies show that various essential oils exhibit significant antibacterial effect. The considerable variation in test results can be attributed to the fact that these are natural products in many cases; the variety of organisms and test methods employed also contribute, to a large extent, to aberration in results. An essential oil can vary considerably in its chemical composition, thus producing a corresponding lack of uniformity in antimicrobial activity. Some essential oils, such as thyme and clove, consistently show good antibacterial activity which is generally attributable to their high phenolic content, namely thymol and eugenol.

Kellner and Kober examined the antibacterial action of 175 oils against nine organisms and classified 21 of the most active oils according to chemical composition.[45] Terpenes were also found to have good antibacterial activity. Maruzella[46] conducted extensive investigations of the antibacterial and antifungal properties of essential oils, perfumes, and aromatic chemicals. He reported a high incidence of activity among these materials both as contact and vapour phase antimicrobial agents.

Assessment of Deodorants

In the case of deodorants, the techniques of assessment are relatively straightforward: conventional microbiological methods of analysing microbial content in properly designed experiments will supply data concerning the efficacy of deodorant compounds and products both *in vitro* and *in vivo*. The ultimate test,

however, for any finished cosmetic deodorant product will involve well designed axillary sniff studies.[47] Although this may appear to be a primitive technique, it is extremely well adapted to a consumer product; for a useful account of these techniques see Rothwell.[48] Final product attributes are a function of the total formula in which the perfume plays a significant role. In the final analysis, it is the well trained nose capable of relating to consumer perception of odour that will aid the determination of the ultimate success or failure of a deodorant product.

Product Formulation—Antiperspirants

Aerosols

Powder-in-oil suspension aerosol antiperspirants using micronized powdered aluminium chlorhydrate and containing 3–4 per cent of active ingredients suspended in an oil base appeared in the USA in the mid-1960s. They have become by far the most preferred applicator type for antiperspirants.

Many combinations of raw materials are available for the formulation of aerosol antiperspirants and their selection must be carefully considered, since the surface chemistry of the system can affect sedimentation and dispersion characteristics of the formula.[49] In addition, formulations must provide maximum antiperspirant and deodorant effectiveness, maximum safety, cosmetic elegance and minimum staining.

A typical powder-in-oil formulation is:

	(2)
	per cent
Aluminium chlorhydrate (micronized)	4·50
Isopropyl myristate	3·70
Fumed silica	0·15
Perfume	*q.s.*
Propellants 11/12 (65:35)	to 100.00

The emollient or carrier for the aluminium chlorhydrate is used to produce a smooth feel on the skin and to help the powder to adhere. Commonly an ester such as isopropyl myristate is used although some products contain volatile silicones to reduce staining of clothes.

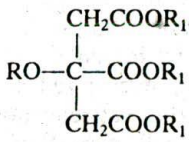
A suspending agent is added to prevent agglomeration of the aluminium chlorhydrate which could lead to valve blockage and leakage. Typical suspending agents are silica and 'Bentone' derivatives. Fumed silica has an extremely fine particle size and forms a coating over the powder particles to prevent the development of hard caking. Floyd[50] has reviewed the effects of montmorillonite clays and silicas on the rheological properties of antiperspirants in aerosol and other product forms.

Aerosols have been under continuing attack by environmentalists, particularly in the USA, because of the 'ozone' depletion theory. It is believed by some that fluorocarbon propellants react with and damage the ozone layer of the atmosphere. A major controversy now rages as to the truth behind the ozone depletion problem, but in the USA and FDA ruled that aerosols for non-essential

uses containing fluorocarbons could not enter the market from April 1979 onward. In the USA aerosol antiperspirants and deodorants are now butane propelled.

Staining of Clothing by Aerosol Antiperspirants. Aerosol antiperspirant compositions in which the astringent material, for example aluminium chlorhydroxide, is dispensed as a solid suspended in an anhydrous hydrophobic liquid vehicle such as mineral soil, isopropyl myristate or isopropyl palmitate have been widely marketed. Although such compositions are effective in reducing perspiration they have a tendency to impart stains to clothing which remain after laundering.

In a patent by Gillette in 1974[51] it was stated that staining due to aerosol compositions could be substantially reduced by using as the liquid vehicle an ester which is miscible with the propellant and which is selected from the group represented by the formula



where R is a hydrogen atom or 2- to 3-carbon acyl group. Examples of compounds include triethyl citrate and acetyl triethyl citrate.

The effectiveness of these esters in reducing staining was demonstrated *in vivo* with about 100 males who were given coded cans of antiperspirants containing parallel triethyl citrate and isopropyl palmitate formulations and new cotton T-shirts. They were instructed to use one product under the right axilla only and the other under the left axilla only. The T-shirt was to be worn for at least four cycles of home laundry. After four weeks, the T-shirts were collected and evaluated. The T-shirt underarm areas in contact with the axilla under which triethyl citrate was used consistently showed substantially less staining than that under which isopropyl palmitate had been used. The confidence level of this observation was greater than 99·5 per cent.

A patent was published by Union Carbide in 1977[52] on the use of volatile cyclic silicone compounds which can be used in place of isopropyl myristate or other emollients commonly used in aerosol antiperspirants to reduce billowing (or clouding) effectively without staining clothing and which impart substantially reduced oiliness to the skin.

Several patents concerned with staining have been granted to Unilever Ltd.[53–55] In one of these it is claimed that a substantial reduction in the level of staining on clothing in repeated contact with antiperspirants can be achieved by incorporating into the antiperspirant composition certain polyalkylene glycols. The invention describes a non-staining aerosol antiperspirant composition of the powder-suspension type containing a colourless water-miscible polyalkylene glycol (such as polypropylene glycol and derivatives) in which a proportion of the hydroxyl groups of the glycols are butylated. The latter substances are supplied by Union Carbide Chemicals Co. under the proprietary names 'Ucon HB' and

'Ucon H'. The term 'polyalkylene glycol' also includes the block copolymers of ethylene oxide and propylene oxide which are supplied by the Wyandotte Chemicals Corporation under the proprietary name 'Pluronic'. A typical formulation described in the patent is as follows:

	(3) *per cent*
Aluminium chlorhydrate	3·50
Fumed silica	0·50
Ucon 50-HB-660	4·77
Pluronic L64D	1·50
Perfume	0·38
Propellants 11/12 (70:30)	to 100

Antiperspirant Sticks

The sodium aluminium chlorhydroxy lactate soap or cologne sticks have been available for several decades now and have often been called antiperspirants. In reality, however, they are deodorants since their efficacy is in the range of only 8–12 per cent sweat reduction. Within the last few years true antiperspirant sticks, utilizing as the active ingredient either the aluminium chlorhydrate propylene glycol complex or micronized aluminium chlorhydrate, have been introduced. These produce a sweat reduction of the order of 40 per cent.

The antiperspirant stick usually consists of a wax-like matrix which serves as a carrier for aluminium chlorhydrate powder and volatile silicone. A low-melting matrix and a high-boiling volatile silicone are necessary in order to conserve the latter during processing. For this reason stearyl alcohol is preferred over stearic acid because of its lower melting point (58·5°C vs 69·9°C).

Typical formulations are as follows:

	(4) *per cent*	(5) *per cent*
*Volatile silicone 7158	46	46
Aluminium chlorhydrate powder	20	20
Stearyl alcohol	24	24
Polyethylene glycol distearate 6000	6	6
*Carbowax PEG 1000	—	2
*Carbowax PEG 1540	4	2

*Union Carbide

Procedure: Heat the stearyl alcohol, Carbowax PEG 1000 and 1540 and polyethylene glycol distearate 6000 to 80°C. When melted, add the aluminium chlorhydrate and mix thoroughly. Cool to 70°C and rapidly mix in the volatile silicone 7158. When mixing is complete, pour the mixture into a stick container. Allow the mixture to cool undisturbed for 24 hours.

Dry compressed antiperspirant sticks using isostatic compaction of aluminium chlorhydrate and microcrystalline cellulose powders have been developed by the FMC Corporation [56]

Dry antiperspirant stick	(6) *per cent*
Powder phase	
Avicel PH-105 (FMC)	52·35
Italian talc	14·30
Aluminium chlorhydrate, Ultrafine (Reheis)	19·00
Dri-Flo Starch 4951 (National Starch)	7·30
Zinc stearate	1·90
Liquid phase	
Volatile silicone 7207 (Union Carbide)	4·80
Isopropylan 33 (Robinson-Wagner)	0·10
Perfume	0·25

Procedure: Blend the powder materials in a V-shell blender for 10 minutes, add the liquid phase and mix via intensifier bar for 5 minutes. Press the powder blend at 2000 psi (14 MPa) in a rigid die.

Avicel microcystalline cellulose is a pure spray-dried material which provides simple binder phase of active astringents.

The advantages of this type of stick are said to be:
(a) high levels of perceived antiperspirancy;
(b) smooth dry application;
(c) no staining or corrosive effect on fabrics.

Antiperspirant Creams

A US patent[57] describes anhydrous antiperspirant creams. While oil-in-water emulsions provide a convenient vehicle for storing and delivering antiperspirant actives, compositions of this type tend to produce an undesirable wet, cold and/or sticky sensation when they are applied to and rubbed into the skin. This can be minimized somewhat by utilizing compositions in anhydrous form. An example is as follows:

	(7) *per cent*
Isopropyl myristate	32·0
Bentone 38 (thickening/suspending agent)	7·0
Ethyl alcohol (gel-promoting agent)	3·0
Zirconium hydroxychloride/aluminium chlorhydroxide/glycine complex	47·0
Silicone (antisyneresis agent)	10·0
Perfume	1·0

This is a substantially anhydrous antiperspirant composition in the form of a cream and is resistant to syneresis.

A normal oil-in-water cream antiperspirant formulation[58] is:

		(8) *parts by weight*
A	* Neo-Fat 18–55	10·6
	Mineral oil	1·0
	Beeswax	1·0
	Glycervl monostearate (pure)	6·4

		parts by weight
B	† Chlorhydrol (50% solution of aluminium chlorhydrate)	32·0
	Perfume	*q.s.*
C	Propylene glycol	5·0
	Sodium lauryl sulphate	1·3
	De-ionized water	to 100·0

* Armak Co., Chicago, USA.
† Reheis Chemical Co., Phoenix, USA.

Procedure: Heat A to 70°–80°C. Add C with agitation and cool to 35°–40°C. Add B and mix thoroughly.

Roll-on Antiperspirants

Roll-on antiperspirants have been on the market for many years. They are generally either emulsion products or aqueous alcoholic solutions thickened with cellulose gums. The aqueous alcoholic products generally dry quicker and are less sticky than the emulsion products. The viscosity of the final product is important to avoid leakage around the roll-ball.

In the following emulsion formulation (*ex* Reheis Chemical Co., USA) magnesium aluminium silicate is used as a thickening agent and emulsion stabilizer and glyceryl monostearate acts as an additional thickening agent and opacifier. The volatile silicone reduces the sticking of the roll-ball due to the drying out of the aluminium chlorohydrate.

		(9) *per cent*
A	Magnesium aluminium silicate	1·0
	De-ionized water	49·0
B	Glyceryl monostearate (acid stable)	8·0
C	Aluminium chlorhydrate (50% soln.)	40·0
D	Volatile silicone	2·0
E	Fragrance	*q.s.*

Procedure: Add magnesium aluminium silicate to water slowly, agitating continually until smooth, and heat to 70°C. Heat B to 75°C and add to 1; mix until temperature has fallen to 50°C. Heat C to 50°C and add to 2; mix until product has reached room temperature. Add D and E and stir for 15 minutes.

	Aqueous–alcoholic roll-on	(10) *per cent*
A	De-ionized water	29·10
B	Propylene glycol	4·00
	*Natrosol 250H (hydroxyethyl cellulose)	0·40
C	Aluminium chlorhydrate (50% soln.)	40·00
D	Alcohol 99% v/v	25·00
	Nonyl phenol ethoxylate (9 mol)	1·00
	Perfume	0·50

* Hercules Powder Co.

Procedure: Heat the water (A) to 70°C. Disperse the Natrosol in the propylene glycol and add this mixture (B) to the water with good agitation. Mix well until the Natrosol is fully hydrated. Add the aluminium chlorhydrate solution. Cool the batch to 30°C. Add D slowly with good agitation.

In this formulation the propylene glycol reduces crystallization of the aluminium salt on the roll-ball and the nonyl phenol ethoxylate is added to solubilize the perfume in the final preparation.

Product Formulation—Deodorants

Deodorant Soaps

The toilet soap market is one of major importance in all countries. The two largest deodorant soap brands worldwide are Armour-Dial's 'Dial', the leading US soap, and Unilever's 'Rexona', which is marketed in most of Europe.

In the USA deodorant soaps are classified as 'drugs'. When reviewing the use of antimicrobial agents used in soaps, the FDA's OTC advisory panel cited a series of studies[59] to support the position that these topical antimicrobials could lead to shifts in the microbial flora, placing the user at risk due to an overgrowth of Gram-negative micro-organisms. Not to be ignored, however, is the safety record of billions of antimicrobial soap bars sold in the USA during the last two decades. No significant medical problems have been reported, and there is no evidence to demonstrate an ecological shift in the skin flora due to the routine use of antimicrobial formulation in deodorant soap and similar products.

The most frequently used antimicrobial agents in soaps at the present time are trichlocarban (TCC), cloflucarban (CF_3) and triclosan (DP300). Prior to their ban, hexachlorophene (G11) and tribromsalan (TBS) occupied the key spots in this application. All but triclosan are active only against Gram-positive organisms when in the presence of soap; triclosan is active against both Gram-positive and many Gram-negative organisms.

Deodorant Sticks

Sodium stearate stick deodorants have been on the market for several years.[60] A typical formulation is given in example 11.

	(11) *per cent*
Sodium stearate	8·0
Ethyl alcohol	74·8
Propylene glycol	10·0
Isopropyl myristate	5·0
Triclosan	0·2
Perfume	2·0

Procedure: Slurry the soap in the cold with organic solvents and triclosan and then heat to 60°–75°C. Stir the mass while hot until clear. Add fragrance and colour as desired at 5°–8°C above the set point of the stick. When it is uniform, pour the soap solution into moulds and allow to cool. Sodium stearate can be prepared *in situ* but critical control is required to avoid excess alkali or fatty acid.

To avoid shrinkage which can occur with alcoholic sticks, particularly if the packaging is poor, non-alcoholic deodorant sticks can be prepared as follows (example 12).

	(12) *per cent*
Sodium stearate	8·0
Propylene glycol	10·0
Perfume	1·0
Coconut diethanolamide	5·0
PPG-3-myristyl ether	68·8
Triclosan	0·2
Water	7·0

The preparation is similar to that described for the alcoholic stick.

Aerosol Deodorants

Aerosol deodorants are based on alcoholic solutions of a bactericide. In some cases a product called a 'deo-cologne' and used as a body spray is based solely on an alcoholic solution of a perfume compound. A typical formula for an aerosol deodorant is given in example 13. Lacquered monobloc aluminium or tinplate containers can be used.

	(13) *per cent*
Triclosan	0·05
Propylene glycol	2·00
Alcohol (99% v/v)	57·45
Perfume	0·50
Propellant 12	40·00

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