

Depilatories

Introduction

Preparations for the removal of unwanted hair have been known for thousands of years. Among them was rhusma, a mixture of quicklime and arsenical pyrites in a ratio of 1:2 used in ancient times by the dancing girls of the East. Before use this product was reduced to a powder and mixed with an aqueous alkali, possibly obtained from wood ashes; another preparation which was used for the same purpose was orpiment which is, essentially, arsenic trisulphide.

There is no record of any development work having been carried out on this subject during subsequent centuries. The attitude taken was that, if one used anything, one used pumice stone and did not talk about such things.

In modern times, however, a rapidly increasing interest in depilatories has been noticed, brought about by changes in fashions, clothing and social customs.

While the term 'depilatory' has been applied to any preparation designed for the removal of superfluous hair (in particular hair occurring on the face and legs, as well as in the axilla) without causing injury to the skin, a distinction must be drawn between the mechanical removal of hair by either plucking it with tweezers or by embedding it in an adherent material which can then be pulled away from the skin bringing the hair with it (a process referred to as epilation), destruction of hair by electrolysis, and the removal of hair after it has been sufficiently degraded by chemical means.

Extensively bibliographed reviews of the historical development and technology of depilatories have been published.¹⁻⁴

Epilation

Epilation has some following because the effect may be slightly longer lasting since, if the epilated hairs take with them the hair bulbs or the hair papillae, there may be a relatively long pause before the hair starts growing in the follicle and reaches the surface of the skin. It is, however, by no means painless and can often cause serious skin damage and subsequent infection, and is therefore frowned upon by doctors.

For many years epilatory preparations were based on mixtures consisting essentially of rosin and beeswax, modified in some instances by the addition of mineral oil and/or waxes. The following examples are illustrative:^{5,6}

	(1)
	<i>per cent</i>
Rosin	75.0
Beeswax	25.0

	(2) per cent
Light coloured rosin	52.0
Yellow beeswax	25.0
Paraffin wax	17.0
Petrolatum	5.0
Perfume	1.0

Procedure: Melt the rosin and waxes, mix and add the petrolatum, then, when the temperature drops to about 60°C, add the perfume and pour the melted mass into suitable moulds. When this wax is used it is melted and painted over the surface to be dehaired.

In addition to rosin and waxes, mineral or vegetable oil may be included (for example at a level of about 15 per cent). Camphor is often included for its cooling effect which reduces the discomfort experienced when the hair is pulled off. A local anaesthetic, for example benzocaine, to enhance this effect and an antibacterial compound will reduce the chance of infecting the skin after damage or exposure.

There has been no dramatic development of a 'painless' epilatory in the industry. Such developments as have taken place have been concerned with modifications in the method of application, such as the provision of a flexible backing strip, and also the provision of a preparation that does not require melting prior to use but can be applied cold, the preparation being based upon a mixture of glucose and zinc oxide.⁷ The use of a 'rubber solution', in which the solvent evaporates and the rubber film is stripped off, is covered in a US patent.⁸

Several more recent patents describe epilating compositions. A French patent⁹ describes depilating waxes in strip form and quotes the following composition as an example:

	(3) parts
Rosin	1700
Vegetable oil	900
Triethanolamine	100
Benzoin	10
Balsam Tolu	10
Lemongrass bouquet	5
Butyl <i>p</i> -aminobenzoate	10
Alcohol	5

The wax is spread on the rough side of a strip of kraft paper, the smooth side of which is silicone-treated. Other patents describe the use of fresh lemon juice in a syrup-type epilatory paste;¹⁰ a solution of cold water-soluble dextrin in glycerin;¹¹ an epilatory tape impregnated with a tacky substance;¹² a film-forming solution which is applied to skin, allowed to dry and peeled off;¹³ a low-melting depilatory wax composition.¹⁴

Maxwell-Hudson¹⁵ has described a 'home-made' depilating formula based on caramelized sugar, lemon juice and glycerin.

Gallant¹⁶ has given a detailed account of professional techniques for depilatory waxing treatments.

Electrolysis

The mechanical methods mentioned above are temporary and often only relatively effective since the papillae and hair bulbs are not always removed and hair soon-reappears. The most effective method of depilation is undoubtedly electrolysis which entails inserting a needle into the hair follicle and complete destruction of the hair root by means of a weak DC current. This method is practised in beauty salons and by some dermatologists but is expensive and time-consuming since every hair must be treated individually, and even a competent operator can only deal with 25-100 hairs per sitting.

Chemical Depilation

The term 'depilatory' as used nowadays refers to preparations intended for the chemical breakdown of superfluous hair without injury to the skin.

The advantage of such preparations is that they avoid any danger of cutting or abrading the skin in regions such as the underarms, where it is difficult to see the area clearly and even more difficult to guide a razor over the complicated contours. There is also a widespread belief that shaving increases the rate of hair growth or the coarseness of the hair. Although these beliefs are unfounded in fact, chemical depilatories have the apparent advantage that they discourage the regrowth of hair if they are applied regularly. There seems to be no scientific explanation for this, but possibly it arises from a gradual removal of keratinous debris from the mouth of the hair follicle, which allows removal of the hair at a deeper level.

Since the hair shaft is of similar composition to the skin (both are derived from keratin), a small degree of local damage may occur as the result of applying such preparations, particularly if the depilatory is kept in contact with the skin for any length of time and the pH is sufficiently high, when the horny layer of the skin will also be attacked.

Provided that the skin is reasonably healthy, that the time of application of the depilatory is not too long, and that this is correctly formulated, very little if any damage will result. In formulating depilatory preparations, therefore, care should be taken to ensure that they will react with the hair preferentially and that their effects will be sufficiently rapid to cause disintegration of the hair before causing any damage to the underlying and surrounding skin.

With the above aims in mind, the desirable requirements of a depilatory may be defined as follows:

- (1) Non-toxic and non-irritant to the skin.
- (2) Efficient in action, removing hair rapidly, preferably in 4-6 minutes.
- (3) Preferably odourless.
- (4) Stable on storage.
- (5) Harmless to clothing.
- (6) Preferably cosmetically elegant.

In line with the requirement for a rapid depilation, depilatory preparations usually contain as their active component an alkaline reducing agent. The latter will cause the hair fibres to swell and produce a cleavage of the cystine bridges between adjacent polypeptide chains as a preliminary to the complete degradation of the hair

Sulphides

The use of sulphides has been known, as pointed out at the beginning of this chapter, for a very long time: however, it was not until 1885 that, in the United States, the first patent was taken out for the use of barium polysulphide for removing hair. In April 1891, the use of the monosulphide, polysulphide and sulphhydrate of strontium for the same purpose was patented.¹⁷ These preparations were, however, mixtures rather than creams, the first depilatory in cream form being developed in 1921.

Compositions based on alkali and alkaline earth sulphides are capable of producing rapid depilation, particularly if used together with a suspension of lime.

The alkali sulphides such as sodium sulphide were, however, found to be too drastic in action. Their depilatory action is linked to their hydrolysis and the formation of sulphhydrates and sodium hydroxide. The latter acts as a primary irritant and will produce erythema. Even a 2 per cent aqueous solution of sodium sulphide will have a pH of 12. Although it will disintegrate hair within 6-7 minutes, it will simultaneously damage the stratum corneum. It is, therefore, no longer used in depilatory preparations on the market.

Strontium sulphide is a much milder depilatory, but must be used at a higher concentration than sodium sulphide to produce an equivalent dehairing action. Preparations containing strontium sulphide, although largely replaced by those based on thioglycollates, are still available. They are very effective and work within 3-5 minutes after application.

While some people are sensitive to such preparations (as indeed are some people to shaving soaps), the products appear to be innocuous if used according to the directions of the manufacturer. The main reason for their loss in popularity is that, in common with other sulphides, they generate the odour of hydrogen sulphide on application (and not infrequently on storage). This odour is most intense when the product is washed off, owing to hydrolysis of the sulphide. It is advisable, therefore, to remove the bulk of the product with a spatula before washing, and it is the usual practice to include such a spatula, made of wood or plastic, in the pack. It also serves to apply the product in the necessary thick layer (1-2 mm). Under no circumstances should the final washing be omitted.

In addition to the active agent, a depilatory preparation may contain a humectant such as glycerin or sorbitol. A thickening agent, for example methyl cellulose, may sometimes be incorporated, so as to thicken the solution sufficiently to allow it to remain in contact with the hair as long as necessary.

For a sulphide depilatory, the following formula will be found effective:

	(4) per cent
Strontium sulphide	20.0
Talc	20.0
Methylcellulose	3.0
Glycerin	15.0
Water	42.0

This may also be prepared using an emulsion base for smoothness and stability.

The formulation of depilatories depends upon very careful adherence to detail; slight departures from formulation in the process of manufacturing can produce remarkable differences between the efficacies of different batches of supposedly the same product. For this reason any formulation can be little more than a general guide.

Despite their disadvantages, sulphide-based depilatories are preferred by many black-skinned men for removing facial hair because of their comparatively rapid action. This subject is covered later in this chapter.

Stannites

In the 1930s considerable attention was devoted to 'soluble stannites'. For example, the use of sodium stannite as a preferred salt of tin with Rochelle salt as a stabilizer was covered in a US patent¹⁸ published in 1933.

Another US patent¹⁹ drew attention to the fact that, while the stannites have no appreciable odour, they suffer from instability, forming stannates in the presence of water. This patent proposed the use as stabilizers of water-soluble organic compounds having three or more carbinol hydroxy groups, or three hydroxyl groups other than those in a carboxyl group and also soluble silicates; specific examples are triethanolamine, dextrine, sugars and—in the case of the silicates—potassium or sodium metasilicate. A British patent²⁰ describes the addition of aqueous stannous chloride to aqueous sodium hydroxide containing sodium silicate to give a solution having pH less than 12.6 (12.3). A French patent²¹ also claims a method for the preparation of a stable stannite. However, the stabilizers recommended in these patents were not found to be effective and did not produce stable preparations.

Substituted Mercaptans

The majority of depilatories available today are substituted mercaptans which are used in the presence of alkaline reacting materials, for example calcium thioglycollate, in conjunction with calcium hydroxide. These preparations possess less odour than the sulphide type, but take longer to act. They are safer on the skin than sulphides, and can therefore be used on the face—an area where superfluous hair can cause great distress and where women have a strong psychological aversion to using a razor. In general, thioglycollate preparations are more attractive than the sulphide type. However, their slowness in attacking the coarse resistant hair of the underarm has left a market open for sulphide depilatories used for this purpose only.

It is often said that depilatories can be used for smoothing the legs, but so much of the product is required to cover each leg that it becomes uneconomic for most users. In any case, the legs are easy to shave.

Thioglycollates

Thioglycollate-based preparations are non-toxic and stable at concentrations at which they are used, that is between 2.5 and 4 per cent. At concentrations of less than 2 per cent w/w they act too slowly to be of any use, while nothing will be gained in terms of effectiveness if their concentration is raised above 4 per cent. At the concentrations at which they are used, they may produce depilation in 5–15 minutes, this again depending on the pH of the preparation. This should

not be less than pH 10.0 and should preferably be about pH 12.5 to produce depilation within a fairly short time and without irritating the skin.

The use of thioglycollate in depilatories stemmed from the research conducted by Turley and Windus²² and was heralded by patents which were issued in France,²³ Britain²⁴ and the United States.²⁵

The British patent²⁴ granted to Bohemen covered the use of calcium thioglycollate in a cream base. The base had the formula:

	(5) per cent
Stearyl alcohol	9.0
Sulphonated stearyl alcohol	1.0
Water	90.0

Sixty-six parts of the above base were mixed with 10 parts of hydrated lime and 4 parts of 90 per cent thioglycollic acid, whereupon the cream liquefied and was stiffened by the addition of at least 20 parts of precipitated chalk.

A US patent²⁶ issued in 1944 to Evans and McDonough covered the use of substituted mercaptans (thioglycollic acid) in conjunction with an alkaline-reacting material and a perfume. Substituted mercaptans having polar groupings are preferred. The patentees claim that in order to obtain a desirable depilating action, the depilating agent must conform to certain general rules:

- (1) pH value should be between pH 9.0 and pH 12.5.
- (2) Concentration of mercaptans should be between 0.1 and 1.5 mol per litre.
- (3) The alkaline ingredient must have an ionization constant greater than 2×10^{-5} .
- (4) In order to prevent skin damage, it is desirable that the concentration of the alkaline material in solution be not greater than twice the equivalent concentration of the mercaptans.
- (5) Paste form is the most satisfactory.
- (6) Natural gums are used to give stable formulations.

Basic formulae for preparing cream, semi-fluid and powder depilatories have been offered by Evans Chemetics:²⁷

Depilatory cream	(6) per cent
Evanol	6.5
Calcium thioglycollate	5.4
Calcium hydroxide	7.0
Duonol WA paste	0.02
Sodium silicate '0'	3.43
Perfume	q.s.
Distilled water	to 100.0

Procedure: Heat the water to 70°C. With stirring add the Duonol and Evanol; continue stirring until melted and dispersed. Discontinue heating and cool/stir to room temperature. Add the calcium hydroxide and perfume. Add the calcium thioglycollate and stir until uniform.

<i>Semi-fluid depilatories</i>	(7)	(8)
	<i>per cent</i>	<i>per cent</i>
<i>Cream base</i>		
Distilled water	60.0	60.0
Cetyl alcohol	6.0	6.0
Brij 35	1.0	1.0
<i>Final product</i>		
Distilled water	17.3	17.2
Calcium thioglycollate	5.4	5.4
Calcium hydroxide	6.6	10.4
Strontium hydroxide	3.7	—
Perfume	<i>q.s.</i>	<i>q.s.</i>
Cream base (as above)	67.0	67.0

Procedure: Prepare the cream base at 70°C and allow to cool to room temperature. Add the calcium thioglycollate to the bulk of the water and mix well; add the calcium hydroxide slowly with stirring, followed by the strontium hydroxide and any remaining water. Combine the two parts and stir well, adding the perfume at this point.

<i>Powder depilatory</i>	(9)
	<i>per cent</i>
Calcium thioglycollate	20.0
Calcium hydroxide	23.1
Strontium hydroxide 8H ₂ O	8.9
Sodium lauryl sulphate powder	1.5
Cellosize QP.100M	1.0
Magnesium carbonate USP	45.2
Perfume	0.3

Procedure: Mix the calcium thioglycollate, calcium hydroxide, strontium hydroxide, sodium lauryl sulphate and Cellosize. Blend the perfume thoroughly with the magnesium carbonate. Add the latter to the former and blend thoroughly. (N.B. This formula contains a much higher level of thioglycollate than is permitted for sale with the EEC.)

The slower activity of thioglycollates has led to attempts to accelerate the depilatory action by incorporating substances which cause swelling of the hair fibres. Urea was considered for this purpose, but could not be used since it decomposes at the normal pH of depilatory preparations. Attempts were made, therefore, to find other compounds which could accelerate the rate of depilation in compositions containing mercaptans and which would remain stable at the pH at which these depilatory preparations are normally used.

In a L'Oreal patent,²⁸ melamine and dicyandiamide, or a mixture of these two compounds, were claimed to have an accelerating effect on depilation and it was proposed that they be used in depilatory compositions at levels ranging between 0.5 and 2 parts per part of (for example) thioglycollic or thiolactic acids or their calcium or strontium salts.

Other L'Oreal patents²⁹ suggest the use of lithium salts of thioglycollic and mercaptopropionic acids for improving the rate of depilation by virtue of their good solubility. The sodium and potassium salts are equally soluble but they are

irritant to the skin. The quicker action of the lithium salts also permits them to be used at a lower concentration and at a lower pH than the calcium and strontium salts, which in turn will reduce the risk of irritating the skin.

A series of patents³⁰ proposes the use of sodium metasilicate with thiourea as synergistic accelerators for calcium thioglycollate. Morillère *et al.*³¹ suggest the use of a blend of copolymers of N-vinyl lactam and a hemiester of an unsaturated dicarboxylic acid.

Another means of accelerating the rate of depilation is by increasing the temperature. Beecham workers³² have proposed a two-part product contained in a tube-within-a-tube; one part is anhydrous and contains calcium oxide, the other contains water. Upon extrusion the two parts mix and generate heat.

An anhydrous depilatory composition in stick form has been patented³³ which is claimed to form, on contact with wetted skin, a cream capable of complete depilation in less than 10 minutes without producing any offensive odours during that time. The stick comprises a depilating agent, a solid basic substance, a solid base and a perfume. The depilating agent is a thiol derivative, preferably calcium thioglycollate; it constitutes 10–35 per cent by weight of the composition. The solid basic substance is an alkaline earth metal hydroxide or carbonate, or a mixture of these two; it is used in sufficient amount to provide a pH of 10.5–12.5 in a saturated aqueous solution.

The function of the solid base is to protect the sensitive facial skin from possible irritation by the active ingredient and to confer emolliency. It consists of the following: (1) a sterol, preferably an unsaponifiable lanolin fraction; (2) a solid inert organic filler to provide hydrophilic and emollient properties and body, and to prevent the penetration of externally applied water. The filler, which will usually constitute up to 75 per cent by weight of the solid base, may include petrolatum, paraffin wax, microcrystalline wax, fatty alcohols, spermaceti, beeswax and others; (3) a nonionic polyalkenoxy-type water-in-oil emulsifier, to provide homogeneity to the final composition and to supplement the emollient and hydrophilic properties of the organic filler. Commercially available compounds representative of this class are Polychols, Solulan, Atlas products G-1441, G-1471 and ethoxylated lanolin derivatives such as Lanogel and Ethoxylan.

Unlike depilatory pastes containing thiol derivatives, which are inherently unstable because of the decomposition of their active agents in the presence of water and give rise to an offensive odour, the depilatory compositions described in the patent, being anhydrous, are claimed to be indefinitely stable.

Another series of patents³⁴ describes an emulsified depilatory containing a Kritchevsky-type alkanolamide condensate which, it is said, may stay in contact with the skin for extended periods without causing irritation or other side-effects.

Sliwinsky³⁵ has described an aerosol depilatory which is sprayed onto the skin and then expands to a foam; this is based upon calcium/sodium thioglycollate and Polawax (Croda). A product which behaves similarly has been patented by Webster;³⁶ this utilizes lithium/sodium thioglycollate, thiolactate or thioglycerol together with sodium lauryl ether sulphate. International Chemical Co. have also patented³⁷ an aerosol depilatory foam product.

The EEC Cosmetics Directive³⁸ and the UK Cosmetic Products Regulations 1978³⁹ limit the use of thioglycollic acid in depilatories to a maximum of 5 per cent with a pH value not to exceed 12.65.

Other 'Thio' Compounds

Thioglycollic acid is the most economical and effective active agent of this type. However French legislation prohibits this material for products for home use. Several alternative 'thio' compounds have been used successfully and notable among these are 2-mercaptopropionic (thiolactic) acid, 3-mercaptopropionic acid, and 3-mercaptopropane-1,2-diol (thioglycerol).

An aerosol gel depilatory based on strontium thiolactate has been described.⁴⁰ A Swiss patent⁴¹ claims a non-irritant, rapid-acting depilatory 'soap' bar:

	(10) per cent
Thiolactic acid	30.5
Urea-sorbitol complex	25.5
Strontium hydroxide	4.5
Calcium hydroxide	4.5
Sodium lauryl sulphate	35.0

A gelled depilatory based on thioglycerol with polyethyleneglycol ethers of fatty alcohols or alkylphenols has been described.⁴²

Bristol-Myers took out a patent⁴³ in which the active depilating agent is a molecular complex (1:1, 0.5:1, or 1:0.5) of thioglycerol with a nitrogen base of the Deriphat or Miranol type. These are said to be highly effective depilators at pH 8.5-10.5.

A US patent⁴⁴ claims the use of 1,4-dimercaptobutanediol and related compounds in which the hydroxyl groups are substituted by alternative polar groups.

Enzymes

Depilatory preparations based on the enzyme keratinase have also been developed which do not have the unpleasant odour of sulphide or even thioglycollate depilatories, and are non-irritant. However, they are not quite as effective. Keratinase was isolated from *Streptomyces fradiae* by Noval and Nickerson⁴⁵ and found to be capable of digesting keratin.

Keratinase is used in depilatory preparations in a purified form, buffered to a pH within the range of 7-8, with an activity of 200 k units per mg. The k unit is defined as the amount of enzyme which will digest wool keratin so as to produce an increase in optical density of 0.04 at 280 nm.

A paste depilatory described in an embodiment example of a patent granted to Mearl Corporation⁴⁶ contained 3.3 per cent w/w of keratinase (200 k units/mg).

Facial Depilatories for Black Skin

The special problems of the black-skinned male in removing facial hair have been described by Shevlin⁴⁷ and de la Guardia.⁴⁸

The facial hair of the black male is often curly and wiry. Shaving hairs leaves the exposed ends with sharp points and as the hairs regrow these sharp points can actually turn back onto and penetrate the skin, causing a clinical condition called *pseudofolliculitis barbae*. For this reason many black men will not shave but prefer to use a depilatory which not only gives a closer 'shave' but leaves the hair tip soft and blunt so that it does not puncture and re-enter the skin.

Conventional thioglycollate-based depilatories take 15–20 minutes to remove beard hair which is regarded as far too long. Effectiveness outweighs cosmetic elegance and the tendency is to use a powder depilatory which must be mixed with water before use but which effects adequate hair removal in 3–7 minutes.

In the USA the active ingredients commonly used in powder depilatories⁴⁸ are barium sulphide and calcium thioglycollate. The former is the most popular because of its effectiveness and despite its offensive odour. However, powders based on calcium thioglycollate are said to be gaining favour since they are less odorous and therefore more easily perfumed, though less effective.

It should be borne in mind, however, that in EEC countries barium salts are prohibited from use in cosmetics and that the upper limit for calcium thioglycollate (trihydrate) is 10 per cent (corresponding to 5 per cent thioglycollic acid).

The 'Ideal' Depilatory

The 'ideal' depilatory, one which would have no odour, would remove hair in about 1 minute, could be used regularly without any complaints of irritation; one that could replace the daily task of shaving has yet to be devised. When such a product arrives it will certainly have a market.

Some interesting avenues of exploration were opened up by studies on the depilating effect of certain unsaturated compounds.

Ritter and Carter⁴⁹ reported as follows:

... When commercial polymerization of chlorobutadiene was undertaken in an aqueous emulsion, some of the employees began to lose their hair after a few weeks or months. The loss of hair could be much reduced by frequent and complete change of the air in which they were working. The hair loss was predominantly on the scalp, and hair always grew again when the employees were transferred to other occupations. Microscopical examination of the hair showed that it came out at the root, a bulb being present at one end of each hair shaft, but there was no evidence of change in the shaft itself. A composite product containing various cyclic and short-chain polymers of chlorobutadiene was prepared: when two drops of this were placed on the back of a mouse or guinea pig, the area covered by the solution became completely denuded of hair in 4–10 days. In about 3 weeks hair was again visible over the denuded area and in 6 weeks it had completely regrown . . .

The interesting part of this observation is that previous developments have been in connection with preparations which are intended to swell the hair near the mouth of the follicle and reduce its tensile strength to an extent that allows it to be 'cork-screwed' away very readily. Since the hair and skin are both composed of keratin there is not a very wide margin between what will attack the

one and irritate the other. The above observation shows the possibility of a different method of attack: not damage to the hair (and skin) *per se*, but merely a detachment of the hair bulb from the hair follicle—such damage being, apparently, temporary since the hair grew again in from 3–6 weeks.

Another observation which could be of some relevance to the development of new depilatories was made by Flesch,⁵⁰ who found that squalene and a group of lipid-soluble unsaturated compounds (with $—C=C—$ groups) caused reversible complete baldness when applied to the skin of laboratory animals. These compounds include the synthetic dimers of chloroprene and certain esters of allyl alcohol, naturally occurring vitamin A, oleic and linoleic acids. Flesch postulated that the depilation is caused by the reaction between the $—C=C—$ bonds and the sulphhydryl group of epidermal protein. Although Flesch was not able to depilate human beings with any of these unsaturated depilatory agents, these findings suggested that human sebum may have an influence in hair growth.

Evaluation of Depilatory Efficacy

Yablonsky and Williams⁵¹ described a procedure for determining the efficacy of depilatories. It involves the measurement of the cross-sectional diameter and the length of a hair immersed in a solution of a depilatory, and observing the time of maximum hair swelling. Sigmoid curves are obtained when both the length and width of swelling hair are plotted against time. The slope maxima of these sigmoid curves may be used to define an index of depilatory effectiveness *in vitro*. No test results were given. In a later paper,⁵² Yablonsky describes a simplification of the method.

Elliot⁵³ designed a depilometer to simulate practical use conditions as closely as possible. In-use tests gave good correlation and rapid screening of formulation variables is possible using this technique.

Elliot found considerable variation in depilating times between individuals but in general leg hair is easier to remove than axillary hair, which is similar to head hair.

Table 11.1 Relative Efficacy of 'Thio' Compounds at 5 per cent Concentration, adjusted to pH 11.0–12.0

'Thio' compound	Average depilation time* (min)
2-Mercapto-ethanol	4.0
Thioglycerol	6.5
Thioglycollic acid	7.5
3-Mercaptopropionic acid	8.0
2-Mercaptopropionic acid	11.0
Thiodiglycol	15.0
Thiomalic acid	15.0

* Average of times for all alkalis used for neutralization. Some combinations were found to be more effective.

Various 'thio' compounds were studied together with the effect of different alkalis, pH values and concentration. Table 11.1 summarizes the relative efficacy of various 'thio' compounds at a concentration of 5 per cent with sufficient alkali to adjust the pH value to 11.0–12.0. Table 11.2 gives similar data found for different alkalis. Elliot showed convincingly that a concentration of 5 per cent 'thio' compound is sufficient; increased concentrations do not increase the speed of depilation appreciably.

An earlier L'Oreal patent²⁹ reported the results shown in Table 11.3.

Table 11.2 Relative Efficacy of Various Alkalis

Hydroxide	Average depilation time (min)
Sodium	5.7
Lithium	5.7
Potassium	6.5
Barium	6.5
Calcium	7.1
Strontium	8.3

Table 11.3 Depilatory Activity of Thioglycollic Acid and Thiolactic Acid Neutralized with Various Alkalis (mercapto-acid concentration 0.4M, pH 12.5)

Cation	Thioglycollic acid		Thiolactic acid	
	Depilation time (min)	Effect on skin	Depilation time (min)	Effect on skin
Calcium	7	0	10	0
Barium	12	0	7	0
Strontium	5	0	7	0
Sodium	4	+	5½	+
Potassium	3½	+	4	++
Lithium	3½	0	5	0

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Shaving Preparations

The typical man tends to regard the removal each day of 20 000–25 000 terminal hairs protruding 250–500 μm from the skin at angles of 30 to 60 degrees¹ and covering a facial area of 250 cm^2 , as something of a chore. To minimize the trauma of shaving, a wide range of preparations is now available that prepare the beard and face for shaving, increase speed and comfort during the shave and confer a feeling of well-being after shaving. The choice of shaving preparation is highly individualistic; however, it is generally recognized that different forms of beard preparation are required for 'wet' (razor blade) and 'dry' (electric razor) shaving. This results from the contrasting mechanisms of hair cutting, which can be inferred from the appearance of the ends of hairs cut by the two implements. The description of shaving preparations has therefore been divided into three sections: wet shaving preparations, dry shaving preparations and after-shave preparations.

WET SHAVING PREPARATIONS

Introduction

The main functional requirements of a wet shaving preparation are to soften the beard, to lubricate the passage of the razor over the face and to support the beard hair. In addition, the preparation should be non-irritating to the skin, should assist in removing shaving debris from the face, should be stable over a range of temperatures, resistant to rapid drying out and collapse, non-corrosive to the razor blade and easily rinsed from the razor and face. There is good evidence for the hair softening and lubrication functions of the shaving preparation, but little has been reported on the hair-supportive role.

Beard Softening

Beard softening results from changes in the mechanical properties of hair by absorption of water. Hair absorbs 31 per cent of its dry weight of water at 100 per cent relative humidity; the relationship between water absorption and relative humidity is non-linear and the swelling of hair is highly anisotropic.² The force required to cut water-saturated beard hair is about 65 per cent less than that for dry hair.³

The hydration of hair is accelerated by increases in temperature; however, views differ on the time taken to hydrate hair completely. This ranges from 2 minutes at room temperature, as measured by the force required to cut beard hair,³ through 2½ to 3 minutes at 49°C (120°F), as measured by creep of scalp hair extrapolated to the thicker beard hair,¹ to 6 minutes at 43°C (110°F) as measured by changes in the elasticity of hair.⁴

The established view on beard softening is based on measurements of the creep and elasticity of hair, supported by practical shaving tests. This suggests that the rate of softening of the beard can be increased by the addition of a wetting agent to the water, increasing the pH of the water and the removal of sebum from the hair. More recent work³ suggests that the force required to cut the hair is not reduced by the use of wetting agents, soap solutions or shaving creams below the value for water alone. Similarly, changing the pH over the range 4.0 to 9.1 and the presence of sebum on the hair do not influence the cutting force. The importance of the shaving preparation in beard softening clearly differs according to which set of results is accepted.

Skin Lubrication

There is little published work on the contribution of skin lubrication to the comfort, closeness and speed of wet shaving. Early work by Naylor⁵ on the coefficient of friction of plastic materials on skin indicated that friction was lower if the skin was dry, greasy or very wet, but higher if the skin was merely moist. Other work has shown that skin friction is reduced by surfactant solutions, mineral oils⁶ and silicone fluids.⁷ The force of friction on skin is not a linear function of the normal load^{7,8} as suggested by Amonton's law, the deviations being attributed to the elastic behaviour of skin.

The frictional force between a razor blade and facial skin has been measured using a razor with built-in strain gauges.⁹ The frictional properties of dry skin were shown to be higher than for wet skin although the absolute values vary for different areas of the face. The type of shaving preparation used does influence the frictional properties to the extent that it is possible to distinguish between different aerosol shaving foam formulations. It is generally found that the second stroke of the razor over a given part of the face yields a higher frictional force than the first stroke, presumably because the first stroke effectively removes most of the shaving preparation. Shavers apparently adjust the applied load on the razor according to the shaving preparation used; the lower the frictional force between the razor and skin, the higher is the applied load and the closer the resultant shave.

One can only speculate on the mechanism of lubrication by the shaving preparation since it depends on the load applied to the razor, the area of contact with the face, the velocity of the razor across the face and the viscosity of the preparation. At high loads per unit area and low shaving speeds, boundary lubrication is likely to predominate so that for a low coefficient of friction the shaving preparation should have a high viscosity and form a condensed film which interacts strongly with skin to preserve the integrity of the lubricant film. At low loads per unit area and high shaving speeds, hydrodynamic lubrication is likely to predominate. The viscosity of the shaving preparation should be high enough to give a film thickness sufficient to prevent asperity contact, but thereafter the viscosity should be as low as possible.

Beard Softening Cream

For many, washing the face with soap and water is an adequate pre-shave preparation for the attainment of a satisfactory shave with a razor blade and

shaving foam. Where this is felt to be inadequate, pre-shave preparations are available to wet and soften the beard and to lubricate the skin; these are often referred to as beard softeners. They are particularly helpful to those with easily abraded skin or large diameter beard hair (since the hydration time varies as the square of the radius of hair, assuming that the diffusion of water into hair obeys Fick's laws). Brushless, non-lathering shaving creams, although satisfactory in terms of their lubricating action, often do not soften the beard sufficiently quickly or adequately. The application of a beard softener containing soaps, synthetic surfactants or possibly urea prior to the application of a brushless cream will allow a more complete wetting and softening of the beard and ensure a close and smooth shave. Such a formulation may contain a lime soap dispersing agent to improve the wetting action in hard water, a soap-compatible anti-bacterial agent, menthol and a preservative.

A beard softening cream recommended by Keithler¹⁰ has the following composition:

	(1) per cent
Stearic acid	13.8
Stearyl alcohol	2.0
Isopropyl palmitate	1.9
Paraffin oil	2.0
Lanolin	2.0
Tween 60	2.4
Span 60	1.0
Triethanolamine	1.0
Dupanol C	1.0
Water	72.4
Perfume	0.5

Bell¹¹ gives another example of a beard softening preparation with the following composition:

	(2) per cent
Coconut oil fatty acids, double distilled	4.20
Oleic acid (with low linoleic acid content)	5.60
Propylene glycol	5.00
Triethanolamine	2.85
Monoethanolamine	1.26
Tergitol NPX	2.00
Demineralized water	79.09

Procedure: Mix the fatty acids together and stir into propylene glycol. Add the amines and stir until a clear solution is obtained. Finally mix in the Tergitol and perfume if required, followed by the water.

Tergitol NPX (alkyl aryl polyethylene glycol ether) is used in example 2 to disperse insoluble lime soaps and to improve the wetting action in hard water. Pre-shave liquids, creams and gels based solely on synthetic surfactants have

been developed from hair shampoo formulations and these are particularly effective beard softeners in hard-water areas.

Lather Shaving Cream

Criteria for a Good Lather Shaving Cream

The undoubted success of foamed shaving preparations is probably due to their economy in use and ability to supply water to the beard by drainage through the plateau borders formed at the junctions of bubbles in the foam, thereby maintaining the hair in a fully water-saturated condition. The requirements of a good lather shaving cream are as follows:

- (1) It must produce a rich copious lather composed of small bubbles.
- (2) It must be non-irritant.
- (3) It must have good wetting properties.
- (4) It should be smooth, soft and entirely free from lumps.
- (5) It must adhere readily to both face and brush and yet be easily removed on rinsing.
- (6) It must retain a satisfactory consistency and texture over all temperature conditions likely to be encountered in use.

When evaluating foamed shaving preparations, such as lather shaving cream or aerosol shaving foam, attention should be paid to the following points:

Ease of transfer to the face.

Ease of spreading on the face.

Wetting and drainage properties of the foam.

Comfort and closeness of shave.

Foam texture, rigidity and rheology.

Foam stability.

Ease of removal of the lather and shaving debris from the razor and basin.

Acceptability and compatibility of the perfume.

Compatibility with the container.

Effect on the life of the razor blade.

Formulation

Lather shaving creams are concentrated dispersions of alkali metal soaps in glycerol and water. To maintain the desired level of foamability, consistency and product stability, careful control of the manufacturing process is essential. Even the slightest change to the formulation or manufacturing procedure can result in a disastrous phase separation of the cream at slightly elevated temperatures. One must therefore be prepared for problems in the scale-up of laboratory formulations.

Lather shaving creams normally contain 30 to 50 per cent soaps. Formulations based on stearic acid alone do not produce a sufficiently voluminous lather and it

is usual to add some coconut oil fatty acids. The ratio of stearic acid to coconut oil varies considerably in different products but the inclusion of about 25 per cent coconut oil with 75 per cent stearic acid will usually be found satisfactory. A mixture of sodium and potassium hydroxides is used to saponify the fatty acids. It has been suggested¹² that a 5:1 ratio of potassium hydroxide to sodium hydroxide with 3-5 per cent free fatty acids will give shaving creams of the correct degree of plasticity. A cream containing a high level of sodium soaps tends to be thick and stringy, from which it is often difficult to produce a good lather. Lather creams can be made with potassium soaps alone but these tend to be less stable.

In order to prevent premature drying out of the cream, up to 15 per cent of a humectant is usually added. This is normally glycerol, but sorbitol or propylene glycol can be used. Humectants also have the effect of making the creams softer; propylene glycol has the greatest influence on the texture of the cream. An improvement in the properties of the cream and the lather has been claimed¹³ by replacing glycerol with 1,3-butylene glycol. Emollients such as lanolin, cetyl alcohol, mineral oil and fatty acid esters should be kept to a low level (1 per cent) if the lathering properties are not to be impaired. Other additives to lather shaving creams, such as synthetic surfactants as foam stabilizers, cooling agents, antibacterial agents, etc., are discussed more fully under aerosol shaving foams.

The pH value of a lather shaving cream is generally around 10. The apparent paradox of a high pH and free fatty acid can be explained in terms of the mixing process. Pockets of unneutralized alkali remain, even under well-controlled manufacturing conditions, because of the high viscosity of the product. As part of the quality control on lather shaving creams, the level of free fatty acid should be determined as a check on the efficiency of mixing during manufacture. The free fatty acid level is one of the factors which influences the maximum temperature at which the cream retains a stable consistency. Above this temperature, free fatty acid rises to the surface of the product, in a similar manner to the creaming of an emulsion, and the functioning of the cream is seriously impaired.

Free fatty acids and the less water-soluble stearate soaps are responsible for the characteristic pearlescence of lather shaving creams. The pearlescence is a result of the formation within the cream of liquid crystalline phases which, in addition to improving its appearance, can increase the stability of the foam generated. The rate at which the liquid crystalline phases form depends on the method of manufacture, in particular the rate of cooling and the amount of stirring. It is normal practice amongst manufacturers to store the cream for some time before packing to allow the structure to develop. The slight change in the consistency and foam stability during the immediate post-manufacturing period should be taken into account when testing production batches of lather shave cream.

Much of our knowledge on lather shaving creams is still empirical; however, further insight may be obtained by consulting the literature on soap manufacture. The following formulation will serve as a guide to experimentation, but the manufacture of a good shaving cream, which will stand up to various climatic conditions, is very much an art

	(3) per cent
Stearic acid	30.0
Coconut oil	10.0
Palm kernel oil	5.0
Potassium hydroxide	7.0
Sodium hydroxide	1.5
Glycerin	10.0
Water	36.5
Perfume	q.s.

Procedure: Mix half of the stearic acid with the oils, melt by steam heat, and bring to a temperature of 75°–80°C. Run in the alkali, water and glycerin and stir well until saponification is complete. The remainder of the melted stearic acid is now added together with any water which may have been lost during manufacture. The perfume is added at 35°C.

An Atlas formula quoted by deNavarre¹⁴ is as follows:

	(4) per cent
Stearic acid	36.0
Coconut oil	9.0
Potassium hydroxide	8.0
Sodium hydroxide	1.0
Sorbitol (70% solution)	3.0
Water	43.0
Preservative, perfume	q.s.

Procedure: Heat the coconut oil to 75°–80°C. Dissolve the alkalis in half of the water and add to the coconut oil. When saponification is complete, add melted stearic acid (70°C) in a thin stream followed by the sorbitol solution, preservative and the remainder of the water. The mixture is then cooled. The perfume may be added at 35°C, or after the emulsion has cooled to room temperature. A check is carried out for completeness of saponification and the free fatty acid content is adjusted to between 3 and 5 per cent. The product is eventually packed into tubes.

Lather Shaving Stick

A lather shaving stick can be prepared from a mixture containing 80 per cent fatty acid soaps, 5–10 per cent glycerol and 8–10 per cent water. The ratio of the fatty acids and the ratio of potassium to sodium soaps should be similar to those described under lather shaving creams. After mixing, the composition is chipped, dried and milled with any other components required, such as perfume, colour or an opacifier. The soap flakes are packed to the desired shape using a soap plodder.

Aerosol Shaving Foams

Aerosol shaving foams are oil-in-water emulsions in which propellant droplets, liquefied under pressure, form a substantial part of the oil phase. When the

emulsion is discharged to the atmosphere, the dispersed propellant droplets vaporize, producing a foam consisting of propellant vapour bubbles surrounded by an aqueous surfactant phase.

Some of the early patents on aerosol shaving foams provide some useful pointers to the influence of the soap composition on the appearance and properties of the foam. The first aerosol shaving foam patent, granted to Spitzer,¹⁵ protected the use of fluorocarbon propellants in aqueous soap solutions enclosed in a pressure-resistant container. Triethanolamine stearate at levels of 8–12 per cent was given as the preferred soap together with smaller amounts of triethanolamine soaps of coconut fatty acids to prevent gelling at low temperatures. Potassium soaps were also said to give satisfactory shaving foams but sodium stearate can only be used at very low concentrations because of its tendency to gel. A later patent granted to Colgate-Palmolive¹⁶ suggested that triethanolamine soaps alone do not make a satisfactory aerosol shaving foam because of a tendency for the emulsion to foam inside the container. As a result, the dispensed foam contains large bubbles and a substantial proportion of the emulsion cannot be expelled from the container. The foams described in the patent contain from 4 to 15 per cent soaps, mainly triethanolamine stearate with minor proportions of potassium and sodium stearates, as in example 5

	(5) per cent
Triethanolamine stearate	8.0
Sodium stearate	1.0
Potassium stearate	4.6
Water	72.5
Perfume	0.9
Borax	0.5
Propellant (fluorocarbon)	12.5

Another patent granted to Colgate-Palmolive¹⁷ claimed that aerosol shaving foams containing less than 4 per cent of potassium soaps produced the best results in softening hair and reducing its resistance to cutting by the razor blade. Soaps of mono- and diethanolamines were also considered suitable for this purpose, but triethanolamine soaps were found to be ineffective. Since the foam produced by such dilute soap solutions was rather unstable, synthetic thickening agents were included in the compositions. Particularly preferred are water-soluble salts of polyacrylic acid and its derivatives, with a mean molecular weight between 100 000 and 200 000, used at concentrations ranging between 0.5 and 3 per cent. These polymers also provide additional lubrication for the razor blade on skin. A ratio of stearic to coconut fatty acid of 80:20 was claimed to give a better beard-softening effect than other fatty acid mixtures when used at low concentrations. A large proportion of free fatty acid is retained to improve lubricity and foam stability. Other lubricants such as cetyl alcohol or glycerol monostearate are also incorporated to improve the feel of the skin after shaving, while nonionic emulsifiers are present to enhance the emulsification of the free fatty acid.

An example of a shaving foam concentrate from the patent had the following

composition:

	(6) per cent
Potassium soap from stearic acid/coconut oil fatty acids (80:20)	1.5
Potassium polyacrylate (polyacrylic acid mol. wt 100 000-200 000)	1.0
Polyvinylpyrrolidone	0.5
Stearic acid/coconut oil fatty acids (80:20)	3.0
Castor oil	3.0
Lauric acid diethanolamide	0.5
Polyoxyethylene sorbitan monolaurate	0.5
Perfume	0.5
Water	89.5

Guidance on Formulation

The following general guidance can be given in the formulation of aerosol shaving foams.

Fatty Acids. Saturated long-chain fatty acids containing 12 to 18 carbon atoms at a level of 7-9 per cent are the main components of aerosol shaving foams. Lower-molecular-weight fatty acids such as those found in unstripped coconut oil cause skin irritation. The ratio of the fatty acids can be varied widely to produce foams with different physical properties. The presence of stearic acid is not essential to an aerosol foam as might be inferred from the early patents. A high proportion of stearic acid in the fatty acid mixture tends to give stiffer foams and a reduction in the number of shaves per can. Replacing some of the stearic acid with lauric acid tends to produce softer foams and improves the expulsion characteristics.

Bases. Triethanolamine, potassium hydroxide or mixtures of the two are the preferred bases for the saponification of the fatty acids. Sodium hydroxide is rarely used and then only as a minor constituent. Mono- and diethanolamines are used occasionally but care is needed to avoid skin irritation. Triethanolamine soaps tend to give closer-knit foams than potassium soaps, particularly with fluorocarbon propellants.

It is common practice to adjust the quantity of base so that the formulation contains 1-3 per cent free fatty acid. The free fatty acid can improve the appearance and lubricity of the foam and, by complexing with the soap, increase foam stability. However, this may be at the expense of reducing the amount of available foam and increasing the rate at which the foam dries out on the face.

Surfactants. A wide variety of anionic and nonionic synthetic surfactants can be used in shaving foams to improve such properties as the emulsion stability (for example, self-emulsifying glycerol monostearate), the wetting properties of the foam (for example, sodium lauryl ether sulphate), the water dispersibility of the foam and shaving debris (for example, polyethoxylated fatty alcohols, the foam stability (for example, lauric diethanolamide) and emolliency (for example, ethoxylated lanolins). Because of the complex nature of the interactions between surfactants, soaps and free fatty acids, their interfacial properties in the emulsion and foam are not easily predicted.

Humectants. Polyols such as glycerol, sorbitol or propylene glycol are usually added to shaving foam concentrates at a level of 3–10 per cent. By their ability to bind water, they reduce the tendency of the foam to dry out on the face.

Lubricants. To assist the passage of the razor over the face and to provide emolliency, additional lubricants such as mineral oils, silicone fluids, lanolin or isopropyl myristate can be included at a level of 1 to 2 per cent, to supplement the effects of the free fatty acid. Water-soluble polymers such as polyvinyl pyrrolidone, sodium carboxymethyl cellulose or polyacrylic acid and its derivatives can also improve lubrication and increase foam stability. Polyvinylpyrrolidone is said to act as an anti-irritant, that is, to reduce the irritancy caused by other compounds.

Propellants. Aerosol shaving foams contain either 7–10 per cent fluorocarbon propellant or 2.8–3.5 per cent hydrocarbon propellant. The fluorocarbon propellants are usually 40:60 to 60:40 weight ratio blends of dichlorodifluoromethane and dichlorotetrafluoroethane. The hydrocarbon propellants are mixtures of *n*-butane, isobutane and *n*-propane.

The higher the concentration of propellant, the lower the foam density, the stiffer the foam and the greater the number of shaves that can be obtained from a given weight of the emulsion. Foams having a density less than 65 g l^{-1} are likely to be difficult to spread on the face and have little beard-softening capability.

In spite of the higher cost, fluorocarbon-propelled shaving foams became very popular, possibly because of the relative ease of forming close-textured, stable foams. Following the Rowland and Molina¹⁸ hypothesis of stratospheric ozone depletion by fluorocarbon propellants and legislation in the USA, all US aerosol shaving foams are now based on hydrocarbon propellants. The best selling UK aerosol shaving foams are also based on hydrocarbon propellants.

Perfume. Soap-compatible perfumes are used at a level of 0.15–0.65 per cent.

Cooling Agents. Physiological cooling agents are often added to shaving foams to counteract the 'after-glow' associated with shaving. The most frequently used cooling agent is menthol at a concentration of 0.05–0.2 per cent. The volatility of menthol means that its cooling effect on skin is transient and its dominant odour is almost impossible to mask. A group of compounds ranging in chemical type from carboxamides to ureas to phosphine oxides have been shown to possess physiological cooling properties.¹⁹ Many are as effective as menthol but without the disadvantages associated with the volatility of menthol. At a level of 0.1–0.2 per cent in shaving foams, the cooling effect can last for 5–15 minutes after application.

Colour. Foams may be coloured by the use of D&C or FD&C dyes. A very low concentration should be used to avoid staining the skin and towel.

Preservatives. Many shaving foams do not require a preservative; however, when necessary 0.2 per cent of a mixture of methyl and propyl *p*-hydroxybenzoate should suffice.

Antioxidants are sometimes required to avoid rancidity in formulations containing even low levels of unsaturated compounds.

Corrosion Inhibitors. Again these are not normally required with suitably lacquered containers. Borax (0.04 per cent, 10 mol) can be used with tinplate containers and 0.25 per cent of sodium silicate 35° Be solution with aluminium containers.

Bacteriostats, etc. 0.05 per cent trichlorohydroxydiphenyl ether (Irgasan DP300) and 0.05 per cent allantoin should reduce skin infections and promote healing of cuts.

Pilomotor Agents. It is claimed that a closer shave can be obtained by incorporating into the shaving preparation compounds having pilomotor activity—that is, ability to cause the contraction of the arrectores pilorum (hair follicle muscles). This contraction causes the beard hair to be pushed farther above the skin surface line by about 0.2–0.3 mm. A hair cut in the elevated position will retract below the skin surface as the follicle muscle returns to normal. Such patented compounds included: imidazolines,²⁰ for example, 2-(2',5'-dimethoxy-4',6'-dimethylbenzyl)-2-imidazoline; 2-amino-imidazolines;²¹ morpholines,²³ for example 2-(3'-hydroxyphenyl)-morpholine; and 2-(phenylamino)-1,3-diazacyclopentenes-(2).²³

A number of the above compounds can also be used to the same effect in lather shaving creams, brushless shaving creams and pre-electric shave lotions.

A statistical study of the formulation of aerosol shaving foams²⁴ examined the importance of a number of variables such as soap concentration, fatty acid type, free fatty acid concentration, polyol type and concentration, and propellant type and concentration. The concentrate was evaluated in terms of viscosity, pH, density and stability, while the discharge properties and foam were evaluated in terms of the number of shaves per can, residue in the can after discharge, foam density, foam strength, drying time and bubble size. A number of the findings of the study have been included in this section.

Example Formulations

<i>Fluorocarbon-propelled shaving foam</i>		(7)
		<i>per cent</i>
A	Stearic acid	5.6
	Palmitic acid	2.2
	Isopropyl myristate	1.0
	Coco monoethanolamide	0.3
B	Sodium lauryl ether sulphate (40% solution)	3.5
	Triethanolamine	3.9
	Glycerol	5.0
	Water (deionized)	78.5
	Perfume	<u>q.s.</u>
	Concentrate	91.5
	Propellants 12/114 (40:60)	8.5

<i>Aerosol shaving cream (Croda Chemicals Ltd²⁵)</i>		(8)
		<i>per cent</i>
A	Stearic acid	4.0
	Lauric acid	2.0
	Liquid lanolin (Fluilan)	1.0
B	Cromeen*	3.0
	Triethanolamine	2.5
	Water (deionized)	87.5
	Perfume	<i>q.s.</i>
Concentrate		92.0
Propellants 12/114 (40:60)		8.0

* Cromeen (Croda Chemicals Ltd) is a substituted alkyl amine derivative of various lanolin acids.

<i>Hydrocarbon-propelled aerosol shaving foam</i>		(9)
		<i>per cent</i>
A	Palmitic acid	5.0
	Lauric acid	1.0
B	Sodium lauryl sulphate	1.0
	Polyethylene glycol (400) monolaurate	0.5
	Polyacrylic acid (40% aq.) mol.wt 100 000	1.5
	Triethanolamine	2.0
	Potassium hydroxide	0.8
	Glycerol	5.0
	Water (deionized)	83.2
	Perfume	<i>q.s.</i>
Concentrate		96.9
Propellants, isobutane/propane		3.1

Procedure: The general procedure for making all aerosol shaving foams is to heat parts A and B separately to 75°C. Add A to B with vigorous stirring and allow to cool to 35°C, when the perfume is added. The aerosol container is charged when the concentrate has reached room temperature.

Consistent Aerosol Shaving Foam

The properties and expulsion characteristics of aerosol shaving foams change significantly as the container is emptied. Typically, the last 10–15 per cent of the product is wet and runny and may be poorly expelled. This is a familiar problem to the aerosol formulator and one which the consumer has reluctantly learned to accept. It is not possible to overcome this problem just by increasing the propellant content, since this causes the foam initially dispensed to be unacceptably stiff and dry. An interesting solution proposed by Mace and Carrion²⁶ involves the use of a concentrate formulation which absorbs just enough liquid propellant to give foam of the correct density. Excess propellant is added to form a discrete reserve layer which can supply all the vapour needed to fill the increasing head space. Hence the foam-forming composition remains unchanged as the container is emptied. This approach may impose constraints on the formulation and it would be necessary to educate the consumer not to shake the container before use. A versatile but relatively expensive means of obtaining a

consistent product is provided by the use of a barrier pack, in which the propellant providing the driving force to expel the liquid concentrate is separated from the foam-generating composition by either a piston or a flexible bag. Foams with very uniform properties throughout the life of a barrier pack have been reported.²⁷ Such a container is used in the post-foaming gel example.

A novel means²⁸ of maintaining the consistency of an aerosol foam is to use propellant-swollen rubber as a source of additional propellant. Propellant vapour is released from the rubber only when the vapour pressure in the head space falls. Hence the properties of foam dispensed from a full container are unaffected by the presence of additional propellant. When the emulsion is expelled, the head space volume increases and there is a small but sharp drop in vapour pressure. The vapour pressure is restored to slightly below the original value by the release of vapour directly or indirectly from the reservoir and not solely from the emulsion. In this way the ratio of concentrate to propellant in the emulsion, which determines foam density, is not reduced to the same extent with the reservoir as would normally be the case.

The benefits of using a rubber reservoir have been demonstrated by the following formulation:²⁹

	(10)
	per cent
Palmitic acid	5.0
Potassium hydroxide	1.0
Sodium lauryl sulphate	2.5
Lauric diethanolamide	1.5
Polyethylene glycol (6000) monostearate	2.0
Water (deionized)	88.0
<i>Fill for a 6 oz aerosol container</i>	<i>weight (g)</i>
Concentrate	177.0
Butane 40 propellant	7.6
Ethylene/propylene rubber	3.0

A conventional package without the reservoir would contain 5.1 g propellant (Butane 40) and 177 g concentrate.

After an appropriate period of storage to allow absorption of some of the propellant by the rubber, the total volume of usable foam was 25 per cent greater when the reservoir was used and the expulsion characteristics remained satisfactory until the container was empty. The proportion of usable contents was increased by the use of the reservoir from 79 per cent to over 95 per cent.

Heated Shaving Foam

The interest in heated shaving foams derives from the improvement in beard softening as a result of increasing the temperature. Heated shaving foam can be obtained either by an exothermic chemical reaction between components which are kept separate within the aerosol container or by bringing the foam into contact with a heat exchanger connected to a hot water supply. Products relying on an exothermic redox reaction require a dual dispensing aerosol valve, the inner compartment containing hydrogen peroxide and the outer compartment containing the soap solution, propellant and a pyrimidine, a thiourea, a sulphite or a thiosulphite.

Whatever the means of heating the foam, conventional aerosol shaving compositions are generally unsuitable because at higher temperatures these form large unstable bubbles and the foam lacks the body necessary for satisfactory shaving. Compositions that are claimed to be suitable for heated aerosol shaving foams³⁰ are based on aqueous solutions of triethanolamine stearate, superfatted with free stearic acid. The presence of lower-molecular-weight fatty acids tends to reduce the stability of the foam at elevated temperatures. This can be compensated for to some extent by increasing the concentration of stearic acid which has the ability to thicken the heated soap solution. The inclusion of propylene glycol or of nonionic surfactants, which will produce much richer and more viscous foams at room temperature, tends to give foams of a watery consistency at elevated temperature.

Satisfactory formulations can be obtained with 8–15 per cent triethanolamine stearate, 1 per cent triethanolamine coconut oil soap and 2 or 3 per cent stearic acid. At lower levels of triethanolamine stearate (7–12 per cent) a satisfactory composition will be obtained with 2 per cent triethanolamine coconut oil soap and 3 or 4 per cent stearic acid.

Scum-free Aerosol Shaving Foam

Soap-based shaving preparations leave on the basin and razor an unsightly deposit that is not readily rinsed away. The deposit, known as lime soap curds or scum, is particularly noticeable in hard-water areas and consists of water-insoluble calcium and magnesium soaps and free fatty acids. The deposit can be reduced by the addition of lime soap dispersing surfactants to a conventional formulation. Even the best lime soap dispersing agent should be present at two to three times the concentration of soap to prevent scum formation. Formulations containing low concentrations of soap and high concentrations of surfactant produce unstable foams. It is possible to restore stability to the foam by the addition of long-chain fatty alcohols such as myristyl alcohol.³¹ An example of a scum-free aerosol shaving foam containing a low concentration of soaps is as follows:

		(11)
		<i>per cent</i>
A	Palmitic acid	1.95
	Myristic acid	0.62
	Myristyl alcohol	2.10
B	Polyoxyethylene (20) cetyl ether	5.23
	Lauric diethanolamide	5.23
	Propylene glycol	0.82
	Glycerol	3.54
	Triethanolamine	1.54
	Water (deionized)	78.97
	Perfume	<i>q.s.</i>
	Concentrate	91.5
	Propellants 12/114 (40:60)	8.5
or	Concentrate	97.0
	Propellant (Butane 48)	3.0

Soap-free Aerosol Shaving Foams

The improvement in the foam stability in example 11 is brought about by molecular complex formation between the long-chain fatty alcohol and the polyoxyethylene fatty ether. The interaction of long-chain fatty acids and fatty alcohols with polyoxyethylene fatty ethers in fluorocarbon propelled shaving foams has been investigated by Sanders.³² Many of these soap-free formulations showed increases in emulsion viscosity and stability and in foam stability and stiffness. However, it has been observed that many soap-free emulsions undergo an irreversible phase separation when maintained at 37°C for a few weeks, such that, even after vigorous shaking to re-emulsify the solid phase, the contents cannot be expelled as a foam.

Certain nitrogen-containing surfactants in combination with myristyl alcohol are claimed³³ to form stable soap-free aerosol shaving foams which do not undergo irreversible phase separation when stored at elevated temperatures. Such foams do not form a deposit in hard water and will often completely disperse the scum formed by the pre-shave wash with soap. With soap-free formulations it is possible to use hypoallergenic surfactants and the pH can be adjusted to the slightly acid value of skin.

An example of a soap-free aerosol shaving foam is as follows:

	(12) per cent
A Myristyl alcohol	2.1
B Dicarboxylated lauric imidazoline 40% solution (Cycloteric DL)	5.1
Polyethylene glycol (1000) monolaurate	5.5
Propoxylated polyol (Emcol CD-18)	0.7
Glycerol	5.0
Water (deionized)	81.6
Perfume	q.s.
Citric acid	q.s.
	<hr/>
Concentrate	97.0
Propellant (Butane 48)	3.0

Procedure: Heat parts A and B separately to 75°C. Add A to B with vigorous stirring. The perfume is added after cooling to 35°C. The pH of the concentrate is adjusted to the desired value by the addition of citric acid.

A soap-free aerosol shaving foam containing anionic sarcosinate surfactants, given in Croda Chemicals Technical Literature,³⁴ is as follows:

	(13) per cent
A Fluilanol	5.0
Crodaterge LS	3.0
Crodaterge OS	4.0
Pentol mineral oil	1.0

	<i>per cent</i>
B Propylene glycol	5.0
Triethanolamine	1.0
Water (deionized)	81.0
Perfume	<i>q.s.</i>
Concentrate	95.0
Propellant isobutane/propane	5.0

Post-foaming Aerosol Gel

Products of this type are discharged from an aerosol container as a stable gel which, when spread on the face, is claimed to improve the wetting of the skin and beard. The foam is subsequently formed *in situ* on the surface of the skin by the vaporization of low-boiling-point aliphatic hydrocarbons. The product is packaged in an aerosol container with a barrier to separate the post-foaming gel from the propellant required for expulsion. The barrier pack ensures that a homogeneous gel is discharged, substantially free of bubbles, which can produce a self-generated lather of uniform consistency and density throughout the life of the product. The post-foaming gel consists essentially of an aqueous dispersion of soaps, water-soluble gelling agents and a post-foaming agent having a vapour pressure of 6–14 psi (41–96 kPa) at 37°C, for example saturated aliphatic hydrocarbons or halogenated hydrocarbons. Miscellaneous additives such as humectants, emollients, foaming aids, perfume, etc., can also be included in the formulation.

Two examples of post-foaming gels of different foam stiffnesses, given in a patent assigned to S.C. Johnson & Son Inc.,³⁵ had the following compositions:

	(14)	(15)
	<i>per cent</i>	<i>per cent</i>
Stearic acid (95% purity)	2.000	2.250
Palmitic acid (97% purity)	5.800	6.500
Polyoxyethylene (2) cetyl ether	1.000	1.000
Hydroxyalkyl cellulose (Klucel HA)	0.067	0.075
Carbopol 934	0.180	0.225
Propylene glycol dipelargonate	2.750	2.750
Sorbitol (70% solution)	10.000	10.000
Propylene glycol	3.300	3.300
Triethanolamine	4.200	4.750
Water (deionized)	67.953	66.400
Fragrance, dye	<i>q.s.</i>	<i>q.s.</i>
<i>n</i> -butane	0.550	0.550
<i>n</i> -pentane	2.200	2.200
Foam stiffness	29.0 g cm ⁻²	69.8 g cm ⁻²

Procedure: Prepare the soap intermediate by adding an aqueous solution of sorbitol and triethanolamine to the fatty acids and polyoxyethylene (2) cetyl ether at 80°C. Add separate solutions of the Klucel HA in aqueous propylene glycol and Carbopol 934 in water to the soap intermediate at 27°C. Disperse the hydrocarbons in an equal volume of propylene glycol at 4°C and mix with the remainder of the formulation in such a way as to avoid trapping air in the gel.

The gel is immediately transferred to the inner compartment of a barrier aerosol dispenser and the valve crimped in place. The outer compartment is pressurized with about 10 ml of a mixture of propane and isobutane having a vapour pressure of approximately 46 psi (317 kPa) at 25°C.

Brushless or Non-lathering Cream

Brushless or non-lathering shaving creams are oil-in-water emulsions. They contain components similar to those in vanishing creams, the main difference being that the concentration of oils and emulsifying agents tends to be higher in the shaving preparations. Ideally, the cream should vanish on completion of the shave, leaving the face free from irritation and with a matt appearance. Since a too rapid disappearance of the cream would be deleterious to the comfort and closeness of the shave, it should be possible at the very least to rub any remaining cream into the skin after the shave.

The popularity of brushless creams is said to be due to their convenience, in that they eliminate the need for a brush and give a faster shave. The thick film of lubricant on the face can provide emolliency and protection to the skin by reducing razor drag during shaving. The lower pH value of brushless creams (7.5–8.5) lends support to the suggestion that they cause less irritation, particularly on broken skin, than lather creams of pH 10. The disadvantages of brushless creams are that more is required per shave than with a foam preparation, the cream is often difficult to rinse from the razor and it can leave the skin feeling greasy. Owing to the slower uptake of water from the emulsion by the hair, the beard-softening action of brushless cream is reported to be less effective than a foam preparation. This may result in a more rapid dulling of the blade edge. To promote beard softening, it is normally recommended that the face is washed with soap and water before applying the cream to the wet face.

Formulation

The oil phase of a typical brushless cream comprises: 4–10 per cent lubricant (for example mineral oil, long-chain fatty acid esters, petrolatum); 10–25 per cent stearic acid to provide a superfatting action and assist the characteristic pearlescent appearance of the cream; and 0–5 per cent emollient (for example lanolin, cholesterol, cetyl alcohol, stearyl alcohol, spermaceti). Spermaceti is widely recommended as a means of preventing the cream from vanishing too rapidly. The aqueous phase usually contains 1–5 per cent soaps (for example potassium or triethanolamine stearate), 0–5 per cent synthetic surfactant to improve emulsion stability, beard wetting and rinsibility (for example glycerol monostearate, sulphonated fatty alcohols, fatty acid amides), 0–1 per cent thickening agent which will also improve emulsion stability (for example gum tragacanth, sodium alginate, polyvinylpyrrolidone, polyacrylic acid and its derivatives), and 2–10 per cent humectant to prevent drying-out of the cream (for example glycerol, sorbitol, propylene glycol). It is normal to add a preservative, for example esters of *p*-hydroxybenzoic acid, to this type of formulation. Other additives, such as perfumes, cooling agents, bacteriostats, etc., as discussed under aerosol shaving foam preparations, can also be included.

The composition of a typical brushless shaving cream is as follows:

	(16) per cent
Mineral oil	9.0
Lanolin	0.5
Stearic acid	14.5
Carbopol 934	0.5
Triethanolamine	2.5
Triethanolamine lauryl sulphate	1.0
Glycerol	5.0
Water	67.0
Preservative, perfume	q.s.

Procedure: Heat the oil, lanolin and stearic acid to 75°C. Disperse the Carbopol 934 in cold water and add the glycerol, surfactant and triethanolamine. Add the oil phase to the aqueous phase at 75°C with vigorous stirring. Cool the mixture rapidly, the perfume being added at 45°C.

The composition of a brushless shaving cream quoted in *Seifen-Öle-Fette-Wachse*³⁶ is given in example 17.

	(17) per cent
Stearic acid	18.0
Lanolin	4.0
Propylene glycol monostearate	4.0
Isopropyl palmitate	4.0
Glycerol	2.0
Triethanolamine	1.0
Water	66.8
Perfume	0.2

The presence of silicone oil in a brushless shaving cream is said to impart a pleasant 'feel' on application and give enhanced razor glide. A formulation given in a *Union Carbide Bulletin*³⁷ had the following composition:

	(18) per cent
A Stearic acid	18.0
Mineral oil	5.0
Silicone fluid L-45 (1000 cS)	1.0
Polyoxyethylene (20) sorbitan monostearate	5.0
B Sorbitol (70% solution)	5.0
Borax	2.0
Triethanolamine	1.0
Water	63.0
Preservative, perfume	q.s.

Procedure: Heat the oil phase to 90°C; heat the aqueous phase separately to 95°C and add to the oil phase with stirring.

Carbowax 1500 may be used in place of oils to formulate so-called non-greasy brushless shave creams:³⁸

	(19)
	parts
A Carbowax 1500	45.0
Stearic acid	37.5
B Triethanolamine	3.0
Potassium hydroxide	1.6
Water	2.0
Sodium alginate	3.5
Water	178.0
Propylene glycol	12.0
Carbitol	15.0
Perfume	q.s.

Procedure: Heat A to 70°C and stir in B. Add the sodium alginate dispersed in water at 70°C followed by the remaining components. The perfume, dissolved in part of the Carbitol, is added when the cream has cooled to 50°C; pour the cream at 45°C.

As with lather shaving creams, the rate of cooling and the amount of stirring can affect the consistency of the product. Cooling the product under vacuum will help to reduce aeration during the manufacture of the cream.

It is possible to obtain a satisfactory brushless shaving cream without using high concentrations of fatty acids. Self-emulsifying glycerol monostearate at a level of 10–25 per cent is a suitable emulsifier for the oils and this produces more translucent creams with better emollient properties than standard creams. An example of this type of cream is as follows:³⁹

	(20)
	per cent
Glycerol monostearate	10.0
Mineral oil	3.0
Lanolin	5.0
Glycerol	3.0
Stearic acid	2.0
Potassium hydroxide	0.1
Water	76.9

Brushless Shaving Stick

Thomas and Whitham⁴⁰ describe a brushless shaving stick which can be applied directly to the face. It is claimed that the continuous thin smear left on wetted skin provides adequate lubrication for the shaving operation. The stick is composed of fatty or waxy materials to which hydrophilic properties have been imparted by a suitable emulsifier, for example soap or a partial fatty acid ester of a polyhydric alcohol. This ensures that the product is readily wetted by, but is not more than very sparingly soluble in, water. Pigment, dyestuff or opacifier is incorporated to indicate the presence of the composition on the face.

The following example is quoted:

	(21)
	<i>per cent</i>
Sesame oil	35.35
Spermaceti	45.80
Stearin	7.60
Soap	5.00
Monoglycerides of coconut oil fatty acids	3.00
Titanium dioxide	2.00
Perfume	1.25

Novel Compositions for Wet Shaving

There are a number of products, often referred to as shaving assisting compositions, which function in a slightly different manner from conventional soap-based shaving preparations. These novel compositions place a greater emphasis on the protection of skin during shaving by the provision of an effective layer of lubricant. They are applied directly to the face or to the blade edge and can be used without any other type of wet shaving preparation. Alternatively, they can be considered as a pre-wet shaving preparation.

An example⁴¹ of a composition based on mineral oil is as follows:

	(22)
	<i>per cent</i>
Mineral oil	95.97
Diocetyl sodium sulphosuccinate (Aerosol OT)	1.44
Lanolin	0.96
Silicone fluid (DC 400)	0.67
Octadecanol	0.48
Fragrance	0.48
Preservative	<i>q.s.</i>

The preparation is applied to moist (but not wet) skin that has been washed with soap and warm water. The oils and octadecanol provide lubrication and act as a barrier to the evaporation of water, thereby preventing dehydration of the skin and beard hair.

A synergistic action between nonionic and ionic surfactants and silicone fluids is claimed⁴² to protect the skin during shaving, facilitate the cutting of the beard and to protect the blade from corrosion between shaves. The compositions can be applied as a lotion or cream and can be used with or without a conventional shaving preparation.

An example of an alcoholic lotion is as follows:

	(23)
	<i>per cent</i>
Methylphenylpolysiloxane (DC-555)	6.6
Dimethylpolysiloxane (DC-200, 350 cS)	6.6
Polyoxyethylene (20) sorbitan monooleate (Tween 80)	6.6
Polyoxyethylene (20) sorbitan monolaurate (Tween 20)	6.6
Diocetyl sodium sulphosuccinate	0.5
Water	25.8
Ethyl alcohol (95%)	47.3

Other preparations make use of the lubricating properties of water-soluble gums and polymers, to which synthetic surfactants, humectants, emollients and oils can be added. Assertions have been made that the anionic soaps and surfactants present in shaving creams tend to emulsify sebum, with the result that the skin is deprived of its natural protection and is left dry, exposed to adverse atmospheric conditions and to the abrading action of the razor blade.

Shaving preparations based on oil-in-water emulsions have been proposed by Clairol.⁴³ These compositions contains dimethylpolysiloxane (200–500 cS) emulsified with 0.3 to 0.7 per cent polyoxyethylene lauryl ethers in 87–95 per cent water which has been thickened with 0.2–1.0 per cent Carbopol neutralized by triethanolamine to pH 6.5–7.2. The silicone fluid is said to form a protective layer on the skin, thereby preventing the emulsification of sebum, reducing razor drag and minimizing skin irritations.

DRY SHAVING PREPARATIONS

Introduction

It is generally recognized that electric shavers do not cut the beard as close to the skin surface as a razor blade. This was confirmed in a study by Bhaktaviziam *et al.*⁴⁴ which also showed that the ends of hair observed 24 hours after shaving with an electric razor showed ragged edges and some vertical splitting of the hair shaft. Both electric and blade shaving result in the removal of skin, the amount removed for an individual being dependent on the pressure applied to the face. Generally, the closer the shave the greater the amount of skin damage. It has been suggested⁴⁵ that pre-electric shave preparations may not increase the quality of the shave but may assist in reducing skin damage.

In contrast to blade shaving where it is preferable to soften the beard, when using an electric razor the beard should be dry with individual hairs raised and stiffened so that they can be caught between the razor's combs and removed. The removal of the film of perspiration from the face reduces the friction between the razor and skin and prevents the beard from being slippery and elusive to the cutting edge of the electric razor. This is achieved in different ways by the two most popular forms of pre-electric shave preparation: the lotion, based on an alcoholic solution, and the talc stick. It should be noted that a completely contrary view of the function of a pre-electric shave preparation has been expressed in a patent granted to the Sunbeam Corporation,⁴⁶ where it is claimed that the removal of moisture from the skin and beard prior to electric shaving is not desirable: that in fact water softens the beard and by causing hairs to swell and to become elongated ensures a smoother, more efficient and closer shave. Furthermore, alcoholic lotions are claimed to cause shrinking of the hair into the follicle, making it more difficult to obtain a close, clean shave. The preparations claimed in the patent are oil-in-water emulsions containing 5–20 per cent by weight of fatty acid esters such as isopropyl myristate, and an

emulsifying agent which is a mixed alkali metal/amine salt of polyacrylic acid.

Pre-electric Shave Lotion

In formulating a pre-electric shave lotion the following attributes are considered desirable:

- (1) Adequate astringency to stiffen the beard and possibly to stimulate the hair follicle muscles.
- (2) Quick drying to allow rapid evaporation of any moisture present on the face.
- (3) A pH below the iso-electric point of keratin to prevent swelling of the hair (that is, pH 4.5–4.8).
- (4) Provision of a coating on the skin on which the razor will glide, thereby preventing irritation of the skin and providing lubrication for the cutting edge of the electric razor.
- (5) Freedom from any substances likely to corrode the cutting head.
- (6) Absence of any lubricants likely to have an adverse effect on plastic components of the electric shaver.

The alcoholic pre-electric shave lotions may be either astringent or oily. The astringent lotions are intended primarily to dry and stiffen the hairs and, theoretically at least, to assist in raising them. The astringent effect of the alcohol can be further enhanced by the inclusion in the preparation of mildly astringent substances such as aluminium chlorhydroxide, zinc phenolsulphonate or lactic acid. Menthol or camphor may be included to give a cooling effect together with a suitable antiseptic and a low level of lignocaine as an analgesic. Compounds having pilomotor activity may also be added to pre-electric shave preparations.

Lotions of the oily type aim to deposit on the face a film of lubricant which reduces the drag of the cutting head against the skin. It has been shown⁷ that a film of silicone oil substantially reduces the frictional force between skin and a smooth steel probe. The mechanism involved is hydrodynamic lubrication—that is, the frictional force is dependent on the viscosity of the lubricant. Perhaps the most frequently used lubricants for this type of product are the esters of higher fatty acids such as isopropyl myristate. By suitable choice of lubricant type and concentration, it should be possible to provide for a comfortable shave even in warm humid conditions without leaving the skin feeling oily. It is claimed by some that the oily type of preparation lengthens the life of the cutting edge of the electric razor because of its lubricating action.

Example Formulations

<i>Astringent pre-electric shave lotions</i>	(24) <i>per cent</i>
Ethanol	45.0
Sorbitol	5.0
Lactic acid	1.0
Water	49.0

	(25) per cent
Zinc phenolsulphonate	1.0
Distilled extract of witch hazel	40.0
Ethanol	40.0
Water	18.8
Menthol	0.1
Camphor	0.1

	(26) per cent
Aluminium chlorhydroxide (50%)	5.0
Isopropyl myristate	5.0
Ethanol	80.0
Perfume	q.s.
Colour	q.s.
Water	to 100.0

<i>Lubricant pre-electric shave lotions</i>	(27) per cent
Isopropyl myristate	20.0
Ethanol	80.0
Perfume	q.s.
Antiseptic	q.s.

	(28) per cent
Ethanol	77.0
Isopropyl myristate	13.0
Oleyl alcohol (cosmetic grade)	4.0
Perfume	1.0
Distilled water	5.0
Colour	q.s.

A pre-electric shave lotion containing a pilomotor agent was quoted in a patent assigned to E. Merck A-G.²⁰ It had the following composition:

	(29) per cent
2-(2',5'-dimethoxybenzyl)-2-imidazoline	0.1
Citric acid	2.5
Polyvinyl pyrrolidone	0.5
Isopropyl myristate	3.5
Alcohol (96%)	80.0
Perfume	q.s.
Water	to 100.0

Pre-electric shave lotions may be applied directly to the face by a roll-on type of applicator. In such circumstances it may be necessary to adjust the viscosity and wetting properties of the lotion to prevent seepage round the ball when the applicator is inverted.

Collapsible Foam Pre-electric Shave Lotion

To aid the transference of the pre-electric shave lotion from the hand to the face, quick-breaking aerosol foams have been developed. The foam is quite stable and confined to a limited area as dispensed, but breaks to a thin liquid when sheared or warmed by body heat. The foam concentrate typically contains 55–70 per cent of an aqueous ethanol solution, 4–10 per cent of a lubricant, 0.5–5 per cent of a surfactant which should be soluble in only one of the miscible solvents but form a clear homogeneous solution on addition of 3–10 per cent of a liquefiable propellant to the concentrate. The persistence of the foam when left undisturbed on the hand can be varied from a few seconds to several minutes depending on the proportions of alcohol, water and propellant and the type and concentration of surfactant. The mechanism of foam stabilization is complex but appears to rely on the partial insolubilization and loose molecular structure formation by the surfactant in the aqueous ethanol solution once the propellant has evaporated. The foam collapses on shearing because the bubble walls are extremely thin compared with those of soap-based aerosol shaving foams.

The surfactants found to be suitable for most quick-breaking aerosol foams are nonionic emulsifiable waxes composed of polyethylene glycol ethers of cetyl and stearyl alcohol and auxiliary emulsifying agents, for example Polawax A-31 (Croda Chemicals Ltd), Promulgen Types D and G (Robinson Wagner Co.). The addition of lubricant oils to the concentrate can cause problems of instability; however, a limited number of compounds have been shown⁴⁷ to possess the right combination of dry lubricity, solubility in aqueous ethanol solutions and initial foam stability. Examples include di-isopropyladipate, dimethyl sebacate, diethyl succinate and propylene carbonate.

The composition of a collapsible foam pre-electric shave lotion disclosed in a patent assigned to Yardley⁴⁷ was as follows:

	(30) per cent
Di-(2-methoxy-2-ethoxy)ethyl adipate	2.4
Denatured ethyl alcohol (95%)	68.1
Polawax A-31	4.9
Water	21.9
Isobutane	2.7

Pre-electric Shave Gel Stick

Solid pre-electric shave sticks of the cologne type can be formed by gelling ethanol with sodium stearate in the presence of glycerol and a suitable lubricant.

Pre-electric Shave Talc Stick

Talc is used as the main component in some pre-electric shave preparations to absorb perspiration and sebaceous secretions from the skin and to confer its characteristic slip so that the head of the shaver will glide smoothly over the face. A reduction of 50 per cent in the frictional force between skin and polished steel was observed⁷ after treating the skin with talc. Colloidal kaolin is usually present

in the preparation to improve the moisture-absorbing capacity and adhesion to the skin. Zinc or magnesium stearate is included to enhance both adhesion and slip. Magnesium carbonate or precipitated chalk serves as the carrier for the perfume as well as increasing the absorbent properties. An important stipulation is that powders for pre-electric shave purposes should be free from grit to avoid abrading the cutting edge of the electric razor. This can be achieved by grinding the powders before use.

The most convenient way to apply the talc preparation to the face is to form it into sticks. The sticks can be moulded from an aqueous dispersion of the powders using colloidal magnesium aluminium silicate (Veegum) as the binder.

A formula for a pre-shave talc stick was given in a Technical Bulletin of the R.T. Vanderbilt Co. Inc.⁴⁸ It had the following composition:

		(31)
		<i>parts</i>
A	Veegum	1.9
	Water	30.0
B	Zinc stearate	4.7
	Light magnesium carbonate	1.9
	Perfume	<i>q.s.</i>
	Talc	91.5

Procedure: Add the Veegum slowly to water with continuous agitation to produce a smooth dispersion. Absorb the perfume with the magnesium carbonate, add the zinc stearate and disperse them in the talc. Add A to the powder blend B and mix to a smooth paste. Pour into moulds and allow to dry until hard. The sticks are finally dried in an oven.

It is claimed that the resulting sticks do not break easily and that they have excellent rub-off qualities. The degree of rub-off and the strength of the stick can be controlled by the level of the binder.

A method for the manufacture of talc sticks without the use of a binder in the talc was disclosed in a US patent⁴⁹ which quoted the following formula:

		(32)
		<i>per cent</i>
	Talc	50
	Zinc oxide	10
	Chalk	10
	Kaolin	10
	Colloidal silica	20

The sticks are formed by compression moulding the powder mixture at pressures ranging between 450 and 600 psi (3–4 MPa), then coating, except on the end, with a suitable film-forming polymer to protect them against cracking or crumbling.

Pre-electric Shave Powder

A loose powder which can be used as a pre-electric shave preparation is illustrated by example 33.

	(33) <i>per cent</i>
Talc	50.0
Kaolin	14.0
Magnesium carbonate	12.0
ANM powder (etherified starch)	10.0
Cetyl alcohol	3.0
Glycerol monostearate	1.0
Zinc stearate	4.0
Zinc oxide	5.5
Perfume	0.5

To overcome the problems of handling the powder and to avoid spillage, pre-electric shave powders have been packed in aerosol containers. A low-pressure propellant mixture and careful selection of actuator are required to produce a soft, dry spray which does not result in excessive 'bounce' of fine particles from the target surface.

Zinc oxide, zinc stearate, kaolin and calcium carbonate all tend to agglomerate in the presence of propellant and cannot be used in powder aerosols. Minor portions of colloidal silica (Aerosil), magnesium carbonate, magnesium stearate and starch can be used to improve the dispersion of talc in the propellants. Isopropyl myristate or mineral oil (0.5–1 per cent) can be used as a lubricant and also to aid dispersion. The total powder content of these compositions rarely exceeds 15 per cent of the total weight in order to avoid blockage of the valve or actuator.

Example 34⁵⁰ illustrates the possible composition of a pre-shave powder aerosol:

	(34) <i>per cent</i>
Talc	80.0
Aerosil	5.0
Starch	4.5
Magnesium stearate	5.0
Light magnesium carbonate	5.0
Perfume	0.5

This powder base is passed through a 200 mesh sieve and packed into aerosol containers as follows:

	<i>per cent</i>
Powder base	15
Propellant 11	60
Propellant 12	25

AFTER-SHAVE PREPARATIONS

Wet or dry shaving causes the removal of skin as well as hair from the face. The total quantity of skin and hair removed can vary by a factor of 4 or more, depending on the individual. Similarly, the percentage of skin in the shaving

debris can range between 25 and 75 per cent.¹ Much of the skin removed is the epidermal horny layer which would be shed naturally without shaving. The skin trauma associated with shaving occurs when the outer horny layer is penetrated. Damage is most likely to occur at follicular hairshaft openings.¹ A second source of irritancy in shaving is from the shaving preparation. The degreasing effect of soaps and synthetic surfactants can increase skin permeability and allow alkali and other irritants to reach the Malpighian cells.⁵¹

The purpose of an after-shave preparation is to relieve the slight irritation or 'after-glow' and confer a pleasant feeling of comfort and well-being after shaving. This is achieved by giving a slight coolness, anaesthesia, mild astringency or emolliency to the skin. At the same time, the preparation should be antiseptic and help to keep the skin free from bacterial infection during the short time it takes to recover from the slight degree of injury inflicted during the shaving operation. The extent to which these properties are emphasized depends on the type of formulation. The materials used in after-shave preparations will be discussed principally in the context of lotions.

After-shave Lotion

In its simplest form, an after-shave lotion is a clear aqueous ethyl alcohol solution containing a perfume. The desired balance of mild astringency and coolness is achieved by controlling the ratio of ethyl alcohol to water. Analysis of popular UK brands of after-shave lotion shows that they contain 50–70 per cent by weight ethyl alcohol. Other countries, notably Germany because of the tax structure, use much lower concentrations of alcohol. US sources recommend 40–60 per cent by volume of alcohol to obtain the balance of properties; however, manufacturers of popular brands tend to use alcohol levels similar to those in the UK.

The commercial success of an after-shave lotion is largely dependent on the perfume and the way in which the product is marketed. Many different perfume types, for example spicy, chypre, sandalwood, leather and tobacco, have been successful. The creation of a stable balanced perfume, which is free from components likely to cause skin irritation or sensitization, is the province of the perfumer.

The chemical composition of the perfume determines the maximum concentration at which it can be used in a particular water–alcohol mixture. It may be necessary with some perfumes to increase the alcohol content in order to achieve the required perfume level. In a situation where it is undesirable to increase the alcohol content or reduce the fragrance level, it is common practice to use a solubilizer to obtain a clear lotion. Nonionic surfactants with a hydrophile–lipophile balance (HLB) number in the range 15–18 are often found to be the most effective solubilizers, although anionic surfactants have also been used. For more detailed information, reference should be made to published work^{52–54} on the effectiveness of surfactants in solubilizing specific perfume oils. The solubilization of a perfume does not appear to reduce its stability or to cause a deterioration in the odour.⁵² Sugar-based surfactants, for example sucrose esters, sucroglycerides and ethoxylated sucroglycerides may make useful perfume solubilizers in after-shave lotions since they are said⁵⁵ to cause less

defatting of the lipid layer than the more usual polyoxyethylene derivatives of fatty acids and alcohols and are therefore less likely to cause skin irritation.

A perfume oil containing resins, terpenes and certain crystalline materials is more difficult to solubilize and may require several times as much surfactant as perfume oil. A perfume based on terpeneless oils, alcohols, compounds of low molecular weight and polar compounds will require less surfactant. The type and level of solubilizer required is determined by dissolving the perfume and surfactant in alcohol and titrating with water to the required alcohol/water ratio. The optimum level of surfactant is that which just gives a clear micellar solution that remains stable over an appropriate range of temperatures (0° – 40° C).

Humectants and emollients are frequently added to after-shave lotions at levels not exceeding 5 per cent. Polyols such as glycerol, sorbitol and propylene glycol help to maintain the water content of the skin. Glycerol has the best humectant properties of the group, but propylene glycol is often preferred because of its greater solvent power, lower viscosity and higher volatility. The feel of the skin can be improved by the addition of long-chain fatty esters, for example isopropyl myristate or lanolin. Quantities are often limited by their low solubility in aqueous alcohol solutions. Water-soluble lanolin derivatives can be used at higher levels to provide emolliency and to assist in the solubilization of the perfume oil.

Cooling of the skin results from the evaporation of the alcoholic solution. The effect can be augmented by the physiological cooling effect of menthol. The level of menthol should be kept below 0.1 per cent because of its lachrymatory properties and because its odour can upset the balance of the perfume. Odourless cooling agents¹⁹ may be more appropriate for this type of product. Menthol is also said to cause slight surface anaesthesia of skin; however, it is preferable to achieve this effect with lignocaine at a level of 0.025–0.05 per cent.

The mild astringency of the alcohol can be supplemented by witch hazel extract or even zinc and aluminium compounds such as zinc phenolsulphonate, aluminium chlorhydroxide or alcohol-soluble aluminium chloride complexes.

In a study of the effects of after-shave lotions on skin flora, Theile and Pease⁵⁶ showed that an aqueous solution containing 55 per cent by weight ethyl alcohol reduced the facial flora count by over 90 per cent immediately after application, the count returning to the pre-application level after six hours. With the same alcoholic solution containing a perfume, the skin flora count was again reduced by over 90 per cent immediately after application and was still 35 per cent below the pre-application level after six hours. This accords with the well-established antimicrobial activity of many perfume oils. Although alcoholic solutions reduce facial flora, tests *in vitro* demonstrate that they are unable to inhibit the growth of bacteria and fungi on agar plates. Some inhibitory action is found with fragranced alcoholic solutions, but a much greater effect can be achieved with quaternary ammonium compounds. The addition of 0.1 per cent benzalkonium chloride to an after-shave lotion was found to double the zone of inhibition of facial bacteria growth.

Cationic surfactants are wide-spectrum germicides which can kill or inhibit growth of organisms over a wide pH range. Quaternary ammonium compounds, for example cetyl trimethyl ammonium bromide, can be used in after-shave preparations provided that anionic surfactants have been used to solubilize the

perfume. Anionic surfactants have some activity against Gram-positive and yeast organisms but are rarely effective against Gram-negative bacteria. Nonionic surfactants are not considered to be germicidal. However, a significant development is the finding that monoesters formed from polyhydric alcohols and lauric acid (Lauricidin) have germicidal activity and they are GRAS materials.⁵⁷ This offers the possibility of perfume solubilization and germicidal activity in a single compound. More powerful bacteriocides and fungicides are available but these would require careful evaluation to ensure compatibility with the lotion and freedom from skin irritation or sensitization.

Soap-based shaving preparations tend to leave the skin slightly alkaline, whereas the pH value of normal skin is 5 to 6. Formerly it was suggested that boric acid was a useful component in after-shave lotions, both as an antiseptic material and as a neutralizer of any residual alkalinity. There is a slight possibility of boric acid intoxication by absorption through damaged skin and therefore it is preferable to use lactic or benzoic acid.

Allantoin is frequently added to after-shave lotions at a level of 0.1–0.2 per cent to promote wound healing.

Example Formulations

A basic after-shave lotion, not requiring solubilization of the fragrance, can be made up as in example 35.

	(35)
	per cent
Ethyl alcohol, specially denatured	60
Propylene glycol	3
Water, demineralized	36
Perfume	1

Procedure: Dissolve the perfume and propylene glycol in the alcohol and add the water slowly, stirring well to avoid locally high concentrations of water precipitating the less soluble components of the perfume. Allow the solution to stand for several hours at about 4°C, then filter.

	(36)
	per cent
Hyamine 10-X (25%)	0.250
Ethyl alcohol	40.000
Menthol	0.005
Benzocaine	0.025
Water	59.720
Perfume	q.s.

	(37)
	per cent
Witch hazel extract	15.00
Ethyl alcohol	10.00
Alum	0.50
Menthol	0.05
Ethyl <i>p</i> -amino benzoate	0.05
Glycerol	5.00
Water	69.40

An aerosol after-shave lotion (example 38) is given in a Technical Bulletin⁵⁹ by Esso Chemicals.

	(38) per cent
Hexadecyl alcohol	0.8
Ethyl alcohol	53.7
Distilled water	33.0
Polawax A-31	2.0
Perfume	0.5
Propellant 12/114 (40:60)	10.0

A formulation containing colloidal alumina⁶⁰ gives a cooling astringent lotion with excellent lubricity:

	(39) per cent
A Baymal alumina	2.10
Water	57.90
B Alcohol (74 OP)	36.950
Polyethylene glycol (400) distearate	3.000
Menthol	0.025
Camphor	0.025
Preservative, perfume	q.s.

Procedure: Parts A and B are prepared separately using heat as required to dissolve the PEG distearate in the alcohol. The two parts are mixed cold.

Some components of perfumes are notorious for their instability when exposed to ultraviolet light. It is not unusual to find that, after exposure to direct sunlight for a few months, an after-shave lotion in clear glass bottles develops a characteristic 'bottle-odour', quite unlike the original fragrance. Accelerated testing of the ultraviolet light stability of the packaged product should therefore be included in the evaluation of after-shave preparations. Many manufacturers circumvent the problem by using opaque or chromium-containing glass bottles to package the lotion.

Quick-break Foam After-shave

To aid the transference of the after-shave lotion from the hand to the face, quick-breaking aerosol foams have been developed. The principles of the action of this type of product have been discussed in the section on collapsible foam pre-electric shave lotion.

A quick-breaking after-shave lotion from the General Chemical Division of Allied Chemical⁶¹ is given in example 40.

	(40) per cent
A Polawax A-31	1.50
Ethyl alcohol (SDA No. 40)	62.10

	<i>per cent</i>
B Menthol	0.05
Camphor	0.05
Perfume	0.30
C Emcol E-607	0.20
Allantoin	0.10
Water (distilled)	35.70
	<hr/>
Concentrate	92
Propellants 12/114 (20:80)	8

Procedure: Warm part A to 45°C to dissolve the Polawax; cool to 37°C and add part B. Heat part C to 80°C to dissolve the components; cool to 37°C and add to the solution of A and B. Fill while still warm.

Crackling Foam Aerosol After-shave Lotion

After-shave preparations have been formulated that are dispensed from an aerosol container as a foam and which exhibit a crackling sound when subjected to shear during application to the face. Compositions of this type are said to be oil-in-water emulsions, the continuous aqueous phase containing suitable emulsifiers and the oil phase consisting of the liquefied propellant and propellant-soluble materials. The propellant, a fluorochlorocarbon, constitutes 75–95 per cent by weight of the emulsion.

An example⁶² of a crackling aerosol after-shave lotion is as follows:

	(41) <i>per cent</i>
Di-isopropyl adipate	0.778
Perfume	1.090
Menthol	0.060
Tergitol-XD*	0.500
Water	9.572
Propellant 114	88.000

* Monobutoxy ether of polyethylene-polypropylene glycols mol. wt 2500 (Union Carbide).

Procedure: Blend the first three components and stir the resulting mixture into water containing Tergitol-XD. Cool this emulsion to 1°C and add 17.6 parts by weight of Propellant 114, pre-chilled to 1°C. Stir the resulting mixture until a uniform emulsion is formed, when the balance of the Propellant 114 (70.4 parts by weight) can be added. The resulting mixture is placed in pre-chilled (1°C) aerosol containers and the valve is crimped in place.

After-shave Gel

An aqueous alcoholic gel can be formed by neutralizing a carboxyvinyl polymer with a base. The amount of gelling agent (usually less than 1 per cent) and the degree of neutralization controls the stiffness of the gel. The gel may optionally contain a physiological cooling agent and an emollient which is soluble in the alcoholic solution.

Example 42 gives an after-shave gel from a B.F. Goodrich Chemical Co. Bulletin.⁶³

	(42) per cent
Ethanol	45.1
Water	53.0
Carbopol 940	1.0
Menthol	0.1
Di-isopropylamine	0.8
Perfume oil	q.s.

Procedure: Dissolve the perfume and menthol in the alcohol and then slowly stir in most of the water (a solubilizer can be used to obtain a clear solution). Disperse the Carbopol 940 in the aqueous alcoholic solution. Reduce the speed of the mixer and slowly add the di-isopropylamine dissolved in the small quantity of retained water.

The resulting product should be a crystal-clear gel, which is subject to degradation by ultraviolet light. It is preferable, therefore, to package it in coloured or opaque containers. Alternatively, UV stabilizers can be added to the formulation.

A similar formulation,⁶⁴ containing Viscofas X 100 000 (1 per cent) neutralized by tri-isopropylamine (0.1 per cent) in place of Carbopol and di-isopropylamine, can be prepared by dispersing the Viscofas in water at 90°C, allowing it to cool to room temperature before adding the alcohol and then the tri-isopropylamine.

Salts of glycyrrhizic acid, derived from licorice roots, can be used to form transparent gels at pH values from 2 to 6. The strength of the gel can be increased by the addition of water-soluble metal salts, for example zinc sulphate, alum, zinc phenolsulphonate.

<i>Astringent after-shave gel</i> ⁶⁵	(43) per cent
Dipotassium glycyrrhizinate	1.0
Citric acid	0.5
Zinc sulphate	0.2
Zinc phenolsulphonate	0.2
Ethyl alcohol	10.0
Propylene glycol	5.0
Water	83.1
Perfume, preservative	q.s.

Procedure: A mixture of dipotassium glycyrrhizinate, alcohol and propylene glycol is prepared and the perfume added. Heat this mixture to about 50°C and add an aqueous solution of citric acid, the zinc salts and preservative. The resulting solution is cooled to around 10°C and allowed to stand overnight.

After-shave Cream and Balm

The astringency of after-shave preparations containing more than 50 per cent by weight alcohol can be irritating to skin which has been excessively damaged by

shaving or over-exposure to sun and wind. Increasingly, manufacturers are introducing creams or balms into their range of after-shave preparations. The formulations used to obtain the soft-textured, oil-in-water emulsions are often similar to vanishing or moisturizing creams. There is some advantage to be gained from using soap-free compositions in that the pH of the emulsion can be adjusted to the slightly acid value of normal skin.

<i>Soap-free after-shave cream</i> ⁶⁶		(44)
		<i>per cent</i>
A	Glycerol monostearate S/E (Teginacid H)	10.0
	Mineral oil	10.0
	Petrolatum	6.0
	Tegiloxan 100	0.5
	Lanolin	3.0
	Cetyl alcohol	3.0
B	Glycerol	3.0
	Citric acid	0.2
	Potassium aluminium sulphate	0.1
	Water	64.2
	Perfume	<i>q.s.</i>

<i>Opaque hydro-alcoholic balm</i> ⁶⁷		(45)
		<i>per cent</i>
A	Amerchol L-101	5.0
	Isopropyl lanolate	1.0
	Polyethylene glycol (1540) monostearate	3.0
B	Carbopol 934	0.5
	Water	60.0
	Triethanolamine	0.5
	Ethyl alcohol	30.0
	Perfume	<i>q.s.</i>

Procedure: Add the Carbopol 934 slowly to the water at room temperature with rapid agitation. Mix thoroughly until a thin cloudy dispersion is obtained. Heat the Carbopol solution and the oil phase A separately to 75°C. Add the Carbopol solution to the oil phase and stir for 5 minutes to emulsify before adding the triethanolamine. Cool with stirring to 38°C. Add the alcohol and perfume and continue cooling.

After-shave Powder

The main purpose of after-shave powders, as of all other after-shave preparations, is to alleviate any discomfort produced by shaving and leave the face cool and refreshed. The additional possible functions of an after-shave powder are to cover minor skin defects and to mask any unacceptable shine produced by an excessively oily brushless shaving cream, leaving the face with a smooth matt appearance. Further functions can be added if desired, for example, the cooling effect produced by menthol, mild astringency by the incorporation of an aluminium salt, antimicrobial activity, agents to sooth irritation and to promote healing of minor wounds.

The important properties of an after-shave powder are slip, adherence and absorbency. Covering power is less important in after-shave powders than in the closely related face powder compositions. The main component of an after-shave powder is talc which provides slip and absorbency. Absorbency can be improved by the presence of kaolin or magnesium carbonate, while covering power is provided by precipitated chalk, zinc oxide or titanium dioxide. Colour is obtained from cosmetic-grade pigments. An ochre will produce a light tan effect, whereas an iron oxide will give a light pink colour. A mixture of these two pigments will produce a tone which will make the powder less conspicuous on the average Caucasian skin. Such a powder must adhere well to skin and so metallic soaps, for example zinc stearate, are usually added to the formulation.

The method of manufacture is very similar to that of face powders and talcum powders. Control of particle size is important and if necessary mixing should be preceded by a grinding process. Powder-grade perfumes should be absorbed by precipitated chalk before incorporation into the powder mix.

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Foot Preparations

Introduction

Although a large proportion of the adult population appears to suffer foot discomfort in one form or another, it is really amazing how little personal attention is lavished upon the much maligned human foot, although foot fatigue affects adversely both the physical and mental wellbeing of the sufferer, and leads to a sharp decline in the individual effort. Moreover, this effect is cumulative and ultimately often ends in various forms of stomach ailment plus the original foot discomfort (tired and aching feet lead to ill-humour, and meals eaten in a bad temper to indigestion).

This is not really surprising when we consider that the human foot has to maintain the whole weight of the body. In spite of the fact that it is equipped with a multitude of sweat glands, unequalled in any part of the skin surface except the palmar surfaces of the hands, it is, under the dictates and necessities of modern civilization, encased first in a stocking and then in a shoe or boot. The organic components of perspiration which accumulate in the shoes provide, particularly under warm and humid conditions, a good substrate for the growth of various types of micro-organism. Although socks and stockings are frequently changed and washed and also foot baths are taken, nevertheless bacteria remain in the shoes and clean socks may be reinfected. Such infection may further be promoted by poor ventilation as caused, for example, by impermeable rubber and synthetic resin soles and uppers, or by nylon stockings. The products formed by bacterial decomposition give rise to malodours, which are particularly pronounced when foot care is inadequate.

Influence of Footwear

Hole¹ reports on the interrelationships between modern footwear and the health of the feet. The disposal of sweat from the foot is inhibited by footwear and the moisture absorption and transmission properties of old and new shoe materials was studied. Leather is extraordinarily effective in absorbing and transmitting water vapour. Manmade materials, on the other hand, are relatively impermeable to moisture vapour and thus to sweat and can have therefore a considerable influence on foot health. Wear trials have shown that it is the properties of the upper material which have by far the greatest effect on sweat accumulation in shoes.

Sweat accumulation in footwear has a direct effect:

- (i) on mechanical properties of foot skin;
- (ii) on physicochemical properties of the shoe material;
- (iii) on encouragement of microbiological growth in the skin and the shoe materials.

It must be emphasized that there is no substitute for a well-fitting shoe, and a foot that is anatomically healthy. A sufferer from a foot ailment must select sensible and properly fitting footwear and, if suffering from what is commonly known as weak arch (a common complaint in those persons whose work entails long hours of standing, for example shop assistants, policemen, plant operatives and laboratory technicians), requires an adequate foot support in the form of an arch support or foot easer to be fitted by an operator experienced in this branch of work.

Foot Malodours

Sehgal² points out that hard skin, which is a layer of flat cells (stratified squamous epithelial cells) bonded together by desmosomes and penetrating tonofibrils, is largely keratin, and this together with perspiration and fungi is a feeding ground for the skin's resident micro-organisms; bacterial decomposition gives rise to the bad odours. The contribution of *Staphylococcus epidermidis* and *Trichophyton floccosum* in creating shoe and foot odours has been established.³ The bacteria responsible for the breakdown of perspiration and fungi impart a musty or mouldy odour to the shoe and foot and this seems to be due to the skin rather than the shoe. However, other odours can arise by interactions with the material of the shoe.

Foot Ailments

Neglect of the feet may lead to one or more of the following unpleasant conditions (Schroder⁴): penetrating odour of sweaty feet, caused by bacterial decomposition of the sweat and skin debris; burning and itching sensation between the toes; painful, tired and swollen feet; softening of the toenail bed; moist skin irritation, creating ideal conditions for fungal infections.

Common foot disorders have been summarized by Chalmers:⁵

Corns—caused by friction and pressure, do not have roots and may be due to structural deformity.

Bunions—misaligned joints which become swollen and tender; basically due to weakness of the muscle structure, but heredity and ill-fitting shoes may contribute.

Calluses—protective hard skin growth over areas where repeated pressure or friction occurs; as most calluses are symptoms of some underlying disorder they cannot be eliminated permanently until the basic cause is corrected.

Verrucae—often mistaken for corns, are contagious and usually quite painful; they tend to spread if not treated.

In-growing toenails—usually due to improper trimming but heredity, injury and infection may contribute.

Athlete's foot—a common skin disease of fungal origin.

Foot Infections

Chalmers^{5,6} has given excellent reviews of this subject. The feet spend long periods covered with socks or stockings and encased in footwear. This results in persistently warm and moist conditions which form an ideal environment for microbial proliferation and activity. In consequence, socks and stockings should be changed and laundered daily; what is not so well appreciated is that, whenever possible, shoes should not be worn for two consecutive days but allowed to dry out.

In a hospital study reported by Chalmers⁶ the incidence of tinea pedis (including tinea unguium) was 40·8 per cent in 348 men examined. Of the infections, 50 per cent were due to *Trichophyton interdigitale*, 26 per cent to *Trichophyton rubrum*, 0·7 per cent to *Epidermophyton floccosum*, 4·1 per cent to non-dermatophytes (nails only), 11·7 per cent to mixed infections and 7·5 per cent were microscopically positive but not identified.

The use of communal washing and bathing facilities is a major cause of spread of such infections. Even laundering failed to eliminate *T. interdigitale* from bedsocks and in the hospital study mentioned above it was suggested that infected socks were an even more important source of cross-infection than bathroom floors. The supreme importance of hygienic cleansing of communal bathrooms, showers, etc., is clear; regular cleansing with germicidal products to remove skin debris and microbial contaminants is essential.

The most prevalent kinds of foot infection are caused by fungi—mycosis. The well known mycosis 'athlete's foot' has almost become an international disease. Athlete's foot, also referred to as tinea pedis, trichophytosis pedis and ringworm of the feet, is a complaint usually caused by the fungus *Trichophyton mentagrophytes* and less frequently by another fungus *Epidermophyton inguinale*. A chronic variety of tinea pedis, which often affects the nails and which is very resistant to treatment, is caused by *Trichophyton rubrum*. Athlete's foot is not as widespread as many people believe it to be. It is reckoned that in the temperate climatic conditions prevailing in the United Kingdom its incidence in the population as a whole is not greater than about 4 per cent. The complaint is more common among athletes, students, schoolboys and, in general, among those who bathe communally. In its commonest form the condition results in maceration and peeling between the toes, while in warmer weather a more active eruption of vesicles may occur in the interdigital areas and on the soles.⁷ Tinea pedis is generally confined to one foot at a time.

There are other conditions resembling ringworm, and for treatment to be effective a correct diagnosis must be made, preceded by microscopical examination and if necessary by culturing. In this connection mention must be made of another affliction of the feet, namely dermatitis of the feet, which may be produced by dyes and chemicals from socks, shoe leather or rubber. Unlike tinea pedis, however, the eruptions are symmetrical and do not affect the interdigital areas but only the back and side of the feet.

Hyperhidrosis of the feet may also cause redness and maceration of the skin of the soles and between the toes, but again it can be differentiated from athlete's foot by its symmetry and the fact that it is not confined to the interdigital areas between the fourth and fifth toes as is the case in athlete's foot.

As far as athlete's foot is concerned, the sources of infection are usually flooring and bath mats in bathing establishments and shower rooms in factories and mines used by barefooted individuals suffering from fungal infections of the feet. Dermatophytes affect, in the first instance, the horny layers of the skin, but eventually produce inflammatory symptoms which vary in intensity, and which in the case of interdigital mycoses are not very easy to treat because causative organisms stay deeply in the crevices of the skin.

Foot Care and Hygiene

It is an undeniable truth that the feet, while needing more care and attention than most other parts of the body, in actual fact generally get far less. Good foot care extends to the choice and treatment of socks, stockings and, above all, shoes.

The feet should be washed at least once a day with soap and water, and after washing should be dried thoroughly, especially between the toes, and dusted with a talcum or foot powder. If infection is suspected or likely to have been encountered, both the soap and the powder should certainly contain an antiseptic agent.

The use of bactericidal compounds in toiletries is becoming widespread but in many products such use may be dubious. However, in foot products which must cope with conditions highly favourable to micro-organisms, the use of bactericides and fungicides is certainly justified.

There are many types of foot preparation in existence. Some are used to provide relief for tired and aching feet, others to soften cornified skin or to combat foot perspiration, and there are those used for alleviating skin irritations, eruptions and infections and for providing an antibacterial or antifungal effect.

Products of general toilet utility can also be used for these purposes and even marketed as foot products; the basic requirements are no different from those of similar products used for other parts of the body. For instance, foot lotions may be formulated on the lines of a skin tonic or mild astringent lotion.

Bathing the Feet

Being an extremity of the body, and not having adequate exercise, the human foot, particularly when constricted in ill-fitting shoes, or by tight elastic or other suspenders around the leg, is prone to an inefficient circulation. Bathing the foot in hot water stimulates the blood circulation, eliminates stale sweat secretions and temporarily reduces bacterial infection. If the bath is alkaline it softens the hard keratinous layer of the skin, corns, calluses, etc.

Proprietary bath salts for the feet consist essentially of alkaline salts, often in conjunction with an oxveen-releasing substance such as sodium perborate. In

some of the oxygenated foot bath salts, catalysts such as manganese borate and enzymes have been used to accelerate the release of oxygen. Other types of preparation are formulated so that the final bath solution approximates in its composition to sea water. Chalmers⁵ proposes the following formulae for bath salts for the care of the feet. Examples 1 and 2 are powder alkaline oxidizing foot fresheners; examples 3 and 4 are mineral foot baths for relieving aches and strains in tired feet:

	(1) per cent	(2) per cent	(3) per cent	(4) per cent
Sodium sesquicarbonate (needles or powder)	94.4	94.0	—	—
Sodium lauryl sulphate (powder)	0.2	0.5	—	—
Methyl salicylate	0.2	—	0.1	—
Menthol	0.2	0.1	—	0.1
Eucalyptol	—	0.2	—	—
Pineneedle oil	—	0.2	—	0.1
Sodium perborate	5.0	—	—	—
Sodium percarbonate	—	5.0	—	—
Sodium dichloro-isocyanurate (6% active chlorine)	—	—	0.1	0.1
Dowfax 2A	—	—	—	0.2
Sea salt crystals	—	—	99.7	—
Magnesium sulphate crystals (Epsom salts)	—	—	—	99.4
Perfume	—	—	0.1	0.1
Colour	<i>q.s.</i>	<i>q.s.</i>	<i>q.s.</i>	<i>q.s.</i>
Bath dose: grammes per 4 pints (2½ litres) water at 40°C	20	20	150	150

Artificial sea-salt powders are sometimes used in foot baths and relief is sometimes attained by their use. Usually the main sea-water constituents of cheap commercial quality are purchased separately and mixed in an approximation of sea-water, the powder being put into packets. This may be tinted and perfumed. Example 5 is such a product. One part of this powder is sufficient for 20 parts of water for a full strength foot bath.

	(5) parts
Potassium iodide	1
Potassium bromide	2
Magnesium chloride	250
Calcium chloride	125
Magnesium sulphate	250
Sodium sulphate	500
Sodium chloride	1500
Colour, perfume	

A bubbling foot bath tablet which releases oxygen and carbon dioxide, may be formulated as follows:⁸

	(6)	
	<i>per cent</i>	
Lathanol LAL	26.0	
Tartaric acid powder	26.0	
Salicylic acid	1.0	
Sodium bicarbonate powder	25.0	
Sodium sesquicarbonate powder	9.0	
Sodium hexametaphosphate	4.0	
Sodium perborate	5.9	
Perfume	1.5	or <i>q.s.</i>
Calflo E	1.5	
Colour: FD & C Blue no. 1	0.1	or <i>q.s.</i>

'Luxury' liquid or cream foot baths with herbal and/or deodorant properties may be formulated along the lines of conventional foam baths:

<i>Luxury foot bath</i> ⁹	(7)	
	<i>per cent</i>	
Tegobetaine L7	50	
Aminoxid WS35	3	
Tego 103S	5	
Undecylenic diethanolamide	2	
Lactic acid	5	
Water	35	
Perfume, colour	<i>q.s.</i>	

<i>Herbal foot bath</i> ⁴	(8)	
	<i>per cent</i>	
A Zetesol 856T	10.0	
Water	52.8	
Extrapone Urtica Special	1.0	
Extrapone Witch Hazel	5.0	
Colourless Distillate Special		
Extrapone Chamomile Special	0.5	
Extrapone Alpine Herbs Special	2.0	
Salicylic acid 10% solution*	20.0	
Foromylen F10	0.3	
B Neo-PCL water-soluble	2.0	
Fungicide DA	5.0	
C Menthol recryst. puriss	0.4	
Perfume oil	1.0	

* Salicylic acid 10% solution:

Borax	5.0
Salicylic acid	10.0
Water	85.0

Heat to near boiling point to dissolve the salicylic acid.

<i>Deo-Foam bath for the feet</i> ⁴		(9)
		<i>per cent</i>
Texapon Extract N25		55
Comperlan KD		6
Salicylic acid 20% solution*		25
Foromyen F10		2
Water		7
Neo-PCL water-soluble		1
Perfume oil		4
* Salicylic acid 20% solution:		
Borax		8
Salicylic acid		20
Water		72

Heat to near boiling point to obtain a clear solution.

Foot Powders

Lehman¹⁰ states that foot powders are recommended in the US Army; they keep the feet dry and if they contain a fungicidal or fungistatic agent a better opportunity is presented for a more continuous application as perspiration dissolves the medicament. In shoes they help to prevent reinfection. Lehman quotes the following formula:

	(10)
	<i>per cent</i>
Thymol	1
Boric acid	10
Zinc oxide	20
Talc	69

Another simple fungicidal dusting powder for the feet is proposed by Goldschmiedt.⁸

	(11)
	<i>per cent</i>
Zinc undecenoate	10.00
Undecenoic acid	2.08
Pine oil	0.47
Starch	50.00
Light kaolin	37.45

The Quaker Oats Co.¹¹ suggests a foot powder containing an antiperspirant:

	(12)
	<i>per cent</i>
Talc	82.65
'Oat-Pro'	3.00
Microdry	10.00
Syloid 72	2.00
Ottasept extra	0.15
Zinc oxide	2.00
Perfume	0.2

Foot powders with various deodorant and antiperspirant additives have been offered in aerosol spray form, as in examples 13 and 14.

<i>Aerosol foot powder</i> ⁴	(13)
	<i>per cent</i>
Talc	92.0
Zinc stearate	1.0
Irgasan DP.300	0.2
Santocel 54	2.8
Span 85	2.0
Isopropyl myristate	1.0
Perfume oil	1.0
	<hr/>
Powder base	15
Propellants 11/12 (50:50 or 65:35)	85

<i>Women's foot spray</i> ¹²	(14)
	<i>per cent</i>
Fragrance	0.35
Menthol crystals	0.10
Talc 'lo micron'	8.35
Acetol	1.00
Chloroxyleneol	0.20
Propellants 12/11 (40:60)	90.00

Foot Sprays

Foot sprays are intended principally to cool and refresh the feet. They usually contain antimicrobial agents, sometimes an antiperspirant material, and may contain an absorbent powder. They may be sprayed through socks or stockings and therefore are suitable for 'emergency' treatment.

The following three formulae, two for aerosol sprays respectively from Croda and RITA, and one for a non-aerosol pump spray from RITA, illustrate modern products. Of example 16 it is claimed, 'This soothing, cooling spray provides relief for hot tired feet and leaves them feeling soft and smooth'; example 17 is described as: 'A clear liquid solution for packing in a manually operated spray dispenser which dries quickly and tack-free leaving the feet cool and refreshed'.

<i>Antiperspirant foot spray</i> ¹³	(15)
	<i>per cent</i>
Talc USP	34.0
Cab-o-sil M5	2.0
Microdry	5.0
Procetyl AWS	4.0
PVP-VA Copolymer E-735	4.0
Menthol USP	0.5
Ethanol anhydrous	50.5
	<hr/>
Concentrate	15.0
Propellant 114	35.0
Propellant 12	50.0

<i>Aerosol foot deodorant spray</i> ¹⁴	(16) <i>per cent</i>
Ammonyx 4002	0.125
Menthol (racemic)	0.125
2-Ethyl-1,3-hexanediol	2.25
Laneto 100	0.25
Ethanol anhydrous	27.25
Perfume	<i>q.s.</i>
Propellants 11/12 (50:50)	70.00

<i>Foot deodorant spray solution for pump spray</i> ¹⁴	(17) <i>per cent</i>
Ethanol 96%	28.00
Versene	0.03
Perfume	<i>q.s.</i>
Hyamine 10X	0.25
Laneto 50	2.00
Deionized water	68.62
Silicone fluid DC-556	0.10
Camphor	0.50
Menthol (racemic)	0.50

Procedure: Dissolve all of the ingredients in the ethanol and then add the water.

Foot Creams

Foot massage is extremely relaxing: in fact the Chinese believe that simply massaging and manipulating the feet can relieve all tension and even cure diseases.¹⁵ Techniques for professional foot massage have been described by Gallant.¹⁶

Foot creams are a suitable adjunct to massage and may contain antimicrobials, antiperspirants, mildly keratolytic agents, vasodilators to stimulate circulation, cooling agents, as well as providing emolliency and skin-softening properties. A simple emollient and deodorant foot cream may be formulated as follows:

	(18) <i>per cent</i>
Glyceryl monostearate (self-emulsifying)	15.0
Lanolin	1.0
Sorbitol syrup 70%	2.5
Glycerin	2.5
Antimicrobial agent	0.25-0.50
Water	to 100.0

Many of the formulae given under foundation creams may be adapted for foot creams. In general the amount of fatty materials is restricted. Some spermaceti substitute or high-melting wax, or fatty acid such as stearic acid, may be included to give a waxy film rather than a greasy layer on the foot. Camphor and methyl salicylate are commonly included to give a cooling sensation; a trace of menthol may be used for a similar purpose. The formula in example 19 is, in

general, along these lines. Three more sophisticated formulae are given in examples 20-22.

	(19) per cent
Glyceryl monostearate (self-emulsifying)	12.0
Mineral oil	2.0
Glycerin	5.0
Spermaceti substitute	5.0
Camphor	1.0
Methyl salicylate	1.0
Water	73.9
Preservative	0.1

	(20) per cent
<i>Foot cream</i> ¹⁷	
A Ottasept extra	1.00
Lexemul AR	16.00
Cetyl alcohol	1.00
Amerchol L-101	3.00
Solulan 98	0.50
Mineral oil	3.00
B Alcloxa	0.25
Propylene glycol	5.00
Distilled water	69.95
C Perfume	0.30

Procedure: Heat A and B to 75°C. With rapid stirring add B to A. Cool with steady stirring and add perfume at the creaming point.

	(21) per cent
<i>Foot antiperspirant cream</i> ¹⁷	
A Stearic acid	2.00
Genapol S200	8.00
Cetyl alcohol	10.00
PCL Liquid	2.00
Cholesterol	0.30
B Sorbitol syrup 70%	5.00
Water, preservative	45.90
Allantoin	0.20
Aluminium hydroxychloride 23 (Hoechst)	20.00
C Salicylic acid	5.00
Fungicide DA	0.20
D Perfume	0.20
Irgasan DP.300	0.20
Polyglycol 400	1.00

Procedure: Heat A to 70°C, B to 75°C. Add the salicylic acid and Fungicide DA to A just before emulsification. Add B to A with stirring. Cool with steady stirring adding mixture D at 40°C. Mill if desired.

<i>Oil-in-water foot massage emulsion</i> ⁴		(22)
		<i>per cent</i>
A	Neo-PCL, self-emulsifying	25.0
	Propyleneglycol dipelargonate	3.0
	Hostaphat KL340N	0.5
B	Water	65.9
	Propylene glycol	5.0
	Preservative	0.3
	Borax	0.1
C	Perfume oil	0.2

Procedure: Heat A and B to 75°C and emulsify. Cool with stirring, adding the perfume at 40°C.

Corn and Callus Preparations

Corn cures or paints contain salicylic acid in collodion either with or without cannabis extract. Other preparations include lactic acid, trichloroacetic acid, glacial acetic acid:

	(23)
	<i>per cent</i>
Salicylic acid	10
Lactic acid	10
Flexible collodion BP	80

	(24)
	<i>per cent</i>
Salicylic acid	10
Cannabis extract (BPC 1949)	10
Flexible collodion BP	80

Five per cent castor oil may be added to the above if desired, for its plasticizing effect.

For callus softening, alkaline products are used, such as:

	(25)
	<i>per cent</i>
Tribasic sodium phosphate	8
Triethanolamine	12
Water	80
Perfume (alkali stable)	<i>q.s.</i>

	(26)
	<i>per cent</i>
Potassium hydroxide	0.5
Glycerin	15.0
Water	84.5

Example 26 should be used with care and must not be left in contact with the skin as it is caustic.

A corn remover in gel form has been described:³⁷

	(27) <i>per cent</i>
Salicylic acid	12
Benzoic acid	6
Pluronic F.127	47
Water	35
Perfume, colour	<i>q.s.</i>

Ten volume strength hydrogen peroxide applied on cotton wool for several minutes has mild but valuable skin-softening properties, and may be followed with advantage by a warm oil massage.

In the late 1950s products appeared which removed hard skin from feet, elbows, etc., by making ingenious use of the 'balling' property of wax-containing emulsions. The emulsion, presented as a milk or thin cream, is pressure-sensitive and breaks when rubbed on the skin. The solid disperse phase then aggregates to form large discrete particles which roll on the skin, collecting loose skin cells. The addition of latex and/or finely divided silica improves the efficiency. The product is effective on clean skin but the presence of oil or grease may cause it to 'smear' rather than 'roll'. The emulsion can be made pressure-sensitive by using minimal quantities of the correct type of emulsifier. The following formula will serve as a basis for experiment:

	(28) <i>per cent</i>
Stearic acid	1.0
Beeswax	4.0
Cetyl alcohol	0.5
Paraffin wax	12.0
Triethanolamine	0.6
Sorbitol syrup 70%	5.0
Veegum	0.5
Water	76.4

Chilblain Preparations

Chilblains are a condition resulting from poor circulation and an inadequate supply of blood to the hands and feet. As Gourlay¹⁸ points out, the 'first sign of a chilblain developing is a local redness and irritation which comes on while in bed or on sitting in front of the fire'; subsequently the pain intensifies and 'broken' chilblains may occur. Gourlay has drawn attention to the fact that, while chilblains occur relatively commonly in Britain and Europe, they are rare in Canada and the USA, and he has recorded the successful treatment of some cases with orally administered nicotinic acid (believed to be effective because of its vasodilator action).

Winner and Cooper-Willis¹⁹ tested an ointment having the composition given in example 29.

	(29) per cent
Phenol	1.0
Camphor	6.0
Balsam of Peru	2.0
Soft paraffin	25.0
Hard paraffin	7.5
Anhydrous lanolin	58.5

The instructions given were either (a) to immerse the affected part in hot water at bedtime, to dry it carefully and apply the ointment; or (b) to rub in the ointment night and morning. Medical officers reported that the ointment eased the pain and caused rapid healing, some describing it as the best remedy they had met. Winner and Cooper-Willis considered this ointment as an efficient palliative which probably acted by stimulating local circulation.

Although good results in the treatment of chilblains have been claimed by the administration of vitamin K,²⁰ it would appear that the best prophylactic measure to take, in our present state of knowledge, is to keep the feet and hands warm with woollen gloves, socks, etc.

Most proprietary products are based on the use of local anaesthetics in appropriate bases which will relieve irritation. They may also stimulate circulation.

Athlete's Foot Preparations

Treatment of tinea pedis is actually outside the sphere of interest of the cosmetic chemist, particularly if the condition is aggravated by eczema and by secondary bacterial infections. Certain preparations, however, such as those used to prevent the infection, or those used during the post-therapeutic stage to prevent re-infection, are within the scope of cosmetic chemistry.

There has been a marked increase in the number of preparations for the treatment of athlete's foot since the introduction of aerosol sprays and powders. The antiseptics that are mainly present in aerosol foot preparations are selected primarily for the control of fungi, but they have also an important function as deodorizing agents to inhibit the growth of odour-producing bacteria. A considerable amount of information has appeared on the treatment of athlete's foot, and good reviews of the subject have been published by Lesser²¹ and Chalmers.⁶

Salts of certain fatty acids such as propionic and undecylenic acids, often used in conjunction with the free acids, have been claimed to give good results in the treatment of *Trichophyton* and other dermatophytes. Keeney²² quoted the formulae given in examples 30 and 31. Little difference in the clinical efficacy of these two ointments was found.

<i>Propionate ointment</i>	(30) per cent
Sodium propionate	16.4
Propionic acid	3.6
Propylene glycol	5.0
<i>n</i> -Propyl alcohol	10.0
Carbowax 4000	35.0
Zinc stearate	5.0
Water	25.0

<i>Undecylenate ointment</i>	(31) per cent
Undecylenic acid	10.0
Triethanolamine	6.0
Propylene glycol	14.0
Carbowax 1500	10.0
Carbowax 4000	40.0
Water	20.0

These acids rarely cause any adverse reaction on the skin. Undecylenic acid is often used in conjunction with zinc undecylenate, which is similar to zinc stearate and, as claimed in a *Schimmel Brief*,²³ would be more suitable for use in aerosol powders than in pressurized lotions. A great drawback of undecylenic acid is its unpleasant odour, resembling that of perspiration malodour. This disadvantage can be overcome, however, by using derivatives of the acid, namely its monoethanolamide (Fungicide UMA, Loramine U185), diethanolamide (Fungicide DA, Loramine DU185), or monoethanolamidodisulphosuccinate (Loramine SBU185). These substances combine the fungicidal effect of undecylenic acid with surfactant properties and are claimed to be non-irritant.

An example of an antifungal foot powder based on a mixture of salts of propionic and caprylic acids is illustrated by the following composition:

	(32) per cent
Calcium propionate	15.00
Zinc propionate	5.00
Zinc caprylate	5.00
Propionic acid	0.25
Talc	74.75

A foot product in gel form is illustrated by example 33.

	(33) per cent
Ethanol 96%	72.0
Water	21.0
Undecylenic acid	5.0
Carbopol 940	1.0
Di-isopropanolamine	1.0

Commercially available antifungal agents which have been shown to be effective against dermatophytes of the *Trichophyton* and *Epidermophyton* species include:

- Bronopol (Boots)²⁴
- Dichlorophen (BP)
- Fungicides DA and UMA (Dragoco)²⁵
- Hibitane (ICI)²⁶
- Irgasan DP.300 (Ciba-Geigy)²⁷
- Loramines DU.185, SBU.185 and U.185 (Rewo)²⁸
- Myacide SP (Boots)²⁹
- Tolnaftate (BP)³⁰
- Vancide 89RE (Vanderbilt)³¹

Other Developments

Among newer developments are 'odour-destroying insoles' with absorbent and deodorant properties,³² a foot care kit with 'everything you need' for the care of the feet³³ and a synthetic fibre 'foot sponge' for use with soap to remove thick hard skin.³⁴

A recent patent³⁵ describes a deodorizer for the foot, etc., based upon an ion-exchange material such as ion-exchange cotton.

Scholl have taken out a patent³⁶ for the use of vanillin for treating athlete's foot through various product forms, or in a controlled-release device.

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Insect Repellents

Introduction

Insect repellents may legitimately be considered as toilet preparations, especially since they may be presented in cosmetic form or even in combination with other functional attributes, notably with sunscreens.

Much of the earlier work on insect repellents was concerned with the protection of military personnel in the field. More recent studies have been associated with insects as disease vectors in man and with the protection of animals, especially dairy cattle, to give substantially increased milk yields.

In a symposium on insects and disease,¹ Maibach *et al.*² reported that the relative attractiveness of man's skin to the mosquito, *Aedes aegypti*, depended upon a balance between the attractiveness of certain elements of the sweat and the repellency of skin lipids. Novak³ reported on the various attractants for the mosquito: colours, intensity of light, humidity, temperature and odours. Wright and Burton⁴ discussed the mode of action of insect repellents in a study on pyrethrum.

Current thoughts on the mode of action of mosquito repellents have been reviewed.⁵ It is proposed that the mosquitoes 'home in' on convection currents from warm, living animals, and respond to increases in relative humidity. A defence therefore is to prevent the moisture sensors from functioning normally which, it is claimed, can be achieved by chemical repellents that physically block the pores of the cuticle. Molecular size and shape and absorption forces are the controlling factors.

The repellent factors in the skin lipids have been reported⁵ to be straight-chain C₉—C₂₀ unsaturated fatty acids among which 2-decenoic acid is one of the most potent.

The possibility of achieving insect repellency by oral means has been discussed;¹ one of the potential drugs is thiamine hydrochloride.⁵

Most efficacy studies on insect repellents have involved a 'time of protection' factor but Burton and his co-workers at the British Columbia Research Council⁶⁻⁸ reported a new method whereby a chemical can be tested for 'intrinsic repellency' against the mosquito, *Aedes aegypti*, and other insects. The method depends upon the concentration of a repellent in air required to neutralize the effect of a 'standard attractive target'; results for some 47 compounds were reported.⁷

Repellent Materials

Prior to 1940 the commonly used insect repellent materials were such strongly odorous substances as citronella oil, clove oil and camphor, which by modern

Insect Repellents

standards are relatively ineffective. Müller⁹ reports the following essential oils as having insect repellent properties: bergamot, birch tar, cassia, cedrus atlantica, cedarleaf, citronella, eucalyptus, fennel, pine oil sylvestris, lavender, laurel leaf, melissa, clove, peppermint, pimento, pennyroyal, West Indian sandalwood, sassafras, tea-tree and wormwood.

The outbreak of World War II and the need to conduct operations in many tropical areas led to an exhaustive investigation¹⁰ into the question of insect repellents; as a result of comprehensive screening tests for primary irritation and skin toxicity properties, some 4000 compounds were reduced, first to 42 compounds, and then, as a result of further intensive testing, to 18.

It must be pointed out that the requirements and conditions of use for insect repellents by military personnel differ from those for use by the civilian population, since the former are composed mainly of young adults under close medical supervision, whereas potential civilian users would include the very young, the aged, and the infirm. On the other hand, among the numerous requirements for military personnel was the use of the preparation under tropical conditions, that is, heavy perspiration and application to large areas of the body surface, and this is more rigorous than the requirement for use in a more temperate climate.

Among the materials considered safe for use were:

Dimethyl phthalate

2-Ethyl-1,3-hexanediol (Rutgers 612)

A mixture of the following composition:

Dimethyl phthalate	6 parts
2-Ethyl-1,3-hexanediol	2 parts
'Indalone' (butoxypranoxy)	2 parts

Di-isopropyl tartrate

Cyclohexyl acetoacetate

Hexahydrophthalic acid diethyl ester

Piperonyl ether butoxide

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Among the better known substances considered safe for use was butyl-3,4-dihydro-2,2-dimethyl-4-oxo-2H-pyran-6-carboxylate (butoxypranoxy).

Martindale¹¹ points out that complete protection against biting insects (in the worst environments) requires application both to skin and to clothing. Repellents usable on the skin may also be used on clothing (except that caution must be exercised with rayon); the reverse is not necessarily so. Effective repellents for clothing include benzyl benzoate, butylethylpropanediol, dibutyl phthalate, and diethyltoluamide. When repellents are applied to the skin complete coverage must be achieved; mosquitoes will bite through any 'holes' in the protective film.

A WHO Report¹² recommends the most suitable repellents for many common biting insects.

Gilbert¹³ reported that the best mosquito repellents were, for skin application: diethyltoluamide, chlorodiethylbenzamide, ethylhexanediol, dimethyl phthalate, dimethyl carbate and butoxypranoxy; for clothing: butylethylpropanediol, ethyl hexanediol and diethyltoluamide.

Gouck¹⁴ reported the most effective tick repellents to include butoxy-pyranoxyl, diethyltoluamide, dimethyl phthalate and benzyl benzoate which gave 99 per cent protection on clothing. Diethyltoluamide and benzyl benzoate were most effective against fleas, giving better than 90 per cent protection on clothing. Diethyltoluamide, dimethyl phthalate and ethylhexanediol used on skin or clothing are effective against chiggers and mosquitoes.

Dimethyl Phthalate

Dimethyl phthalate is a colourless, almost odourless liquid, boiling point 282°–285°C, slightly soluble in water (1/250) and miscible with most organic liquids.

It is an effective repellent against blackflies, mosquitoes, midges, mites, ticks and fleas¹¹ and is usually applied as a cream or lotion containing upwards of 40 per cent; any less is ineffective. It is said to prevent the bites of mosquitoes for 3–5 hours on the skin unless washed off with profuse sweating, and for about a week on clothing—though dibutyl phthalate is preferred for this application as it is less volatile and less easily washed off.

Dimethyl phthalate is non-toxic but may cause local slight temporary smarting in sensitive persons. Smith¹⁵ reported that the minimum effective dose for protection against *Aedes aegypti* is between about 1.15 mg and 3.5 mg per square centimetre of skin. Its main disadvantage is its solvent action for certain plastics materials and it should not be allowed to come into contact with rayon garments or with plastics spectacle frames.

Dimethyl Carbate

Chemical name: dimethyl-bicyclo-(2,2,1)-heptano-2,3-dicarboxylate. Dimethyl carbate is a white to straw-coloured crystalline solid, setting point 35°C, soluble in water (1.5 per cent), in mineral oil (5–6 per cent), and very soluble in esters and vegetable oils.¹⁶

It has been described as an effective insect repellent¹⁷ and has been used by the US military forces, usually in combination with other materials, though it seems to find little use nowadays.

Ethylhexanediol

Chemical name: 2-ethylhexane-1,3-diol. *Other names:* Ethohexadiol (USP), octylene glycol, Rutgers 612, 6–12 (Union Carbide).

Ethylhexanediol is a clear, colourless, almost odourless (but reminiscent of witch hazel) oily liquid, boiling point 244°C, which is slightly soluble in water (1/50) and is miscible with alcohol, isopropyl alcohol, propylene glycol and many other materials.

Granett and Haynes¹⁸ report on the historical development of ethylhexanediol at Rutgers University during World War II and describe its properties at length. It is stable under extreme storage conditions and its solvent action for plastics and synthetic fibres is weak. It is the subject of an early patent granted to Union Carbide.¹⁹

McClure²⁰ claimed ethylhexanediol to be among the best mosquito repellents. It will also repel biting flies, gnats, chiggers and fleas for about 4 to 8 hours when applied neat, but proportionately less when used in more dilute applications. Granett and Haynes,¹⁸ reporting on comparative effectiveness studies against dimethyl phthalate, found ethylhexanediol to be almost always better against mosquitoes and to be remarkably effective against other insects. They showed a protection time of about eight hours on the skin and eight days on clothing, though the latter was affected by rain. It is stated to be particularly effective when used in conjunction with dimethyl phthalate and butoxypranoxy.¹¹

In a study of its protective efficacy against *Aedes aegypti*, Smith¹⁵ found that the minimum effective dose ranged from about 80 to 280 μg per square centimetre of skin. No synergistic effect has been found between ethylhexanediol and diethyltoluamide.²¹ Extreme toxicity tests and large-scale use by military forces indicate its safety and lack of irritant properties.¹⁸

Butoxypranoxy

Chemical name: butyl-3,4-dihydro-2,2-dimethyl-4-oxo-2H-pyran-6-carboxylate. *Other names:* butyl mesityl oxide, 'Indalone' (US Industrial Chemicals Inc. proprietary name).

Butoxypranoxy is a yellow to pale reddish-brown liquid with a characteristic aromatic odour, insoluble in water and glycerin, but miscible with alcohol, propylene glycol, other glycols, light mineral oils and vegetable oils.

Butoxypranoxy is an effective repellent; lotions containing 20–45 per cent will give protection for 4–6 hours and even longer. It has been used mainly in conjunction with dimethyl phthalate and ethylhexanediol.

Butoxypranoxy also possesses modest sunscreening properties and it is claimed that a 0.1 mm film gives complete absorption of ultraviolet light up to 350 nm. However it is prudent to include a small amount of a more active ultraviolet absorber to achieve effective suncreening.

Butoxypranoxy hydrolyses on storage in the presence of more than 10 per cent water and preparations containing it must therefore be formulated with a lower water content.

Diethyltoluamide

Chemical name: N,N-diethyl-*m*-toluamide. *Other names:* DET, DEET, Detamide, Delphene or Metadelphene (Hercules Powder Co.).

N,N-diethyl-*meta*-toluamide is a colourless liquid with a faint pleasant odour, almost insoluble in water and glycerin, but miscible with alcohol and isopropyl alcohol. The commercial material contains a minimum of 95 per cent of the *meta*-isomer.²²

Diethyltoluamide was developed by the US Department of Agriculture for use by troops during the Korean War in 1951. Of the three isomers (*ortho*-, *meta*- and *para*-) the *meta*-isomer was found to be 10 per cent more effective. Gilbert, Gouck and Smith^{23–25} found N,N-diethyl-*m*-toluamide and *o*-ethoxy-N,N'-diethylbenzamide superior or equal to the standard US Army repellent M2020. Diethyltoluamide containing about 70 per cent of the *meta*-isomer was found to be generally more effective than ethylhexanediol and other repellents both for skin and clothing.

Diethyltoluamide is effective against blackflies, chiggers, mosquitoes, ticks and fleas.¹¹ Clyde and Kingazi²⁶ found in laboratory studies that diethyltoluamide was an effective mosquito repellent for 18–20 hours compared with 4–4½ hours for a 40 per cent dimethyl phthalate cream. It has been reported to be the most effective repellent against *Aedes aegypti*.²¹ Smith¹⁵ showed that the minimum effective dose for protection against *Aedes aegypti* ranged from 50 µg to 77 µg per square centimetre of skin.

Among the properties of diethyltoluamide are claimed²⁷ its great persistence, resistance to wiping action, resistance to sweating and its non-oily nature.

Major and Hess²⁸ reported N-ethoxy-N-ethyl-*m*-toluamide to have considerable toxicity to mosquitoes *Aedes aegypti* and to repel stable flies *Stomoxys calcularis* but not houseflies *Musca domestica*.

Two new toluamides, N-(*m*-toluyl)-2-methyl piperidine and N-(*m*-toluyl)-4-methyl piperidine, have been found particularly effective against stable flies.²⁹ They may be used in a variety of formulations ranging from ointments to sprays and are said to repel a large number of troublesome arthropods.

MGK Repellents

McLaughlin Gormley King have formulated a range of repellent compositions, using patented materials, under the designation 'MGK Repellents for Personal Use' which are said to utilize the latest developments in repellent materials and to provide maximum protection.³⁰ Advantages claimed over older formulae are:

- (1) Best combinations available for stable flies, horse flies, deer flies and blackflies—frequently more of a problem than mosquitoes on beaches, golf courses, etc.
- (2) Excellent mosquito repellency.
- (3) Protection against ticks, fleas and chiggers.
- (4) No adverse effects on synthetic fibres, except for a slight darkening of rayon.
- (5) Plasticizing effect not as intense as compositions dependent upon diethyltoluamide alone or dimethyl phthalate.

'MGK Intermediates', a range of repellent compositions, are based upon blends of diethyltoluamide with MGK-264 (N-octyl bicycloheptene dicarboximide), an insecticide synergist; with MGK Repellent 11 (2,3:4,5-bis-(2-butylene)-tetrahydro-2-furaldehyde), primarily a fly repellent; and with MGK Repellent 326 (di-*n*-propyl isochinomerate), also primarily a fly repellent.

'MGK Intermediates' have the following compositions (per cent):

Intermediate No.	1995	2007	2020	5134	6339	5582
Diethyltoluamide	86	76.92	80	70	67	—
MGK-264	8	15.38	12	20	11	66.6
MGK Repellent 11	3	3.85	4	5	22	16.7
MGK Repellent 326	3	3.85	4	5	—	16.7
Typical usage level	25%	32.5%	25%	10–15%	9–15%	3–6%

1995 gives maximum protection against mosquitoes, less against other biting flies; 2007 has greater repellency to all flies and mosquitoes; 2020 is a

general-purpose composition with excellent mosquito repellency; 5134 is a general-purpose repellent giving excellent repellency to mosquitoes and good repellency to all flies and insects; 6339 will provide excellent mosquito repellency as well as being particularly effective against such insects as blackflies and sand flies; 5582 is a fly repellent generally used in combination with diethyltoluamide or another repellent of choice.*

MGK Repellent 326 should not be used in alcohol-based preparations when transesterification may occur; however, it is perfectly satisfactory in isopropyl alcohol. It sometimes shows instability in water-based systems, especially if alkaline.

Other Repellents

Benzyl Benzoate. This is the best repellent for chiggers and one of the best for fleas and ticks.¹² However, it should not be used on the skin as it may cause eruptions in sensitive persons. It is usually applied to clothing where it is very effective and its action persists after washing.

Dibutyl Phthalate. This is slightly less effective than dimethyl phthalate but preferred to the latter for impregnating clothing as it is less volatile and less easily removed by washing.

Butylethylpropanediol. This is used for the treatment of clothing and should not be used on the skin. It is an ingredient of M-1960 (butylethylpropanediol 30 per cent, butylacetamide 30 per cent, benzyl benzoate 30 per cent, emulsifier 10 per cent), used by the US Army for impregnating clothing; it is effective against blackflies, mosquitoes and other insects.¹¹

Butoxypolypropyleneglycol. This is reported to be very effective against the house fly *Musca domestica*.³² Under the name of Crag Repellent (Union Carbide Agricultural Chemicals) marketed for use on cattle, etc., but no longer approved for use on dairy and meat cattle in the USA.³¹

Di-n-butyl Succinate (Tabatrex). This is reported to be effective against the house fly *Musca domestica*.³² It is used for agricultural purposes but no longer approved for use on dairy and meat cattle in the USA.³¹ A patent³³ claims the use of the di-n-butyl succinate and, as a synergist, a fatty material such as oleic acid, ricinoleic acid, propyl oleate or benzyl oleate.

Undecenoic Acid. This is an effective insect repellent but its disagreeable odour is difficult to mask.¹¹

Repellent 790 (E. Merck, Darmstadt). This is a proprietary repellent of undisclosed composition, possibly based upon caprylic acid diethanolamide.³⁴ It is said to have a broad spectrum of activity, to be highly potent, with a sustained action and well tolerated by the skin. It is claimed to be as effective as diethyltoluamide against mosquitoes and three times as effective as the latter against the house fly.³²

Moskitox (Dragoco). This is a proprietary composition based on diethyltoluamide, dimethyl phthalate and hexylene glycol.

Other Developments

Ralston and Barrett³⁵ have reported that decyl, undecenyl and dodecyl alcohols, and aliphatic nitriles with 10–14 carbon atoms are highly repellent to flies. The inherent odour of these materials precludes their use in cosmetic preparations.

A Russian investigator, Nabokov,³⁶ reported that anabesine sulphate, an alkaloid from the plant *Anabasis aphylla* (*Chenopodiaceae*) which has been used in Russia as an agricultural insect repellent for many years, would confer protection for 10 hours when applied to the skin as a 5 per cent lotion. It was stated to be harmless to the skin and health of the person treated. The material was also said to be non-odorous.

Shambaugh and his co-workers³⁷ studied the repellency of some phenylphenols to houseflies; the most effective of these were biphenyl and 4-chloro-2-phenylphenol. A mixture of these with phenol, *o*-phenylphenol and 6-chloro-2-phenylphenol was more effective than any single compound.

Weaving and Sylvester^{38,39} and Wright and Burton⁴ have investigated pyrethrum as an insect repellent.

Quintana and his co-workers have carried out several studies on potential materials for use as long-lasting insect repellents: esters of undecanoic acid with phenols, especially resorcinol, hexachlorophene, 4-chloro-resorcinol and 4-chlorophenol;⁴⁰ esters of undecanoic acid with dihydroxyacetone, specifically 1,3-di-undecanoyl-oxyacetone and 1-undecanoyloxy-3-hydroxyacetone were shown to have long-lasting insect repellent activity on the skin;⁴¹ the mono-hexanoate, mono-propanoate, mono-benzoate and mono-undecanoate esters of dihydroxyacetone were studied and the long-lasting insect repellency of dihydroxyacetone mono-hexanoate was particularly noteworthy.⁴²

A patent⁴³ taken out by Stepanov *et al.* claims an insect repellent containing 20–90 per cent hexamethylenecarbamide to provide protection against mosquitoes, gnats, sand flies, blackflies, houseflies, fleas and ticks. In an example, an ointment containing a mixture of this compound (30 per cent) and dimethyl phthalate (52 per cent) was said to provide protection for 24–36 hours against mosquitoes and sand flies; an emulsion containing 75 per cent applied to cloth was said to protect for 5 months or more.

Two patents to Dow Corning^{44,45} relate to derivatives of tetra-silaadamantane as insect repellents.

Gualtieri *et al.*⁴⁶ investigated a number of acetals, amino-acetals, carboximide-acetals and aromatic esters on the skin for repellency to mosquitoes. The amino-acetals showed the highest degree of repellency but did not rival diethyltoluamide in duration of protection.

Klier and Kuhl⁴⁷ evaluated a number of derivatives of *N*-disubstituted *beta*-alanine. Several *N*-alkyl esters of 3-(*N*-*n*-alkyl-*N*-acyl)-aminopropionic acid and of 3-(*N*-*n*-alkyl-*N*-carboxyalkyl)-aminopropionic acid were effective repellents for mosquitoes on the skin, equal to diethyltoluamide. One compound in particular, ethyl 3-(*N*-*n*-butyl-*N*-acetyl)-aminopropionate showed high mosquito repellency and extremely low toxicity and was well tolerated by the skin.

Formulation

In formulation, quantities of repellent of the order of 10 per cent or more are generally recommended and a trend towards the use of higher levels has been noted.³⁰

Limitations of certain repellent materials must be taken into account when formulating, such as the tendency of dimethyl phthalate, especially, to attack some plastics and fibres, and the instability of butoxy pyranoxyl in the presence of water levels above 10 per cent. MGK Repellent 326 and 'MGK Intermediates' containing it should not be used in alcohol-based compositions, though isopropyl alcohol is permissible, and water-based systems should be approached with caution. MGK Repellent 11 should not be used in the presence of 2-aminopropanediol (AMPD).³⁰

Insect repellents may be formulated into the whole gamut of cosmetic product forms and formulae abound in the literature for lotions, oils, milks, creams, aerosol sprays, foams, 'quick-break foams', pump-sprays, towelettes, gels and sticks.

It has been pointed out³⁰ that under normal conditions of use—on the beach, golf-course and other holiday and pleasure pursuits—it is biting flies and other insects that are the problem and not mosquitoes, and products should be formulated accordingly. A significant trend is the logical combination of an insect repellent and a sunscreen into a single product to provide dual protection.

Formulae for a representative range of products follow. It is worth noting that more sophisticated products might be developed utilizing the more advanced formulation techniques available in the field of sunscreen preparations; product attributes and formulation problems are often similar.

Lotions

Lotions may be simply solutions of an insect repellent in alcohol with or without the addition of modifiers to moderate oiliness or to give a better skin feel. Aqueous-alcoholic products may be formulated using a solubilizer though clearly these will have considerably less wash-off resistance. Solutions may also be in other more or less volatile solvents (see later under 'Repellent Oils').

<i>Alcoholic lotion</i>	(1)
	<i>per cent</i>
Dimethyl phthalate	33
Alcohol 96%	67
<i>Clear aqueous-alcoholic lotion</i> ⁴⁸	(2)
	<i>per cent</i>
Tween 80	15
Repellent 790	10
Alcohol 96%	30
Water, purified	45

Aerosol Sprays

Examples 3,³² 5³⁰ and 6³⁰ are insect repellents; example 4 is a combined sunscreen and repellent.

	(3) <i>per cent</i>	(4) <i>per cent</i>
Repellent 790	20	15.0
Eutanol G	15	15.0
Sunscreening substance 3573	—	2.5
Isopropyl alcohol	65	67.5
Concentrate	50	50
Propellant 11	25	5
Propellant 12	25	45
	(5) <i>per cent</i>	(6) <i>per cent</i>
MGK Intermediate 5734	15	10-25
Isopar E	30	} 70-55*
Isopropyl alcohol	51	
Nitrous oxide or carbon dioxide	4	—
A-46 Isobutane/propane	—	20

* All isopropyl alcohol, all Isopar E, or a blend of the two.

Pump Sprays

Owing on the one hand to current disquiet and the regulatory position regarding chlorofluorocarbon aerosol propellants, and on the other to the development of much improved spray pumps, an interest has developed in personal repellents which can be dispensed by this method. Tested formulae³⁰ include:

	(7) <i>per cent</i>	(8) <i>per cent</i>
MGK Intermediate 5734	15	—
MGK Intermediate 2007	—	32.5
Isopar E	15	15.0
Isopropyl alcohol	70	52.5

Repellent Oils

Since most repellent materials are oily by nature and there is a need to use fairly high levels to achieve efficacy, application as an oil is advantageous. Modern materials allow the formulation of products minimizing inherent oiliness on the skin to produce aesthetically acceptable products. Formulation experience in the sunscreen field, where this is a popular method of application, can be called upon. Pressurization to give aerosol-dispensed products is straightforward. An added dimension may be given by the inclusion of moderately volatile 'oils' such as the Isopars or volatile silicones.

Example 9 gives a simple general-purpose formula.

	(9) <i>per cent</i>
Mineral oil, light	40
Vegetable oil	30
Isopropyl palmitate	20
Repellent (of choice)	10

<i>Hydrophilic repellent oil</i> ⁴⁸	(10)
	<i>per cent</i>
Atlas-G-1086	7.5
Repellent oil	20.0
Mineral oil, light	42.5
Isopropyl myristate	29.0
Perfume	1.0

<i>Aerosol sunscreen/insect repellent oils</i> ⁴⁹	(11)	(12)
	<i>per cent</i>	<i>per cent</i>
Dimethyl phthalate	4	6.0
Moskitox	5	6.0
Prosolal S8	5	4.2
PCL Liquid	24	23.0
Arachis oil	10	—
Isopropyl myristate	40	60.0
Mineral oil, viscous	10	—
Antioxydol	1	—
Perfume oil	1	0.8
	<hr/>	<hr/>
Concentrate	40	40
Propellants 11/12 (50:50)	60	60

Creams and Liquid Creams

Stable creams are less easy to formulate owing to the high levels of repellent material needed for effectiveness and their inherent emulsification problems. Once again, techniques learned from formulating sunscreens can be very useful.

The following formula for a midge repellent cream, avoiding emulsification, was proposed by the Scottish Scientific Advisory Committee:⁵⁰

	(13)
	<i>per cent</i>
Dimethyl phthalate	67
Magnesium stearate	10
Zinc stearate	23

Procedure: The mixture is gelled by means of heat.

Another non-emulsified cream has the following formula:⁵¹

	(14)
	<i>per cent</i>
Ethylhexanediol	18.6
Butoxypranoxyl	18.6
Dimethyl phthalate	55.8
Ethyl cellulose	2.7
Cellulose acetate-butyrate	2.3
Propyleneglycol monostearate	2.0

Examples 15 and 16 illustrate the use of ethylhexanediol in combination with zinc stearate and polyethyleneglycol.

	(15) per cent	(16) per cent
Ethylhexanediol	30.0	30
Zinc stearate	20.0	20
Stearic acid	4.8	—
Potassium hydroxide 41% aqueous solution	1.8	—
Water, purified	43.4	20
Carbowax 4000	—	30

A simple emulsion formula is proposed by Croda:⁵²

	(17) per cent
A Diethyltoluamide	20
Polawax	7
Ceto-stearyl alcohol	12
Crillet 3 (Polysorbate 60)	1.5
B Water, Purified	59.5
Perfume, preservatives	<i>q.s.</i>

Procedure: Heat A and B separately to 70°C. Add B to A with high shear mixing. Cool with low shear mixing.

A pleasant, non-greasy oil-in-water lotion has been described⁵³ which uses Veegum as emulsion stabilizer:

	(18) per cent
A Veegum	1
Water	64
B Diethyltoluamide	25
Stearic acid	4
Sorbitan monostearate	4
Polysorbate 60	2
Preservative	<i>q.s.</i>

Procedure: Add the Veegum to the water slowly, stirring continuously until smooth. Heat to 70°C. Heat B to 75°C, add B to A and mix until cool.

An elegant, glossy, soft sunscreen-insect repellent cream (example 19) suitable for squeeze-bottle or tube packaging has been described.⁵⁴ It is said to spread easily and rub in without whitening, to be without objectionable oiliness or tackiness and to provide good protection against the elements.

	(19) per cent
A Amerchol L-101	3.50
Modulan	1.00
MGK Intermediate 5734	12.00
Escalol 506	1.20
Tinuvin P	0.05
Arlacel 165	5.00
Cetyl alcohol	1.50

B	Carbopol 940	0.21
	Water, purified	75.34
C	Triethanolamine	0.20
	Perfume, preservatives	q.s.

Procedure: Slowly add the Carbopol to the water with fast stirring. Mix until thoroughly dispersed. Add B at 75°C to A at 75°C with stirring. After emulsification, add the triethanolamine. Continue mixing and cool to 32°C.

Another elegant sunscreen-insect repellent lotion has been proposed by Malmstrom:⁵⁵

	(20)	
	per cent	
A	Nimlesterol D	5.00
	Emerest 2400	5.00
	Mineral oil 70 visc.	18.00
	PEG-23 lauryl ether	5.00
	Methyl paraben	0.20
	Propyl paraben	0.10
	Cetyl alcohol	0.10
	Emersol 132	3.00
	Diethyltoluamide	10.00
	Escalol 506	1.20
B	Water	48.95
	Carbopol 934	0.25
	Emsorb 6915	2.00
C	Triethanolamine	1.20

Procedure: Heat A and B to 80°C. Add A to B slowly with stirring. Mix thoroughly and add C. Cool with stirring.

Gels

A good gel is an excellent way of presenting an insect repellent which may have an alcoholic, aqueous or oil basis. Certain of the formulae presented earlier in this chapter as creams are, in reality, opaque gelled oils; however, gels are usually thought of as being clear or almost so. Simple Carbopol-based gels may be prepared as in example 21.

<i>Personal repellent gel</i> ³⁰	(21)
	per cent
MGK Intermediate 5734	10-15
Isopropyl alcohol	50
Water	31-36
Carbopol 940	2
Ethomeen C-25	2

Procedure: Disperse the Carbopol smoothly in the isopropyl alcohol-water mixture using high shear mixing; low shear mix until the Carbopol is fully swollen. Add the MGK Intermediate, then add the Ethomeen, when a stiff gel will form.

The above formula will give a slightly hazy, pale green product. A clear, bright, soft gel, with additional emolliency, may be formulated as follows:⁵⁴

	(22) per cent
MGK Intermediate 5734	10.00
Alcohol 96%	50.00
Carbopol 940	0.75
Water	28.25
Di-isopropanolamine, 10% aqueous	8.00
Solulan 98	3.00
Perfume, preservatives	q.s.

Procedure: Disperse the Carbopol in the water using high shear mixing. Mix the MGK Intermediate and the alcohol, reduce the speed of mixing and add. Add the di-isopropanolamine solution followed by the Solulan 98 and mix until uniform.

Sticks

Sticks have proved generally to be less effective owing to the difficulty of transferring enough repellency to the skin. However, two formulae are of interest as typical products; one is a soap-alcohol gel-stick and the other a wax-based product.

In example 23 an MGK Intermediate is used which does not contain Repellent 326 because the latter has been found to decompose rapidly in soap-based sticks. It is said to remain firm at elevated temperatures and to be semi-clear.

<i>Personal repellent stick</i> ³⁰	(23) per cent
A MGK Intermediate 6561	20.0
Isopropyl alcohol	64.5
Glycerin	5.0
Sorbo sorbitol syrup	4.0
B Sodium stearate	6.0
Stearyl alcohol	0.5

Procedure: Heat A to 55°–65°C and stir until uniform. Add B and heat to 65°–70°C with stirring until clear. Immediately pour into moulds and cool.

<i>Wax-type repellent stick</i> ³²	(24) per cent
A Repellent 790	20
B Lanolin	25
Paraffin wax m.p. 68°–72°C	20
Spermaceti (or substitute)	20
Mineral oil, viscous	15
Colour, perfume	q.s.

Procedure: Melt B to 75°C, mix and stir in A. Add perfume at 55°–60°C. Pour into moulds at 39°–40°C.

A US patent⁵⁶ disclosed a stick-type product (example 33) containing a high proportion of active repellent in a soap base. It was plasticized with glycerin and was claimed to be transparent, stable at the extremes of temperature normally encountered, non-brittle and easily applied to the skin.

	(33) parts
Dimethyl phthalate	18.2
Ethylhexanediol	18.0
Isopropyl alcohol (91%)	31.5
Sodium stearate (powdered)	20.3
Glycerin	12.1
Distilled water	3.5
Colour solution	1.2
Perfume	1.2

Procedure: Mix the first three ingredients together and add the sodium stearate, glycerin, water and colour solution to the mixture. Heat to 81°–82°C. with occasional stirring. When a clear solution is obtained (usually 7–10 minutes), remove the heat source and allow to cool to 60°C. Add the perfume and pour into moulds; cool to room temperature.

In making such sticks, at least 30 per cent of repellent should be present; the gelling agent may consist of beeswax with the addition of other oils, fats and waxes to obtain the desired consistency.

Towelettes

Paper or fabric towelettes for applying various toiletry and cosmetic products have become increasingly popular, including their use for insect repellents. A suitable impregnating solution can be prepared as follows.³⁰

	(34) per cent
MGK Intermediate 5734	10–25
Isopropyl alcohol	56–50
Water	34–25

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Sunscreen, Suntan and Anti-sunburn Products

SUNLIGHT AND THE HUMAN BODY

Introduction

Exposure to sunlight can have both beneficial and harmful effects on the human body, depending on the length and the frequency of exposure, the intensity of the sunlight and the sensitivity of the individual concerned.

The most obvious effect of exposure to the rays of the sun is first of all erythema of the skin, followed by the formation of a tan which seems to have been adopted by the present civilized world as a symbol of physical health. In actual fact, development of a tan is a protective reaction of the human body to minimize any damaging effect of solar irradiation.

The intensity of erythema (reddening) produced on the skin following exposure to sunlight depends on the amount of UV energy absorbed by the skin. Erythema usually starts to develop after a latent period of 2–3 hours and reaches its maximum intensity within 10 to 24 hours after exposure.

Tanning

The tanning ability of an individual is genetically predetermined and depends on his capacity to produce melanin pigment within the melanocytes.

Tanning responses are stimulated by erythemogenic (as well as longer) wavelengths in the ultraviolet and visible radiation ranges. There are three types of tanning response:

- (i) immediate tanning;
- (ii) delayed tanning;
- (iii) true tanning, also referred to as melanogenesis.

Immediate tanning is stimulated by energy between 300 nm and 660 nm and its maximum efficacy lies between 340 nm and 360 nm. It entails the immediate darkening of unoxidized melanin granules present in the epidermal layer of the skin, near its surface. It reaches a maximum about one hour after exposure to radiation and begins to fade within 2–3 hours after exposure.

Delayed tanning involves the oxidation of melanin granules present in the basal cell layer of the epidermis and their migration towards the surface of the skin. It may start as early as one hour after exposure, reaches a peak after some ten hours and then fades rapidly after 100 to 200 hours following exposure.

Delayed tanning and also true tanning are stimulated primarily by the so-called erythemogenic radiation, that is, between wavelengths 295 nm and 320 nm.

True tanning starts about two days after exposure and reaches a maximum about two to three weeks later.

Beneficial Effects of Sunlight:

Moderate exposure of the human body to sunshine results, psychologically and physiologically, in a general sense of fitness, peace of mind and general well-being. Also it has certain definite beneficial effects on human health. It stimulates blood circulation, increases the formation of haemoglobin, and may also promote a reduction in blood pressure. Furthermore, it plays a vital part in the prevention and treatment of rickets by producing—through the activation of 7-dehydrocholesterol (provitamin D₃) present in the epidermis—vitamin D, which enhances the absorption of calcium from the intestine.

It has been used in the treatment of certain types of tuberculosis, such as the tuberculosis of glands and bones, and the treatment of certain skin diseases such as psoriasis. It is also believed to exert a beneficial influence on the autonomous nervous system and to reduce the susceptibility of individuals to various infections. Finally, by producing melanin and causing thickening of the skin, it plays an essential part in the formation of the body's natural protective mechanism against sunburn.

Adverse Effects of Sunlight

Solar irradiation can have both short-term and long-term adverse effects.

Sunburn

The short-term effect, as far as the skin is concerned, is a temporary damage of the epidermis, manifesting itself in the known symptoms of sunburn. These may range in severity from a slight erythema to painful burns and blistering accompanied in more severe cases, when large amounts of the skin have been affected, by shivering, fever and nausea, and sometimes pruritus.

According to Keller,¹ the symptoms of sunburn are the direct result of damage or destruction of cells in the prickle cell layer of the skin, possibly through denaturing of its protein constituents. Histamine-like substances released by the damaged cells are responsible for the dilation of blood vessels and erythema. They also cause swelling of the skin (oedema) and stimulate the basal cells of the skin to proliferation.

During the latent period preceding the appearance of sunburn symptoms, photochemical degradation products formed as a result of solar irradiation are believed to trigger a series of free-radical reactions leading to the formation of the biologically active substances referred to above, which diffuse into the dermal blood vessels and produce the symptoms described.

As a result of experiments conducted in the USA with exposure to mid-day sunshine in June, Luckiesh² arrived at the following definitions of four degrees

of sunburn:

- (1) *Minimal perceptive erythema*—a slight, but discernible red or pink coloration of the skin, produced in 20 minutes.
- (2) *Vivid erythema*—a bright red coloration of the skin, not accompanied by any pain, produced in 50 minutes.
- (3) *Painful burn*—characterized by both vivid erythema and pain ranging from mild to intense, produced in 100 minutes.
- (4) *Blistering burn*—characterized by an extremely high level of pain accompanied by vivid erythema and possibly systematic symptoms with blistering and peeling, produced in 200 minutes.

Sunburn does not leave any scars. A slight burn protected from further exposure to sunlight will disappear within 24–36 hours. More severe burns will generally heal within 4–8 days. As the inflammation subsides, it will be followed by peeling of the skin.

Chronic Exposure

Chronic exposure to intense sunlight, to which sailors, farmers and construction workers are often subjected, entails more serious hazards such as, for example, the development of skin cancer. It may also produce degenerative changes in the connective tissue of the corium, and result in the so-called premature aging of the skin. This is evidenced by the thickening of the skin, the loss of natural elasticity and the appearance of wrinkles, all resulting from the loss of the skin's water-binding capacity. There is also an increased tendency to form skin blemishes.

Excessive exposure to solar radiation can also aggravate or be the direct cause of some skin diseases, ranging from a transient dermatitis to skin cancer. Certain types of dermatitis are produced by photo-sensitization following solar irradiation in the presence of certain dyestuffs and chemicals such as tetrachlorosalicylanilide. Another example is Berlock dermatitis, an irregular discoloration of the skin, resulting from the application of bergamot oil or cologne spirit to the skin followed by exposure to sunlight. Lerner, Denton and Fitzpatrick³ have suggested that psoralens present in bergamot and other citrus oils are responsible for Berlock dermatitis.

There is some evidence to support the view that excessive sunlight is a major factor in the production of skin cancer and that the erythemogenic and carcinogenic wavelength limits of ultraviolet radiation coincide. Consequently, according to Piers,⁴ a higher incidence of skin cancer would be expected to occur in regions with sunlight rich in the shorter ultraviolet rays.

Roffo⁵ has shown that malignant growths occur mainly in those regions of the body that receive the greatest amount of light, such as the neck, head, arms and hands. Passey⁶ stated that seamen who were exposed to intense sunlight over a number of years developed cancer of the skin more often than others. It is also known that fair-skinned people are far more susceptible to skin cancer than people with a deeper pigmentation, and that Negroes are noted for their resistance to skin cancer, an indication that a dark pigmentation protects non-whites against the harmful effects of sunlight.

Auerbach⁷ found a constant rate of increase in the incidence of skin cancer when moving southwards towards the equator, which doubled for every 3°48' reduction in latitude, the increase in incidence thus being related to an increase in the exposure of individuals to sunlight in southern latitudes over that in northern latitudes.

The realization of the existence of long-term hazards of solar irradiation led some dermatologists to advocate the adoption of precautionary measures on a wider scale than practised hitherto. Kinos,⁸ for example, suggested the inclusion of sunscreens in make-up bases, face powders and after-shave lotions, and claimed that 2,4-dihydroxybenzophenone in an alcohol and silicone oil vehicle affords excellent protection for photosensitive individuals, and will also prevent tanning.

Solar Radiation and its Effect on Skin

Solar radiation consists of a continuous spectrum of wavelengths ranging from the infrared through the visible light to the ultraviolet region. The infrared radiation comprises wavelengths longer than 770 nm, the visible light wavelengths are between 400 nm and 770 nm, while ultraviolet radiation comprises wavelengths between 290 nm and 400 nm.

The skin responds differently to radiations of different wavelengths. The reddening of the skin produced by visible and infrared radiation (390–1400 nm) will appear immediately and subside rapidly at the end of the exposure. Radiation between 320 nm and 390 nm induces pigmentation but is not erythemogenic. Erythema is essentially brought about by exposure to ultraviolet radiation between 320 nm and 290 nm but will also be induced by radiation at shorter wavelengths.

Many workers have concerned themselves with defining whether, and which, separate parts of the ultraviolet spectrum give rise to sunburn and suntan. In the interests of standardization many have used artificial sources of ultraviolet radiation such as arc lamps of various types. It must be remembered that the total radiation from these sources will include some radiation with a wavelength as low as 200 nm, and although the lower wavelengths are filtered from sunlight by ozone in the upper atmosphere, the cosmetician has at times to concern himself with tanning by artificial sunlamps, as well as by the sun's rays.

Luckiesh and Taylor⁹ carried out some classical work in this field and established spectral curves of tanning and erythema production. Using a range of filters to isolate narrow bands of wavelengths from radiation generated by an electric arc lamp, behind a water screen to absorb heat, they found that the action on the exposed areas depended on the wavelength of the energy to which they had been exposed. Erythema and tanning were assessed immediately after exposure, on the next day and at weekly intervals thereafter. By examining the skin under ultraviolet light, they concluded that erythema and tan may be produced simultaneously but a strong erythema may obscure the tan.

With respect to wavelength they found that at wavelengths above about 330 nm the areas appeared somewhat brownish and tanned immediately after exposure. Later an erythema developed together with the tan. Wavelengths of

334.2 nm and 366.3 nm were especially effective in producing tan with minimum erythema. At wavelengths about 295–315 nm there was no immediate visible effect, but after a few hours a definite erythema set in. After a few days the erythema subsided and a tan formed. At 250–270 nm the erythema was quite superficial and disappeared in a few days with no resultant tan.

They found no difference in the rate of fading of erythema of tan produced by the different wavelengths.

The conclusions reached were that the spectrum erythema curve cannot be separated from the tanning effectiveness curve at wavelengths above 295 nm, at least for those tanning effects which may be apparent within 12 hours, when the erythema has approximately reached its maximum.

When using intermittent sub-erythema exposures, Luckiesh and Taylor found that a single exposure of 40 per cent less duration than one which produced neither tan nor erythema when applied intermittently, would produce erythema or tan. These results appeared to indicate that if tanning is desired, exposures should be long enough to produce some erythema.

Blum¹⁰ classified radiation below 320 nm as erythema and that of 300–420 nm as melanogenic.

To sum up the above and other works, the ultraviolet range can thus be subdivided into the following three bands:

- (1) The UV-A range, also referred to as long-wave ultraviolet radiation, has wavelengths ranging from 320 nm to 400 nm with a broad peak at 340 nm. This range is believed to be responsible for the direct tanning of the skin without a preliminary inflammation, possibly due to the photo-oxidation of the leuco form of melanin already present in the upper layer of the skin; it is, however, weak in producing erythema.
- (2) The UV-B range of the ultraviolet radiation lies within wavelengths of 290 nm and 320 nm. It is also referred to as the sunburn radiation or middle UV radiation, and it has a peak of effectiveness around 297.6 nm. This is the erythemogenic range of UV responsible for producing sunburn as well as for irritating reactions which lead to the formation of melanin and the development of tan.
- (3) The UV-C range, also referred to as the germicidal radiation or short UV radiation, comprises wavelengths from 200 nm to 290 nm. Although it is damaging to tissue, it is largely filtered from sunlight by ozone in the atmosphere. It can, however, be emitted by artificial UV sources. While it is not effective in stimulating tanning, it can cause erythema.

The A, B and C bands of UV radiation emit different amounts of energy and produce an erythema reaction at different time intervals after exposure. About 20–50 joules cm^{-2} of UV-A radiation are required to produce minimally perceptible erythema compared with only 20–50 mJ cm^{-2} of UV-B energy and 5–20 mJ cm^{-2} of UV-C energy.

In the case of UV-A energy, erythema of the skin produced as a result of exposure to this radiation attains its maximum intensity at about 72 hours after exposure, while in the case of UV-B radiation, the erythema reaction reaches its maximum intensity within 6–24 hours after exposure.

The proportions of energy of different wavelengths, furthermore, will vary with many other factors, such as the time of day, season, altitude, latitude, humidity and presence of smoke or dirt particles in the atmosphere.

The E-viton Concept and the Minimum Erythema Dose

To quantify erythemal energy, Luckiesh and Taylor⁹ adopted as a unit of erythemal flux, independent of the wavelength, the E-viton equivalent to 10 microwatts of radiant energy at 2967 nm wavelength where the erythemal effect is greatest.

The unit of intensity of the erythemal flux is 1 E-viton cm^{-2} (also referred to as the Finsen).

The measurement of intensity is indirect and based on the premise that, to produce a minimum perceptible erythema on an average untanned skin, exposure of approximately 40 E-viton min cm^{-2} of skin is required. Thus a minimally perceptible erythema (MPE) is produced by one of the following exposures:

- 1 E-viton cm^{-2} acting for 40 min
- 10 E-viton cm^{-2} acting for 4 min
- 40 E-viton cm^{-2} acting for 1 min

The intensity of solar erythemal ultraviolet energy in E-viton cm^{-2} on a horizontal plane with hourly variations on three specific days is shown in Figures 15.1 and 15.2.

The energy required to produce a minimum perceptible erythema is nowadays referred to as the MED (minimum erythema dose). It has been determined for both monochromatic and polychromatic radiation. Rottier¹¹ used the time required for the ultraviolet erythema (as distinct from heat erythema) to

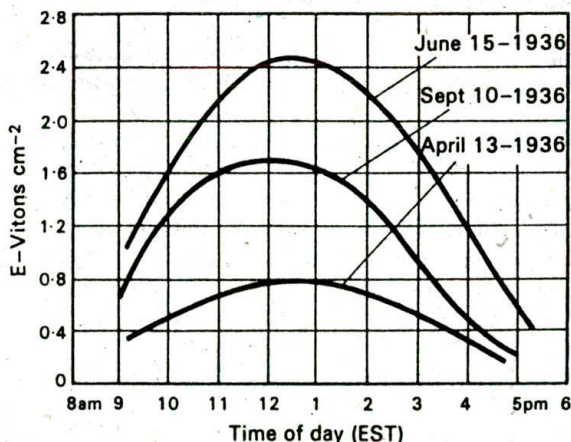


Figure 15.1 Erythemally weighted or antirachitic UV energy incident on a horizontal plane on three clear days in April, June and September. Exposure to approximately 40 E-viton min cm^{-2} produces a barely perceptible erythema on average untanned skin. (Courtesy American Perfumer)

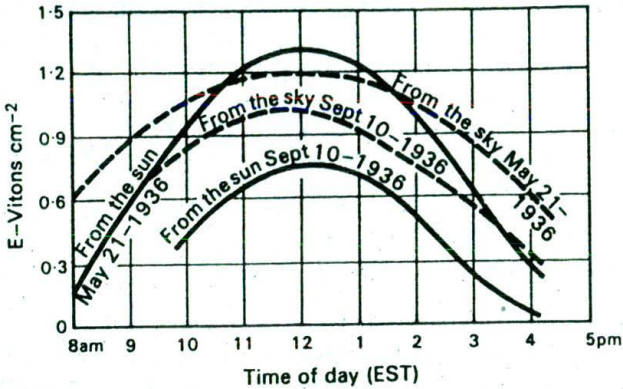


Figure 15.2 Erythemally weighted or antirachitic UV energy incident on a horizontal plane from the sun and from the entire sky on two clear days in May and September. (Courtesy American Perfumer)

develop and fade as a measure of the severity of the erythema reaction. The UV erythema appears several hours after damage is done to the skin and the period of latency depends on the ultraviolet dose. Thus the latency associated with 1 MED is 8–10 hours, whereas with 8 MED it can decrease to 1–2 hours. The erythema produced by a dose greater than 3 MED may persist for several days, while 24 hours after such a dose there may be an oedema lasting several hours. Higher doses may cause severe oedema for days, while erythema may last for months, although it may be imperceptible under a heavy tan.

Each wavelength has a specific minimal erythema dose, and a plot of log MED ($s\text{ cm}^{-2}$) against wavelength (nm) for wavelengths 250 nm to about 550 nm gives an 'action spectrum' which shows skin to be most sensitive to radiation of wavelength 250–297 nm, and much less sensitive to longer wavelengths.

Kreps¹² studied the relative response of 'normal Caucasian skin' to monochromatic radiation and found that it varied markedly with the wavelength of the radiation.

The production of erythema and the subsequent production of melanic pigment are both at a maximum at a wavelength of 296.7 nm and decrease by factors of 10 at each of the following wavelengths: 307, 314, 330, 340 nm.

There have been slight differences in the definitions of MED. According to one definition, it is the amount of energy from any source required to produce a minimally perceptible redness reaction of the skin. Anderson¹³ defined it as the time in seconds required for a ultraviolet lamp to produce an area of erythema developing after six hours and still just visible after 24 hours. Blum and Terus¹⁴ define MED as the quantity of electromagnetic radiation required per unit area to produce a minimally perceptible erythema at a specific time after exposure. It is nowadays usual to define MED as the time of exposure to any particular source of UV (sun or UV lamp) required to produce an erythema which develops after six hours and is still just visible after 24 hours.

The energy quantification of sunburn-producing radiation proposed by Luckiesh is illustrated in Table 15.1, in which the degree of sunburn resulting from

Table 15.1 Energy Quantification of Sunburn-producing Radiation⁹

Degree of erythema	Exposure (min)	E-vitons (s cm ⁻²)	MED value
Minimally perceptible erythema	20	2 500	1.0
Vivid erythema	50	6 250	2.5
Painful sunburn	100	12 500	5.0
Blistering sunburn	200	25 000	10.0

different times of exposure is related to the intensity of erythema flux and the minimum erythema dose (MED).

The length of time required to produce minimally perceptible erythema, and thus 1 MED, depends both on the quantity of energy emitted by the radiation source and on the response of a given individual's skin to sunlight, which in turn will depend on its pigmentation. Less time is required to produce a MED in light-skinned than in dark-skinned individuals. The MED for a dark-skinned Negro has been reported to be about 33 times higher than that for a Caucasian with a light complexion.

Reactions to exposure to sunlight also vary with season and the time of day. For example, at sea level the UV energy of sunlight is greatest between 10 a.m. and 2 p.m. in midsummer, with a maximum of UV-B energy falling on the skin at noon. In the early morning or late afternoon, when sunlight falls on the skin at a lower angle, the intensity of the solar energy is considerably lower and sunburn is unlikely to occur.

The different exposure times required to produce various degrees of sunburn in the average unprotected, untanned Caucasian can be seen in Table 15.2, which also illustrates the differences in exposure to produce the same effects at different latitudes. The time of exposure to produce sunburn may further be considerably shortened by reflection of additional UV light from snow and white sand.

Table 15.2 Exposure Times to Various Degrees of Sunburn¹⁵

Degree of sunburn	MED value	Length of exposure (min)	
		New Jersey (lat. 40°N)	Florida (lat. 25°N)
Minimal erythema	1	21	10
Vivid erythema	2	42	25
Painful sunburn	4	50	50
Blistering sunburn	8	165	120

Protective Mechanism of the Skin

The two factors which are mainly responsible for the skin's natural protection against sunburn are the thickness of the stratum corneum and the pigmentation of the skin.

A number of workers who investigated the nature of the protective mechanism of the skin have shown that solar radiation increases the mitotic rate of epidermal cells, causing a thickening of the stratum corneum in the course of 4–7 days, and making it thereby more impervious to the passage of erythemogenic radiation.

Some degree of protection against sunburn is conferred by an increased melanin content of the epidermis. Granules of melanin which are formed in the basal cell layer of the skin following the action of UV-B radiation migrate upwards towards the stratum corneum and the skin surface, where they are believed to be oxidized by radiation of the UV-A range. These granules are eventually shed during exfoliation, causing the skin to lose its immunity to sunburn.

The painful after-effects of solar irradiation of the unprotected skin which so often follow sunbathing can normally be prevented by a gradual exposure. The initial exposure (allowing for the sensitivity of the individual concerned) should not exceed 5–15 minutes, and should be progressively extended, the daily increase in exposure being of the order of 40 per cent over the preceding day. This should ensure development of full immunity to sunburn within 10–12 days. Maximum pigmentation can be achieved after above 100 hours of exposure.

It has been suggested by Hais and Zenisek¹⁶ that urocanic acid present in the stratum corneum to the extent of 0.6 per cent may act as a natural physiological screening agent, in that it absorbs ultraviolet radiation within the 300–325 nm range. Its elution from the skin during bathing may explain the increased susceptibility of the skin to sunburn.

Rottier¹¹ proposed an arbitrary classification of people into three groups according to their reaction to sunlight.

Group 1. 'The insensitives' with good habituation and pigmentation.

Group 2. 'The sensitives' with bad habituation and no pigmentation.

Group 3. 'The diseased' with a pathological skin reaction to sunlight.

He pointed out that in Holland people belonging to Group 1 would acquire 1–3 MED 306 in 1–3 hours, at first exposure of the trunk to the summer sun. This would not harm their skin. Repetition of such doses on the following days would gradually produce a red-brown tan. The subjects after one week's exposure would easily tolerate 8–10 hours sunlight a day, even at Mediterranean latitudes.

People in Group 2 would acquire 4–10 MED 306 at the first exposure of one hour. This may cause a disagreeable sunburn in the evening. People in this group can never expose themselves to the sun for such long periods as those in the first group, and they remain as red as lobsters without much tanning.

Insensitive people do not require a high screening factor, and in order to acquire tan, they will need a fairly strong erythema. As sunscreen they will normally use an oil which does not screen out the short wave UV. Sensitive subjects, on the other hand, will require real protection against UV in order to withstand longer exposures without any disagreeable sunburn.

A more recent classification of skin types and the characteristics of appropriate sunscreen products for their protection are given below (page 240)

SUNSCREENS AND SUNTAN PREPARATIONS

Introduction

The purpose of sunscreens and suntan preparations is to prevent or minimize the harmful effects of solar radiation or to assist in tanning the skin without any painful effects.

Classification of Sunscreens According to Application

Depending on their intended application, sunscreens may be classified as follows.

- (1) Sunburn preventive agents are defined as sunscreens which absorb 95 per cent or more of UV radiation within wavelengths 290–320 nm.
- (2) Suntanning agents are defined as sunscreens which absorb at least 85 per cent of UV radiation within the wavelength range from 290 nm to 320 nm but which transmit UV light at wavelengths longer than 320 nm and produce a light transient tan. These agents will produce some erythema but without pain.

Sunscreens in both of these categories are chemical sunscreens absorbing a specific range of UV radiation. In some instances the same sunscreen may be employed in both product classes but at different concentrations (lower in a suntan product).

- (3) Opaque sunblock agents aim to provide maximum protection in the form of a physical barrier. Titanium dioxide and zinc oxide are the most frequently used agents in this group. Titanium dioxide reflects and scatters practically all radiation in the UV and visible range (290–777 nm), thereby preventing or minimizing both sunburn and suntan.

It should be emphasized nevertheless that opaque sunblock agents based on inorganic materials are not the only compounds claiming to confer maximum protection against solar radiation. 'Supershade 15', a product of the Plough Corporation which contains a combination of 7 per cent octyl-dimethyl-*p*-aminobenzoic acid ester and 3 per cent oxybenzone is claimed to have a sun protection factor of 15 (see page 240) and to give complete protection against UV-B. It is also claimed that its regular use may prevent skin cancer.

Other products which will be mentioned in this chapter are palliatives and simulative preparations. Palliatives are designed to alleviate the pain and irritation resulting from excessive exposure to sunlight; many of them are purchased from the local chemist and druggist. Simulative preparations are designed for those who wish to feign a brown skin in the minimum of time and with the least possible pain or trouble. These are essentially preparations which stain the skin brown, or promote the synthesis of melanoid materials in the skin.

Sunscreen Agents

Sunscreens should either scatter the incident light effectively, or they should absorb the erythema portion of the sun's radiant energy. Opaque powdered materials, when applied to the skin either in the dry state or when incorporated

into suitable vehicles, will serve to scatter the ultraviolet light falling upon them. As discussed under Face Powders, in Chapter 18, zinc oxide is the most effective of such powders and is superior to titanium dioxide in this respect. Other powders which may be employed for this purpose with, however, very much less efficiency, are kaolin, calcium carbonate, magnesium oxide, talc, etc. Obviously the particle size of the powder employed is a factor of considerable importance in such preparations.

Although powders of this type rank fairly low in the sales of anti-sunburn preparations, when applied as a second line of defence over a suitable sun-screening foundation, their light-scattering possibilities should not be ignored.

The most important class of sunscreens are those which operate by absorbing the erythema ultraviolet radiation. The properties necessary in a sunscreen are:

- (1) It must be effective in absorbing erythrogenic radiation in the 290–320 nm range without breakdown which would reduce its efficiency or give rise to toxic or irritant compounds.
- (2) It must allow full transmission in the 300–400 nm range to permit the maximum tanning effect.
- (3) It must be non-volatile and resistant to water and perspiration.
- (4) It must possess suitable solubility characteristics to allow the formulation of a suitable cosmetic vehicle to accommodate the requisite amount of sun-screening.
- (5) It must be non-odorous or at least sufficiently mild to be acceptable to the user and be satisfactory in other relevant physical characteristics such as stickiness, etc.
- (6) It must be non-toxic, non-irritant and non-sensitizing.
- (7) It must be capable of retaining its protective capacity for several hours.
- (8) It must be stable under conditions of use.
- (9) It must not stain clothing.

Non-toxicity and dermatological acceptability are important because, as Draize¹⁷ has pointed out, 'sunscreens are unique as cosmetics in that their manner of use may involve multiple and extensive daily applications to large areas of the body surface and, in addition, they may be applied to skin already damaged by sun or wind burn'. Moreover they may be used on persons of all age groups and in varying conditions of health.

Draize further pointed out that pharmacological and toxicologic tests should establish an 8-fold margin of safety and that this involves acute and sub-acute dermal toxicities and potential sensitization studies.

During World War II, systematic investigations were carried out of a number of materials likely to provide protection against sunburn to soldiers fighting in tropical countries and airmen shot down over tropical islands. This led to the introduction of many new organic materials which in turn had to be screened for efficacy and toxicity.

An extensive list of sunscreens was compiled by Klarmann.¹⁸ It included the following substances:

Para-aminobenzoic acid and its derivatives (ethyl, isobutyl, glyceryl esters; *para*-dimethylaminobenzoic acid).

- Anthranilates (i.e. *ortho*-aminobenzoates; methyl, menthyl, phenyl, benzyl, phenylethyl, linalyl, terpenyl and cyclohexenyl esters).
- Salicylates (amyl, phenyl, benzyl, menthyl, glyceryl and dipropylene-glycol esters).
- Cinnamic acid derivatives (menthyl and benzyl esters; alphaphenyl cinnamonnitrile; butyl cinnamoyl pyruvate).
- Dihydroxycinnamic acid derivatives (umbelliferone, methyl-umbelliferone, methylaceto-umbelliferone).
- Trihydroxycinnamic acid derivatives (esculetin, methylesculetin, daphnetin, and the glucosides esculin and daphnin).
- Hydrocarbons (diphenylbutadiene, stilbene).
- Dibenzalacetone and benzalacetophenone.
- Naphthosulphonates (sodium salts of 2-naphthol-3,6-disulphonic and of 2-naphthol-6,8-disulphonic acids).
- Dihydroxy-naphthoic acid and its salts.
- Ortho*- and *para*-hydroxybiphenyldisulphonates.
- Coumarin derivatives (7-hydroxy, 7-methyl, 3-phenyl).
- Azoles (2-acetyl-3-bromoindazole, phenyl benzoxazole, methyl naphthoxazole, various aryl benzothiazoles).
- Quinine salts (bisulphate, sulphate, chloride, oleate and tannate).
- Quinoline derivatives (8-hydroxyquinoline salts, 2-phenylquinoline).
- Uric and violuric acids.
- Tannic acid and its derivatives (e.g. hexaethylether).
- Hydroquinone.

Klarman pointed out that isomerism plays an important role in determining absorptive capacity and illustrated this fact with absorption (absorption) curves for *ortho*-, *meta*-, and *para*-aminobenzoic acids, which indicated the superiority of the *para*-isomer over the *ortho*- and *meta*-isomers. By way of contrast, *ortho*-hydroxybenzoic (salicylic acid) has a high absorption value for erythral radiation, whereas *para*-hydroxybenzoic acid has practically none.

In experiments on protective skin preparations for the prevention of sunburn carried out on behalf of the US Army Air Forces, a large number of products were investigated.¹⁹ It was felt that since men marooned on life rafts, or in the desert, might be subject to very severe solar exposure without shelter, and to either very high or very low temperature conditions as well as to spray and waves, it was essential that the substances chosen should give effective protection, should be stable at freezing and at tropical temperatures, should be free from rancidity, non-irritant, non-toxic, and should be waterproof. Although the requirements for such preparations were exceedingly stringent, and are not likely to be generally encountered in the case of toilet preparations, the results obtained in this investigation indicate a number of substances which are of very definite value. For use by the US Forces sunscreens were required to show an absorption of 99 per cent at 297 nm with a film thickness of 0.001 in.

The screening agents tested included titanium dioxide, zinc oxide, phenyl salicylate, yellow petroleum jelly, amber petroleum jelly, zinc oxide ointment, lotions containing menthyl salicylate, a proprietary sun-preparation, dark red veterinary petroleum jelly, and several other grades of petroleum jelly. Various

types of bases included water-in-oil emulsions of lanolin and petroleum jelly, vanishing cream base, and petroleum jelly base.

A dark red petroleum veterinary jelly (Standard Oil Co., New Jersey) was quite opaque to erythema energy and used on its own gave complete protection to the skin in an exposure equivalent to 20 hours of the strongest sunlight measured during a four-year period in Cleveland. This compound was found to be non-irritant and to adhere tenaciously to the skin. Phenyl salicylate (salol) was also found to be an excellent sunscreen when used at a level of 10 per cent in a suitable base, such as petroleum jelly, particularly in a jelly having erythema screening properties of its own. Experiments showed phenyl salicylate to be non-toxic. Zinc oxide was also found of definite value in preventing sunburn, but not in conjunction with phenyl salicylate with which results were not so good when zinc oxide was added. Titanium dioxide was not found to be a very dependable protective judged on a specimen containing 20 per cent in yellow petroleum jelly. Yellow petroleum jelly was found to possess dependable screening properties against ultraviolet energy at wavelengths 296.7 nm and 302.2 nm, far more than those possessed by white petroleum jelly.

Of the very large range of compounds possessing satisfactory absorption characteristics which have been listed repeatedly in the literature, sunscreens have, in practice, been confined to *p*-aminobenzoates, *p*-dialkylaminobenzoates, salicylates and cinnamates, and frequently mixtures of these compounds have been employed. A combination of benzyl cinnamate and benzyl salicylate in an emulsion base was used in the first commercial sunscreen preparation marketed in the USA in 1928.

A number of proprietary products have been based upon menthyl salicylate. Unlike some salicylates, the menthyl ester of salicylic acid is non-irritant, odourless and initially acts as a satisfactory sunscreen at concentrations of about 10 per cent. However, as pointed out by deNavarre,²⁰ menthyl salicylate undergoes chemical change on exposure to light with the result that its screening properties are considerably diminished. Menthyl anthranilate, marketed by Givaudan under a proprietary designation, was claimed to give maximum effectiveness at about 4 per cent concentration.

Other proprietary sunscreen preparations include 'Solprotex' of Firmenich, 'Prosolal 58' of Dragoco, the 'Antivirays' of A. Boake Roberts and 'Giv-tan F' of Givaudan. 'Giv-tan F', which is 2-ethoxyethyl-*p*-methoxycinnamate, was claimed by the manufacturers to have a sunscreen index of 14.4 (see Table 15.6); this is of the same order as ethyl-*p*-dimethylaminobenzoate which has an index of 14.8.

The following five sunscreen agents were recommended by the US Department of Health, Education and Welfare²¹ for inclusion in 'a base such as mineral oil, cold cream or ethyl alcohol' at the levels stated:

	<i>per cent</i>
Cycloform (isobutyl <i>p</i> -aminobenzoate)	5.0
Propylene glycol <i>p</i> -aminobenzoate	4.0
Monoglyceryl <i>p</i> -aminobenzoate	2.5
Digalloyl trioleate	5.0
Benzyl salicylate and benzyl cinnamate (2% each)	4.0

Giese, Christensen and Jeppson²² listed the extinction coefficients at 297 nm of a number of sunscreens, together with some of their physical properties (Table 15.3).

Pernich and Gallagher²³ examined transmission spectra of various sunscreens and found the following substances to be efficient sunscreens:

Ethyl *p*-dimethylaminobenzoate
Isobutyl *p*-aminobenzoate
Coumarin
8-Methoxycoumarin
5,7-Dihydroxy-4-methylcoumarin
6-Aminocoumarin
Umbelliferone
Benzyl- β -methyl-umbelliferone
Benzylacetophenone

Some other compounds, claimed to be effective sunscreens, have been disclosed in patent specifications.

One patent²⁴ claims that protection against erythema is obtained by the application to the skin of hydrazones of *ortho*- and *para*-aminobenzaldehydes, and of *ortho*- and *para*-aminoacetophenones. Acetylated aminocinnamates have been claimed as effective and stable sunscreens in another patent.²⁵

Two other patents cover the use of organosilicon compounds with suncreening properties. These are not easily washed off the skin. One example of such a compound is a reaction product of carbethoxyethyltriethoxysilane with *p*-aminobenzoic acid, which absorbs light in the range 260–310 nm.²⁶

Another example²⁷ of an active UV-absorbing organosilicon compound is one produced by reacting ethyl-*p*-(*N*-butylamino) benzoate with gamma aminopropyltriethoxysilane. The resulting compound is said to absorb light in the 240–330 nm region.

The transmission spectrum obtained by Pernich and Gallagher for ethyl *p*-dimethylaminobenzoate is reproduced in Figure 15.3.

Stambovsky²⁸ expressed the view that esters of *para*-aminobenzoic acid in comparable concentrations possessed the highest absorption capacity of any chemicals then available. He stated that out of twenty-seven actively promoted suntan products on the US market in 1955, nineteen employed derivatives of aminobenzoic acid or salicylic acid.

Sunscreens compositions containing esters of *p*-dimethylaminobenzoic acid with C₅—C₁₈ monohydric alcohols have also been patented.²⁹ The suitability of sunscreens for commercial application is determined by their screening efficacy, solubility and their stability in given formulations. The higher esters of *p*-dimethylaminobenzoic acid are claimed to have UV absorption screening properties superior to those of the lower alkyl esters of both *p*-aminobenzoic acid and dimethylaminobenzoic acid.

In general, esters of *p*-dimethylaminobenzoic acid are more effective sunscreens than esters of *p*-aminobenzoic acid and superior to them in respect of stability, storage and use. They are also less reactive when incorporated in the usual type of cosmetic formulations.

Table 15.3 Sunscreens—Extinction Coefficients at 297 nm²²

Compound	State	Solvent	Molecular weight	Extinction coefficient	Concentration (%)
Ethyl <i>p</i> -dimethylaminobenzoate	Solid	Alcohol	194.13	27 000 27 300	1 × 10 ⁻⁴ 2 × 10 ⁻⁴
Ethyl <i>p</i> -aminobenzoate	Solid	Alcohol	165.19	21 750 21 450	2 × 10 ⁻⁴ 2 × 10 ⁻⁴
Isobutyl <i>p</i> -aminobenzoate	Solid	Alcohol	193.13	23 200 22 800	2 × 10 ⁻⁴ 2 × 10 ⁻⁴
Menthyl anthranilate	Liquid	Alcohol	275.374	941 956	5 × 10 ⁻⁴ 5 × 10 ⁻⁴
Homomenthyl salicylate	Liquid	Alcohol	390.38	6 720 6 720	2.5 × 10 ⁻⁴ 2.5 × 10 ⁻⁴
Phenyl salicylate	Solid	Alcohol	214.08	3 850 3 900	5 × 10 ⁻⁴ 5 × 10 ⁻⁴
Menthyl salicylate	Liquid	Alcohol	276.19	4 540 4 600	5 × 10 ⁻⁴ 5 × 10 ⁻⁴
Amyl salicylate	Liquid	Alcohol	208.12	4 150 3 970	5 × 10 ⁻⁴ 5 × 10 ⁻⁴
Isoamyl salicylate	Liquid	Alcohol	208.12	348 381	5 × 10 ⁻⁴ 5 × 10 ⁻⁴
Benzyl salicylate	Liquid	Alcohol	228.13	4 060 4 200	1 × 10 ⁻⁴ 1 × 10 ⁻⁴
Cinnamic acid	Solid	Alcohol	148.06	705 693	1 × 10 ⁻³ 1 × 10 ⁻³
Benzyl cinnamate	Solid	Alcohol	238.11	1 908 1 979	1 × 10 ⁻⁴ 1 × 10 ⁻⁴
Homomenthyl cinnamate	Liquid	Alcohol	300.32	505 530	5 × 10 ⁻⁴ 5 × 10 ⁻⁴
β-Methyl umbelliferone	Solid	Alcohol	176.066	8 510 8 560	5 × 10 ⁻⁴ 5 × 10 ⁻⁴

2-Naphthol-6-sulphonic acid	Solid	Water	304.28	3 310	5×10^{-3}
				3 240	
2-Naphthol-8-sulphonic acid	Solid	Water	304.28	2 010	1×10^{-3}
				1 830	
3-Hydroxy-2-naphthoic acid	Solid	Alcohol	188.17	3 470	5×10^{-4}
				3 330	
Acetanilide	Solid	Alcohol	135.08	162	1×10^{-1}
Violuric acid	Solid	Alcohol	157.05	4 800	1×10^{-3}
				4 700	
Benzylacetophenone	Solid	Alcohol	208.196	24 200	1×10^{-4}
				23 900	
Quinine sulphate	Solid	Alcohol	548.39	3 500	4×10^{-4}
				3 500	

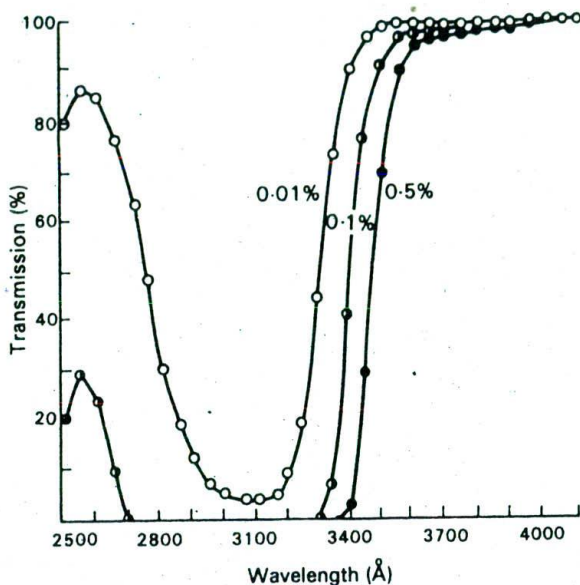
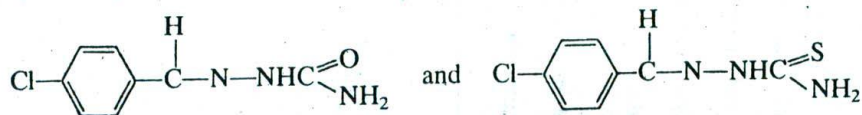


Figure 15.3 Transmission spectra of 0.5 cm layers of different concentrations of ethyl-*p*-dimethylaminobenzoate (in alcohol)

As far as esters of *p*-dimethylaminobenzoic acid are concerned, the lower esters are appreciably soluble in water, but insoluble in oils, and as a result of this are easily removed from the skin during bathing or by perspiration. With increasing molecular weight the esters become progressively less susceptible to removal by water, thus conferring longer lasting and more effective protection against erythema.

The higher alkyl esters (for example amyl, hexyl, heptyl and octyl esters) of *p*-dimethylaminobenzoic acid are oily liquids which are said to form continuous and adherent films which are not easily removed by water, exercise, abrasion or washing. Their solutions in mineral, vegetable and animal oils are claimed to remain completely homogeneous on storage for prolonged periods of time.

Sunscreening compositions fairly stable to actinic radiation, which are not readily removed from the skin, have been claimed by the GAF Corporation. As the active sunscreens, these compositions employ compounds prepared by condensing a benzaldehyde with a keto or thioketo hydrazine. Compounds specifically claimed are:



These sunscreens may be used in combination with conventional additives.

Selection of a suitable base which will not be easily removed from the skin, and will therefore ensure a long period of protection against sunburn has been

the subject of a patent granted to Boots Pure Drug Co.³⁰ The patented compositions contain a sunscreen, preferably ethyl *p*-dimethylaminobenzoate, in a cosmetically acceptable diluent or carrier comprising not less than 5 per cent of castor oil.

Polymeric Sunscreen Materials

All the compounds conventionally used as sunscreens have a relatively low molecular weight and many of them are fairly quickly removed from the skin on contact with water, necessitating further applications of the product if protection against erythema is still required. An attempt to avoid the necessity of re-applications has led to the development of water-insoluble but alkali-soluble polymeric sunscreens.

Formulations described in a patent of the National Starch and Chemical Corporation³¹ contain at least 1 per cent of an alkali-soluble, UV-absorbing polymeric sunscreen in a suitable vehicle. The polymer in question is produced from at least two essential comonomers:

- (1) An ethylenically unsaturated compound capable of absorbing UV radiation of the erythemogenic range, but transmitting radiation which produces suntan (exemplified by certain substituted acrylates, methacrylates and benzoates as well as some ethers of 2,4-dihydroxybenzophenone, 2,2,4-trihydroxybenzophenone and ethers of benzotriazole derivatives).
- (2) An acidic comonomer specified as an ethylenically unsaturated carboxylic acid containing at least one free carboxyl group (for example acrylic acid, methacrylic acid, itaconic acid, crotonic acid, etc.).

Compared with non-polymeric sunscreens, the polymeric sunscreens disclosed in the patent are very resistant to removal by fresh or sea water. By virtue of their free carboxylic groups, however, they may be readily removed from the skin, merely by the application of a dilute, mildly alkaline aqueous solution, such as soap and water, which converts the water-insoluble polymers into their water-soluble and readily removable alkaline salts.

Several more recent patents relate to sunscreens or sunscreen compositions which are substantive to the skin and resistant to water and perspiration, therefore providing a more lasting protection. An example of a compound with such properties mentioned in one patent³² is a sunscreen comprising a 50 per cent by weight solution, in isopropanol, of a polymer produced from the 4-(3-acryloxy-2-hydroxypropyl) ether of 2-(2,4-dihydroxyphenyl) benzotriazole, vinyl acetate and ethyl hydrogen maleate.

Another active agent in a sunscreen composition, with a high absorption of UV radiation and capable of depositing a continuous film substantive to the skin, is a fluorescent concentrate recovered from dark green or red petrolatum.³³ 2-Hydroxy-4-methoxybenzophenone-5-sulphonic acid was the active ingredient of yet another patent.³⁴

Sunscreen compositions have also been disclosed which contain as active agents highly substantive sulphonium salts³⁵ such as *para*-nitrobenzamide propyldodecylmethyl sulphonium bromide. These were quoted to have prominent absorption peaks within the wavelength range of 250 nm and 400 nm, which

is wider than those of the majority of commercially available sunscreens; they also adhere well to the skin.

Another patent disclosed compositions containing sunscreens with absorption peaks between 280 nm and 320 nm used in a cosmetically acceptable vehicle in combination with an alcohol-soluble polyamide resin; these were capable of forming protective films, substantive to the skin and resistant to water and perspiration.³⁶

Skin Types and Recommendations for the Choice of Sunscreens— The Sun Protection Factor

The extent to which a sunscreen product protects from sunburn and other harmful effects of exposure to sunlight varies with the individual skin type. A classification system for suncreening products³⁷ comprises five product category designations (PCD) to meet requirements of consumers with different types of skin.

Individuals can be classified into six groups according to skin type and tanning history:

- I Always burns easily; never tans (sensitive).
- II Always burns easily; tans minimally (sensitive).
- III Burns moderately; tans gradually (light brown) (normal).
- IV Burns minimally; always tans well (moderate brown) (normal).
- V Barely burns; tans profusely (dark brown) (insensitive).
- VI Never burns; deeply pigmented (insensitive).

The 'sun protection factor' (SPF) system has been developed by the Plough Corporation to define the relative effectiveness of sunscreen agents to protect the skin. It was subsequently recommended by the Over-the-Counter (OTC) Panel of the US Food and Drug Administration as a means of numerically identifying the efficacy of various sunscreen products and to provide for consumers a guide to the products suitable for particular types of skin. The SPF has been defined as the ratio:

$$\left(\frac{\text{UV energy required to produce a minimal erythematous dose (MED) on protected skin}}{\text{UV energy required to produce one MED on unprotected skin}} \right)$$

or as the ratio between the UV exposure required to produce a minimally perceptible erythema on protected skin, and the exposure that will produce the same erythema on unprotected skin. The formal definition of SPF by the OTC Panel was

$$\text{SPF value} = \frac{\text{MED(PS)}}{\text{MED(US)}}$$

where MED(PS) is the minimum erythematous dose for protected skin after the application of 2 mg cm^{-2} or $2 \mu\text{l cm}^{-2}$ of the final formulation of the sunscreen product, and MED(US) is the minimum erythematous dose for unprotected skin, that is skin to which no sunscreen product has been applied. The larger the SPF, the greater the protection the sunscreen can confer

The OTC Panel has proposed that all sunscreen products should be rated for the consumer according to the degree of protection they can provide, the rating numbers to range from 2-8. Products with a rating of 8 would thus provide the maximum protection to individuals who always burn easily and never tan, while products with a rating of 2 would be suitable for those who rarely burn and who tan profusely. Thus, for the skin-type groups listed above, sunscreen products with the following SPFs are recommended:

<i>Skin type</i>	<i>SPF</i>
I	8 or more
II	6-7
III	4-5
IV	2-3
V	2
VI	None indicated

The product category designations recommended to consumers in selecting the types of sunscreen product providing various SPFs are as follows.

PCD 1: Minimal Sun Protection Product	Provides an SPF value of 2 to under 4 and offers the least protection, but permits suntanning.
PCD 2: Moderate Sun Protection Product	Provides an SPF value of 4 to under 6 and offers moderate protection from sunburning, but permits some suntanning.
PCD 3: Extra Sun Protection Product	Provides an SPF value of 6 to under 8 and offers extra protection from sunburning, and permits limited suntanning.
PCD 4: Maximal Sun Protection Product	Provides an SPF value of 8 to under 15 and offers maximal protection from sunburning, permitting little or no suntanning.
PCD 5: Ultra Sun Protection Product	Provides an SPF value of 15 or above and offers greatest protection from sunburning, permitting no suntanning.

It has been pointed out that some people when first using this scale may misjudge the reactivity of the skin to sunlight. It has also been mentioned that elevated heat and humidity, sweating and swimming may lower the SPF value at any one time for an individual.

In practical terms, a person who usually gets red in the sun after 20 minutes should be able to stay in the sun for 120 minutes if he applies a sunscreen of extra protection (SPF 6), that is 20 minutes \times 6, provided the product is not washed off or removed by sweat. A product in the maximal protection category (say,

SPF 8) would protect the average person who would get sunburn in 40 minutes or be exposed to sunlight in the dangerous sunburning hours between 10 a.m. and 2 p.m., for $40 \times 8 = 320$ minutes. However, once the skin has become accustomed to the sun (developed protection through pigmentation) the individual's self-protection period is longer, and since the risk of sunburn has become smaller he may gradually replace a product with a high PCD by a product with a lower PCD.

Highly sensitive individuals needing mainly protection against sunlight are recommended to use a product in the 'ultra protection' category (SPF 15 or more).

For the guidance of consumers the OTC Panel has recommended that the following labelling statements are prominently placed on the principal display panels of appropriate products:

1. For minimal sun protection products (SPF 2)—
'Stay in the sun twice as long as before without sunburning'.
2. For moderate sun protection products (SPF 4)—
'Stay in the sun 4 times as long as before without sunburning'.
3. For medium sun protection products (SPF 6)—
'Stay in the sun 6 times as long as before without sunburning'.
4. For maximum sun protection products (SPF 8)—
'Stay in the sun 8 times as long as before without sunburning'.
5. For ultra sun protection products (SPF 15)—
'Stay in the sun 15 times as long as before without sunburning'.

Product Classification According to Safety or Efficacy

The OTC Panel has classified active sunscreen ingredients into three categories (Table 15.4). Products in Category I are generally recognized as safe and effective. Products in Category II are not generally recognized as safe or effective and are misbranded. The data relating to products in Category III are not yet sufficient to permit their final classification. A period of two years has been recommended to complete studies that may enable products in Category III to be switched to Category I.

In Europe, the proposed third amendment (1981) to the EEC Cosmetics Directive lists six sunscreen agents that may be contained in cosmetic products, and a further 36 sunscreen agents that may provisionally be contained in cosmetic products. These are given in Table 15.5.

Evaluation of Sunscreen Preparations

When formulating sunscreen preparations it is necessary to assess the efficiency both of the sunscreen and of the prototype products. This is done by examining their absorption characteristics spectrophotometrically in terms of concentration, thickness of liquid through which the light passes, and wavelength. The absorption characteristics may be expressed as a percentage of incident radiation absorbed or transmitted, or as the optical density. The last named is the logarithm of the ratio of the intensities of the radiation before and after passage through the solution. It has the advantage that it is directly proportional to the concentration and to the thickness of the material, hence calculation is simple.

Table 15.4 Classification of Sunscreen Ingredients—US FDA OTC Panel

I SAFE, EFFECTIVE

Compound	Dosage limit (%)				
<i>p</i> -Aminobenzoic acid	5-15				
2-Ethoxyethyl- <i>p</i> -methoxy cinnamate (Cinoxate)	1-3				
Diethanolamine- <i>p</i> -methoxy cinnamate	8-10				
Digalloyl trioleate	1-5				
2,2-Dihydroxy-4-methoxybenzophenone (Dioxybenzone)	3				
Ethyl-4-bis-(hydroxypropyl)aminobenzoate	1-5				
2-Ethylhexyl-2-cyano-3,3-diphenyl acrylate	7-10				
Ethylhexyl- <i>p</i> -methoxy cinnamate	2-7.5				
2-Ethylhexyl salicylate	3-5				
Glyceryl aminobenzoate	2-3				
3,3,5-Trimethylcyclohexyl salicylate (Homosalate)	4-15				
Lawsone with dihydroxyacetone	<table border="0"> <tr> <td style="border-left: 1px solid black; padding-left: 5px;">Lawsone</td> <td>0.25</td> </tr> <tr> <td style="border-left: 1px solid black; padding-left: 5px;">DHA</td> <td>3.0</td> </tr> </table>	Lawsone	0.25	DHA	3.0
Lawsone	0.25				
DHA	3.0				
Menthyl anthranilate	3.5-5				
2-Hydroxy-4-methoxy benzophenone (Oxybenzone)	2-6				
Amyl- <i>p</i> -dimethylamino benzoate (Padimate A)	1-5				
2-Ethylhexyl- <i>p</i> -dimethylamino benzoate (Padimate O)	1.4-8				
2-Phenylbenzimidazole-5-sulphonic acid	1-4				
Red petrolatum	30-100				
2-Hydroxy-4-methoxybenzophenone-5-sulphonic acid (Sulisobenzene)	5-10				
Titanium dioxide	2-25				
Triethanolamine salicylate	5-12				

II NOT SAFE, NOT EFFECTIVE

2-Ethylhexyl-4-phenylbenzophenone-2'-carboxylic acid
3-(4-Methylbenzylidene)-camphor
Sodium 3,4-dimethylphenyl glyoxylate

III UNCLASSIFIED

Allantoin combined with aminobenzoic acid
5-(3,3-Dimethyl-2-norbornylidene)-3-penten-2-one
Dipropylene glycol salicylate

The absorption characteristic of a chemical is frequently expressed as the molar extinction coefficient, i.e. the calculated optical density of a 1 cm layer of a molar solution, or the specific extinction coefficient, i.e. the calculated optical density of a 1 cm layer of a 1 per cent solution.

However, Stambovsky,³⁸ when discussing the technical causes of commercial failure of suntan preparations on the US market, warns against relying too much upon spectrometric data in selecting sunscreen agents and suggests that their value is limited to initial qualitative examination.

Kumler and Daniels³⁹ constructed a sunburn curve for which the ordinates were the products of the ordinates of the solar radiation curve and an erythematic curve derived from experimental data. This curve ranged from

Table 15.5 Classification of Sunscreen Ingredients—EEC Cosmetics Directive (Proposed Amendment)

Compound	Dosage limit (%)
SUNSCREEN AGENTS WHICH COSMETIC PRODUCTS MAY CONTAIN	
<i>p</i> -Aminobenzoic acid	5
3-(4-Trimethylammonio-benzylidene) camphor methosulphate	6
Homomenthyl salicylate (3,3,5-trimethylcyclohexyl salicylate)	10
Phenyl salicylate	4
2-Hydroxy-4-methoxybenzophenone	10
2-Amino-6-hydroxypurine (guanine)	2
SUNSCREEN AGENTS WHICH COSMETIC PRODUCTS MAY PROVISIONALLY CONTAIN	
N-propoxylated ethyl- <i>p</i> -aminobenzoate	5
Ethoxylated ethyl- <i>p</i> -aminobenzoate	10
Amyl <i>p</i> -dimethylaminobenzoate	5
Glyceryl <i>p</i> -aminobenzoate	5
2-Ethylhexyl <i>p</i> -dimethylaminobenzoate	8
2-Ethylhexyl salicylate	5
Benzyl salicylate	7
3,3,5-Trimethylcyclohexyl-N-acetylanthranilate (homomenthyl-N-acetyl anthranilate)	2
Potassium cinnamate	2
<i>p</i> -Methoxycinnamic acid salts (potassium and diethanolamine)	8
	(expressed as acid)
Propyl <i>p</i> -methoxycinnamate	3
Salicylic acid salts (potassium and triethanolamine)*	5
Iso-amyl <i>p</i> -methoxycinnamate	10
2-Ethylhexyl <i>p</i> -methoxycinnamate	10
2-Ethoxyethyl <i>p</i> -methoxycinnamate	5
Digalloyl trioleate	4
2,2',4,4'-Tetrahydroxybenzophenone	10
2-Hydroxy-4-methoxy-4'-methylbenzophenone	4
2-Hydroxy-4-methoxybenzophenone-5-sulphonic acid and sodium salt	5
	(expressed as acid)
2-Ethylhexyl-4'-phenylbenzophenone-2-carboxylate	10
2-Phenylbenzimidazole-5-sulphonic acid and its potassium and triethanolamine salts	8
	(expressed as acid)
β -Imidazole-4(5)-acrylic acid and its ethyl ester	5
	(expressed as acid)
2-Phenyl-5-methylbenzoxazole	4
Sodium 3,4-dimethoxyphenylglyoxylate	5
Dianisoylmethane	6
5-(3,3-Dimethyl-2-norbornylidene)-3-pentene-2-one	3
3-(3-Sulpho-4'-methylbenzylidene) camphor	6
3-(4'-Sulphobenzylidene) camphor	6
3-(4'-Methylbenzylidene)-d,l-camphor	6
3-Benzylidene-d,l-camphor	6
Methoxybenzylidene cyanoacetic acid and its n-hexyl ester	5
4-Isopropylidibenzoylmethane	5
<i>p</i> -Isopropylbenzyl salicylate	4
Cyclohexyl- <i>p</i> -methoxycinnamate	1
2-(<i>p</i> -Toluy)-benzoxazole	10
ter-Butyl-4-methoxy-4-dibenzoylmethane	5

* pH of the finished product must be such that the acid is not liberated. Not to be used for children under 3 years of age.

296 nm to 326 nm with a maximum at 308 nm. In their view a compound had to fulfil two requirements to be regarded as an effective sunscreen. Firstly, it would have to superimpose on the entire sunburn curve. Secondly, it would have to possess high absorption properties at 308 nm. This latter qualification was later proposed by Kumler⁴⁰ as the basis for a simple and rapid method for the relative evaluation of sunscreens. He measured the optical density of 0.1 per cent solutions in a 0.1 mm silica cell at 308 nm and converted the results to a sunscreen index (SI) which corresponds to the OD of a 1 per cent solution in a 1 mm cell. Forty-five compounds are ranked in decreasing order of screening effectiveness in Table 15.6, headed by ethyl *p*-dimethylaminobenzoate.

If the absorption characteristics of the chosen material are known, the concentration required in a product to produce the desired effects can be calculated, taking into account the probable film thickness to be applied.

Film Thickness

Film thickness can, of course, be estimated readily by measuring the area covered by a known amount of the preparation applied in a practical manner.

Bergwein⁴¹ considered that, when dealing with sunscreen preparations in the form of fatty ointments, the thickness would be within the range 0.007–0.01 mm, and in the case of oily and aqueous preparations it would be within the range 0.005–0.007 mm.

This gave rise to another concept, that of a critical layer thickness, which was proposed by Masch,⁴² to provide an indication of the thickness of the protective film which would ensure a 90 per cent absorption by the suntan preparation. The critical layer thickness can be derived for any wavelength, but preferably at the wavelength corresponding to the maximum erythemogenic radiation, by the equation $S = 10/E$, where S is the critical layer thickness in μm and E is the extinction coefficient for a 0.1 per cent solution in a 1 cm cell.

The US Army specification of 99 per cent absorption at 297 nm by a film 0.001 in thick has already been stated; normal commercial sunscreens usually fall considerably short of this and transmit 15–20 per cent of the erythemogenic radiation.

Kreps,⁴³ who published a spectrophotometric method of evaluating the erythema protection and tanning properties of suntan preparations, gave results for six commercial preparations which, he stated, transmitted between 1 and 17 per cent of the erythema energy and from 63–85 per cent of the tanning energy.

Stambovsky,⁴⁴ who dealt very fully with the ultraviolet screening requirements of commercial suntan preparations, suggested that for persons of average ultraviolet tolerance a suntan film should not transmit more than 20 per cent of solar erythema radiation, while for therapeutic-type products he suggested a transmission of not more than 5 per cent.

Having established the probability of the sunscreen's effectiveness *in vitro* the next step is to check its toxicity and dermatological acceptability before proceeding to examination *in vivo*.

Evaluation *in vivo*

It is general practice in examination *in vivo* to use an artificial sun-ray lamp with a filter and to test on a portion of the body which is not usually exposed to the sun

and thus retains its sensitivity to erythema radiation. Stambovsky's method⁴⁵ is typical. The filter used is practically impervious to radiation below 280 nm; at 295 nm it transmits 50 per cent and at 300 nm 72 per cent of the incident radiation.

The first stage in the evaluation is a calibration to determine the time required to produce the minimum perceptible erythema with the lamp at a given distance from untreated untanned skin. With a 500 watt lamp 12 in (305 mm) from the skin, one minute is typical. In a typical experiment a number of half-inch sectors are outlined on the inner surface of the forearm with strips of adhesive tape and numbered. The first sector, with the others covered, is exposed to the lamp for a unit period, say 30 seconds. Another sector is then exposed, with the first one, for a further period. This is repeated until all the sectors have been exposed for successively increasing periods. Readings are taken after about 10–12 hours at which time the test of the particular sunscreen is started.

In the second stage of the investigation the test product is applied to the other arm which is divided into sectors and exposed in the same way as before, except that, now the skin is protected, the units of exposure can be two or three times as long. After 10–12 hours the sector showing the minimum erythema can be seen and a comparison of the exposure times for the same effect with and without the test product will indicate the factor by which the sunscreen has lengthened the safe exposure. Several such tests with any given substance will increase the accuracy of determining its protective efficiency.

However, it must not be forgotten that there is no complete analogy between the erythema radiation of the sun and that of the quartz mercury lamp. One important factor of dissimilarity is the occurrence in the solar radiation of infrared energy which induces hyperaemia in the skin; this, in turn, produces a stronger erythemic response than would be produced in a non-hyperaemic skin. Pre-heating the skin with an infrared lamp to induce hyperaemia will cause a 33 per cent increase in its sensitivity to ultraviolet radiation.

All the tests described have been rather protracted, involving strong exposure of the skin of human subjects to radiation and long periods over which the observations were made. This hampers development work to some extent.

A method developed by Master *et al.*,⁴⁶ using thin film techniques claims to allow the evaluation of sunscreens by means of transmission measurements without dilution, using the sunscreens either alone on quartz slides or applied to excised portions of human skin. To obtain more accurate measurement of the total radiation passing through the skin, a Cary spectrophotometer fitted with integrating spheres was used in place of the xenon arc monochromator, which only measures that portion of the radiation which is not scattered.

As far as the evaluation of sunscreens *in vivo* is concerned, it now seems likely that the evaluation procedure based on the SPF value system introduced by the Plough Corporation and mentioned earlier will become the standard procedure for testing the efficacy of sunscreens. The added advantage of this system, as has already been shown, is that it can be correlated with proposed product category designations to help consumers to select the sunscreen preparations most suitable for their particular types of skin.

Table 15.6 Sunscreen Index (SI) based on Optical Density, of a 1 per cent Solution at 308 nm

Compound	SI
Ethyl <i>p</i> -dimethylaminobenzoate	14.8
Ethyl <i>p</i> -aminobenzoate	9.6
Isobutyl <i>p</i> -aminobenzoate	9.2
Propyl <i>p</i> -aminobenzoate	9.0
<i>n</i> -Butyl <i>p</i> -aminobenzoate	8.0
β -Methyl umbelliferone	7.7
<i>p</i> -Aminobenzoic acid	7.4
Dehydroacetic acid	7.0
3-Carboxycoumarin	6.6
Benzilidene camphor	6.6
Heliotropine	6.5
Umbelliferone acetic acid	6.0
Salicylic acid	4.3
Sodium <i>p</i> -aminosalicylate	4.3
Menthyl salicylate	4.0
Salicylamide	3.9
Methylenedisalicylic acid	3.0
3-Carboxycoumarin	3.0
Thiosalicylic acid	2.7
Brightener W/450	2.7
<i>p</i> -Hydroxyanthranilic acid	2.6
Sodium salicylate	2.4
Digalloyltrioleate	2.3
α -Resorcylic acid	2.2
Salicylaldehyde	2.2
<i>p</i> -Aminosalicylic acid	1.9
Dipropyleneglycol salicylate	1.9
Pyribenzamine	1.8
Pyrianisamine maleate	1.7
Sodium gentisate	1.7
Fluorescent white	1.6
Ethanolamide of gentisic acid	1.5
Ethyl gallate	1.4
Sodium sulphadiazine	1.2
Ethyl vanillate	1.1
Sodium sulphapyridine	0.95
Lauryl gallate	0.85
Totaquine	0.80
Barbituric acid	0.19
Chlorophyll	0.15
Amberlite IR-4-B	0.15
Salicyl alcohol	0.05
Anisic acid	0.01
Uvitex RBS	0.01
Uvitex RS	0.005

Determination of SPF

The test procedure recommended by the OTC panel of the FDA³⁷ for determining the Sun Protection Factor of a sunscreen preparation after UV-B and UV-A irradiation of the skin includes the use of a specified standard homosalate solution, to ensure a uniform evaluation of sunscreen preparations by different laboratories. Test subjects may be exposed to sunlight or preferably to a xenon arc as the preferred source of artificial light.

Among advantages claimed for the use of xenon arc tests *in vivo* are:

- (1) Its continuous emission spectrum simulates that of the sun in the UV region, with a comparable output in the 290–400 nm range.
- (2) It provides a constant spectrum at a constant angle with a high output, and the spectrum is stable when used over a long period of time.

Among disadvantages arising from the use of a xenon arc are:

- (1) The full solar spectrum 'is low in the visible and infrared wavelengths.'
- (2) 'Its use is time-consuming if only one test site can be irradiated at a time.'

Advantages offered by the exposure of test subjects to sunlight include:

- (1) Test conditions approximate more closely the actual conditions under which sunscreen preparations are used.
- (2) Test subjects are exposed simultaneously to the full solar spectrum, heat and humidity.
- (3) Several sunscreen preparations can be tested simultaneously.

However, these advantages can be offset by variable weather conditions, variable radiation intensity and variable heat-induced sweating and changes in the sun angle to the body surface. Although these variables can present difficulties in determining the total erythema exposure they can be successfully overcome by the use of a recording radiometer such as the Robertson-Berger (R&B) meter which is capable of monitoring and reproducing solar erythema exposures.

The R&B meter is said to record a measure of the cumulative amount of UV radiation passing through its filters and photosensors after each interval of 30 minutes. A count of approximately 400 has been estimated to produce 1 MED on 'typical' Caucasian skin.

Other recording radiometers used permit the continuous measurement of the sun's intensity in joules m^{-2} .

When using natural sunlight to test the efficacy of sunscreens, the exposure of individual subjects to the sun should be completed during one continuous exposure period even though the exposure of different subjects may not be on the same day. For any one test, solar exposure of all subjects must be completed within two weeks and must be conducted at the same geographical location. The sun intensity during each exposure should be measured continuously by an R&B meter or other recording radiometer and recorded in either joules m^{-2} or R-B counts.

According to the OTC Panel, 6×10^6 joules m^{-2} as measured by a recording radiometer will evoke 1 MED on subjects with skin types I and II when read 16–24 hours later.

If the recording R-B meter is used, 400 counts are equivalent to 1 MED in skin type III subjects and MEDs as low as 200 counts may be expected of skin type I subjects.

When using a solar simulator such as the xenon arc lamp, the measurement units used to obtain one MED for the calculation of the SPF value will be time units, usually seconds.

Regardless of the light source employed, differences may arise in interpreting the results of tests *in vivo* because the same dose of UV radiation will produce different intensities of erythema in different people. This will necessitate the determination of the MED for each subject irrespective of the radiation source.

Test Panel. Only fair-skinned individuals with skin types I, II and III as previously defined should be selected, and a group of at least 20 subjects should be used for each panel. The size of panel arises from the fact (among others) that testing of MED is done in 25 per cent increments of exposure which are reasonably close to standard deviations observed in test results; the standard error should not exceed ± 5 per cent. Each test subject should be examined for the presence of suntan, sunburn or any dermal lesions. The test area is the back of subjects between the belt line and the shoulder blade and should be outlined with ink and subdivided into at least three test sub-areas of at least 1 cm^2 . For each test usually 4-5 sub-sites are employed.

Both test sunscreen preparations and the standard sunscreen preparation are applied to the test sites in amounts of 2 mg cm^{-2} or $2 \mu\text{l cm}^{-2}$, to ensure use of a standard film.

One series of exposures is administered to the untreated, unprotected skin to determine the test subject's inherent MED; the time intervals employed are a geometric series represented by $(1.25)^n$ in which each exposure time interval is 25 per cent greater than the previous one.

The protected test sites (standard or test sunscreen preparations) are usually exposed to UV light the following day. The exact series of exposures to be given is determined by the MED of the unprotected skin. An example is quoted in the Federal Register to illustrate this point. The idea is to provide a series of exposures in which the shorter exposure times produce no effect on the skin, whereas the longer exposure times at 16-24 hours later produce light and moderately red exposure sites.

The SPF of the test product is then calculated from the exposure time interval required to produce the MED of the protected skin and from the exposure time interval required to produce the MED of the unprotected skin (control site).

Water Resistance and Perspiration Resistance of Sunscreens

The efficacy of sunscreen preparations also depends on their ability to form substantive films on the skin, which are resistant to removal by water or perspiration. It is therefore appropriate to include in the evaluation of sunscreen preparations tests for assessing their water and perspiration resistance.

The OTC Panel recommends the use of an artificial light source in such tests because of certain difficulties which are encountered when test subjects are exposed to sunlight, for example lack of protection of test subjects' untreated skin against sunburn or difficulty in determining the quantity of sunlight striking the skin when it is immersed.

A period of copious sweating of 30 minutes under controlled environmental conditions is considered to be an appropriate test for determining resistance to perspiration and for making substantivity claims for a sunscreen preparation. Such a claim will be allowed if the sunscreen preparation under test retains its original PCD after the test. The claim 'resists removal by sweating' is also appropriate if the product proves to be water resistant, since water immersion is a more severe test than sweating.

Tests for water resistance and waterproof claims are more easily conducted and more reproducible if carried out in an indoor pool. The test to determine the water resistance of a sunscreen preparation is carried out after 40 minutes of moderate activity in water, and that to test the claim that a given product is waterproof after 80 minutes of moderate activity.

Since sunscreens dissolve much more slowly in sea water than in fresh water, because of its salt content, the indoor pool should contain fresh water.

Efficacy of Sunscreens

The efficacy of a sunscreen preparation depends on the amount of harmful (erythemogenic) solar radiation which it is capable of absorbing, and hence it depends on the absorption range of the active sunscreen, its absorption peak, concentration employed, substantivity to the skin and its resistance to water and perspiration, and also on the nature of the solvent employed and other constituents present.

The molar absorptivity of a sunscreen in the erythemogenic and photosensitization ranges of the UV spectrum can also be used as a criterion of the relative effectiveness of a sunscreen agent. The larger its value at a specified wavelength, the greater the ability of the sunscreen agent to absorb UV radiation at this wavelength. The effectiveness of sunscreens with a low molar absorptivity can be increased by raising the concentration of the active ingredient in the preparation.

Other factors which can influence the effectiveness of a sunscreen preparation are:

- (i) pH;
- (ii) the solvent system employed;
- (iii) the thickness of the residual film on the skin;
- (iv) the stability of the product during the time it is employed.

A change in the pH, for example an increase in the H^+ ion concentration, will change the ratio of ionized and nonionized fractions of the sunscreen agent and result in a shift in the absorption range (and absorption peak) away from the erythemogenic range of 290–320 nm with a consequent reduction in efficacy.⁴⁷

In practically all aromatic UV absorbers, addition of solvents can also produce a shift of their absorption range. Thus the absorption peak of *p*-aminobenzoic acid in 100 per cent isopropanol was moved from 287.5 nm to 267.5 nm in 100 per cent water.⁴⁸ Mineral oil is another example of a medium which can produce a shift of the absorption range of sunscreens to a lower wavelength. Change of solvent, can, therefore, adversely affect the protection given by the sunscreen agent.

On the other hand, 2-ethylhexyl palmitate is very stable to UV radiation and has practically no effect on the absorption peak.

Formulation of Sunscreens

Work on the lines already described in this chapter will have established the type and amount of active material necessary to yield a suitable product, and formulation becomes largely a matter of selecting a suitable vehicle. Sunscreens can be presented in almost any of the product forms which can be applied to skin so as to give a continuous film, ranging from aqueous or alcoholic lotions, through liquid and semi-solid emulsion products to non-aqueous lipid preparations. Included also are gels and aerosols.

Points which should be considered in building formulae are:

- (1) Convenience in use, remembering that the product will often be used out of doors, will be carried to the beach and may be placed on irregular surfaces, which will influence the type of product, package and closure.
- (2) The sunscreen should be present in sufficient quantity to be effective (see earlier in this chapter).
- (3) The sunscreen and the vehicle should be compatible. From the point of view of the product the sunscreen may be dissolved in either the aqueous or non-aqueous phase, but it should be remembered that, in use, water and alcohol will evaporate from the product leaving the sunscreen dissolved or dispersed in the non-volatile portion of the cream, which may itself contribute to the sunscreen activity, or in the skin surface lipids.
- (4) Consideration should be given to the properties desirable in the film of non-volatile material left on the skin. It is probably neither necessary nor desirable that the sunscreen should penetrate to any depth in the skin so that there is no special need for readily absorbed materials, except in so far as some absorbance may be required so that the product can contribute to keeping the skin supple. The choice between lipids of various types and hydrophilic materials such as glycerin or sorbitol is one for the manufacturer to make, based on such factors as the degree of greasiness, tack or wetness required, bearing in mind that the product may be used on sandy beaches, or may be required to adhere to the skin while bathing, or may come in contact with clothing.

With these points in view the formulator will be able to select from formulae given elsewhere in this book. Some formulae which have been recommended and which illustrate particular points or types of preparation are given below:

<i>Lotion, primarily aqueous, with a small amount of thickener</i> ⁴⁹	(1) per cent
Filtrosol B	7.0
Methyl cellulose	0.5
Glycerin	2.0
Ethyl alcohol	10.0
Water	80.5
Perfume	q.s.

<i>Lotion, primarily alcohol, with oleyl alcohol as residual lipid</i> ⁵⁰		(2)
		<i>per cent</i>
Giv-tan F		1.5
Ethyl alcohol (denatured)		65.0
Oleyl alcohol		10.0
Water		23.5
Perfume		<i>q.s.</i>

<i>Clear sunscreen lotion</i> ⁵¹		(3)
		<i>per cent</i>
Isobutyl <i>p</i> -aminobenzoate	5.0	
Tween 20	9.0	
Alcohol SD-40	45.0	
Water	41.0	

Example 4 is a thickened aqueous alcoholic lotion with small amount of hexadecyl alcohol which is claimed to be a good vehicle for suntan oils, since it is relatively non-greasy and non-tacky after application to the skin.⁵²

		(4)
		<i>per cent</i>
Isobutyl <i>p</i> -aminobenzoate	1.9	
Hexadecyl alcohol	4.7	
Isopropyl alcohol	52.6	
Water	40.3	
Carbopol 934	0.5	
Di-isopropanolamine to pH 6.0	<i>q.s.</i>	

<i>Alcoholic lotion including silicone as the residual vehicle</i> ⁵³		(5)
		<i>per cent</i>
Sunscreen agent		1.0
L-43 Silicone (Union Carbide)		5.0
Ethyl alcohol		94.0
Perfume		<i>q.s.</i>

<i>Gel with a hydrophilic residue</i> ⁵⁴		(6)
		<i>per cent</i>
Sunscreen (water soluble)	5.0	
1,2,6-Hexanetriol	15.0	
Distilled water	80.0	
<i>in addition:</i>		
Carbopol 934	0.1	
Sodium hydroxide 10%	0.42	

<i>Gel containing mineral oil and a high proportion of nonionic (lanolin) derivative</i> ⁵⁵		(7)
		<i>per cent</i>
Filtrosol A. 1000 (Schimmel)		2.0
Crodafos N.3 neutral		6.80
Volpo N.3		4.06
Volpo N.5		2.72
2-Ethyl-1,3-hexanediol		3.42
Mineral oil 65/70 vis.		13.0
Distilled water		68.0
Perfume, preservative		<i>q.s.</i>

*Oily product containing a mixture of vegetable and mineral oil*⁵⁴

	(8)
	per cent
Filtrosol A 1000	3.0
Lantrol	2.0
Isopropyl myristate	12.0
Olive oil	13.0
Mineral oil	70.0

*Non-greasy oil based on isopropyl palmitate and silicone*⁵³

	(9)
	per cent
Sunscren (oil-soluble)	1.0
Silicone fluid L-45 (100cS)	10.0
Isopropyl palmitate	89.0

*Water-in-oil emulsion with an oil-soluble sunscren*⁵⁴

	(10)
	per cent
Sunscren (oil-soluble)	3.0
Mineral oil	34.0
Atlas G-1425	2.0
Avitex ML	5.0
Beeswax	2.0
Isopropyl myristate	0.5
Petroleum jelly	7.5
Water	46.0

*Oil-in-water emulsion with a low oil content of non-greasy character*⁵⁰

	(11)
	per cent
Giv-tan F	1.5
Diethylene glycol monostearate	2.0
Stearic acid	3.5
Cetyl alcohol	0.4
Isopropyl myristate	4.0
Triethanolamine	1.0
Triethanolamine lauryl sulphate	0.75
Water	86.85
Perfume, preservative	q.s.

*Cream with a moderate oil content, chiefly mineral*⁵⁵

	(12)
	per cent
A Giv-tan F	2.0
Glyceryl monostearate (self-emulsifying) (5% soap)	7.0
Spermaceti wax	2.0
Mineral oil	20.0
Stearic acid (triple pressed)	2.0
Polychol 5	1.0
B Water	63.8
Glycerin	2.0
Preservative	0.2
C Perfume	q.s.

Procedure: Add B to A at 70°C. Stir until the cream has cooled to 40°C.

*Low oil content vanishing cream containing Veegum*⁴⁹

	(13) per cent
Filtrosol A	5.00
Stearic acid	6.00
Cetyl alcohol	0.50
Veegum	2.28
Water	85.42
Borax	0.50
Potassium hydroxide	0.30
Perfume, preservative	q.s.

Weakly basic products are said to promote tanning.

Oil-in-water cream with a moderate oil content of mixed character

	(14) per cent
Sunscreen, etc.	q.s.
Glyceryl monostearate (self-emulsifying)	16.0
Cetyl alcohol	1.0
Mineral oil	10.0
Seesame oil	10.0
Glycerin	7.0
Water	to 100.0
Antioxidant, preservative, perfume	q.s.

Water-in-oil cream with an oil:water ratio similar to example 14

	(15) per cent
Ethyl <i>p</i> -diethylaminobenzoate	1.0
Mineral oil	9.0
Ozokerite	2.0
Microcrystalline wax	1.0
Paraffin wax	5.0
Petroleum jelly	2.0
Lanolin	3.0
Isopropyl myristate	10.0
Arlacel 83	1.5
Glycerin	5.0
Preservative, perfume	q.s.
Water	to 100.0

Examples 16 and 17 are creams containing colloidal alumina, which has been claimed to enhance the water-resistance of suntan preparations. As with examples 14 and 15, one is water-in-oil and the other oil-in-water, but in this case the difference is due to the use of different emulsifiers and different amounts of oil.⁵⁶

	(16) per cent	(17) per cent
A 2-Ethylhexyl salicylate	5.0	5.0
Mineral oil	30.0	10.0
Myverol 18-71	10.0	—
Stearic acid	2.2	—
Tween 80	—	3.5
Span 80	—	1.5
Preservative	0.2	0.2
B Baymal	3.5	5.6
Water	49.1	74.2

Examples 18 and 19 are aerosol sunscreen oils. Example 18⁵⁴ is based on mineral oil, while example 19⁵³ is alcohol-based, contains silicone and is non-greasy.

	(18) per cent
Filtrosol A 1000	3.0
Mineral oil	75.0
Eutanol G	8.0
Lantrol	2.0
Isopropyl myristate	12.0
Perfume	q.s.
Concentrate	40
Propellants 11/12 (50:50)	60

	(19) per cent
Sunscreen agent	5.0
Isopropyl myristate	25.0
L-43 Silicone	5.0
Perfume oil	1.25
Lanolin oil	2.5
Menthol Racemic USP	0.25
Absolute alcohol	61.0
Concentrate	20.0
Propellants 11/12 (75:25)	80.0

	(20) per cent
<i>Aerosol quick-breaking foam, substantially non-greasy</i> ⁵³	
Myristic acid	1.3
Stearic acid	5.0
Cetyl alcohol	0.5
Isopropyl myristate	1.3
Glycerin USP	5.0
Sunscreen agent	1.0
L-43 Silicone fluid	1.0
Triethanolamine	3.0
Distilled water	80.6
Benzyl alcohol	1.0
Perfume oil	0.3

<i>Aerosol product that combines sunscreen activity with insect repellency</i> ⁵⁵	
	(21)
	<i>per cent</i>
Dipropylene glycol monosalicylate	4.0
Polawax A.31	3.0
Ethyl alcohol 74 OP	47.0
Distilled water	31.0
Ucon lubricant 50 HB 660	5.0
Dimethyl phtalate	10.0
Perfume	<i>q.s.</i>
Concentrate	92.0
Propellants 12/114 (20:80)	8.0

Perfumes. Exposure to sun invariably results in an increased sensitivity of the skin, due to release of histamine. The irritant effect of many essential oils and other perfume components is well known, and is likely to be intensified under those conditions. It is essential, therefore, to exert very good care in the selection of ingredients, and also keep the perfume at a low concentration, preferably about 0.2 per cent.

Heavy Sunscreens

There exist preparations on the market, the object of which is to inhibit pigmentation completely. This class of products also includes preparations which are applied to the skin with the sole object of providing a mechanical barrier to sunlight, such as calamine lotion or heavy make-up. Many attempts have been made to develop cosmetic products which would inhibit the formation of freckles or any skin lesions resulting from exposure to sunlight or other UV light sources. Like other sunscreen preparations, these products are commercially available in cream, lotion or aerosol foam form. Among compounds which have been proposed for inclusion in such products by virtue of their sunscreensing properties, the following have been mentioned:

In creams:

- 2-hydroxy-4-methoxy-4'-methylbenzophenone (Uvistat)
- 1 per cent of 3-benzoyl-4-hydroxy-6-methoxybenzophenone
- 3-15 per cent of *p*-aminobenzoic acid
- 5-10 per cent of aesculin
- 10 per cent of salol in yellow vaseline
- 10 per cent of methyl salicylate in an ointment base

In lotions:

- 10-15 per cent *p*-aminobenzoic acid in 70 per cent alcohol
- 5-10 per cent tannic acid in 25-30 per cent alcohol

PALLIATIVE PREPARATIONS

Preparations for the relief of sunburn may be formulated on the basis of calamine lotion or other zinc preparations.

In connection with this, manufacturers should note that sun 'burns' are quite capable of producing exactly the same injury as steam burns, and the consequent risk of infection by bacteria and of absorption of the damaged proteins is still present. For this reason such preparations should be antiseptic.

<i>Calamine lotion type</i>	(22)
	<i>per cent</i>
Colloidal calamine	20.0
Glycerin	5.0
Water	75.0
Antiseptic	<i>q.s.</i>

Nadkarni and Zopf⁵⁷ have suggested the following improved calamine lotion:

	(23)
Zinc oxide	8.0 g
Prepared calamine	8.0 g
Polyethylene glycol 400	8.0 cm ³
Polyethylene glycol 400 monostearate	3.0 g
Lime water	60.0 cm ³
Water	to 100 cm ³

Triethanolamine stearate milks are also soothing:

	(24)
	<i>per cent</i>
Triethanolamine stearate	4.80
Liquid paraffin	10.00
Water	85.20
Antiseptic	<i>q.s.</i>

If desired, 10 per cent colloidal calamine may be added to this mixture, which is prepared by heating the stearate and oil to 70°C and adding to the water at the same temperature, or preferably by preparing the triethanolamine stearate *in situ*. The choice of a suitable antiseptic is a matter of individual preference; many of the chlorinated bisphenols (see Chapter 35) are good germicides and are non-irritant and innocuous in ordinary concentrations. For badly burnt areas the inclusion of a local anaesthetic or analgesic is indicated, but in view of the dangers of absorption this should be chosen with care. Monash⁵⁸ studied the topical anaesthesia of unbroken skin using six different preparations in alcoholic, hydrophilic ointment base and petrolatum vehicles. A 2 per cent alcoholic solution acted within 45–60 minutes, while a 5 per cent concentration of active ingredients in the two ointments produced topical anaesthesia within 60–90 minutes. The hydrophilic ointment acted more rapidly than the petrolatum base. The effects lasted 2–4 hours. Removal of 10–15 cell layers using adhesive tape reduced the period for anaesthesia to between 1 and 4 minutes. The author suggested that the mechanism of penetration through untreated skin was entry via the follicles and lateral spreading through the follicle walls near or just below the lower level of the external barrier, and thence through the stratum mucosa to reach the papillary portions of the dermis. Aerosol, lotion and cream products

containing benzocaine and the germicide triclosan are available.⁵⁹ The treatment of a serious burn should be carried out under medical supervision.

In general greasy preparations should not be used in the treatment of sunburn. They only retain the heat of the burn and prevent the use of an antiseptic capable of mixing with the secretions and preventing bacterial infection.

All such preparations should be either aqueous solutions or oil-in-water emulsions which are capable of exerting both a protective and cooling effect.

ARTIFICIAL SUNTAN PREPARATIONS

Stains

The enhanced colour of suntan may be regarded either as functional, to prevent skin damage by absorption of erythema radiation, or as cosmetic, to indicate the health and well-being of the subject. In either case the effect may be obtained by the use of staining materials. From ancient times materials such as walnut juice have been used. Water-soluble dyes, however, will streak on exposure to rain or moisture, and oil-soluble materials have been recommended. A vegetable product may be obtained by extracting a mixture of cudbear and henna with ten parts of warm deodorized olive oil, the ratio of the vegetable dyestuffs being adjusted to give the desired shades.

A more modern practice is to use suitable oil-soluble dyestuffs in less greasy lipid material.

Heavily pigmented face powders or modifications of the 'cosmetic stocking' may also be used. In conjunction with suitable shades of make-up, excellent effects may be obtained.

Systemic Materials

None of the sunscreens mentioned above is able to speed the rate of skin tanning, although such a product, if safe in use, would obviously command a significant market.

In 1947, Fahmy and Abu-Shady⁶⁰ isolated the active principles from the plant *Ammi Majus* (Linn.), known in ancient folk-medicine practised in Egypt for restoring pigmentation in vitiliginous skin. Subsequently it was shown that taken orally or applied topically these extracts could bring about re-pigmentation after exposure of the skin to sunlight.

Among these compounds possessing photosensitizing properties are the alkoxy-psoralens, and methoxsalen (8-methoxy-psoralen) has been investigated extensively both as a treatment for vitiligo and also as a possible cosmetic tanning preparation.

Sulzberger and Lerner⁶¹ in a report to the AMA Committee on Cosmetics, reviewed the introduction of orally administered drugs (psoralens) claimed to accentuate tanning. They reported that problems associated with the use of the oxy-psoralens to cure vitiligo were far from solved, cosmetically satisfactory re-pigmentation being obtained in only one out of every seven patients treated. Local application, probably the most pigment-stimulating method of use, causes severe oedema, erythema, blistering and pain when the skin is subjected to natural or artificial ultraviolet radiation.

Increased pigmentation is said to occur after ingestion of 10–20 mg of methoxsalen when the skin is exposed to sunlight within 2–4 hours.

Daniels, Hopkins and Fitzpatrick⁶² carried out a clinical trial using 106 subjects to assess the effectiveness of a daily dose of 10 mg of methoxsalen in producing tanning of the skin. It was demonstrated that these results did not discriminate between the methoxsalen tablets and a placebo tablet. Subsequently, Stegmaier⁶³ gave 20 mg daily doses of methoxsalen using a lactose placebo as a control. He concluded that this material ingested in sufficient dosage increased tanning (98 per cent confidence level) and decreased burn (90 per cent confidence level).

A suntan-promoting tablet was introduced on the USA market under the name TAN-IF-IC with 8-methoxypsoralen as the active principle. Other components of the tablet were carefully balanced vitamins to ensure the presence of tyrosine, copper and some of the vitamin B group. After ingestion, exposure to the sun produced, in the matter of a few days, a tan which was sometimes equivalent to the suntan previously achieved by a full summer's exposure. In addition, it was said to protect the skin by accelerating the body's production of melanin, the increased pigmentation acting in the normal way as a protection against sunburn. It was claimed as the only oral suntanning agent and sun protectant, but was later withdrawn.

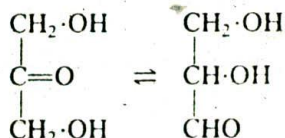
Dihydroxyacetone (1,3-dihydroxy-2-propanone)

In 1959 there appeared on the USA market a colourless after-shave lotion which claimed to produce gradual tanning of the skin—the effect appearing within 6 hours of application. Examination of this product showed that the colouring of the skin was confined to the upper cell layers of the skin. The active principle used at a level of up to 2.5 per cent was dihydroxyacetone (DHA).

In 1960 a patent⁶⁴ was published covering the use of dihydroxyacetone for tanning the human epidermis. This patent included eight claims covering lotions, creams, ointments and dusting powder including dihydroxyacetone at a level of 0.2–4.0 per cent.

In the years which followed, numerous publications appeared and it seems that the reaction involved had first been described some years before in journals devoted to dental research.^{65–67} Thus this product is an excellent example of cross-fertilization from one field of research to another.

More detailed investigation^{68,69} showed that the DHA reacts with free amino groups in the skin proteins, and in particular⁷⁰ with the free amino group in arginine. It is suggested that the DHA exists in tautomeric isomerism with glyceraldehyde:



and that the aldehyde undergoes a Schiff-type reaction with amino or imine groups of keratin forming aldehyde-amino products which condense and polymerize to form dark-coloured melanoidins.

This scheme of reaction is in accord with later work by Laden and Zielinski,⁷¹ who showed that the reaction is not specific to DHA but is general to many α -hydroxymethyl ketones. DHA is, however, one of the best compounds for giving colour (but see below—Erythrulose).

Although there were some reported cases of skin irritation on normal and abnormal skin by the use of products containing DHA,^{68,72-76} considerable evidence soon accumulated to show that DHA is innocuous.⁷²

Aqueous solutions of DHA do not spread well and produce relatively little tanning. Alcohols and surface-active agents increase the apparent rate of tanning.⁷⁷ The reaction decreases with increasing pH, solutions having a pH value in excess of 8.0 producing no colour reaction.

A DHA suntan lotion proposed by Fuhrer⁷⁸ consisted of:

	(25) per cent
DHA	4.0
Ethanol (95%)	28.0
Methyl <i>p</i> -hydroxybenzoate	1.0
Sorbitol syrup (70%)	3.0
Boric acid powder	1.0
Allantoin	0.3
Distilled water	60.7
Perfume	2.0

A US patent⁷⁹ assigned to Plough Inc. covered the use of dihydroxyacetone in conjunction with sunscreens agents which do not contain active amino groups, within a pH range of 2.5-6.0. These formulations were claimed to have a shelf-life of more than 6 months. They simulate skin tanning and also protect the skin from sunburn.

Dihydroxyacetone/Juglone or Lawsone Combinations. A mixture which stains the skin and then protects it against excessive sunburn was described by Fusaro and Runge.⁸⁰ It consists of a 3 per cent solution of dihydroxyacetone in 50 per cent isopropanol, also containing 0.035 per cent of juglone or lawsone. The former is chemically 5-hydroxy-1,4-naphthoquinone and is obtained from walnut shells; the latter is 2-hydroxy-1,4-naphthoquinone, derived from henna. On repeated applications to the skin, and after the skin has been washed with soap and water, this mixture produces a brownish tan colour, the shade of which can be governed by the number of applications. It has been claimed that the stain which is produced on the skin absorbs 95 per cent of the ultraviolet radiation and 20 per cent of the infrared radiation reaching the skin. Protection is conferred to the skin only after the colour has been developed, and is then maintained by re-application of the mixture at intervals from 2-7 days. Natural tan may still be acquired after the product has been applied to the skin, but only very slowly.

Erythrulose

Another compound which has been proposed in cosmetic preparations as an artificial tanning agent for the skin is butane-1,3,4-triol-2-one, $\text{HO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, also referred to as erythrulose. A L'Oréal

patent covering its use⁸¹ states that the preferable concentration of this compound is between 0.5 and 10 per cent by weight, depending on the degree of bronning of the skin desired. According to the same patent, erythulose may be used in combination with a UV absorber; alcohol and a surface-active agent may also be present to promote penetration into the skin. It can be presented in the form of a lotion, cream or gel as well as in compositions packed in pressurized containers. Formulation of an alcoholic spray of erythulose for use in an aerosol pack is illustrated by example 26.

(26)	
Concentrate	
Erythulose	3 g
Propylene glycol	0.2 g
Ethyl alcohol 99.8% q.s.	100 cm
Fill	parts
Concentrate	33
Trichloromonofluoromethane	33
Dichlorodifluoromethane	33

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