PART TWO

The Nails and Nail Products

Chapter Twenty-one

The Nails

Biology of the Nails

Structure

Nails [1,2] are translucent plates, composed of hard keratin, which protect the top surfaces of the end joint of each finger and toe. Each lies upon a *nail bed*, to which it appears to be fused, except at the far or *distal* end where there is a free margin. At the near or *proximal* end a paler *lunula* is visible, and the posterior margin is slightly overlapped by a narrow extension of the horny layer of the epidermis which is known as the *cuticle*.

Development and Formation

The nails start to develop in the nine-week human embyro from invaginations, or *nail folds*, of epidermis on the dorsal tip of each digit, and by the twentieth week they are complete. Exactly how the plate is formed and continues to grow has been the subject of some discussion. The traditional view is that the bed plays no part and that the nail is formed solely by proliferation of keratinizing cells from a *proximal matrix* which starts at the proximal limit of the fold, possibly involves a little of the adjacent roof, and extends below the nail to the distal margin of the lunula (Figure 21.1a). This interpretation was supported by autoradiographic studies in which tritiated glycine was injected into the squirrel monkey, a primate with flat nails very like human ones.[3] However, similar experiments on human volunteers suggested that there was some activity in the nail bed.[4]

A second view[5] is that the nail is formed in three layers. The dorsal and intermediate nail comes from the traditional matrix, but there is also a ventral layer which is formed from the nail bed distal to the lunula (Figure 21.1b). A third view[5] divides the nail bed into three zones, namely a proximal fertile matrix, an intermediate sterile bed, and a distal fertile matrix, the *solehorn*, which contributes a small quantity of material to the underside of the nail (Figure 21.1c).

The view of Samman[1,2] is that all three modes of nail formation can occur in normal subjects, but that the participation of the distal and intermediate parts of the bed is commoner in pathological conditions.

Histology, Ultrastructure and Composition

The epidermis of the nail bed is similar to that of the skin, but has no *stratum lucidum* or *stratum granulosum* and no hair follicles or sweat glands. It probably moves forward with the growth of the nail.[6] The epidermis of the matrix is thick and passes into the substance of the plate, which is formed by changes similar to keratinization in the superficial epidermis.[7] The appearance of the lunula is

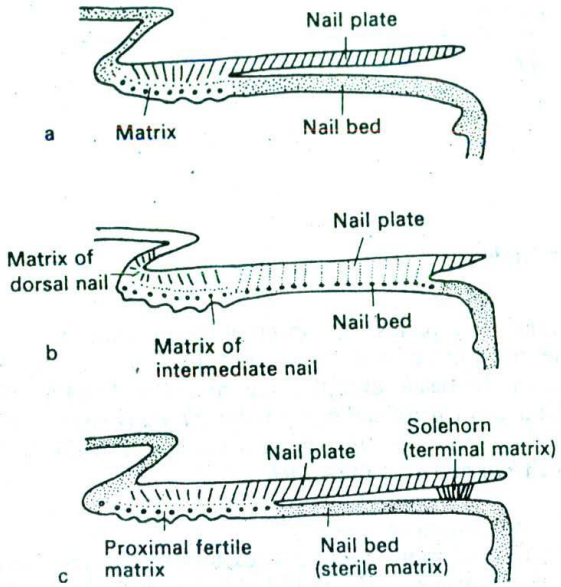


Figure 21.1 Possible methods of nail formation (after Samman[1])
a Traditional view: the nail plate is formed solely from a single proximal matrix
b Hypothesis that ventral layer of nail plate is formed from the nail bed
c Third view that distal terminal matrix, which is separated from proximal matrix by intermediate sterile matrix, contributes some material to underside of nail

probably due to a combination of incomplete keratinization in the nail plate and looseness of connective tissue in the nail bed.[8]

The nail plate is made up of impacted and adhering layers of flattened cells which have lost their nuclei. The cells contain hard keratin, similar to that of hair (see Chapter 23), with a high sulphur content, mainly in the form of cysteine, which comprises about 9–12 per cent of the weight of the nail.[1,9] The keratin fibrils are mainly orientated parallel to the nail surface from side to side.[10,11] There is a natural cleavage between the harder dorsal nail and the more pliable intermediate nail. Nail contains about 7–12 per cent of moisture[12] and 0·15–0·76 per cent of fat, a little more (1·38 per cent) in infants.[13] Calcium constitutes about 0·02–0·04 per cent of the weight, and could not contribute to the hardness.[10,14,15] Even this amount may be derived from the environment. Other trace elements have been detected and measured in nail clippings.[16]

The nail bed and matrix have a rich supply of blood from two arterial arches which lie below the nail plate.[1,2]

Rate of Nail Growth

Nails, unlike hairs, grow continuously throughout life. Le Gros Clark and Buxton[17] measured the rate in undergraduates and schoolchildren by notching the nail about 2 mm from the margin of the lunula and recording its progressive

displacement in each succeeding month. They found no differences over the age range of 19 to 23 years, no sexual difference, and only a very slight difference between hands, growth on the right being faster. However, there were differences between fingers, growth being fastest on the third digit and least on the little finger. Dawber[18] has confirmed these observations. Bean,[19–22] by studying his own thumb for over 30 years, found some slowing-down followed by a levelling-out. The rate of fingernail growth varies between 0·5 and 1·2 mm per week.[2,17,18,23] On average, it is higher in psoriasis,[18] idiopathic oncholysis[24] and as a result of inflammatory change, and it may be temporarily depressed in infective diseases such as measles or mumps.[25] To replace a finger nail completely takes about 5½ months; toe nails need 12–18 months.[2]

Pathology of the Nails

Abnormalities of structure and appearance of the nails are of many kinds and can have many causes: genetic, infective or environmental. For a full account of the various conditions that affect nail growth and the ways in which they affect it, the reader is referred particularly to Samman.[2] Here abnormalities will be briefly surveyed, with the purpose of enabling the cosmetician to recognize the extent to which each may be ascribable to traumatic causes or local infection as distinct from underlying disease.

Absence of Nails

Complete absence of nails from birth, *anonychia*, is rare, and appears to be associated in several ways with other hereditary defects. In *nail patella syndrome*, complete absence of thumb nails, or a grossly defective nail less than half the normal length, is associated with reduction in size or absence of the knee caps and other skeletal anomalies.

Nail Shedding

Nails can be lost either by loosening at the base or by separation from the nail bed. Shedding can follow trauma or severe illness, or can be caused by drugs. More serious loss with scarring sometimes follows damage, defective circulation, lichen planus, epidermolysis bulbosa or drug eruptions.

Onycholysis

The separation of the nail from its bed, *onycholysis*, is fairly common. There are many causes but quite often none can be found. It may result from external damage, fungal infections, dermatitis or a drug eruption, or it may be associated with psoriasis, defective peripheral circulation, hypo- or hyper-thyroidism, or other disorders.

Of particular interest are reports of its causation by cosmetics. Nail hardeners containing formaldehyde,[26] nail varnish containing phenol[27] and dental acrylic polymerized *in situ* to strengthen the nail[28] have all been implicated.

Brittleness

Brittle nails are common. While sometimes they may be associated with impaired peripheral circulation as in Raynaud's disease, iron deficiency

anaemia, congenital defects, diffuse alopecia or infections, the cause is often unknown.

Environmental factors are certainly important. Nails are kept pliable by their moisture content, and long thin nails are especially susceptible to very dry atmospheres. Frequent immersion of the hands is conducive, and Silver and Chiego[29] believed that soaps and detergents remove the protective lipids from the keratin.

The continuous use of nail varnishes and varnish removers has also been blamed.[30] Woolcott[31] investigated the reactions of twenty-five business women using the same brand of nail lacquer, and found that although nearly half of them showed brittleness and splitting of the nails, the rest were unaffected.

Tyson[32] reported in 1950 that oral ingestion of 7 g of gelatin per day for three months restored normal appearance and texture to fragile fingernails, and a number of other investigators have confirmed this.[33–37] In an extensive investigation, Michaelson and Huntsman[38] claimed that 2 g per day was enough to produce a significant increase in hardness within one month in five out of seven test subjects. Samman[2] simply recommends avoidance of frequent immersion and nightly use of a hand cream containing equal parts of salicylic acid ointment (2 per cent) and glycerin of starch.

Striations

Longitudinal striations are common in healthy nails, and become more prominent with aging, as well as in lichen planus, Darier's disease and defective peripheral circulation. An uncommon condition is median dystrophy, in which the nail plate has a longitudinal split, just off centre.

Regular transverse striations can occur as a developmental anomaly. Severe depressions, known as Beau's lines, indicate a period of severe systemic disability, such as measles, mumps, pneumonia or coronary thrombosis, which interferes with growth of the nail.

Koilonychia

In koilonychia or 'spoon nails' the nails are thin, soft, and depressed in the centre. The condition results from iron-deficiency, usually, but not invariably,[39] associated with anaemia. There are other causes; it is, for example, not uncommon in motor mechanics,[40] where perhaps it is due to softening with oils or soaps.

Splitting

The splitting of nails horizontally, so that pieces of the surface break away, is very common in women, and the main causes are probably repeated immersion in water and the use of varnish and varnish removers.

Pitting

Pitting of the nails is found in dermatitis and fungal infections, in association with alopecia areata and, most commonly, in psoriasis.

Leukonychia

Leukonychia is complete or partial whitening of the nail plate. Complete leukonychia occurs very rarely as an inherited abnormality; often epidermal

cysts are associated with it. Partial leukonychia is very common, and may take the form of white spots or white transverse streaks. It may be associated with many types of illness and is found in chronic arsenical poisoning, but in the punctate cases there is usually no discernible cause.

A white appearance of the nails is not necessarily due to leukonychia; it may result from changes in the bed, not in the plate. Such a condition has been described in association with cirrhosis of the liver.[41]

Discoloration

Nails may be discoloured for a wide variety of reasons. External causes include hair or other dyes, nicotine and medicaments such as mercury, dithranol and picric acid. Tints may leak out of nail varnish and penetrate the nail.[42,43]

Abnormal formation or very slow growth of the nail will produce colour changes. Psoriasis, in particular, among other abnormalities, causes opaqueness and discoloration, and so can several other skin conditions.

In the *yellow nail syndrome* as described by Samman and White[44] the nails almost cease to grow and several months later become yellow or greenish. They may also be thickened and curved from side to side. The condition is accompanied by oedema and changes in the lymphatic system. Yellowish, green or grey nails can also occur as growth of nails slows down in old age.

Fungal or candidal infections which partly destroy the nail often cause brown discoloration. Infection by *Pseudomonas aeruginosa* under the nail will stain it black or blue.

Systemic drugs can alter the colour in many ways. Prolonged administration of tetracycline may occasionally turn nails yellow. Mepacrine makes them bluish, and chloroquine may produce blue-black pigmentation of the nail beds.[45]

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Chapter Twenty-two

Manicure Preparations

A complete manicure treatment can involve a number of different cosmetic preparations concerned with the cleansing and preparation of the nail and its decoration. These will be dealt with below, somewhat in order of their use.

CUTICLE REMOVER

When the free edge of the nail has been shaped, by mechanical means such as cutting or filing, the next problem is to shape the base of the nail. Where the skin adjoins the nail it becomes cornified and the dead cells, together with sebum, form an irregular appendage which grows thick and ragged and partially obscures the 'halfmoon' or lunule. Some improvement can be effected by mechanically loosening and pushing back the cuticle, but removal of excess cuticle by cutting is unsatisfactory and cuticle removers are used.

Cuticle removers are based principally on alkaline materials in liquid or cream form. One of the most effective and relatively cheap materials is potassium hydroxide and 2–5 per cent of this material in aqueous or aqueous–alcoholic solution formed the basis for many early preparations. The incorporation of humectants such as glycerin or propylene glycol, at a level of 10–20 per cent, served to counteract the irritation potential of alkali hydroxides and also to retard evaporation and increase viscosity. The latter effects can also be achieved by the use of suitable water-soluble gums or hydrocolloids.

Milder but correspondingly less effective preparations can be obtained by using alkaline polybasic salts such as trisodium phosphate or tetrasodium pyrophosphate, with the possible addition of 2–3 per cent sodium, or triethanolamine, lauryl sulphate.

An example of a basic formula is:

	(1)
	per cent
Trisodium phosphate	8·0
Glycerin	12·0
Water	80·0
Perfume	*q.s.*

Still milder products incorporate alkanolamines such as monoethanolamine or isopropanolamine at 8–10 per cent or triethanolamine at, say, 10–12 per cent.

To improve the convenience in use of cuticle removers attempts have been made to present them in cream form, which will also reduce the potential risk of damage to furniture, carpets, etc. Example 2 gives a basic formula suggested[1]

for such a preparation:

	(2) *per cent*
Sorbitan monopalmitate	2·0
Polyoxyalkylene sorbitan monopalmitate	2·0
Mineral oil	15·0
Water	81·0
Cuticle remover	*q.s.*

Procedure: Heat the first three items to 65°C. Emulsify at this temperature with the water, except for a portion used to dissolve the cuticle remover, which should not, in this case, be alkali hydroxide. Mix the emulsion and the solution of cuticle remover when cold.

Special emulsions have to be prepared to allow the incorporation of highly alkaline materials. Example 3 is typical:

	(3) *per cent*
Cetyl alcohol	2·5
Myristyl alcohol	3·5
Polyoxyethylene (5) lauryl ether	1·0
Glycerin	4·0
Potassium hydroxide	1·6
Water	87·4

Procedure: The water-soluble ingredients are mixed together, heated to 75°C and then added to the mixture of alcohols that has also been heated to 75°C. The resultant cream is then cooled to 45°–50°C and should be filled at this temperature.

A combination of phosphate and caustic alkali can also be used with this type of cream emulsion, although the presence of phosphate can drastically affect the viscosity of the final product. This can be controlled, however, by careful homogenization of the cooled emulsion.

Care must be taken in packing all such alkaline preparations in glass containers which should be fitted with alkali-resistant stoppers such as rubber or plastic. Even so, the more alkaline preparations are liable to give rise to glass etching and silicate precipitates. The latter can be masked by the use of opaque containers or, it is claimed, prevented by the inclusion of potassium oleate or about 1 per cent of the tetrasodium salt of ethylenediaminetetra-acetic acid. Trends in legislation are now towards the requirement of warning labelling of these products, either by naming the caustic material (for example, 'Contains sodium hydroxide') or by specifying the pH of the product.

Cuticle Softeners

Another type of preparation which has been employed is the cuticle softener in cream form, which by its action and emolliency facilitates subsequent mechanical removal of the cuticle. Quaternary ammonium compounds are prominent in this class of preparation. Their softening action is the result of their affinity for

protein, and increases with increasing molecular weight. Cetyl pyridinium chloride and stearyl dimethyl benzyl ammonium chloride are typical materials used at 3–5 per cent. They also exert a bactericidal action. Urea may be added to promote the swelling of keratin and enhance the cuticle softening and lanolin or isopropyl myristate will confer improved emolliency. Nonionic thickening agents such as methylcellulose or hydroxyethylcellulose will increase the viscosity.

NAIL BLEACH

Nail bleaches are solutions or creams used for the removal of ink or tobacco stains, vegetable stains, etc., from the nails. Such stains may yield either to oxidation or reduction, depending on the type of stain. Oxidation may be achieved by the use of hydrogen peroxide, either at 20 vols or diluted to about 1:4, by chlorine compounds such as the hypochlorites and the cyanurates and by sodium perborate and zinc peroxide (the latter two substances decompose in aqueous solution). Use of sulphites with dilute acid is probably the easiest method for achieving reduction in such preparations. These can be packed in two-solution form, one the stabilized oxidizing or reducing agent, the second containing enough acid or alkali to shift the pH sufficiently (when the two solutions are mixed) to render the agent to be employed unstable and hence active.

A one-solution nail bleaching lotion cited in literature[2] had the following composition:

	(4) *per cent*
Hydrogen peroxide (10 vols—3% w/w)	73·5
Ammonia (SG 0·93)	0·5
Rose water	25·0
Preservative	1·0

A number of stain-removing preparations are based on aqueous solutions or organic acids such as citric or tartaric acids and a 4 per cent solution of concentrated hydrochloric acid in water and glycerin has also been recommended[3] for such purposes.

The following formula for an abrasive nicotine stain remover has appeared in *Drug and Cosmetic Industry*:

	(5) *per cent*
Beeswax	10·0
Paraffin wax	5·0
Mineral oil	46·0
Pumice powder	8·0
Borax	0·5
Water	30·0
Perfume	0·5

NAIL CREAM

Nails are not porous in the normal sense of the word. They have no pores through which to 'breathe' or absorb any 'food', or which can become blocked by, for instance, nail varnish. Nevertheless, as explained in the previous chapter, nails can become brittle from various causes and it is natural to wish to apply some preparation to counteract this brittleness, which is probably due to dehydration.

One recommendation for the relief of brittle nails was to massage them with olive oil after having bathed them in warm water. It was stated, however, that nail plates will regain their normal consistency and elasticity only after several weeks.

A more practical preparation is an emollient cream containing a suitable humectant such as one of those already described in earlier chapters. Emollient creams for use as nail creams have been formulated on a lanolin absorption base or on beeswax–borax emulsions. These creams should be applied after soaking the hands in warm soapy water and thoroughly drying them, just before retiring for the night. This treatment should be carried out at least once and preferably 2–3 times per week (that is, on alternate nights) depending upon the condition of the nails. Wearing fingerstalls or gloves may assist the treatment.

Claims have been made that certain fatty substances, in particular cholesterol, appear to assist in maintaining the natural elasticity of the nail. In this connection the water-in-oil emulsifying properties of cholesterol should be borne in mind since it may assist in maintaining the requisite degree of moisture in the keratin. Although much remains to be discovered, it would appear that the use of a nail cream containing oils in an emulsified form with water (and possibly incorporating a mild antiseptic) would be of value.

Any of the cold, vanishing, foundation or all-purpose cream formulae given in the various chapters in this book may be modified slightly—if necessary—for use as a cream for brittle nails, by the inclusion of a little lanolin or other emollient and an adequate amount of humectant.

NAIL STRENGTHENER

The fact that dry fingernails tend to split and break off easily is bound to spoil their appearance and make manicuring difficult and often painful. This has led to the development of various products for strengthening brittle nails and for eliminating brittleness and dryness.[4]

A liquid composition consisting of an aqueous solution of 3 per cent stearyl trimethyl ammonium chloride, 1·5 per cent nonylphenolpolyoxethylene ($10Et_20$ per mol) ether and 0·5 per cent triethanolamine stearate was claimed in US[5] and British[6] patents, for eliminating brittleness and dryness of nails, counteracting the effect of solvents present in nail polish removers and improving the adhesion of nail lacquer applied subsequently.

Other nail-hardening preparations for increasing the resistance of nails to cracking, splitting and laminating were disclosed in another US patent.[7] They were all solutions of water-soluble metallic astringent salts such as, for example,

aluminium sulphate, potassium, sodium and ammonium alums, zinc acetate and zirconium chloride. Treatment consists of wetting the nails by dipping in, or painting with, a 1–5 per cent aqueous solution of the metallic salt, and keeping the nails in contact with the solution for 5–10 minutes at an ambient temperature. If the recommended concentration is exceeded, drying and wrinkling of the skin of the finger tips may occur. These nail-hardening compositions preferably also contain 5–20 per cent of a humectant such as glycerin or propylene glycol to retard evaporation of the aqueous solvent, and to provide an even coating and a 'slightly enhanced penetration'.

A slight bactericidal effect has also been claimed for these salts, which may be further enhanced by the inclusion of other bactericidal substances such as formaldehyde. In one example the nail-hardening composition contained:

	(6) *per cent*
Potash alum	3·00
Glycerin	10·00
Formaldehyde	0·01
Menthol	0·001
Water	to 100·000

Partially polymerized formaldehyde resins have also been used as the cross-linking agent in nail-hardening compositions. However, attention must be drawn to a reaction to the formaldehyde component of a nail hardener reported by Lazer,[8] which resulted in nail damage including subungual haemorrhage, discoloration, subungual hyperkeratosis and dryness of the skin, and necessitated oral administration of a steroid to relieve the accompanying pain and oedema. The use of the preparation had to be discontinued to allow the nails and the skin to return to a normal condition.

In a French patent[9] the use of a solution of dimethylol- or diethylol-thiourea was suggested for a nail-strengthening composition, which also contained a weak acid polymerization catalyst; in an Australian patent application,[10] a nail-strengthening product was described containing a non-toxic cysteine derivative dispersed in a non-toxic carrier.

NAIL WHITE

Nail whites are preparations used to produce an even white edge to the nails. They are based on an inert white pigment such as zinc oxide, titanium dioxide, kaolin, talc or colloidal silica, of which the first two are the best. The pigment forms 20–30 per cent by weight of the preparation, which is generally presented as a stiff paste.

For general purposes a fatty base is preferable. Titanium dioxide is incorporated in the following example:

	(7) *per cent*
Titanium dioxide	38·0
Petroleum jelly	62·0

This simple preparation is readily produced by milling the titanium dioxide into the melted petroleum jelly. Various mixtures of suitable fats and waxes may replace the petroleum jelly as desired.

Nail white pencils have largely replaced nail white creams, since they are easier to apply, are less messy in use, and simply require moistening with water before application to the under-surface of the nail free edge, the pencil then being recapped.

A wax may be used as a base if desired:

	(8) *per cent*
Beeswax	55·0
Hydrogenated cottonseed oil	9·0
Cocoa butter	9·0
Castor oil	8·0
Lanolin base	9·0
Titanium dioxide	10·0

Such a base is ready for use and is not wetted before application. The usual type, which requires preliminary damping, is prepared by massing casein or gum arabic with the inert pigment, or by suspending it in soap, for example sodium stearate base.

The making of white pencils is a job for firms specializing in the manufacture of ordinary pencils and not for the ordinary cosmetic manufacturer. Consistency of the base will have to be adjusted according to plant operating conditions and hence any formulations given here probably bear little resemblance to those actually used by the pencil manufacturers.

NAIL POLISH

A distinction is drawn between those polishes which by abrasive action bestow a gloss on the nail surface, and a nail varnish. The former, by reason of the friction set up in the buffing process, draw the blood to the numerous capillaries of the nail bed and, by increasing the blood supply, may exert some slight stimulating effect upon the growth of the nail. The latter, which depend upon the deposition of a thin film of highly lustrous cellulose lacquer upon the nail plate, have increased enormously in popularity and have largely replaced the abrasive type, although abrasive polish may also be used between two successive coats of varnish to enhance the lustre, in the manner of the French polisher.

Abrasive polishes consist of a suitably finely powdered abrasive which is applied to the nail and then polished with a shaped chamois leather pad. The principal constituents of such powders are stannic oxide, talc, silica, kaolin, precipitated chalk, etc., the first being an excellent abrasive but rather more expensive than the others listed.

	(9) *per cent*
Stannic oxide	90·0
Powdered silica	8·0
Butyl stearate	2·0
Pigment, perfume	*q.s.*

Butyl stearate is included to render the product less gritty and may be replaced, if desired, by oleic acid. The method of preparation is by simple trituration in a mortar or revolving mill. By the addition of a suspending agent, methylcellulose or tragacanth together with glycerin or one of the glycol ethers, they may be prepared in liquid form or compressed into a paste or pencil.

Wax polishing pencils embodying a large proportion of abrasive powder replaced the older powder and block type. They were effective and could be carried and used without the danger of spilt contents:

	(10) *per cent*
Hardened palm kernel oil	22·0
Synthetic wax (high melting point)	7·0
Stannic oxide	71·0

A softer stick may be obtained by omitting the synthetic wax and making a simple mixture of abrasive powder with the hardened oil. Alternatively, a base of rosin, beeswax, ceresin and petroleum jelly, or other suitable combination of waxes, may be employed.

NAIL LACQUER (NAIL VARNISH)

Introduction

The largest and most important group of manicure preparations is that of nail varnish or lacquers. These names give some indication of the progress of this type of preparation from the transparent uncoloured or pale pink natural colours, which were the only ones tolerated at one time, to the vivid shades and even bizarre colours now accepted as a most essential part of modern beauty.

Requirements of a Nail Lacquer

A nail lacquer should fulfil the following requirements.

(1) It should be innocuous to the skin and nails.
(2) It should be easy and convenient to apply.
(3) It should be stable on storage as regards homogeneity, separation, sedimentation, colour and interaction of ingredients.
(4) It should give a film with satisfactory characteristics.

The characteristics of a satisfactory film are:

(1) Even thickness, which demands a satisfactory viscosity of the lacquer, neither too thin nor too thick, and good wetting and flow properties.
(2) Uniform colour, which demands a very finely divided pigment, intimately ground and wetted by the medium.
(3) Good gloss, which implies a very smooth surface and depends upon the properties of the medium.
(4) Good adhesion to the nail.
(5) Sufficient flexibility to avoid brittleness and cracking.

(6) Hard, non-tacky surface, resistant to impact and scratching, which will not adhere to other surfaces nor mark off colour on fabrics or paper.
(7) Satisfactory drying properties—drying time of about 1–2 minutes without development of bloom even in humid atmospheres.
(8) Maintenance of these properties for approximately 1 week.

Ingredients of Nail Lacquer

In practical terms, the main essentials for the manufacture of nail lacquer are a lacquer base with suspending properties and a colouring system. These two components can be broken down into necessary constituents, and these are described before manufacture of the product is considered.

Film-formers

The basic film-forming material in nail lacquers is nitrocellulose, a cellulose nitrate obtained by the reaction of mixtures of nitric acid and sulphuric acid with cotton. In this reaction all three of the alcohol groups in the cellulose ring can be esterified. The degree of esterification or substitution determines the intrinsic characteristics of the nitrocellulose and the degree of polymerization of the cellulose chain governs the viscosity of the product. The nitrocellulose used in nail lacquers has a degree of substitution of approximately two and is known as dinitrocellulose-pyroxylin.

Different grades of nitrocellulose are characterized by their viscosity in organic solvents, for example $\frac{1}{2}$-second or $\frac{1}{4}$-second nitrocellulose, using the US nomenclature based on the falling ball method of determining viscosity. In practice, the grades of nitrocellulose used to manufacture nail lacquers are those which give sufficiently fluid solutions to allow easy application on the nails. Peirano[11] considered a 15 per cent solution of $\frac{1}{2}$-second nitrocellulose to be suitable, giving a viscosity in the range 300–400 cP. Similarly, $\frac{1}{4}$-second nitrocellulose gives a viscosity of approximately 500 cP when dissolved in 20 per cent *n*-butyl acetate.

Films produced by nitrocellulose are waterproof, hard and tough and resist abrasion. However, when used alone nitrocellulose has some drawbacks, namely, poor gloss and a tendency to shrink and to become brittle; adhesion to most surfaces is only moderate. This has resulted in the use of modifying resins to impart adhesion and to improve gloss, and of plasticizers to impart flexibility and to reduce shrinkage. With the use of solvents and diluents one then has the complete range of ingredients used in nail lacquers.

Resins

Wing[12] has pointed out that plasticized nitrocellulose films do not possess a high lustre. Resins such as damar and alkyd resins which were added by manufacturers of industrial enamels were found to be unsuitable for nail lacquers, since they made the films more susceptible to water. In about 1938 resins of the aryl sulphonamide-formaldehyde type were introduced which gave good lustre to nail varnish films and improved their resistance in detergent solutions; such resins have been used in many nail lacquers since that time to impart gloss, improve adhesion and often to increase the hardness of resulting films.

Examples of two commercially available resins of the aryl sulphonamide-formaldehyde type are Santolite MHP and Santolite MS 80 per cent, of which the former is the harder while the latter produces films of greater flexibility. Both of these resins are said to impart high gloss and good flow properties and also to increase the hardness of nitrocellulose. They are also claimed to increase the moisture resistance of nitrocellulose films, and thus to reduce the incidence of water spotting and whiteness of such films. With a dry nitrocellulose:resin ratio of 2:1, the moisture permeability of a film has been claimed to have been reduced to about half of that of an unmodified nitrocellulose film of the same thickness.

These resins are moderately stable to light and soluble in the majority of lacquer solvents and diluents usually employed. It has been pointed out, however, that their solvent release of alcohols other than methyl and ethyl alcohols is slow and that in lacquers which contain these resins the amount of a higher-molecular-weight alcohol should be kept to a minimum. It should also be stressed that, because of the low viscosity of their solutions, relatively large amounts of aryl sulphonamide-formaldehyde resins can be used in many lacquer formulations without adversely affecting the ease of application of such formulations. These resins have the further advantage of making it possible to produce films of a given thickness with fewer applications and a correspondingly smaller solvent loss, thus allowing economies in the use of expensive solvents when manufacturing modified nail lacquer preparations.

Some users develop a sensitivity to aryl sulphonamide-formaldehyde resins; such persons should use a varnish which does not include this resin.

The use of other resins has also been suggested. Cosmetic Laboratories Inc. have claimed production of an improved film with quick-drying properties by an additional use of nylon in amounts of up to 4 per cent of solids. Maleic alkyd resins have also been used because of their compatibility with nitrocellulose and their enhancement of light stability, hardness and solvent release. Other resins that could be investigated include styrene alkyds, melamine-formaldehyde, urea formaldehyde and the acrylics.

Plasticizers

Nitrocellulose is too brittle to be used in lacquers on its own and even the inclusion of a resin will not impart the necessary flexibility to lacquer films. Plasticizers must therefore be included in nail lacquer formulations in order to ensure that the film which remains on the nails after the solvents have evaporated adheres well, is flexible and does not flake off. By virtue of their high boiling point, plasticizers will remain in the film after the solvents present in the formulation have evaporated and render the films pliable. Plasticizers, even at low concentration, will furthermore enhance the gloss of resultant films and will also improve the flow properties of lacquers.

There are two groups of plasticizers:

(i) solvent plasticizers which, as the name implies, are solvents for nitrocellulose;
(ii) non-solvent plasticizers, also referred to as softeners.

The first group, the members of which are true plasticizers, comprises mainly high-molecular-weight esters, with fairly high boiling points and low volatility.

The second group are not solvents for nitrocellulose and are not compatible with it. If they are used in the absence of solvent plasticizers they will form separate droplets on the film once the solvents have evaporated. They must therefore be used in conjunction with true plasticizers which will hold them in solution; under those conditions they will impart additional flexibility to the film.

The most common representative of this group is castor oil which, when used in combination with a true plasticizer in the proportion 1 : 1, at a level of about 5 per cent, produces a very flexible film.

A good plasticizer must:

(a) be miscible in all proportions with the solvent, the nitrocellulose (applies to true plasticizers) and the resins used;
(b) be dermatologically innocuous and free from any sensitizing properties;
(c) have a low volatility;
(d) improve the flexibility and adhesion of the lacquer;
(e) not cause any discoloration of the finished product, that is, it must have moderately good lightfastness;
(f) be stable and odourless, or it must have a pleasant odour, since it does not evaporate but remains in contact with the nail.

Provided that the plasticizer fulfils the above requirements, the criteria which govern the selection of a plasticizer for nail lacquers are its effect on viscosity, on the rate of drying, flexibility, adhesion and gloss. The mention of lightfastness primarily relates to the fact that certain plasticizers, such as tricresyl phosphate, tend to turn yellow when exposed to light, while others will darken.

The amount of plasticizer used in nail lacquers varies from about 25 to 50 per cent based on the dry weight of the nitrocellulose present, and depends on the degree of flexibility required. Some formulations contain a single plasticizer; in others two or more plasticizers may be present among which dibutyl phthalate is one of the most widely used. Phthalates, phosphates, phthalyl glycollates, sulphonamides and citrates constitute the main group of plasticizers used in nail varnishes.

For a list of plasticizers most commonly used in nail lacquer preparations and for a more detailed description of properties of some of them, the reader is referred to a review of nail lacquers in *Manufacturing Chemist*.[13]

Solvents

It will be seen from the list of desirable film properties given earlier that the properties of the solvent, particularly the evaporation characteristics, are of the utmost importance.

It is common practice to rank solvents by their boiling points, which also appear to correlate with the viscosities of the resultant nitrocellulose solutions and hence with the spreading characteristics.

The normal procedure in textbooks appears to be the listing of a number of solvents with their boiling points, from which the experimenter is expected, presumably, to select a judicious mixture of medium-, high-, and low-boiling

solvents, which are generally differentiated as follows:

(1) Low-boiling solvents (with boiling points of up to 100°C) represented, for example, by acetone or ethyl acetate.
(2) Solvents of medium boiling point (100°–150°C) represented by *n*-butyl acetate, considered to be the best all-round solvent.
(3) High boiling point solvents (over 150°) exemplified by Cellosolve, Cellosolve acetate, butyl Cellosolve, and including all nitrocellulose plasticizers which are also solvents for nitrocellulose.

However, although the boiling point will play some part, it is the evaporation rate at temperatures not much above 30°C that is the real concern in this context. This will depend on a number of factors including specific heat, latent heat of evaporation, molecular weight, degree of association, to mention only a few.

In the case of cellulose lacquers, in which a mixed solvent is employed, the effect of the vapour pressure of the mixed solvents on each other, and that of any molecular attraction, has to be considered. Even this by no means exhausts the variable complex factors involved. It suffices, however, to show the difficulties of any purely theoretical selection.

In order to provide some simple approximate factors for evaporation rates of single solvents, a number of solvents were allowed to evaporate under uniform conditions and the times required for complete evaporation of standard volumes were compared with that for a sample of ethyl ether. The results are given in Table 22.1.

Table 22.1 Solvent Evaporation Coefficients based on the Evaporation Rate of a Standard Volume of Ethyl Ether

Solvent	Approximate evaporation coefficient	Boiling range (°C)
Ether, ethyl (0·72)	1·0	34–35
Ether, petroleum (40°–60°C)	1·3	40–60
Methyl acetate	2·0	56–59
Acetone	2·1	55–56
Ether, petroleum (60°–80°C)	2·5	60–80
Cyclohexane	4·2	81
Ethyl acetate	4·8	74–79
Methyl ethyl ketone	5·0	79
Carbon tetrachloride	6·0	77
Ethyl alcohol	9·0	78
n-Butyl acetate	12·8	124–128
Amyl acetate	13·0	137–142
Xylol	13·4	138
Isopropyl alcohol	22·0	80
n-Butyl alcohol	34·0	115–118
Diethylene glycol monomethyl ether	35·0	134
Diethylene glycol monoethyl ether	45·0	135
Ethyl lactate	90·0	150–160

The correct choice of the constituents of the solvents and their proportions is very important for the following reasons:

(1) The thin low-boiling solvents give the necessary mobility to enable the lacquer to spread easily and dry quickly, but if they are present in excess the lacquer may not wet the nail and consequently may spread unevenly.
(2) On the other hand, the higher-boiling, more viscous solvents give body to the lacquer and allow time for it to key on to the nail surface and to flow into an even film, but delay the drying and hardening times.
(3) Too rapid evaporation from the surface of a film may give rise to blushing or blooming, especially in a humid atmosphere.
(4) Evaporation from the surface of a thicker film may give a surface dryness with an underlying softness which can cause wrinkling of the film.
(5) Preferential evaporation of one part of a solvent blend may change the composition of the remaining liquid so much as to disturb the solvent properties, giving rise to premature or partial precipitation of the solid material, with an uneven final effect.

Diluents

Diluents, while not being actual solvents for nitrocellulose, are organic solvents miscible with nitrocellulose solvents. They are used as solvents for modifying resins used in lacquers, since true nitrocellulose solvents are expensive. They also help to stablilize the viscosity of lacquers, but their main value lies in reducing the overall cost of formulations. There are three classes of diluent: (i) the alcohols, (ii) aromatic hydrocarbons and (iii) aliphatic hydrocarbons.

There is a limit, however, to the amount of diluent that can be tolerated by the nitrocellulose solution, which may be defined by the so-called tolerance, or dilution ratio. This has been defined as the maximum diluent–solvent ratio that can be tolerated by a nitrocellulose solution without causing the latter to be precipitated. In addition to the possibility of nitrocellulose precipitating out of solution, the question of viscosity, which governs ease of application, must also be taken into account. Lacquers in which the solvent–diluent ratio approximates to the tolerance ratio have a considerably higher viscosity than those containing a smaller amount of diluent, and will cause difficulties in obtaining a smooth film. The actual tolerance ratio for any solvent–diluent system is determined by titrating a given volume of the nitrocellulose solution with a diluent until the solution becomes cloudy.

It has been pointed out elsewhere that, in the formulation of lacquers, use of a high boiling point diluent with a low boiling point solvent is to be avoided if precipitation of nitrocellulose and 'blushing' of the film are not to occur. In general, when dealing with compositions containing solvent and diluent mixtures, the rate of evaporation of the diluent should be greater than that of the solvent or solvent mixture employed, otherwise the diluent–solvent ratio in the film will steadily increase and eventually the tolerance ratio will be exceeded, causing nitrocellulose to precipitate on the film. As a result, instead of the smooth, clear and continuous film hoped for, a harsh, rough and cloudy film will be produced which will lack adhesion.

Alcohols, especially ethyl and butyl alcohols and isopropanol, are very efficient diluents, their tolerance ratio being 9:1. Butyl alcohol, with an evaporation rate which is neither too rapid nor too slow is preferred to the more volatile ethyl alcohol, which may give rise to chilling. Butyl alcohol tends to lower the viscosity of nitrocellulose solutions. Isopropanol, with its lower cost and ready availability, is the most popular alcohol used.

In nail varnishes, aromatic hydrocarbons such as toluene and xylene are employed. Their tolerance ratio of 3:1 is much lower than that obtained with alcohols; consequently they are not such efficient diluents. They also tend to increase slightly the viscosity of nitrocellulose solutions and to impart poor flow properties to the film. To overcome these disadvantages, a mixture of toluene and isopropanol may be employed as the diluent.

The choice of solvent will also influence the gloss of the films produced. A high boiling point solvent will produce a brighter film than does a low boiling point solvent. For matt films, highly volatile solvents and diluents are still used, but care must be taken that 'blushing' of the film does not occur.

Colours

Insoluble lakes are incorporated in the majority of nail lacquers to produce a suitable shade, together with titanium dioxide in order to confer opacity and creaminess and to produce pastel shades.

Soluble dyestuffs such as erythrosine, carmoisine and rhodamine, which were used at one time in nail lacquers, were found to stain the surrounding skin and the use of such dyestuffs has been virtually abandoned.

As far as the required properties of these pigments are concerned, they are similar to the requirements specified for pigments used in other cosmetic products, namely that they should be non-toxic and non-sensitizing, that they should be non-staining, substantially insoluble in lacquer solvents, free from any tendency to bleed, compatible with other lacquer constituents and moderately stable to light. They should also be of very small particle size, free from gritty particles and should have satisfactory dispersing properties.

The colours used in nail lacquers must conform to appropriate national legislation. In the USA only colours certified by the Food and Drug Administration, or inorganic colours of suitable purity, may be used. In the EEC the colours used must be taken from the positive lists included in the EEC Cosmetics Directive of 1976 and its amendments. Surveys of permitted colorants are given in Chapter 19 and by Van Ham.[14] The most widely employed pigments include the following accepted colours:

D&C Red 6	Colour Index	15850 Na
D&C Red 30		73360
D&C Red 36		12085
D&C Red 9		15585:1
D&C Red 7		15850:1
FD&C Yellow 5		19140
FD&C Yellow 6		15985

As pointed out above, titanium dioxide has been employed to impart opacity and to produce pale shades, while iron oxides are used to produce brown and tan

shades. A range of chemically inert brown pigments derived from dinitrobenzene has been suggested for use in nail lacquers instead of iron oxide.[15] These were said to give more brilliant colours, to have greater tinctorial strength than iron oxide and to be very fast to light; because of their lower specific gravity, they are less liable to settle out.

Pigments for use in coloured lacquers are often supplied in the form of dispersions. These dispersions are formed by dissolving 'colour chips' in the appropriate solvents. 'Colour chips' are mixtures of nitrocellulose, colour and solvents, processed on a roller mill by specialist operators to give solid colour particles that are easily handled. Provided that this processing is satisfactory, no further roller milling of the pigment will be necessary prior to its incorporation into the nail lacquer. The pigment content of coloured lacquers varies from product to product but does not normally exceed 5 per cent. For improved wear resistance, the pigment concentration in nail lacquers should not be lower than 3 per cent.

Pearlescent (Nacreous) Pigments

In addition to the conventional pigments, nail lacquers can incorporate iridescent materials Guanine (2-amino-6-hydroxy purine), a crystalline substance from the scales and body of various fish, has been one of the most frequently suggested. In its pure form it is non-toxic, but there have been references to this material being the cause of dermatitis arising from nail lacquers. This substance has a high refractive index (1.8) and its pearly lustre and brilliance are due (i) to the simultaneous reflection of light both from the upper layers of its transparent crystals and from crystal planes at different depths, and (ii) to the alignment of crystals in the same direction, made possible by their shape and dependent on the degree of dispersion of the crystals in the lacquer. Orientation of these crystals takes place when the nail surface is coated with the lacquer containing the pearl pigment and they remain in this alignment when the film hardens. Natural pearl essence is commercially available in the form of a suspension in a nitrocellulose–butyl acetate lacquer at a level of about 11 per cent and is used in clear or pigmented lacquers at a concentration of between 8 and 10 per cent.

Synthetic pearl pigments are also available; owing to the high cost and scarcity of guanine, these have become the most predominantly used materials. The most popular is bismuth oxychloride. It crystallizes in platelets, has a high refractive index and produces a high lustre and brilliance at low cost. However, the material is denser than guanine and this can lead to problems of settling on standing, within the finished product. Bismuth oxychloride is normally available as 12·5 per cent and 25 per cent suspensions in nitrocellulose–butyl acetate–toluene mixtures to which has been added a small amount of colloidal pretreated clay. This gives the system added suspension power to prevent the bismuth oxychloride settling out. Another pearlescent material gaining increasing popularity is mica coated with titanium dioxide. It is less dense than bismuth oxychloride and therefore can be suspended more easily. However, it is less brilliant and does not have the same covering power as bismuth oxychloride. It is commercially available in nitrocellulose–solvent suspensions and this method of addition to formulations is preferable to the use of the dry powder, which can be difficult to disperse without the use of specialist mixers.

Suspension Agents

The modern trend towards highly pigmented and pearlescent nail lacquers has led to a critical assessment of the ability of traditional nail lacquer formulae to suspend these materials at high concentration. Additionally, consumers have reacted against products showing 'settled out' materials, and thus systems developed to avoid sedimentation soon showed themselves both to be technically superior and to have enhanced consumer acceptance. The suspension properties are obtained by creating a thixotropic system with the use of pretreated colloidal clays such as benzyl dimethyl hydrogenated tallow ammonium montmorillonite (Bentone 27), dimethyl dioctadecyl ammonium bentonite (Bentone 34), or dimethyl dioctadecyl ammonium hectorite (Bentone 38). These clays increase the viscosity of the system to such an extent that the heavy oxide pigments remain in suspension. When a shear force is applied to the system by shaking, or by brushing the product across a nail, the viscosity drops sharply, allowing a smooth application. On standing, the system regains its initial high viscosity. A thixotropic system containing nacreous pigments has been described in a US patent.[16] In modern practice, bentone levels range from 0·5 to 2 per cent, since the viscosity of the system can be enhanced even further by adding small quantities of a polyvalent acid, for example, ortho phosphoric acid, which precludes the use of high levels of bentone and makes the system more controllable.

Formulation

In the preceding paragraphs the desirable properties of nail lacquer constituents have been outlined. These should be taken into consideration in the formulation of such lacquers.

Various tests must therefore be devised to ascertain the flow characteristics of formulations, the rate of drying of lacquer films, the compatibility of their constituents during drying, as well as their appearance, hardness, adhesion and resistance to soap and to detergents. If necessary, formula adjustments have to be made and the tests repeated until the required characteristics are obtained. A good indication of the behaviour of lacquers on fingernails can be obtained from the behaviour of a layer of the lacquer on a clean and clear glass plate. However, this does not obviate the need for studying the products by actual application to the nails. Tests should also be carried out on the flow and evenness of application of lacquer films, their hardness and gloss. Any drag observed on the applicator brush should also be recorded.

Abrasion tests may be used *in vitro* to assess the wear resistance of films. Ultimately, however, assessments of the products *in vivo* must be carried out, employing a large panel of subjects who have applied both the experimental lacquer and the control on different fingernails for a period of one week, and examining the treated nails daily. A summary of evaluation techniques has been given by Shansky.[17]

In connection with the drying of lacquer, the practice of blowing on freshly applied lacquer films to speed up their drying should be discouraged, so as to ensure that no moisture is present which could have an adverse effect on the adhesion and the gloss of the film.

It has already been pointed out that it would be preferable from the point of view of convenience and solvent economy to apply a film in a single application. Since the thickness of the film determines its gloss and resistance to wear, it is desirable to obtain as thick a film as is practical from the point of view of ease of application and the rate of drying. Practical limitations, however, sometimes make it necessary to apply two coats of the lacquer in order to obtain a film of the required thickness. If this is necessary, it is then good practice to allow the first film to dry completely before applying a second coat, otherwise the evaporation of solvent may produce small blisters in the upper layer and give rise to the 'orange peel' effect often observed with quick-drying lacquers.

Formulation of base nail lacquers can be illustrated by the following examples.

Typical nail lacquer base[12]	(11) *per cent*
Nitrocellulose (about ½-second viscosity)	10·0
Resin	10·0
Plasticizer	5.0
Alcohol	5.0
Ethyl acetate	20·0
Butyl acetate	15·0
Toluene	35·0

In more detail, a clear base lacquer can be described as:

		(12) *per cent*
Nitrocellulose (½-second)		18·28
Santolite MS 80	(resin)	6·43
Dibutyl phthalate	(plasticizer)	2·15
Camphor	(plasticizer)	1·88
Ethyl acetate	(solvent)	6·45
Butyl acetate	(solvent)	25·42
Toluene	(diluent)	29·56
Isopropanol	(diluent)	9·83

In a *Monsanto Bulletin*[18] the following nail lacquer base formulation was quoted:

		(13) *per cent*
RS ½-second nitrocellulose		10
Santolite MHP	(resin)	10
Santicizer 8 or 160	(plasticizer)	5
Ethyl alcohol		5
Ethyl acetate		20
Butyl acetate		15
Toluene		35

Resins consisting of polymerization products of acrylic acid and its derivatives may be used in nitrocellulose compositions, and it has been claimed that this will overcome inherent disadvantages of nail varnishes such as shrinkage during

drying, peeling at the edge of the nail, discoloration, thickening of the enamel by evaporation of volatile ingredients when stored in poorly stoppered containers, and failure to achieve proper gloss and durability. A typical formula cited is the following:

	(14) *parts*
Cellulose nitrate	3·2
Denatured alcohol	1·4
Butyl acetate	19·3
Ethyl alcohol	19·3
Toluene	19·3
Propyl methacrylate resin	15·0
Plasticizer	3·2

Both high-boiling and low-boiling solvents are said to be eliminated in the above formula and the enamel produced is said to afford excellent adhesion and to be remarkably resistant to soapy water, alkali, marking and scratching.

Keithler[19] gives an interesting formula containing no nitrocellulose and using a chlorinated biphenol plasticizer:

	(15) *parts*
Polyvinylchloride–acetate copolymer	10·7
Polymethylmethacrylate	7·0
Methyl ethyl ketone	21·5
Sorbitol	20·0
Arochlor 5460	15·0
Tricresyl phosphate	8·0
Ethyl acetate	22·3
Colours	0·5

Manufacture of Nail Lacquer

The preceding sections are to a certain extent theoretical in their approach to nail polish production. One would not, for example, make a nail lacquer by measuring into a mixing vessel the individual materials listed in example 11. In practice it is more usual to buy a base lacquer which incorporates the particular requirements for plasticizer, resin, etc., and mix with it pearlescent materials and pigments, etc. Because of the specialist approach needed to handle and process nitrocellulose and bentone, most cosmetic manufacturers handle nail lacquer production along these lines. Many just fill the finished product as supplied to them from a specialist contract manufacturer, although they themselves may well have developed the shades, etc.

An outline of all the manufacturing procedures involved in nail lacquer production is given in Figure 22.1.

Base Coats and Top Coats

The object of using a base coat is to prevent the chipping of the nitrocellulose film, by forming on the nails a film to which the nitrocellulose lacquer will closely

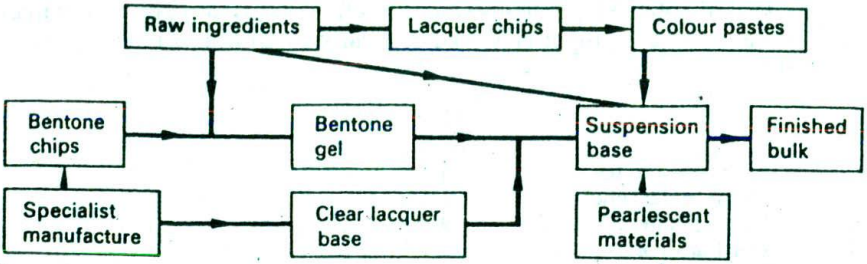


Figure 22.1 Manufacturing routes for nail lacquer production

adhere. Phenol-formaldehyde resins, sulphonamide-formaldehyde resins, alkyd resins and methacrylate are used for this purpose.

Base coats often contain a larger amount of resin for increased adhesion; they dry more rapidly and give a harder film that the normal lacquer film. Films built on a base coat are far less liable to crack than ordinary nail enamels. Clear and pigmented base coat formulations are available with a lower solid content and lower viscosity than normal lacquer formulations.

Top coats are usually clear lacquer films which are applied over the pigmented lacquer film in order to increase film thickness and thus resistance to abrasion and wear, and also to improve gloss. They have a higher nitrocellulose and plasticizer content and a lower resin content than normal nail enamel and they also have a relatively high diluent content and tend to dry rapidly. Three formulae for a base coat, a clear lacquer and a top coat, originally quoted by Peirano[11] and later cited in *Manufacturing Chemist*,[13] illustrate the differences in the composition of such products (examples 16–18).

	(16) Base coat *per cent*	(17) Clear lacquer *per cent*	(18) Top coat *per cent*
Nitrocellulose	10	15	16
Santolite resin	10	7·5	4
Dibutyl phthalate	2	3·75	5
Butyl acetate	—	29·35	10
Ethyl acetate	34	—	10
Ethyl alcohol	5	6·4	10
Butyl alcohol	—	1·1	—
Toluene	39	36·9	45

Enamel Remover

The products used as enamel removers usually consist of simple mixtures of solvents, such as acetone, amyl acetate or ethyl acetate, which may contain small amounts of fatty material to counteract any excessive drying action of the solvents on the nails. Originally castor oil was used, but nowadays esters such as butyl stearate or dibutyl phthalate, fatty alcohols or soaps may be used for the same purpose. An example of an enamel remover is provided by the following formula:

	(19) *per cent*
Butyl stearate	5·0
Diethylene glycol monoethyl ether	10·0
Acetone	85·0

Gamma-valeractone ($C_5H_8O_2$), a colourless and almost odourless solvent, has been suggested[20] by the manufacturers as a nail polish remover. Unlike the majority of organic liquids used for this purpose, GVL (as the compound is known) is completely miscible with water; a 50 per cent solution in water is suggested for use as a nail polish remover. It is stated to be non-irritating to the skin. Yet another solvent suggested for use in enamel removers is butyrolactone.

Another type of enamel remover is the so-called 'non-smeary' remover which is claimed to remove the nail lacquer without smearing the nails or the adjoining skin. These products consist of a mixture of water and water-miscible solvents such as ethyl acetate in which the water content is only of the order of 8–9 per cent.

Cream Nail Enamel Removers

A number of creamy nail enamel removers have been introduced, many of them patented. In general these consist of a fairly high-boiling solvent for the lacquer, introduced into a cream which may contain some lanolin or other emollient material; alternatively they may be composed of a lacquer solvent solidified by means of a suitable wax.

One example of a product of this type disclosed in a US patent[21] had the following composition:

	(20) *per cent*
Paraffin or beeswax	11·5
Lanolin	4·0
Sodium or potassium linoleate	2·6
Methyl ethyl ketone	to 100·0

Dreyling[22] described a creamy nail polish remover which contains about 70 per cent by weight of a substantially anhydrous organic solvent capable of dissolving nitrocellulose, the remainder of the preparation comprising a mixture in the ratios, by weight, of 10 parts of a solid fatty acid such as stearic or palmitic, 2 to 4 parts of ethyl cellulose, 2 to 10 parts of a cosmetic aid (castor oil, olive oil and lanolin) and 2 to 4·6 parts of concentrated ammonia water; example 21 is taken from the patent:

	(21) *parts*
Ethyl acetate	40·0
n-Butyl acetate	40·0
Castor oil	4·0
Perfume	0·1
Ethyl cellulose (60/80 seconds)	2·8
Stearic acid	11·0
Ammonium hydroxide (conc)	3·8

Procedure: Mix the above ingredients (with the exception of the ammonium hydroxide) until complete solution is obtained (heating at 50°–60°C will hasten rate of solution). When the composition forms a clear liquid, add the ammonium hydroxide slowly, stirring the mixture.

An important and critical part of the above invention is stated to lie in the balance existing between the ratios of ethyl cellulose, stearic acid, ammonia and water. Attention is drawn to the fact that, while ammonium stearate produced *in situ* is the emulsifying agent, it does not appear possible to produce a satisfactory preparation by the inclusion of a previously and separately prepared ammonium stearate.

Carter[23] described a cream to remove nail polish consisting of an intimate mixture of water-soluble soap, free stearic acid (in greater proportion than the soap, the two together forming at least 15 per cent of the cream) and a solvent for nitrocellulose. Ochs[24] described a type of preparation comprising 4 per cent lanolin, 11·5 per cent wax, 2–6 per cent alkali metal soap, 5 per cent water and 70–80 per cent of a solvent for cellulose nitrate (for example, methyl ethyl ketone).

In an earlier patent[25] Carter employed bentonite as an emulsifier. This patent points out that in mixtures of oil and water, bentonite collects at the interfacial boundary and acts as a protective colloid to stabilize the emulsion.

A suggested composition from this patent is given in example 22.

	(22) *per cent*
Sulphonated olive oil	10·0
Sodium hydroxide (10%)	1·0
Benzyl acetate	15·0
Acetone	15·0
Titanium dioxide	0·5
Bentonite	2·0
Water	56·5

Procedure: Mix the bentonite with 20 per cent of the water and allow to stand for about 12 hours. Then add the pigment, oil, organic solvents, alkali and the remainder of the water to the suspension in this order, with continuous agitation.

Example 23 gives a useful formula quoted in *Drug and Cosmetic Industry*.[26]

	(23) *per cent*
Stearic acid	9·5
Triethanolamine	3·5
Mineral oil	10·0
Butyl acetate	50·0
Butyl stearate	5·0
Carbitol	5·0
Water	17·0

Nail Drier

Nail driers are aerosol formulations which make use of the rapid evaporation of a propellant to speed up the drying of freshly enamelled nails, by drawing off the solvent present in the nail varnish. Sometimes drying is combined with the deposition of a transparent film of oil over the freshly applied enamel, to reduce its tackiness and to prevent it from smearing if touched.

PLASTIC FINGERNAILS AND ELONGATORS

Plastic fingernails and elongators are largely used to improve the cosmetic appearance of damaged or short stubby nails. They are produced by the polymerization or copolymerization of monomers in the presence of a polymer, a catalyst and a polymerization promoter.[27] A plasticizer, an opacifier, a pigment and a filler may also be included.

The most frequently employed monomer has been methyl methacrylate while poly(methyl methacrylate), polystyrene, polyisobutylene and cellulose acetate have been used as the polymer. If methyl methacrylate is copolymerized with a crosslinking agent such as ethylene dimethacrylate, more brittle polymers with improved solvent resistance are produced. The crosslinking agent polymer is usually employed in amounts ranging between 2 and 10 per cent by weight of the monomer. The actual level at which it is used largely determines the hardness and brittleness of the product. Compounds of improved flexibility may be produced by forming a copolymer containing 5–20 per cent by weight of a higher-molecular-weight ester of acrylic or methacrylic acid such as lauryl methacrylate.

Triphenyl or tricresyl phosphate, dimethyl, diethyl or dibutyl phthalates may be used as plasticizer in amounts ranging between 1 and 10 per cent by weight of the monomer.

Polymerization of methyl methacrylate is a free radical-catalysed reaction entailing the dissociation of the catalyst to free radicals which initiate polymerization. The catalysts which are preferred in the production of nail elongators are benzoyl peroxide or lauroyl peroxide, and they may be used in amounts of up to 3 per cent by weight of the solid constituent of the preparation; usually, however, 1 per cent of the catalyst on the weight of monomer will be adequate. A polymerization promoter is also usually present to induce free radical release and to allow polymerization of component monomers to take place at room temperatures, that is at temperatures appreciably lower than those at which polymerization usually takes place.

Among fillers, silica and aluminium silicate, mica and metallic oxides have been used. The filler may constitute up to about 25 per cent of the solid compositions. Pigments and opacifiers are generally used at a level of 0·1 per cent.

Irrespective of the procedure adopted, it is necessary to prepare the surface of the nail before applying the nail elongator composition by removing any excess cuticle and all traces of any old lacquer from the nail, as well as to smooth any ragged surfaces, so as to ensure good adhesion between the nail surface and the plastic material applied.

The skin surrounding the nail is protected from polymerization taking place on its surface by applying to the skin a material with little adhesion for the plastic, usually a water-soluble resin easily removable with water.

Viola[28] has described in detail the procedure used to form a nail elongator *in situ*. It entails successive applications, first of the liquid monomer and then of the powder containing the catalyst. This is repeated until the nail has been adequatedly lengthened. Once the tip of the nail has been strengthened, the nail is then built up from the centre of the nail to the outer edge.

The ease with which methyl methacrylate and also other vinyl monomers polymerize has led to the incorporation in such compositions of, for example, hydroquinone which gives rise to the actual polymerization inhibitor benzoquinone. The polymerization inhibitor reacts with the chain radicals as they are formed, thereby preventing the addition of monomer molecules. The inhibitor may be removed from the film by washing the monomer with a sodium hydroxide–salt mixture. It is also important to ensure that the catalyst and promoter are not present in excesive amounts, otherwise the inhibitor will not be able to react with all the excess free radicals produced.

To illustrate the composition of solid and liquid components, the following example is quoted from the literature:

	(24)
Solid component	*per cent*
Poly(methyl methacrylate) (granules)	75
Aluminium silicate	23
Benzoyl peroxide	2
Liquid component	
Methyl methacrylate (monomer)	83
Lauryl methacrylate (crosslinking agent)	15
Diethyl aniline (promoter)	2

Procedure: Mix 1·8 parts by weight of the powder component with 1 part by weight of the liquid component; polymerization to a hard plastic material takes place within 15–20 minutes at room temperature.

Compositions and the technique employed in producing natural-looking fingernails have also been described in another US patent;[29] the artificial nails are produced *in situ* by rapid polymerization or copolymerization of a constituent monomer at room temperature in the presence of a polymer and a redox catalyst system.

They are formed from two components, one of which is a primer composition containing a film-forming resin, for example a mixture of poly(methyl methacrylate) and a copolymer of vinyl chloride and vinyl acetate, and the oxidizing component of a redox catalyst system. This component is used to form coatings on the exposed nail bed and the surrounding skin and protects them from irritation by the monomer contained in the second composition. The film-forming solids content of the primer composition should preferably not exceed 25 per cent.

The second composition contains most of the resins for the artificial nails and consists basically of a solution of a polymeric film-forming resin, for example

poly(methyl methacrylate), in a resin-forming monomer, for example methyl methacrylate. It also contains the reducing component of the redox catalyst. Both compositions are stable as long as they are stored separately, but when they are combined the monomer begins to polymerize.

The catalyst system employed in these compositions, as shown in embodiment examples of the patent, consists of benzoyl peroxide as the oxidizing component and N-dimethyl-*p*-toluidine as the reducing component.

NAIL MENDING COMPOSITIONS

Mending compositions described in a British patent[30] are basically mixtures of an adhesive, a fibre reinforcing material and a solvent. The first two components produce a film which forms a strong bond between the broken parts of the damaged fingernail, improving its appearance and preventing further damage, while the solvent, which permits easy application of the composition to the fingernail, will quickly evaporate and allow the reinforced adhesive film to set and to mend the damaged fingernail. These preparations are preferably applied in four coats, each coat being applied in a direction perpendicular to the previous one and allowed to become surface dry before applying the next coat. The nail polish is applied about one hour after the application of the final coat of the mending preparation, to allow all the coats to dry thoroughly.

The preferred organic film-forming material of the mending composition is nitrocellulose. A resin, for example an aryl sulphonamide formaldehyde, is also included to make the film produced by the composition more adherent, flexible and tough, and a plasticizer may be added to make the film flexible. Short rayon fibres (1·5 mm long) and of small diameter (1·5–5 denier) are used as reinforcing agent. Other fibres may also be used if they are not soluble in the mending composition. A gelling agent (preferably silica) is also present, to ensure that the fibres used remain suspended within the adhesive. Solvents specifically mentioned in the patent are ethyl acetate, butyl acetate and toluene used in a combination of 30–50 per cent, 5–20 per cent and 20–30 per cent respectively. Pigments or dyes may also be included to confer the desired colour. The compositions just described are illustrated by example 25. It has been claimed that nail polish can be applied to and removed from such mended nails without difficulty and without disturbing the 'repair'.

	(25) *per cent*
Nitrocellulose	10·3
Aryl sulphonamide formaldehyde resin	4·1
Silica	2·0
Dibutyl phthalate	0·5
Rayon fibres	0·5
Ethyl acetate	46·2
Butyl acetate	5·1
Toluene	31·3

Also patented have been keratin-containing compositions[31] which may be used either as nail varnishes or for the repair of chipped or cracked nails, as well as for producing artificial nails. They are intended to provide coatings that are not incompatible with natural nails. The keratin, which is resistant to various solvents including dilute acids and alkalis, is combined with a suitable water-insoluble bodying agent, for example cellulose nitrate, and dissolved in a suitable solvent, preferably methyl ethyl ketone, or a mixture of ethyl and butyl acetates. Synthetic resins may be included to increase adhesion, solids content and water resistance, and also to enhance gloss. Plasticizers may also be incorporated to avoid excessive brittleness of coatings.

The keratin is used in finely particulate form in the size range of 400 and 20 mesh, its amount according to embodiment examples varying between 5 and 9·5 per cent of the composition.

Coatings obtained with these compositions were claimed to give the necessary strength, body, hardness and adhesion for satisfactory performance of the coatings.

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PART THREE

The Hair and Hair Products

Chapter Twenty-three

The Hair

Introduction

The profound psychological and social significance of hair in Man is in contrast to its complete lack of vital function.[1] For mammals, as a whole, fur provides an insulating coat for the conservation of body heat. Its properties can be adapted to seasonal changes in the environment by periodic moulting of old hairs and their replacement by new ones, and even human hair follicles remain endowed with such cyclic activity. However, Man evolved by the ability to keep cool. The ape, *Ramapithecus*, an ancestor of 10 million years ago, was probably hairy, but the early hominids, as they left the forest and moved to the savannah, started a march towards nudity; the hair on the body became sparser and shorter.

Not all was lost. The eyebrows and eyelashes remained, as did the hair on the scalp, perhaps as a protection from the midday sun for an animal beginning to stand—and walk—on its own two feet. The beard remained as a badge of maleness. And, in both sexes, the genital and axillary hair, which was probably associated with glandular scent-producing units, now became conspicuous.

The Hair Follicle

Development and Structure

The structure of the hair follicle, the method by which it manufactures hair and its cyclic activity are better made understandable by brief reference to its embryonic history.[2,3] Each follicle arises from an interaction between epidermis and dermis.

A thickened plaque of epidermis, lying over an aggregation of dermal cells, extends inwards to form a peg which eventually engulfs a small papilla of dermis to form the *hair bulb*. The epidermal cells surrounding the dermal papilla then proliferate to push outwards a column of keratinizing cells, which is the hair shaft invested in an inner root sheath. A hair canal is formed in the process.

The bulk of the hair shaft consists of elongated, keratinized cells cemented together and is known as the *cortex*. Some, though not all, hairs have a continuous or intermittent *medulla*. The cortex is surrounded by a *cuticle*, which arises from a single line of cells in the bulb, but becomes five to ten overlapping layers. From the outside the cuticular scales appear imbricated, like roof tiles; with the free edges directed outwards (Figure 23.1).

The inner root sheath interlocks with the overlapping cells of the cuticle of the growing hair and moves with it, but the keratinizing cells are desquamated as the hair emerges from the skin. Thus the outer surface of the inner root sheath glides against the stationary *outer root sheath*, which is the innermost part of the follicular wall.

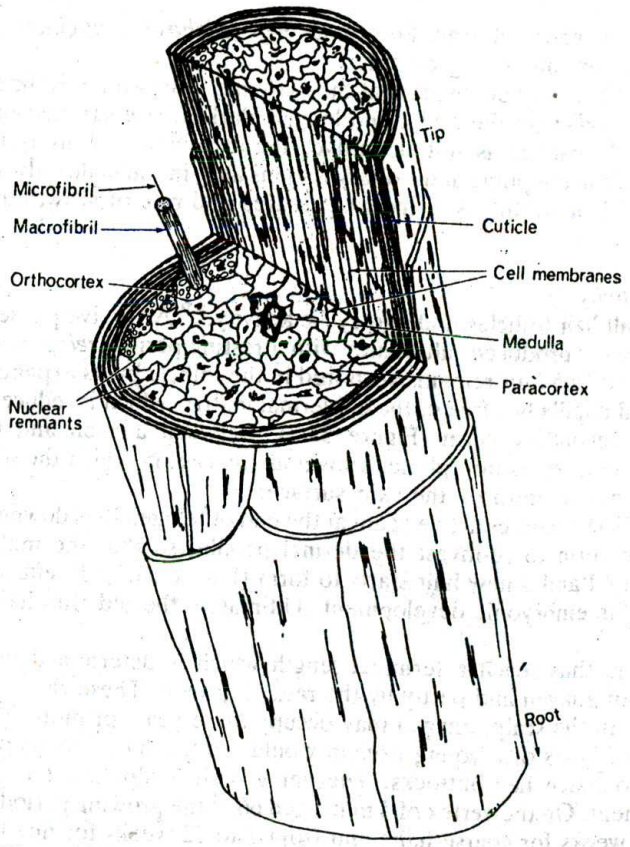


Figure 23.1 Section of a hair fibre (courtesy Unilever Ltd)

During the development of the peg, three bulges appear on its posterior wall. The outermost is the rudiment of the apocrine gland, which remains vestigial except in the genital, axillary and areolar regions, the next is the sebaceous gland, and the innermost is the attachment for the arrector muscle.

As the foetus grows, the first-formed follicles move apart and a new crop of secondary rudiments develop between them. But no new follicles are formed post-natally.[4] The total number of follicles in an adult man is about 5 million, of which about 1 million are in the head and perhaps 100 000 in the scalp.[5] A significant loss occurs with age;[6] young adults have an average of 615 per cm^2 on the scalp, but by the age of 80 the density has fallen to 435 per cm^2.[7] Some follicles are lost in baldness; a comparison over a wide range of ages gave averages of 306 per cm^2 for bald scalps as against 459 per cm^2 for hairy scalps.[7]

The first hairs to grow from hair follicles, which are fine, unmedullated and usually unpigmented, are known as *lanugo* and are normally shed *in utero* in the seventh or eighth month of gestation. Very rarely, lanugo-like hair is found in the adult, even on areas such as the nose and ears which are not normally hairy,

either as an inherited trait known as *hypertrichosis lanuginosa*, or as the symptom of an underlying cancer.

Postnatal hair may be divided, at the extreme, into two kinds: fine, unmedullated, short *vellus* on the body, and longer, darker, *terminal hair* on the scalp. The infantile pattern is not definitive, for at puberty vellus is replaced by terminal hair in the pubic and axillary regions and, in the male only, on the face. This sexual hair continues to increase in area and rate of growth until the late twenties.[2]

Cyclic Activity

Virtually all hair follicles undergo cyclic activity.[8,9] An active phase, *anagen*, in which a hair is produced, alternates with a resting period, *telogen*, in which the fully formed *club hair* remains anchored in the follicle by its expanded base and the dermal papilla lies free of the epidermal matrix, which is reduced to a small, quiescent secondary germ (Figure 23.2). Between anagen and telogen is a relatively short transition phase, known as *catagen*, in which the newly formed club hair moves towards the skin surface.

The follicle becomes active again at the end of telogen by a downgrowth of the secondary germ to re-invest the dermal papilla, so that the matrix becomes reconstituted and a new hair starts to form (Figure 23.3). In effect, the follicle re-enacts its embryonic development. Ultimately the old club hair is shed, or *moulted*.

All hairs thus reach a terminal length which is determined mainly by the duration of anagen and partly by the rate of growth. These characteristics vary with site. In the scalp, anagen may occupy three years or more;[9,10] indeed the untrimmed locks of a young woman would require 6 or 7 years of continuous growth to reach her buttocks. The aging male scalp falls far short of such achievement. On the vertex of a man aged 60,[11] the growing period ranged from 17 to 94 weeks for coarse hairs and from 7 to 22 weeks for fine hairs. On the body, the period of the cycle is much less. In a young male[11] it ranged from 19 to 26 weeks on the leg, 6 to 12 weeks on the arm, 4 to 18 weeks on the finger, 4 to 14 weeks in the moustache, and 8 to 24 weeks in the region under the temple.

Animals show wide differences. For example, in the rat the dorsal hair is fully formed in three weeks and the shorter ventral hair in only 12 days,[12] and in the guinea-pig anagen lasts between 20 and 40 days.[13]

In many animals waves of follicular activity, followed by moulting, pass over the body in symmetrical patterns. In the rat, for example, replacement of hairs starts in the venter and bands of activity and shedding move over the flanks to the dorsum, subsequently spreading to the head and the tail regions.[12] In contrast, in the human scalp each follicle appears to be independent of its neighbours. At any one time an average of 13 per cent (4–24 per cent) of the follicles are in telogen[9,14,15] and about 1 per cent in catagen. Thus in a scalp containing around 100 000 follicles with an average cycle of 1000 days, about 100 club hairs should be shed each day. This is approximately the number recovered in practice.[9,10]

The guinea-pig has been said to resemble man in that moulting is continuous and at random. However, in the newborn animal all follicles are simultaneously active[13] and it seems that for at least 50 days, and probably for much longer,

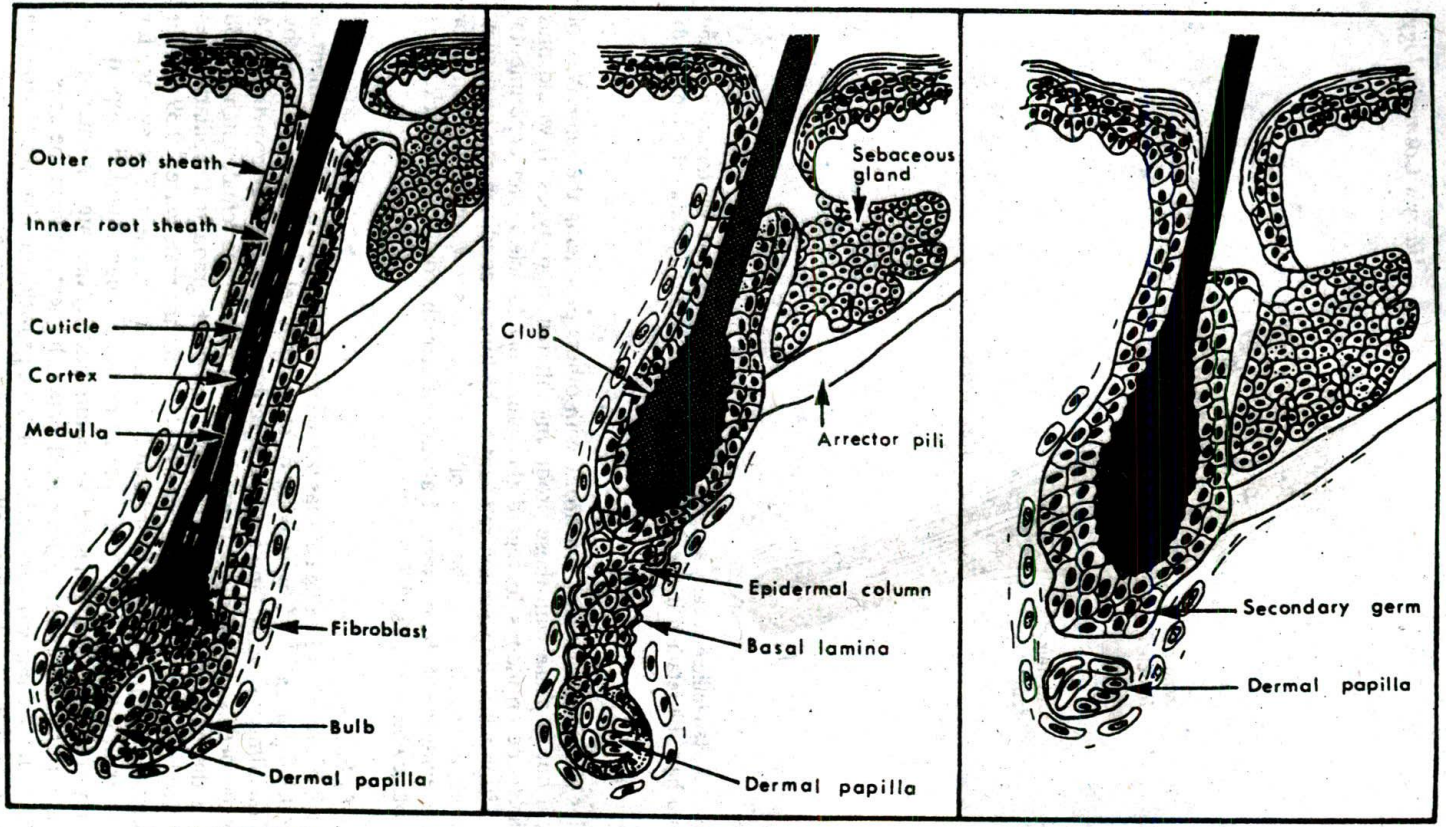


Figure 23.2 The hair follicle cycle

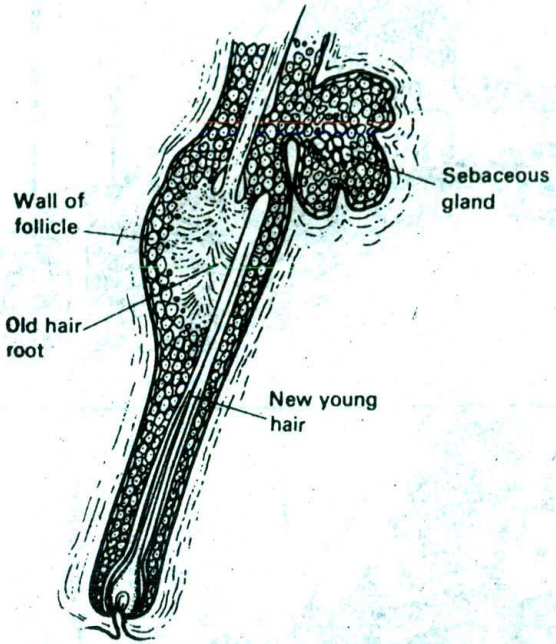


Figure 23.3 Hair follicle in early anagen, prior to shedding. Note newly formed hair, and old club hair still retained in the follicle (after Unna, courtesy Edward Arnold Ltd)

follicles show a measure of synchrony with others producing the same type of fibre, if out of phase with those producing different fibre types. It would thus appear to be erroneous to regard the guinea-pig follicle as an experimental model from which information relevant to the human condition can be drawn. However, at an early stage human follicles may also show some synchrony, for there is evidence of the passage of a wave of growth from front to back in the scalp of newborn infants.[10,16,17]

Rate of Growth of Hair

The rate of growth of human hair has been determined by direct measurement of marked hairs *in situ*,[18,19] by shaving or clipping at selected intervals[20] and by pulse labelling ^{35}S cystine and autoradiography.[21,22] The average growth per 24 hours has been stated to range from about 0·21 mm on the female thigh to 0·38 mm on the male chin.[20] Another study,[19] in which graduated capillary tubes were fitted around growing hairs, gave 0·44 mm for the male vertex, 0·39 mm for the temple, 0·27 mm for the beard and 0·44 mm for the chest. The average for the vertex in women was 0·45 mm per 24 hours. Though scalp hair appears to grow faster in women than in men,[19,23] before puberty the rate is greater in boys than in girls.[15] In both sexes the growth rate is highest between the ages of 50 and 69 years.[24] Some workers believe that the growth rate remains constant in any follicle,[19] others that it usually decreases or increases.[21]

While daily variations in temperature have no effect on hair growth, it seems likely that there are longer-term seasonal changes; for example, the beard grows faster in summer than in winter.[25] It is generally agreed that shaving does not alter the rate of growth,[26] though prolonged irritation may affect the follicle.[27]

Rates may differ considerably between species. Hair growth can be more than 1·0 mm per 24 hours in the rat[12,28,29] and up to 0·6 mm in the guinea-pig, in which it has been clearly shown that the rate depends on the time for which activity of the follicle has been in progress.[30]

Hormonal Influences

There is ample experimental and clinical evidence that hormones influence hair growth. The analysis of their actions is, however, extremely complicated. In considering the extent to which animal models may illuminate the human condition, it is important to distinguish the control of the follicular cycle, concerned with the adaptive function of the moulting, from the control of sexual hair, concerned with adult social interactions. Moreover, hormones may act at more than one point; an action which modifies the structure of the hair, the rate of growth or the duration of the growing phase must be distinguished from one which simply reduces or prolongs the resting period. The failure to make such distinctions has led to many useless experiments and even more fallacious conclusions.

The control of the follicular cycle appears to be exercised at several different levels. First, experiments on rats have demonstrated that each follicle has an intrinsic rhythm which continues when its site is changed[31] or, at least for a period, when it is transplanted to another animal in a different phase of the moult.[32] When hairs are plucked from resting follicles, activity is initiated and at least for a time the follicles remain out of phase with their neighbours. Whether the intrinsic control of the follicle involves the build-up and dispersal of inhibitors[33] or the release of wound hormones when the follicle is epilated,[34] or both, continues to be debated.

The intrinsic cycle is, in turn, influenced by systemic factors, so that, for example, follicles on homografts gradually come into phase with their hosts.[32] Several hormones have been shown to affect the moult cycles in animals. Thus, the passage of the moult in the female rat is accelerated by removal of the ovaries or the adrenals, or by administration of thyroid hormone and, conversely, is delayed by administration of oestrogens or adrenocortical steroids, or by inhibition of the thyroid.[35–37] In a number of mammals moulting is influenced by seasonal changes, in particular of the photoperiod.[38] It seems likely that these act through the hypothalamus, the anterior pituitary and the endocrine system.

Hormones also influence the rate of hair growth and the duration of anagen in the rat. Oestrogen decreases both; thyroxine increases growth but reduces the growing period.[29] This finding suggests that the two hormonal systems act at different points.

Such experimental studies on animals have only a limited relevance in relation to human hair growth, but there are several points of interest. First, it appears that post-partum alopecia (see below) is caused by a disturbance of the hair

follicle cycle brought about by circulating hormones, probably by the high level of oestrogens, in late pregnancy. Secondly, thyroid disturbances are frequently associated with diffuse alopecia. Thirdly, even the human scalp may not be free from environmental influences, for hair fall shows significant seasonal fluctuations.[11,39]

The growth of the sexual hair is brought about by androgens, that is, by male hormones. The first sexual hair to appear is that in the pubic region. In boys it reaches the classical 'female' pattern at an average age of 15·2 years,[40] in girls about $1\frac{1}{2}$ years earlier.[41] In about 80 per cent of men and 10 per cent of women the pubic hair spreads further over the abdomen in a sagittal, acuminate or disperse pattern; this growth may not be complete until the mid-twenties.[42] Axillary hair appears about two years after the start of pubic hair growth and continues to increase until the late twenties.[43] The rate of growth of the beard levels out after the age of 35, but the area continues to increase until the later decades of life.[43]

Castration virtually prevents the development of the beard if it is carried out before the age of 16 years.[43] Performed after the age of 21, it only reduces the extent, and the weight of hair growth per day.[43] There is little doubt that the rising levels of androgen at puberty account for the successive development of pubic and axillary hair in both sexes, and for the growth of the male beard. Equally, androgens are necessary for the development of female *hirsutism*, that is body and facial hair in part or whole of the male pattern. Either abnormally high levels of androgen or an increased response of the pilo-sebaceous apparatus, or both, may be involved. Anti-androgens, namely substances which block the attachment of male hormones to the receptors within the target cells, effectively reduce such hair growth.[44]

Paradoxically, androgens are also a prerequisite for the development of *male pattern alopecia* or *alopecia androgenetica* in subjects who are genetically disposed. Eunuchs retain their scalp hair, even when they have a family history of baldness, unless they are treated with testosterone.[45] However, castration of balding men, though it arrests the process, does not appear to restore luxurious hair growth to areas that are already bald.[46] The condition will be further considered below.

Nutritional Influences

The nutritional requirements of skin and the general consequences of dietary deficiency have been reviewed in Chapter 3. Attention was drawn to the necessity of certain vitamins, particularly some of the B complex, for normal hair growth and keratinization of the epidermis. On the other hand, evidence was presented that vitamin A inhibits the differentiation of the stratified squamous epithelium. Thus hyperkeratotic papular dermatitis is a symptom of vitamin A deficiency, and excess of the vitamin, for example when used in the treatment of psoriasis, appears to cause loss of hair.[47]

Protein deficiency is the cause of the condition *kwashiorkor* and has serious consequences for hair growth. The hair becomes sparse, thin and brittle and loses its pigment. The linear growth may be decreased by as much as one-half;

children with kwashiorkor produced only 59 μm^3 hair tissue per follicle per day compared to a normal figure of 514 μm^3, and the hair was weaker even when corrected for the difference in diameter.[48]

The changes in the hair reflect considerable alterations in the follicles themselves. Thus in a sample of Andean children with kwashiorkor the proportion of follicles in anagen was only 26±6 per cent compared with 66±6 per cent in healthy children of the same age, and even the anagen follicles were severely atrophied, with depletion of pigment and loss of internal and external root sheaths.[49] Even more severe changes were found in children suffering from marasmus; less than 1 per cent of the follicles were in anagen.[50] Marasmus appears to be a condition of chronic protein–calorie undernutrition in which the hair follicles have ceased activity in order to conserve nitrogen, whereas kwashiorkor is an acute condition following more or less normal growth.[50]

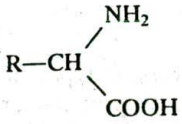
The hair bulb is rapidly affected by experimental protein malnutrition. In male volunteers, the mean root diameters became significantly reduced by the eleventh day of protein deprivation, pigmentation was visibly reduced by the fourteenth day, and there was progressive atrophy and loss of root sheaths.[51] The changes were reversible within days when protein was given. Thus while claims[52] that administration of amino acids will, in certain conditions, improve hair growth should be treated with great caution, the possibility should not be rejected out of hand.

Chemistry of Hair

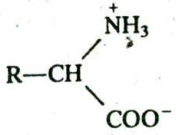
Keratin

The greater part of hair and wool is made up of an insoluble protein material called keratin, which is formed as the ultimate product of the keratinization process which takes place in the follicle. There are also present the vestigial cell membranes, nuclei, etc., but these form a very small fraction of the substance of hair.[53] Small quantities of water-soluble substances are also present, such as pentoses, phenols, uric acid, glycogen, glutamic acid, valine and leucine.[54]

Keratin, like other proteins, is composed of amino acids, substances of the general formula



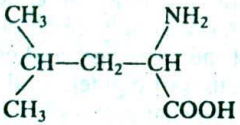
or in the zwitterionic form



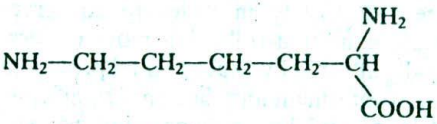
which give rise to the majority of the most characteristic properties of the proteins.

About 25 different amino acids are known to occur in proteins, and of these 18 are found in measurable amounts in keratin. They may be described and characterized by the side-chains R, which may be of three types:

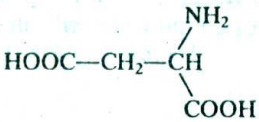
(a) Inert chain as in the amino acid leucine:



(b) Basic side-chain as in the amino acid lysine:

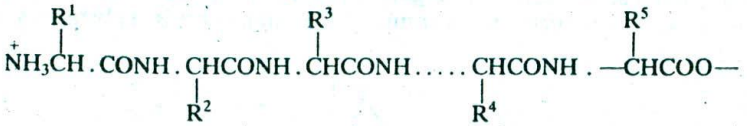


(c) Acid side-chain as in the amino acid aspartic acid:



The incidence of amino acids in hair and wool is given in Table 23.1; the figures for wool are those of Spector[55] and those for hair are by Bell and Whewell.[56]

These amino acids can form large large condensed polymeric structures by the formation of amide links between the acid group of one amino acid and the amino group of another. The type of structure thus formed is a polypeptide of the following type:



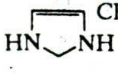
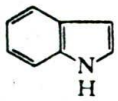
where R^1, R^2, etc., represent various types of side-chain.

Such a structure is common to all proteins, and in itself it is not sufficient to give the molecule the degree of stability and insolubility possessed by hair and wool.

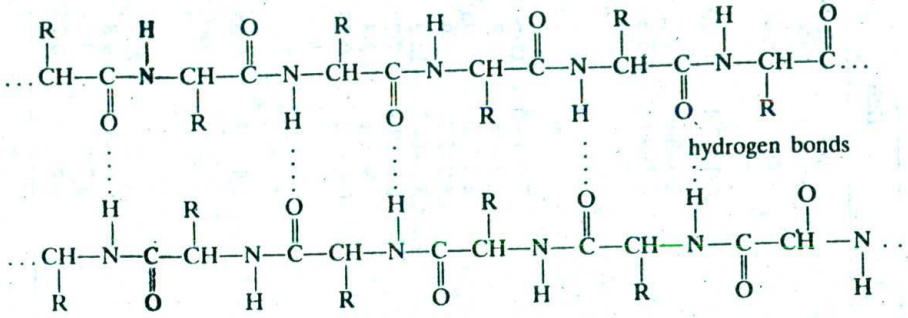
For a protein molecule to have some organized and 'shaped' structure, the polypeptide chains must be very long, and there must also be other bonds to keep the chains in fixed relative positions to one another. These additional bonds can be set up in three ways.

1. *Formation of Hydrogen Bonds between Parallel Polypeptide Chains.* The hydrogen bonds are formed by the interaction of the NH group with a suitably placed CO group.

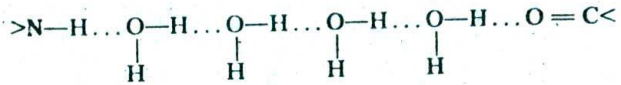
Table 23.1 Amino Acid Composition of Wool[55] and Hair[56]

Amino acid	Formula	Wool (%)	Wool (mole %)	Hair (%)	Hair (mole %)
Glycine	NH_2CH_2COOH	6·8	10·6	4·1–4·2	7·5
Alanine	$CH_3CH(NH_2)COOH$	4·0	5·3	2·8	4·25
Valine	$CH_3CH_2CH(NH_2)COOH$	5·4	5·4	—	—
Leucine	$(CH_3)_2CHCH_2CH(NH_2)COOH$	8·6	7·9	11·1–13·1	12·55
Isoleucine	$CH_3CH_2CH(CH_3)CH(NH_2)COOH$	4·3	3·8		
Phenylalanine	$C_6H_5CH_2CH(NH_2)COOH$	4·0	2·8	2·4–3·6	2·5
Proline		8·0	8·2	4·3–9·6	9·3
Serine	$HOCH_2CH(NH_2)COOH$	9·9	11·5	7·4–10·6	11·6
Threonine	$CH_3CH(OH)CH(NH_2)COOH$	6·5	6·4	7·0–8·5	8·8
Tyrosine	$p\text{-}HOC_6H_4CH_2CH(NH_2)COOH$	5·5	3·9	2·2–3·0	1·95
Aspartic acid	$HOOCCH_2CH(NH_2)COOH$	7·4	6·5	3·9–7·7	5·9
Glutamic acid	$HOOCCH_2CH_2CH(NH_2)COOH$	14·0	11·1	13·6–14·2	12·8
Arginine	$NH_2C(=NH)NH(CH_2)_3CH(NH_2)COOH$	10·6	7·0	8·9–10·8	7·7
Lysine	$NH_2(CH_2)_4CH(NH_2)COOH$	3·3	2·7	1·9–3·1	2·3
Histidine		1·1	0·8	0·6–1·2	0·85
Tryptophan		1·5	0·7	0·4–1·3	0·55
Cystine	$HOOCCH(NH_2)CH_2SSCH_2CH(NH_2)COOH$	13·6	6·6	16·6–18·0	9·8
Methionine	$CH_3SCH_2CH_2CH(NH_2)COOH$	0·7	0·5	0·7–1·0	0·75
Cysteine	$SHCH_2CH(NH_2)COOH$	—	—	0·5–0·8	0·75

When a range of values is quoted, the mole per cent value is calculated from the mean of the range.

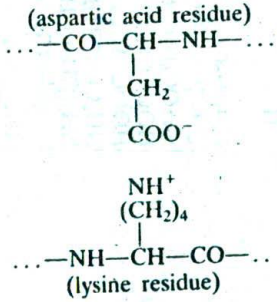


These bonds are very weak individually; but since they are extremely numerous they play a significant part in stabilizing the protein structure. However, the structural strength which they impart to a protein is limited by their property of lengthening to admit any other substance that can form hydrogen bonds, such as water, alcohols, phenols, amines, amides, etc. With water, for instance, the simple bond >N—H . . . O = C< becomes converted to the much more complex and weaker bond:



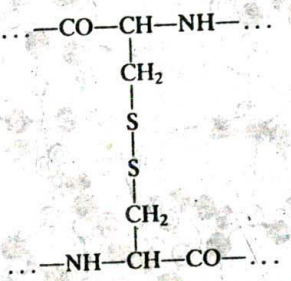
Such entry of water into the bonds is associated with solution of the globular proteins, and swelling characteristics of the more insoluble fibrous proteins.

2. *Formation of Salt Linkages between Acidic and Basic Side-chains.* As some of the side-chains of the polypeptide contain acidic groups and others contain basic groups, there is the possibility of salt formation between them if the groups are favourably placed; thus:



3. *Formation of Disulphide Linkages.* The extreme strength and insolubility of hair keratin is attributed to its large cystine content. This amino acid contains two amino and two carboxyl groups; it can thus enter into two polypeptide

chains which are then linked together by a disulphide bond:



A few disulphide bonds are also believed to be along the main chains.[57,58] Other linkages such as ether cross-links between serine, threonine and tyrosine have been suggested, but there is little evidence for such linkages and the known chemical behaviour of hair can be explained in terms of hydrogen bonds, salt linkages and disulphide bonds.

Hair is thus an intensely cross-linked structure and can be considered as a series of submicroscopic fibrils with both parallel and linked polypeptide chains; X-ray studies show that a considerable proportion of hair has a crystalline structure (effectively a regular structure, though not necessarily crystalline in the sense associated with inorganic materials) known as the α-keratin structure. This has been described in X-ray diffraction terms by MacArthur[59] and Giroud and Leblond.[60]

Of the many structures proposed for α-keratin, the most widely accepted is that due to Pauling and his co-workers.[61–66] These authors propose a structure in which the polypeptide chains have assumed a helical form with 3·7 amino acids per turn of the helix. Each turn of the helix is located relative to the next by hydrogen bond formation between the carbonyl and imine groups of amino acids separated by two other residues (Figure 23.4). The diameter of the helix is roughly 10 Å (1 nm) and the translation per complete turn is 5·44 Å (0·544 nm). The side-chains of the amino acids all project outwards from the helical structure. A similar structure has been proposed for synthetic polypeptides such as poly-γ-methyl-L-glutamate.[67] The theoretical Fourier transform for such a helical structure has been calculated by Cochran and Crick[68] and found to agree closely with the observed patterns. Similar studies have been made by Yakel, Pauling, and Corey[69] and by Fraser *et al.*[70,71] However, Fraser notes from his work on porcupine quill tip that precise comparison is handicapped by interference effects due to the macromolecular organization of the keratin.

To explain some anomalous X-ray results, especially a calculated repeating unit at 5·2 Å (0·52 nm) spacing, Pauling and Corey suggested that the helical structure itself might have a slightly helical axis, and that under these conditions the more closely packed regions of fibres contain structures in which six of these screw-shaped helices have twisted about another, so as to form a compound helix rather like a seven-strand cable (Figure 23.5). The degree of twist in this way depends on the distribution of the side-chains, and the packing of these into the interstices of the 'cable'.

Electron microscopy has been used to study the structure of keratin,[72–75] and Orfanos and Mahrle[76] have used both the transmission and stereoscanning

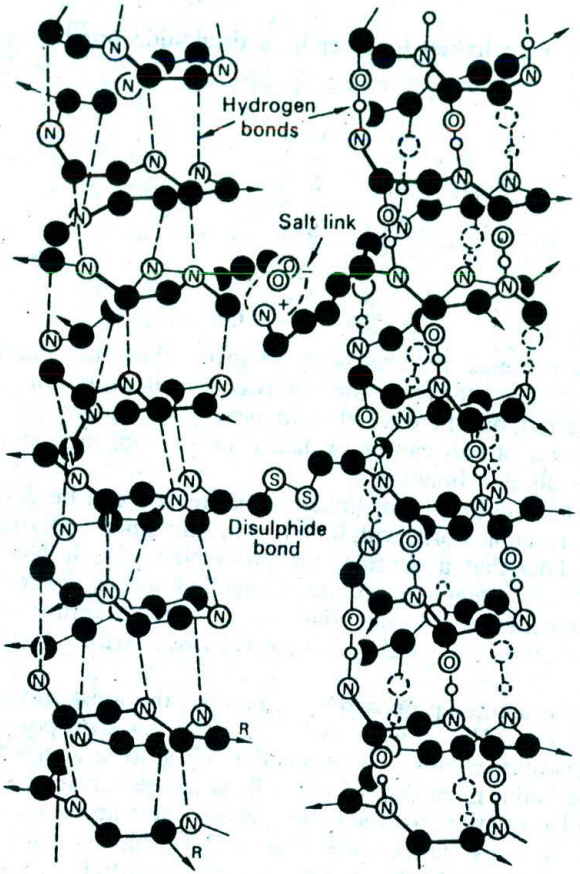


Figure 23.4 Pauling-Corey structure for α-keratin

modes to characterize the surface and structure of human hair following exposure to various hair products. Randebrock[77] has summarized the main morphological features observable in hair as:

	Diameter	
	(Å)	(nm)
Spindle cells	10 000–60 000	1000–6000
Macrofibrils	2000–9000	200–900
Microfibrils	60	6
Protofibrils	20	2
Peptide spirals	7	0·7

Not all the keratin structure is so well organized as the α-keratin structure, owing to irregularities in the material from which the keratin is formed. In

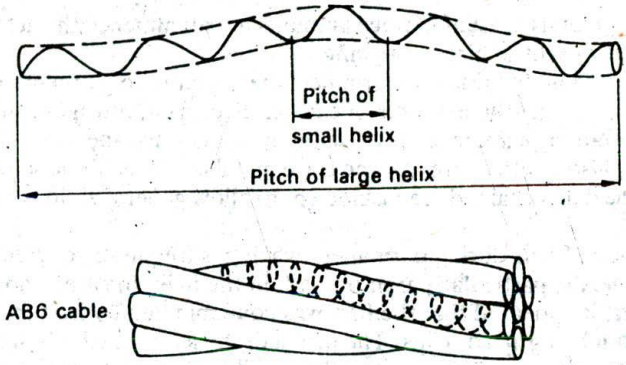


Figure 23.5 Structure of 'crystalline regions' of keratin

addition, the difficulty of packing the side-chains of 18 widely differing amino acids into any sort of regular structure over long sections of the polypeptide chain results in the existence of areas which lack any closely packed 'crystalline' character and which are referred to as the amorphous regions. These are very important in the chemistry of hair, as the amino acids in such regions are not protected from attack by the complexities of the compound helix. Some attempts have been made to estimate the relative amounts of 'crystalline' and 'amorphous' material in hair, but such measurements are difficult to interpret since there is no clearcut distinction between a slightly imperfect 'crystalline' region and a well organized 'amorphous' region. One can only assume that the helical polypeptide chains pack together where they meet in such a configuration as circumstances will permit, and one chain may pass through many crystalline and amorphous regions. The existence of several closely related keratins corresponding to various histological structural features of hair fibres has been postulated by Kuczera.[78]

A concise but detailed review of the amino acid composition, morphology and keratin-fibre histology of human hair and wool has been given by Leon.[79]

The cuticular surface of human hair has received scant attention in the literature, despite its obvious importance to those concerned with the formulation and performance of hair preparations. Keratin organization within the cortex contrasts with the non-helical cross-linked protein structure found in the surface cell layers. The results of amino acid analyses reported by Wolfram and Lindemann[80] show a high sulphur content in comparison with the cortex, accounting for the function of the cuticle as a chemical barrier and perhaps signifying a structural role in physical terms. The progressive loss of cuticle from root to tip has been described by Bottoms *et al.*[81]

Mineral Constituents of Hair

The mineral content of hair, in particular the trace metal content, has been a subject of interest for many years, especially since analytical techniques have been developed that permit the analysis to be carried out on the small samples of hair generally available. Apart from scientific curiosity there is always the

possibility that metals present in trace amounts might influence the action of hair treatments such as bleaching or dyeing.

Bagchi and Ganguly[82] have determined the mineral constituents of human hair and point out that the amounts of carbon, hydrogen, nitrogen, sulphur and phosphorus are approximately of the same magnitude irrespective of age, race and sex. They also quote figures for the trace metal contents of the same samples of hair, but the data obtained are insufficient to allow generalizations to be made (Table 23.2).

Discoloration of hair during permanent waving is frequently attributed to the presence of metals, particularly iron or lead, in the hair. In cases known to one of the authors, it appeared that the hair was contaminated by iron from the use of old and worn hair grips or clips. The origin of the lead, which often amounted to 1000 ppm or more, was less easy to explain. The complaints, which concerned a slightly pinkish brown colour, generally came from subjects with perfectly white or naturally blonde hair, and it was not reasonable to suppose that they had used lead-containing hair colorants.

Tompsett[83] has shown that when the calcium metabolism of the body is disturbed, lead which is normally accumulated in the bones becomes mobile and

Table 23.2 Mineral Constituents and Trace Metal Contents of Various Samples of Hair[82]

	European girl (brown hair) (%)	Hindu woman (black hair) (%)	Mixed hair of thirty male adults—from a hair cutting saloon (%)
Carbon	44·03	44·20	44·60
Nitrogen	13·70	13·68	14·60
Hydrogen	5·58	5·60	5·40
Sulphur	3·80	1·50	3·80
Phosphorus	0·065	0·096	0·08
Chlorine	1·98	2·00	2·00
Water	3·96	4·20	4·10
	(mg/kg)	(mg/kg)	(mg/kg)
Lead	21·0	284·0	47·7
Copper	64·0	62·8	108·0
Arsenic	2·4	2·2	2·2
Zinc	116·0	182·0	212·0
Iron	133·0	126·0	141·0
Manganese	28·4	25·0	38·0
Cobalt	14·2	16·0	18·1
Nickel	5·4	5·5	8·2
Calcium	212·0	188·0	208·4
Aluminium	26·0	26·0	32·0
Silicon	188·0	178·6	150·4
Bismuth	nil	nil	nil
Silver	nil	nil	nil
Antimony	nil	nil	nil
Mercury	nil	nil	nil

can disperse into the blood stream, and hence into all the soft tissues and organs of the body. Unfortunately hair was not included in this investigation, but by analogy with arsenic, which has long been known to deposit in hair and nails, it seems highly probable that this could be the origin of lead in the hair. Further evidence for this theory comes from the work of Strain *et al.*[84] who showed that the zinc content of hair reflected the zinc content of body tissues. Similar results have been found with other metals and there seems little doubt that metals in the blood stream find their way into the hair.

The latest technique to be applied to the determination of the trace element content of hair is that of radioactivation analysis,[85,86] which enables a comprehensive analysis to be made even on a single hair. However, the technique has not, unfortunately, provided a definitive forensic technique for matching hairs.

Bate and various co-workers at Oak Ridge National Laboratory (USA) published a number of papers[87,88] on the subject and concluded that the method has serious handicaps owing to the ease with which hair adsorbs and desorbs traces of metals from externally applied solutions. Coleman *et al.*[89] at the Aldermaston Atomic Research Centre (UK) were also active in this field. They developed a standardized test procedure and a statistical method of evaluating the results. They claimed that by using a profile of 12 elements they could delineate the number of people in the population from whom a hair might have come; alternatively, they could associate the hair with one of a number of suspects whose hair could be sampled and compared. Coleman *et al.* determined the trace element content of human hair based on a random sample of some 800 subjects from England and Wales. They claimed that the difference between male and female hairs was significant and would enable unknown hairs to be 'sexed' with an accuracy of about 90 per cent.

Chemical Properties of Hair

While there is no space here to classify exhaustively all the chemical properties of hair, certain reactions are reviewed which have a direct bearing on the structural details already dealt with.

At the outset, it must be realized that about 50 per cent of the weight of hair keratin is made up of the side-chains of the amino acids, so these have a correspondingly great effect on the properties of the whole material. Because of the variety of these side-chains, the reactions are not clearcut, but the influence of certain groups may be detected in their contribution to the total chemical reactivity. For instance, if the disulphide bonds are broken the hair is weakened, but not destroyed as long as the salt links are intact. Similarly, the action of strong acids in breaking the salt links (by suppressing the ionization of the carboxylic acid groups) will not disrupt the hair unless the disulphide bonds are simultaneously broken. If the hydrogen bonds remain intact it is very difficult to carry out any other reactions with the hair, because it does not swell to admit any other reagents; it is certainly difficult to cause hair to react in non-polar solvents. Alexander[57] suggests, in fact, that most of the mechanical strength of dry hair resides in the hydrogen bonds.

Under normal conditions, however, the hydrogen bonds always contain some water adsorbed from the air, usually around 9 per cent—more or less, according

to the humidity of the atmosphere, etc. In liquid water, hair can take up bound water to about 30 per cent of its own weight.[90]

Hair keratin is insoluble in aqueous salt solutions (except lithium bromide at concentrations over 50 per cent), in weak acids, weak alkalis and saturated neutral urea solution. In acid solutions between pH 1 and 2 moderate lateral swelling occurs because both hydrogen bonds and salt links are broken. The structure remains sound, however, because of the disulphide bonds. In alkaline solutions at pH 10 lateral swelling is intense for the same reasons, and at pH 12 the disulphide bonds begin to break down, lateral swelling becomes limitless and the hair passes into solution. (More details of the effects of alkali on the disulphide bonds will be found in Chapter 28 on permanent waving.)

All three types of bond can be affected by certain other materials such as sodium sulphide,[91,92] sodium thioglycollate,[93] mercaptoethanol,[94] urea-bisulphite,[95,96,97] potassium cyanide,[98] chlorine dioxide[99] and peracetic acid.[100] A mixture of phenol and thioglycollic acid will also dissolve hair keratin[101] as will formamide and urea at high temperatures (140°–160°C). Whewell[102] has reviewed the properties of keratin as a chemical and reports a comprehensive range of reagents that have been used for the modification of wool. Menkart[103] has compared the chemical properties of wool and human hair and has shown that wool is more reactive owing to its lower degree of cross-linking. This work enables the data given by Whewell to be placed in their proper perspective.

The table of amino acid analyses of hair and wool keratin shows that the total number of acid side-chains (from glutamic acid and aspartic acid) is approximately double the number of basic side-chains (from arginine, histidine, and lysine). This means that even if the positions of the amino acids in the keratin structure are favourable to salt linkage, there will still be a large excess of acidic side-chains. Normally these will be neutralized by ions such as ammonium, sodium, etc., and by the traces of other metals in the hair when these exist as cations, but these cations can be replaced by others, just as in an ion exchanger, if the circumstances are favourable. For instance, a high concentration of sodium ions (as in some shampoos) will tend to convert all the surplus acid side-chains into sodium salts; polyvalent ions will tend to replace monovalent ions (Ca^{2+} will replace Na^{+}; Al^{3+} will replace Ca^{2+}), and cations with some surface activity will replace the simpler inorganic ones. This last effect accounts for the readiness with which cationic detergents are adsorbed by the hair, and for the rapid adsorption of cationic dyestuffs such as methylene blue. An interesting example of the base-exchange characteristics of hair can be demonstrated with methylene blue. If hair is carefully washed with dilute sodium chloride solution for about 60 minutes, most of the acidic side-chains will become sodium salts. If such hair is dyed with methylene blue it will rapidly become a deep blue. If, however, the hair is soaked in aluminium sulphate solution, or preferably a more neutral aluminium salt, such as the chlorhydrate, before dyeing with methylene blue, it will only take on a pale blue tint, showing that many of the base-exchange sites are blocked by a fairly stable aluminium complex.

If hair is dispersed by sodium sulphide or 0·5 M sodium cyanide in 0·1 M sodium hydroxide, the solubilized material has a composition similar in amino acid content to the original hair. The isoelectric region of such a solubilized material is at pH 4·1–4·7, showing again the excess of acidic side chains.

Physical methods of evaluating hair damage such as extensometer tests and stress relaxation measurements[104] are well known. Later work has been aimed at obtaining suitable chemical methods for estimating hair damage and a number of different principles, including the swelling effect of lithium bromide, the effect of enzymes and the copper uptake of hair, have been evolved.[105–109]

Hair Colour

Melanin and Melanocytes

Hair colour is caused by pigment granules in the cells of the hair shaft. The effect is produced by the large amount of pigment in the cortex, but granules also occur in the medulla. The pigment is manufactured within melanocytes situated around the apex of the dermal papilla and transferred to the newly formed hair cells from the tips of their finger-like dendrites.[110–112]

The granules themselves are the end product of *melanosomes*. These originate as colourless *pre-melanosomes* in the region of the Golgi and become progressively darker as pigment is synthesized on them and they move peripherally. The granules themselves are ovoid or rod-shaped and vary in length from 0·4 μm to 1·0 μm and in breadth from 0·1 μm to 0·5 μm.[113,114] The darker the hair, the larger the average size of the granules,[115–117] and Negroids generally have larger and fewer granules than Caucasoids. Melanogenesis has been reviewed by Collins[118] and by Fitzpatrick.[119]

The shades of human hair result mainly from two kinds of pigment, *eumelanin*, which is brown or black, and *phaeomelanin*, which is yellow or reddish. Eumelanin is formed from the amino acid tyrosine by oxidation with the enzyme *tyrosinase*. Tyrosine is also the precursor of phaeomelanin, but it seems that the presence of an *o*-aminophenol derived from tryptophane is also necessary.[111,120,121]

Other pigments, which appear to be iron complexes, have been extracted from human red hair,[122–124] red rabbits and red mongrel dogs,[125,126] and given the name of *trichosiderins*. At least three distinct compounds have been isolated.[127] The importance of these pigments is questionable: Boldt[128] has shown that their colour is not due to the iron content, since it has been possible to isolate iron-free alcohols, named pyrrotrichols, which have the same colours as the iron complexes. Moreover, the red colour of human hair is not substantially altered by extraction of the trichosiderins. Thus, although it is admitted that red hair does contain greater amounts of iron than any other shade, its colour is now believed to be due to phaeomelanin.

Biochemistry of Melanogenesis

The first stage in the formation of either eumelanin or phaeomelanin is the oxidation of tyrosine to 3,4-dihydroxyphenylalanine (dopa) by the enzyme tyrosinase.[129–133] The second stage, also catalysed by tyrosinase,[134,135] is the dehydrogenation of dopa to form dopa quinone (Figure 23.6).[136]

Eumelanins involve the formation of indole-5,6-quinone. It now seems likely that eumelanin is not, as once believed, a simple polymer of indole-5,6-quinone units linked through a single bond, but a poikilopolymer of several types of monomer joined by multiple types of bonds, with the incorporation of an

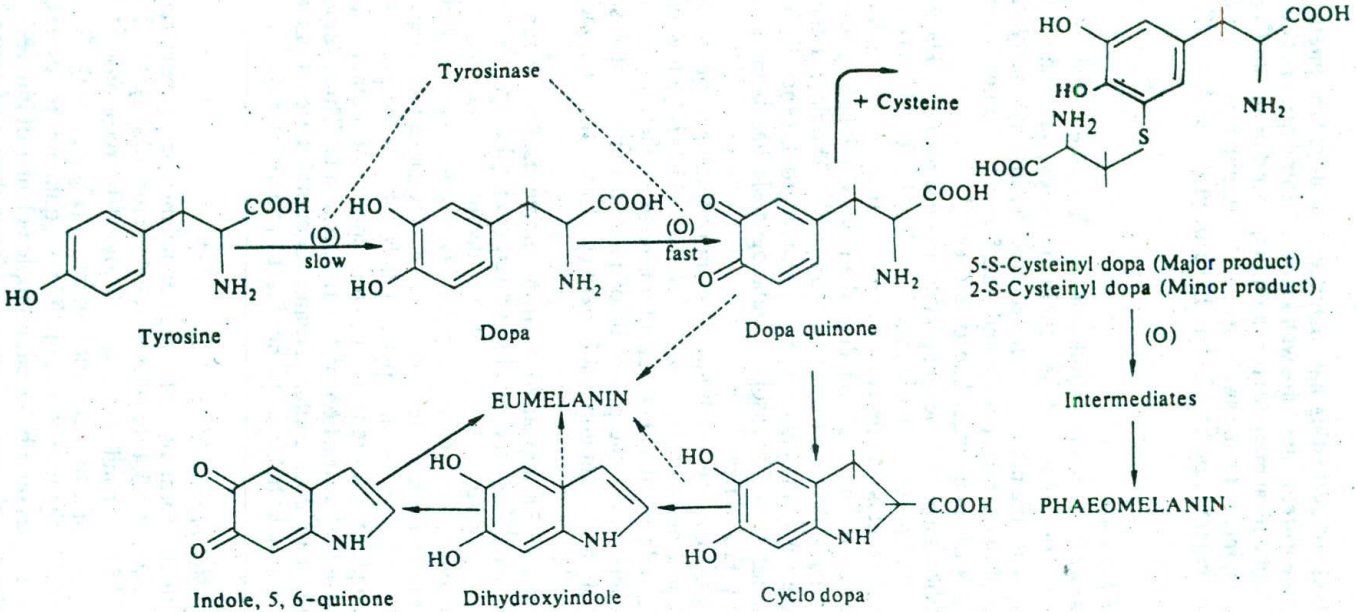


Figure 23.6 Simplified scheme for the formation of eumelanin and phaeomelanin (from Rook *et al.*,[136] courtesy Blackwell Scientific Publications)

assortment of oxidized intermediates. According to Dalgliesh[137] there are four sites at which the molecules could join together. The eumelanin becomes linked to protein.

Phaeomelanins are formed from dopa quinone by a different pathway. The dopa quinone reacts with cysteine to form 5-S- and 2-S-cysteinyldopa,[138] and further oxidation, which is probably non-enzymatic, produces intermediates which form the phaeomelanin polymers.

Tyrosinase contains trace amounts of copper, which can exist in either a cuprous or a cupric state. Tyrosinase activity is also shown by similar complexes containing other polyvalent ions such as cobalt, nickel and vanadium,[139] but their efficiency is lower than that of copper. The activiation of tyrosinase requires trace amounts of dopa to be present,[140] and this can be produced from dopaquinone by ascorbic acid.

A large number of materials can inhibit tyrosinase activity, and therefore pigmentation. Such materials include competitors for tyrosine (3-fluorotyrosine, N-acetyltyrosine, N-formyltyrosine, phenylalanine, 3-aminotyrosine), agents with a complexing activity with the copper prosthetic group of the enzyme (phenylthiourea, diethyldithiocarbamate, BAL, cysteine, glutathione, hydrogen sulphide, cyanides, etc.), compounds which alter the redox potential of the system (hydroquinone, indophenol, etc.), substances which combine with one or other of the intermediates in the melanin synthesis (aniline, *p*-aminobenzoic acid, *p*-phenylenediamine, etc.) and one or two materials (ethers of hydroquinone, pentachloronaphthalenes) where the mode of action is unknown. Useful reviews of such inhibitors are given by Lorincz[141] and Fitzpatrick.[111]

For obvious reasons, few of these materials have been tested *in vivo*. However, α-naphthylthiourea and phenylurea cause greying of hair in rats as long as they remain in the diet, and thiouracil has suppressed pigmentation in man.

Greying of Hair

Greying of hair involves a loss of pigment from the hair shafts and a progressive loss of tyrosinase activity from the hair bulbs. It must be considered as a normal part of aging; in Caucasoids white hairs first appear at the temples at the average age of 34, and by age 50 half the population has at least 50 per cent grey hairs.

Rapid greying of hair (as judged by its overall appearance) after severe emotional stresses has often been recorded, though the belief that the hair of Marie Antoinette and Sir Thomas More turned white overnight may stretch credulity. It is not conceivable that pigment could be destroyed in hair which has already grown. However, there are two possible explanations. One is that 'telogen effluvium' (see below, Hair Disorders) causes sudden shedding of dark hairs from a mixed population, leaving a predominance of white or grey hairs *in situ*; the other is that a traumatic event precipitates loss of hairs by an episode of 'alopecia areata'—the first hairs to regrow are invariably white. However, such a process would take weeks or months rather than hours. Green and Patterson[142] recorded such a case of an engine driver who fell from a stationary engine. His hair came out on the day of the accident, at first in a round patch, which was diagnosed as alopecia. Eventually it spread, until after four months he was completely bald. Two months later a few white downy hairs appeared.

Greying of hair can be experimentally produced in animals by copper or by pantothenic acid deficiency; greying due to copper can be reversed by pantothenic acid.[143] Though it has been claimed that huge doses of *p*-aminobenzoic acid will occasionally restore pigment to grey hair in man[144] there is no known medical treatment by which greying can be consistently reversed. Hair follicles can, however, sometimes produce pigmented or grey hair intermittently; one such condition is a rare anomaly known as *ringed hair* or *pili annulati*.

Hair Disorders

Introduction

Only a brief summary of the major conditions which affect the hair shaft and the hair follicle will be given here. For more comprehensive accounts see works by Orfanos[145] and Ebling and Rook.[136]

The cosmetician may need to be able to recognize several abnormalities of the hair shaft of genetic origin, each of which may be associated with sparse, brittle and often short hair. From these disorders must be differentiated various types of hair loss in which the shafts remain structurally normal.

Hair loss may be either rapid or gradual. Sudden shedding of hair is often, though not invariably, transient, whereas gradual loss, observed only by its long-term effect, is usually hopelessly chronic.

Rapid loss can be further subdivided into two types, according to whether the fallen hair is a club, or a growing hair shed from an active follicle.

Loss of club hairs is known as *telogen effluvium* and seems to have several possible causes. One, namely childbirth, is well established and the ensuing condition is known as *postpartum alopecia*. Loss of growing hairs is known as *anagen effluvium*. It occurs after cytotoxic drugs, and it seems likely that the shedding of hairs in patchy baldness, or *alopecia areata*, is a similar process.

Slowly developing hair loss, causing baldness in a symmetrical pattern, is well known in males, where it is named *male-pattern alopecia* or *alopecia androgenetica*. Diffuse alopecias have been attributed to several causes. It seems likely that much, probably most, diffuse alopecia in women is an inherited androgen-potentiated condition which is the female equivalent of male-pattern baldness.

Defects of the Hair Shaft

Monilethrix: a condition in which the hair shaft is beaded with elliptical nodes about 0·7–1·00 mm apart alternating with constricted internodes which lack any medulla. The hair is brittle and breaks off a centimetre or two above emergence.

Pili torti. The hair shaft is twisted on its axis at intervals, and usually breaks off short.

Trichorrhexis nodosa: a response to physical or chemical injury in which an apparently normal hair becomes swollen and split to form a node at which the hair subsequently fractures. In *trichorrhexis invaginata* the fractured hair telescopes to give a bamboo-like appearance.

Telogen Effluvium
Excessive shedding of normal club hairs after febrile illness (*post-febrile alopecia*) is well authenticated,[10] and other causes, for example antithyroid drugs, anticoagulants and psychogenic stress have been suggested. Kligman[10] has recounted the case of a prisoner who suffered a daily shed of 600–1500 hairs over a period of three months after conviction for murder, but subsequently recovered after a pardon had been granted.

Postpartum Alopecia
The shedding of hair within two or three months of parturition appears to be a telogen effluvium similar to post-febrile alopecia. The cause seems to be a prolongation of anagen by the hormonal conditions of late pregnancy. Lynfield[146] first described, and others have confirmed, that prior to childbirth as many as 95 per cent of the scalp follicles may be in anagen, but that the proportion falls to less than 70 per cent within 2–4 months after parturition, suggesting that the follicles have been precipitated into catagen.

Anagen Effluvium
In contrast to telogen effluvium, loss of anagen hairs is a rapid event. Cytotoxic drugs such as cyclophosphamide, adriamycin and vincristine can produce it in a few days.

Alopecia Areata
Alopecia areata, or patchy baldness, is usually easy to recognize. The lesions are sited asymmetrically, and each starts at a focal point and spreads outwards. The process may take two or more weeks or may, to quote Behrman,[147] be 'so rapid that a completely denuded plaque may appear overnight with the lost hairs found in a heap on the pillow in the morning'.

The margins of the lesions are characterized by the occurrence of short protruding club hairs with a frayed point, often named 'exclamation marks'. As the lesions progress, many follicles in a state of arrested anagen can be found. By plucking hairs successively from a series of concentric rings around the focus of the lesions, it has been shown that an area from which only club hairs can be removed develops at the centre and moves centripetally.[148]

The simplest hypothesis to explain these observations is that initially hairs are shed from all active follicles, leaving only the clubs unaffected. The shearing of hair from follicles moving into catagen produces the protruding stumps of the exclamation marks. However, it is quite possible that follicles are also precipitated into catagen. It should be added that the process does not always produce patchy lesions, but may sometimes occur diffusely, so-called 'diffuse alopecia areata'.

The cause of alopecia areata is a subject of debate. It seems likely that there are several types, probably four, of the disease, differing from each other in the age of onset, clinical features and prognosis.[149] Authors are divided about the role of heredity, some favouring a family history in 10–20 per cent of cases,[150] others finding it in none.[151] Some believe psychological factors are important,[152] others that they play no role.[153] It seems, however, difficult to deny that the condition is in some instances precipitated by mental shock.[154,155]

Various treatments such as ultraviolet light or miscellaneous irritants have been used for *alopecia areata*, but there is no objective evidence that they are of any value. One half of all patients recover within a year of the initial attack, though the incidence of relapse is high.[156] Corticosteroids, given systemically, have been shown to induce regrowth in many cases, though the growth is not always maintained after discontinuation of the treatment. More justifiable is the use of intralesional injections.[157]

Male-pattern Alopecia

No particular expertise is needed to recognize pattern alopecia[158] in the male, for the recession of the hair line, loss of hair from the crown, and the bald pate are only too familiar.[159] In the affected areas the hairs become steadily shorter and finer and, ultimately, cosmetically useless. About a third of the follicles may disappear. A reduction in the length of the growing period is reflected in the increased ratio of telogen to anagen in samples of plucked hair.

Pattern alopecia is inherited, apparently as an autosomal dominant trait, but it is only manifested in the presence of male hormone. Eunuchs retain their scalp hair, even when they have a family history of baldness, unless they are treated with testosterone.[45] Though a correlation with hairiness of the chest has been suggested,[158] baldness does not seem to be associated with other indices of masculinity, such as sebum secretion, muscle size and body hair in general.[160] While the finding that bald scalp has a greater capacity than non-bald scalp to convert testosterone to 5α-dihydrotestosterone *in vitro*[161] suggests that the key to understanding baldness lies in the field of steroid metabolism, no plausible hypothesis of how androgens promote baldness of the scalp but hair growth on the body has yet been proposed.

Diffuse Alopecia

Loss of hair is by no means uncommon in women. Occasionally such loss involves obvious recession of the hair line as in males, but usually it is diffuse.

A number of causes have been proposed. It has long been recognized that thin hair may be associated with hypothyroidism (myxoedema) as well as with hyperthyroidism.

There is some evidence pointing to other factors, such as, for example, iron deficiency[162] and ingestion of amphetamines for weight reduction.[163] However, in many cases (over half of the total in one series studied[163]) no possible cause could be found. It seems likely that these were androgenetic alopecias which had become manifested even within the normal range of female androgen levels.

Hirsutism

Hirsutism may be defined as growth in the female of coarse terminal hair in part or whole of the adult male sexual pattern. At one end of the scale the condition may be obviously associated with other signs of virilism, excessive androgen production and an endocrine pathology. But most cases show no signs of masculinization except hirsutism, and have only slightly or moderately raised androgen levels; some lie well within the range for normal, non-hirsute subjects. The condition appears to result either from abnormal levels of free androgens or from an abnormal response of the hair follicle, or both. Anti-androgens, such as

the steroid cyproterone acetate given orally, have proved effective in management of the condition.[44]

Dandruff

Definition and Etiology

Dandruff is a condition of the scalp characterized by the massive desquamation of small flakes of stratum corneum. It has already been mentioned as a scaling disorder in Chapter 1, where its occurrence and debatable etiology were briefly reviewed.

Discussion about the cause of dandruff revolves around the relative roles of physiological, traumatic and infective factors. Many authors have attempted to correlate dandruff with body disorders or environmental factors. Thus Lubowe[164] has discussed the possible roles of hormones, metabolic faults, diet and nervous tension, as well as inflammatory reactions to topical medicaments and cosmetics. Sefton[165] noted that prisoners of war in Japanese camps in Singapore in 1942–45 had little dandruff and attributed this to shortage of fats in the diet, and it has been claimed that vitamin therapy is effective for some types of dandruff.[166]

The yeast-like organisms, *Pityrosporum ovale* and *Pityrosporum orbiculare* are common members of the scalp flora. *Pityrosporum* can be easily detected with stains such as methylene blue and Nile blue. It does not appear to exist in nature away from human beings and has proved difficult to culture, though this problem has been solved.[167,168] Its ultrastructure has been described by Swift.[169]

Pityrosporum ovale was first described in 1874 by Malassez who believed it to be the sole cause of dandruff.[170] This opinion was later supported by Reddish.[171] The role of *Pityrosporum* in dandruff has been much debated. What is the evidence? Koch laid down the original postulates for proving an organism is the specific cause of a disease as follows:

(i) the organism must be present in every case of the disease;
(ii) it should be collected and cultivated in pure culture;
(iii) inoculation from such culture must reproduce the disease in susceptible animals;
(iv) the organism must be re-obtained from such animals and again grown in pure culture.

There is little doubt that *Pityrosporum* is generally present in cases of dandruff; so are many other micro-organisms, including a number of bacteria and moulds.[172–174] The first postulate might thus appear to be satisfied, were it not for the fact that *Pityrosporum* is also present on scalps which do not have dandruff. The question therefore arises whether there is any relationship between dandruff and the level of infection. Some authors have failed to find any such correlation,[175] others have produced evidence that *Pityrosporum* is, in fact, more abundant in affected than in non-affected persons.[172,176]

The question of whether inoculation of cultured *Pityrosporum ovale* could produce dandruff was investigated by Moore and his associates.[177] Their results are quoted in Table 23.3. The evidence is not overwhelming, but it supports the view that *Pityrosporum* is a causative agent.

Table 23.3 Results of Experimental Inoculation with Pityrosporum ovale to produce Dandruff

Type of innoculation	Reaction			Total
	Positive	Doubtful	Negative	
Intradermal injection of whole cells in saline	22 (79%)	0	6 (21%)	28
Excoriations rubbed with whole culture	19 (40%)	8 (16%)	21 (44%)	48
Excoriations rubbed with whole culture + lipid mixture	12 (48%)	5 (20%)	8 (32%)	25
Exposure of intact skin to culture	9 (50%)	2 (11%)	7 (39%)	18
Application of culture to scalp	6 (100%)	0	0	6

Some further support comes from studies on the effect of antimicrobial preparations. When an aqueous solution of neomycin and nystatin was massaged into the scalp, both the scurf and the microbial flora were reduced.[178] Moreover, it appeared that a reduction in the yeast flora was more effective in controlling dandruff than a reduction in the number of bacteria.[179]

The circumstantial and experimental evidence thus implicates *Pityrosporum* as an agent in dandruff, but does not establish beyond doubt that it is the only cause. Indeed it may well be that the term 'dandruff' covers more than one condition and that dry dandruff needs to be differentiated from greasy dandruff. A further complication is the distinction between dandruff and seborrheic dermatitis. Spoor[180] believed that it was unrealistic to try to separate the conditions, whereas Kligman and his co-workers[181] strongly reject the view that they are in any way related.

Dandruff Therapy

The wide range of treatments that have been used for dandruff reflects the debate about its nature and etiology.

Inasmuch as dry dandruff might be related to external provoking agents such as unsuitable shampoos, alcoholic lotions or waving lotions used too close to the scalp, these should clearly be avoided.

Greasy dandruff has been assaulted by an armoury of materials. Before reviewing them, the difficulties of making an objective assessment of their efficacy should be mentioned. Properly controlled tests are essential, since regular washing, massage and anointment of the scalp will often alleviate dandruff, whatever the materials used. Alexander[182] examined the effects of three treatments:

1. Shampoo base
2. Shampoo base plus tar

3. Shampoo base plus tar plus the sodium salt of the sulphosuccinate of an undecylene alkanolamide

She found that washing with any of the shampoos reduced dandruff for a few days, the tar product reduced dandruff for a longer time than the base alone, while the product containing the additive was even better.

Procedures for clinical evaluation of antidandruff shampoos have been discussed by Van Abbé and Dean[183] and by Kligman and co-workers.[181]

Idson[175] and Lubowe[164] have reviewed the materials used in commercial preparations. Among the reported active ingredients in some forty-seven products were hexachlorophene, tar, salicylic acid, sulphur, resorcinol and cationic compounds.[164]

Germicidal treatments have included resorcinol, thymol and other phenols. Cationic germicides were introduced by Hodges[184] and Neville-Smith[185,186] in the form of therapy with 5 per cent Cetavlon solution, and a later account is given by Speirs and Brotherwood.[187] Sodium sulphacetamide has been used by Duemling[188] and Whelan[189] for the treatment of pityriasis circinata. Trichloromethylmercapto derivatives have been used by Ball[190] in the form of Vancide 89 (trichloromethyl-mercapto-4-cyclohexene-2,2-dicarboximide), again for the treatment of pityriasis circinata, and such materials have been used commercially in treatments for dandruff. Gross and Wright[191] used a 2·5 per cent suspension of tellurium dioxide, which they claimed was safe and effective in the control of pityriasis.

Elemental sulphur is one of the oldest treatments. The most effective form is colloidal sulphur, or milk of sulphur, which contains large amounts of polythionic acids, and these have been combined with cationic materials. Lubowe[192] reports success with 'Sarthionate' (*bis*-lauryltrimethyl ammonium polythionate). Cadmium sulphide suspensions have been used by Kirby.[193]

Selenium disulphide proved to be a very effective compound. Slinger and Hubbard[194] published tables showing complete control of seborrhoeic conditions in 73·3 per cent of severe cases, 84·6 per cent of moderate cases and 95·4 per cent of mild cases, and similarly good results were reported by Slepyan.[195] Further reports are given by Bereston,[196] Matson[197] and Caspers.[198] Brotherton has discussed the effect of selenium compounds on the sulphur metabolism of *P. ovale*,[168] suggesting one possible mode of action on the organism. However, Plewig and Kligman[199] have produced substantial evidence that the compound lowers the corneocyte count and postulated that it controls dandruff by its cytostatic capabilities.

One major difficulty with selenium compounds is that although they are effective they are not cosmetically attractive. Thus products containing selenium oxide or sulphide are invariably dark brown in colour and are not pleasant to use. In addition care must be taken to exclude contact with the eyes. Products containing selenium are considered more to be ethical products for use in severe cases of dandruff, rather than general toiletries, and should be used mainly under advice.

More recently, zinc pyridinethiol-N-oxide (zinc pyrithione, zinc omadine) has been introduced as a safe agent for incorporation into shampoos.[200] Kligman and his associates[181] compared shampoos containing 2 per cent zinc pyrithione

or 2·5 per cent selenium sulphide with a detergent base. Both compounds significantly reduced the corneocyte count, as well as effecting clinical improvement of the dandruff, whereas the bland shampoos had little effect. The zinc pyrithione appeared, however, to act more slowly than the selenium sulphide.

An antidandruff effect slightly superior to that of zinc pyrithione has been claimed for a shampoo containing 1-hydroxy-4-methyl-6-(2,4,4-trimethylpentyl)-2-(1H)-pyridone monoethanolamine salt (Octopirox).[201]

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Chapter Twenty-four

Shampoos

Introduction

Nowadays shampoos constitute one of the main products for personal care used by all strata of the population (age, sex, . . .). In 1977 shampoos represented 43 per cent of the total US haircare market.[1]

Defined in earlier editions of this book as 'suitable detergents for the washing of hair, packaged in a form convenient for use', they have since undergone drastic changes in design and technology in order to respond to multiple requirements, from the most sophisticated to the simplest and which go much beyond the single purpose of cleaning.

As early as 1955, a panel reported that 'women want a shampoo to clean and also to rinse out easily, impart gloss to the hair and leave it manageable and non-drying'. At the same time, it was also stressed that 'the principal trend evident in shampoo formulation is toward surfactants which have a milder effect on the skin; complete elimination of any sting if the product gets into the eye is the objective'.[2]

These are the two basic attributes of the types of shampoo described here and it is these requirements, known as 'conditioning effects' and 'mildness', that shampoo formulators nowadays provide as the indispensable cosmetic counterpart to the original 'cleaning' function.

However, no matter how grand a shampoo may be, its primary function remains that of cleansing the hair of accumulated sebum, scalp debris and residues of hair-grooming preparations. Although any efficient detergent can do this job, cleansing should be selective and should preserve a quantity of the natural oil that coats the hair and, above all, the scalp. Undesirable side-effects have been shown to occur when using some of the best cleansers and indeed some authors include cleansing among the functions of shampoo only as an afterthought.[3,4] The view that shampoos should be 'inefficient' detergents arises mainly from the theory that the after-effects of shampooing—difficulty in combing the hair, roughness to the hand, lack of lustre and 'fly' when the dry hair is combed—are due to excessive removal of oil from the hair. This assumption is at first sight quite reasonable but further examination shows that it is very much oversimplified: if sebum somehow fulfils a natural function of protection, and enhances the lustre and lubricity of the hair, it also possesses the dangerous drawback of attracting and trapping dust and dirt and has a potentially deleterious effect on the maintenance of set and the 'feel' of hair.

Conventional detergents of the anionic type seem to cause unpleasant after-effects to the hair roughly in proportion to their grease-removing power, but many other materials which remove grease will cause no apparent deteriora-

tion in the hair condition. Thus, if the hair is extracted with ether or trichloroethylene it can rapidly be made essentially grease-free, but its condition will be found almost unchanged. The hair will still be smooth, lustrous, and easy to comb and set. Even among detergents, there will be found some which remove relatively little sebum, but leave the hair in bad condition, and others which wash quite thoroughly without harming the hair. So no cause–effect relationship is likely to exist between residual oil and hair condition[5] and it is up to the cosmetic chemist to find the right balance between adequate soil removal and desirable hair condition.

This balance between cleaning and conditioning must be chosen with care, and it must also take into account the type of market to be supplied. People with greasy hair are highly critical of a shampoo which produces effects lasting only for three or four days, while those with dry hair may be more easily satisfied. However, many dry-haired people also use dressings of an oily character which must be removed, and in any case there is a deep-seated feeling, among women in particular, that the process of shampooing is a cleansing, purifying activity, designed to free them from daily accumulation and maturation of grease, dirt, perspiration, cooking smells, dandruff, environmental pollution and so on. In fact, it seems sensible to retain the definition of a shampoo as a suitable detergent for washing the hair with the corollary that it should also leave the hair easy to manage and confer on it a healthy look.

DETERGENCY

The development of a detergent system adapted to hair is a complex problem in itself because of the variability of the substrate and the process, and it is further complicated by the ambiguity of the objective. The substrate to be cleaned is made of the relatively hard but porous keratin of the hair and of the soft keratin of the scalp, the latter being much more sensitive to drying and defatting. While there exists very large individual variation in fibre number and diameter, the average surface area of a female head of hair is calculated to be between 4 and 8 m^2—that is, 50 to 100 times the average scalp area.[6]

The kind of soil to be removed, either natural or captured, varies greatly according to the weather, the life style, the type of work, the physiological functions, the haircare practice and so on.

Although shampoo should 'remove more soil than oil',[7] the problem of cleaning hair is mainly one of grease removal. Hair presents a reasonably hard surface and, unlike cotton and some other textiles, it does not pick up particles of dirt without the intervention of a grease layer. As long as the grease can be removed, it is quite easy to remove the dirt. In order to remove grease from the hair, one must find some agent with a greater affinity for the grease. This function can be accomplished by absorbent solids such as fuller's earth or flour, but solutions of surface-active materials such as those discussed in Chapter 33 (Surface-active Agents) are much more convenient and more commonly employed.

The mechanism of detergent action involves a number of complex physical phenomena—wetting, foaming, emulsifying and peptization—several of which

are imperfectly understood. It appears evident that detergency, that is the removal of dirt, involves the following processes:

1. The detergent solution must be able to wet both the dirt and the substrate which, in the case of a shampoo, is the keratinized hair fibre; hence it must lower the surface tension.
2. The interfacial tension must be reduced to such an extent that it will allow the dirt or oil particles to be displaced by the detergent solution.
3. The dirt particles must be kept dispersed in order that they may readily be washed away.

In a detergent the polar portion of the molecule must have some attraction to the surface to be wetted (in this case the hair) so that the detergent molecules in the interface between the water and the hair will 'drag' the water over the hair surface. In doing so, the detergent solution creeps under the oily layer and lifts it from the surface, eventually causing it to roll up into spherical particles which are then solubilized by the detergent.

The essential difference between a detergent and a simple emulsifier resides in the ability of the polar group of the detergent to displace oil from a surface, and in hair washing this is its most important property. The washing of cotton and similar textiles also requires the removal of strongly bonded metallic ions from the surface, and this complicates the process and the selection of suitable detergent materials.

The evaluation of shampoo detergency is a complicated and difficult process, and there are virtually as many methods as there are laboratories evaluating detergency. The method described by Barnett and Powers[8] is typical and depends on estimating gravimetrically the quantity of soil removed from wool yarn soiled in a standard manner.

Although the public commonly associates 'foam' with detergency, the two are by no means synonymous and many very effective detergents do not foam well. However, foam (or lather) is at least of psychological importance and a shampoo that will not foam adequately will be considered unsatisfactory.

EVALUATION OF DETERGENTS AS SHAMPOO BASES

While measurements such as surface tension and interfacial tension (see Chapter 33 on surface-active agents) may often be used as screening tests to eliminate unsuitable detergents, there seems to be no substitute for practical trials on heads in the selection of detergents for shampoos. There are several reasons why this should be so, the most important being the fact that the after-effects of the shampoo may often be the deciding factor. With the wide range of materials available it is a relatively easy task to find materials that will adequately clean hair and allow for adequate lather. The final criterion which then applies in the selection of the detergent is its effect on the hair.

These effects are best observed in comparative tests on the same head, as hair diameter, quantity, greasiness and previous treatments may all affect the results. Such comparative tests can be carried out by parting the hair in the middle and washing with one detergent preparation on one side, and the alternative on the

other side.[9] Care should be taken to ensure that the amount of mechanical work applied by the operator's hands is the same on both sides, and obviously the temperature of the water, the amounts of rinsing, the water hardness and so on should be kept constant for each experiment. The following are the points to be looked for.

Ease of Spreading. Ease with which the shampoo can be distributed over the hair: some shampoos seem to 'sink into' the hair so that it is difficult to spread them all over the head and to raise a lather.

Lathering Power. An abundance of foam is usually required as a first sensory perception of efficacy, though this may be waived in consideration of achieving greater mildness. Foam has not only a psychological value: it allows assessment of the amount of shampoo necessary to ensure that all functions involved in cleansing are performed.[10] This means that several properties must be considered, such as the speed with which the lather may be generated, the volume, the consistency—whether loose or creamy—and the stability of the lather on the hair.

Efficient Soil Removal. Removal of grime, excess oil and scalp debris in soft and hard water: it has been proposed that cleaning agents should be prescreened *in vitro* by studying the detergent activity on hair switches soiled with synthetic sebum.[5,11]

Ease of Rinsing. Some shampoos rinse away very quickly, others continue to lather after what seems endless rinsing. This latter behaviour can be very annoying to a woman trapped with her head over a basin!

Ease of Combing Wet Hair. This evaluates the roughness and tangling tendency immediately after treatment with the detergent, under conditions where these defects are most apparent. The consumer associates this property with the cleansing action of the shampoo, although, as has been seen, the simple removal of oily material is not the whole story.

Lustre of the Hair. The importance of this to the average consumer is sufficient justification for taking notice of it, but hair that is left dull is also a sign of unsuitability or inefficiency of a detergent. Soaps in hard water, for instance, tend to leave dulling films of insoluble calcium and magnesium soaps on the hair; detergents with insufficient suspending power may redeposit dirt or grease with, again, a dulling effect. The shampooed hair must feel and smell clean and fresh.

Speed of Drying. Drying the hair is one of the most tedious operations in the normal shampooing process and, in the case of treatments carried out in hairdressers' salons, is the most costly in terms of time and equipment. Some detergents leave the hair very wet and slow to dry; others tend to leave behind a slightly hydrophobic surface which sheds water fairly quickly. There is a practical limit to the speeding-up of drying in that a great deal of the water taken up by the hair during shampooing is bound into the hydrogen bonds, and these

are unlikely to be affected by such surface effects as the type of detergent. However, of the total weight of water removed by drying after a shampoo, as little as 20 per cent or as much as 50 per cent may be in the form of surface water, according to the efficiency of the mechanical drying or the type of detergent used.

Ease of Combing and Setting the Dry Hair. When the hair is dry, any roughness induced by the detergent during the shampooing operation appears as a resistance to combing and, more important, a tendency to produce static electricity as the comb is drawn through the hair. This static electricity, which is usually of positive charge (with ebonite or nylon combs; the hair is always positively charged and the comb negatively) can be a serious hindrance to setting, as it makes the hairs repel one another. The more the hair is combed or brushed to set it out in the desired style, the more it flies about and defeats this purpose.

Safety. The shampoo detergent must be safe for use on the scalp, and no irritation, reddening or other discomfort should be caused by its use.

Sorkin *et al.*[12] have described a method of evaluating shampoos in practice using most of the points listed above. The major difficulty with these evaluation procedures is that they depend on the subjective judgment of the operator applying the product and on the variability of the subjects. It is true that these effects can be minimized by using suitable statistical designs, but it would be far better to have applicable instrumental techniques. A review of instrumental methods available for the evaluation of shampoo performance has been given by Prall,[13] with special reference to the measurement of combing resistance of hair, and its correlation with perceived sensory evaluation.

More recently, factor analysis applied to panel evaluation of shampoos for normal, dry and greasy hair was shown by Baines[14] to be a powerful tool for drastically reducing the number of parameters required to describe product performance. At least 90 per cent of the variation of most of the 17 attributes for which shampoos were rated appeared to be accounted for by two orthogonal factors—rate of foam build-up and stability of the first lather, the hair condition being better described by the former—and an oblique factor corresponding to ease of rinsing.

RAW MATERIALS FOR SHAMPOOS

The types of ingredient that go to make a shampoo are the following:

Surfactants (cleansing or foaming agents)
Foam boosters and stabilizers
Conditioning agents
Special additives
Preservatives
Sequestering agents

Viscosity modifiers (thickening or thinning agents)
Opacifying or clarifying agents
Fragrance
Colour
Stabilizers (suspending agents, antioxidants, UV absorbers)

These ingredients may be classified more simply as:

Principal surfactants to provide detergency and foam
Auxiliary surfactants to improve detergency, foam, and hair condition
Additives to complete the formulation and to give special effects

A general coverage of this field is given in Chapter 33 and we deal here only with considerations particular to shampoo formulation.

Principal and Auxiliary Surfactants

Nonionic detergents have sufficient cleansing activity to be considered as shampoo detergents, but very few have sufficient foaming power. They are therefore more often used as auxiliaries; some are remarkable foam boosters and stabilizers, others are used in view of their emulsifying properties and their extreme mildness in non-irritating shampoos. However, new nonionics have been developed which possess good foaming properties *per se* and may be used as the main surfactant.

Cationic detergents would appear to be ideal for shampoos: they can be made to foam well and many of them have reasonable cleaning power. In addition, they also leave the hair in excellent condition—easy to comb and set, lustrous and free of electrostatic charge. Unfortunately they have suffered from two serious disadvantages: a tendency to weigh down hair and a somewhat injurious behaviour, particularly to the corneal eye tissue. However, non-irritating cationics are now obtainable and combination with suitable nonionics and ampholytics helps to reduce the risk of irritation even more.

The remaining two groups of detergents, the anionics and the ampholytics, are both suitable as bases for shampoos. Anionics are by far the most widely used surfactants because of their superior foaming properties and lower cost. However, ampholytics, which used to play only an auxiliary role by virtue of their good hair conditioning properties, now receive increasing favour because of their contribution to mildness.

Anionic Surfactants

Soaps are metallic or alkanolamine salts of fatty acids, mostly provided by saponification of vegetable oils and animal fats. They were the first bases for shampoos.

In soft water, soaps have most of the properties desirable in a shampoo detergent, but they suffer from the disadvantage that soap solutions, especially if they are to be clear, are always alkaline. The alkalinity tends to cause roughening of the scales in the hair cuticle, thus giving a dull appearance, and is potentially damaging to the scalp. These disadvantages may be overcome by a mild acid rinse or by using less alkaline alkanolamine salts.[15]

In hard water, soaps also cause dullness by the deposition of calcium and magnesium soaps on the hair shaft. This can be prevented by the inclusion of lime soap dispersant or of sequestering agents for calcium and magnesium ions, such as salts of ethylenediamine tetra-acetic (EDTA) or polyphosphates, but these agents have no effect on the essential alkalinity of the soap solution. Soap is cheap but its use in shampoos should be considered only for less sophisticated markets, unless as 'special additive'.

Paraffin Sulphonates. These materials were introduced as soap substitutes in Germany during World War II. They earned a bad name for harshness and drying action on the skin and hair, but superior materials of this class have become available.

The C_{12}–C_{15} compounds have good foaming power and solubility, in the form of the sodium salts, and when built up by the addition of monoalkanolamide materials they can form useful cheap detergents for liquid shampoos, but they have never really become accepted.

Alkyl Benzene Sulphonates. The sodium salts of alkyl benzene sulphonates in which the alkyl group is on average a linear C_{12} chain (and hence biodegradable) are produced in bulk for use in household washing powders. They are strong degreasing agents and can be used to prepare low-cost liquid shampoos by formulating with other active ingredients such as alkanolamides. However, they are reputed to leave the hair quite dry and rough, to cause problems of fly-away, and to give a high order of irritation.

TEA dodecyl benzene sulphonate has found use in some 'oily hair'-type formulae (3–5 per cent concentration).

Alpha Olefin Sulphonates. Newly available surfactants, the alpha-olefin derivatives are less irritating than those formerly available and are widely used in powdered bubble baths. The preferred 'cut' is C_{14}–C_{16}. They have the advantages of high foaming properties in the presence of sebum and even in hard water, low cloud point and excellent acid and basic pH stability, which should provide a broad range of use, particularly for building shampoos of low pH.

Alkyl Sulphates. The most widely used anionic detergents in current shampoos are the alkyl sulphates, especially those derived from lauryl and myristyl alcohols. These alcohols, $C_{12}H_{25}OH$ and $C_{14}H_{29}OH$ respectively, are obtained by the catalytic reduction of the fatty acids in coconut and palm kernel oils, and most commercial samples of the detergents contain a mixture of the alcohols in the proportions set by the source of the raw materials.

It is commonly accepted that lauryl sulphates give a greater volume of lather and myristyl sulphates greater richness, so a mixture of the two provides a satisfactory compromise. Cetyl sulphates are usually too insoluble to give a freely-foaming solution, and the octyl and decyl sulphates are definitely lather depressants, so it is preferable to distil the fatty alcohols before sulphation so as to use only the narrow cut containing the C_{12}, C_{14} and a little C_{16} alcohol.

The mixture of alkyl sulphates so obtained from natural fats is generally referred to as 'lauryl' sulphate. However, it should always be remembered that

such materials are mixtures and may vary in their properties according to the source of supply and the narrowness of the cut of fatty alcohols.

Sodium lauryl sulphate tops all other salts for flash foam and foam volume. It is normally obtained as a white powder, consisting largely of the detergent with some sodium sulphate as diluent, or as pastes with varying detergent contents. This material is poorly soluble in cold water, but its solubility increases greatly with temperature so that at the normal shampoo temperature (35°–40°C) quite concentrated solutions can be made. Moreover the process of sulphation by sulphur trioxide now permits the preparation of a highly purified product, practically free of fatty alcohol and of inorganic salt, so that it is available as 28 per cent water solutions of suitable viscosity. Its high cloud point and high viscosity make it more specifically suitable for the paste type of cream shampoo or for powder shampoo; both types are passing out of favour.

Another criticism of the product pertains to its marked detergent and defatting effect and potentiality to be somewhat irritant. This is why alkanolamine salts, claimed to be milder and less defatting, are preferred; these compounds are much more soluble and show a better compatibility with other additives and a lower cloud point. They are usually sold as 30–40 per cent solutions and are yellow, rather viscous liquids with a tendency to darken on storage, particularly on exposure to light. They form the basis of many liquid and lotion shampoos, often with no more additions than colorant and perfume. Triethanolamine (TEA) salt is the more used; monoethanolamine (MEA) salt is usually lighter in colour—MEA is less liable to oxidative spoilage than TEA—and has a slightly lower cloud point at similar concentrations. Usual concentrations of lauryl sulphate in shampoos range between 7 and 15 per cent (anhydrous product).

With all the lauryl sulphates, the inorganic salt content has two main effects. Firstly, it raises the cloud point so that solutions with much inorganic sulphate tend to turn hazy in cold weather. This is due to salting-out of the detergent. Secondly, an increase in the inorganic salt content usually increases the viscosity of the detergent solution. This is often used deliberately to increase the viscosity of products. On balance, therefore, it is as well to specify a low level of inorganic salt so that salt can be added as a viscosity builder. Addition of fatty alcohol has a similar effect. In this respect, MEA lauryl sulphate is more sensitive to viscosity-modifying salts, especially chlorides, than TEA lauryl sulphate.

Ammonium lauryl sulphate has also achieved some popularity because of its lathering quality and good solubility and because it is more stable than the sodium salt with regard to hydrolysis at acid pH (up to 4·5), allowing formulation of shampoos with low pH.

Zinc, calcium and magnesium salts are also available, but they do not seem to have come into general use. Magnesium lauryl sulphate appears to be less hygroscopic than the sodium salt, which makes it attractive for powder shampoos which are liable to cake.

To complete the survey of alkyl sulphates used in shampoos, mention should also be made of those derived from fatty alcohols obtained by Fischer-Tropsch oxidation of paraffins, such as the so-called tridecyl sulphate which is very similar to lauryl sulphate in its properties.

Alkyl Polyethylene Glycol Sulphates (Alkyl Ether Sulphates). While sodium lauryl sulphate is less soluble than the amine salts, it is cheaper, and a considerable amount of work has been carried out on related sodium salts with greater solubility.

If, instead of lauryl alcohol, a polyethoxylated lauryl alcohol is sulphated, the resulting material is so much more hydrophilic that the sodium salts are soluble up to levels of 50 per cent or more.

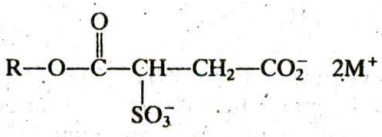
Usually, 2–3 ethylene oxide moles are condensed with the alcohol, 3-ethylene oxide compounds showing better solubility and lower cost. Such materials, widely available, are almost water-white solutions containing about 28 per cent of detergent. They have good foaming properties but, compared with alkyl sulphates, the foam is lighter and more open, collapsing readily in the presence of grease, so that additions of foam booster and stabilizer are required.

They are good cleansers, good solvents for non-polar materials such as fatty additives and fragrances, and they can be adjusted within wide limits of viscosity by the addition of salts such as sodium chloride. They are rapidly gaining favour as principal surfactant in that they are stable in a broader range of pH than lauryl sulphates (though potentially liable to hydrolysis on storage); they display greater mildness, irritancy decreasing with increasing number of ethylene oxide (approaching zero in the Draize rabbit eye test for 7 EO content[16]); and they show reduced tendency to keratin degradation and 'dry hair'.

However, they leave the hair in a condition slightly poorer than that obtained from washing with triethanolamine lauryl sulphate at similar concentrations. Slightly better results on the hair may be obtained with the monoethanolamine, triethanolamine or ammonium salts; however, as with alkyl sulphates, these improvements are often so marginal that the extra cost may not be justified.

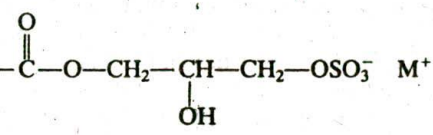
Magnesium salts find their use in some baby shampoos because of their lack of irritation.

Sulphosuccinates.



These surfactants, which contain both a carboxylate and a sulphonate group in the same molecule, are succinic hemiesters: the hydrophobic chain may come, for example, from a fatty alcohol—possibly polyethoxylated—or a polyethoxylated alkyl phenol or a fatty acid ethanolamide ($R{=}R'{-}CONH{-}CH_2{-}CH_2$). Very often they are average foamers and detergents, but they are mild to the skin and evince very low incidence of eye irritation and sting,[17] along with even some conditioning effect. So they find favour in the formulation of a number of mild shampoos, such as 'low pH', 'frequent' and baby shampoos.

Monoglyceride Sulphates.



These sulphation products of monoglycerides, such as monolaurin, have been described in a number of patents.[18] The ammonium salt of coconut acid monoglyceride sulphate was used as a basis for a widely popular US shampoo. In general, apart from the improved solubility of the sodium salt, these detergents seem to behave very much like the lauryl sulphates.

Fatty Glyceryl Ether Sulphonates. $R{-}O{-}CH_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_2{-}SO_3^-\ M^+$

Protected by numerous patents,[19] these surfactants have been developed with an exclusive use. Their main advantage is a good hydrolytic stability at all pH values. They are also said to be mild to the skin and have excellent flash foam.

Isethionates. $R{-}COOCH_2{-}CH_2{-}SO_3^-\ M^+$

Isethionic acid, $HOCH_2CH_2SO_3H$, was one of the first materials successfully used by IG Farbenindustrie to convert fatty acids into synthetic detergents without passing through the fatty alcohol stage.

The esters, originally known as Igepon A (now Hostapon A), display qualities similar to those of the alkyl sulphates with similar chain-length, although the foaming power of 'coconut' isethionate (sodium salt) is not quite as good as that of sodium lauryl sulphate. Very mild for scalp and hair and practically unaffected by Ca salts, they become hydrolysed in solution, which limits their use to powder shampoos and to syndet bars.

Methyl Taurides. $R{-}CO{-}\underset{\displaystyle CH_3}{\underset{|}{N}}{-}CH_2{-}CH_2{-}SO_3^-\ M^+$

The fatty amides of methyl taurine, $CH_3{-}NH{-}CH_2{-}CH_2{-}SO_3H$, were also developed by IGF as the Igepon T (or Hostapon T) series. Less mild than the above esters, the detergents in this class are remarkable for the excellent condition in which they leave the hair after washing.

Acylsarcosinates. $R{-}CO{-}\underset{\displaystyle CH_3}{\underset{|}{N}}{-}CH_2{-}CO_2^-\ M^+$

These are condensation products of fatty acids with sarcosine (that is, N-methyl glycine, an amino acid). They offer very interesting properties. They foam well and impart a good feel to the skin and the hair, which makes them appreciated as auxiliaries for lauryl sulphates or amphoterics. Preferred compounds are sodium myristyl and lauryl sarcosinates. While quite stable at low pH, they somehow lose their foaming characteristics but effect a noticeable thickening.

Another advantage of these anionic compounds is their good compatibility with a wide range of cationics, of which they do not affect the conditioning or bactericidal properties.[20]

Acyl Peptides. $R—CO—NH\left[CH(R)—CO—NH—CH(R)\right]_n COO^- \; M^+$

These are complex mixtures of peptide fatty amides obtained by reaction of a fatty acid chloride with protein hydrolysates. Earlier materials were soiled with large quantities of soaps derived from the unreacted acid chloride, which caused dulling of the hair and the formation of scum. The products available today—Maypons, Lamepons (the best known being the K salt of cocoyl hydrolysed animal protein)—no longer have these drawbacks but leave the hair lustrous, manageable and silky to the touch. They do not foam so well as alkyl sulphates but produce a soft, creamy, easily rinsed lather. They are good dispersing agents of Ca soaps and offer, like the above mentioned sarcosinates, a good compatibility with cationics. More expensive than alkyl sulphates, they are used in mixture with them so as to reduce irritation and impart fine foaming, mildness and conditioning properties.

Protein condensates with coco-fatty acid, oleic acid and abietic acid are more particularly recommended.[21]

Acyl Lactylates. $R—CO\left[O—CH(CH_3)—CO\right]_n O^- \; M^+ \quad n = 1 \text{ to } 3$

These anionic esters are condensation products of a fatty acid and lactic acid. Since they derive from compounds that occur naturally on the skin's surface, they are expected to be well tolerated. A further advantage lies in their substantivity, linked to a capacity to form complexes with proteins.[22] According to the length of the fatty chain, they may show cleansing, foaming, thickening, emulsifying, antistatic or conditioning properties; they are said to improve texture and manageability.[23] They could contribute as substantive humectants.

Polyalkoxylated Ether Glycollates. This class of substance covers ethers of an α-hydroxylated acid and polyalkoxylated fatty alcohols. They are mild and they offer some conditioning properties (increasing with decreasing pH); they are said to result in a creamier foam and to improve lubricity.[24]

The oldest known compounds are polyethoxylated glycollates[25] such as Sandopan DTC (from Sandoz AG—CTFA: Trideceth-7 carboxylic acid):

$$R—O\left[CH_2—CH_2—O\right]_n CH_2—COOH \quad R = C_{13},\ n = 6{\cdot}5$$

More recently polyglycerolated glycollic ethers and thioethers have been patented; they may, in addition, contain oxyethylene or oxypropylene groups.[26]

Nonionic Surfactants

Fatty Acid Alkanolamides. These materials have no great use as shampoo detergents by themselves, but they are of great importance as additives to anionic detergents. The monoalkanolamides (usually monoethanolamides, $RCONHCH_2CH_2OH$, or isopropanolamides, $R—CONHCH_2CH(CH_3)OH$), of the C_{12} to C_{18} acids are waxy solids, insoluble in water but easily soluble in

detergent solutions with gentle warming. They are commonly used with the lauryl sulphates, and the addition to shampoos of between 10 and 15 per cent of lauric monoethanolamide (based on the weight of the lauryl sulphate) has the following effects:

(a) The solubility of the lauryl sulphate is increased—for instance, 15 per cent of sodium lauryl sulphate, normally a paste, can be converted to a clear solution by the addition of 2 per cent of lauric monoethanolamide.
(b) The viscosity of the solution is increased: stearic ethanolamide is a pearlescent thickener.
(c) The after-effects on the hair are better since they exhibit softening properties. Oleic ethanolamides have been recommended as conditioning agents for shampoos.
(d) The volume and the richness of the lather are very much improved.

There is little point in exceeding the ratio of 15 parts of monoethanolamide to every 100 parts of detergent, as higher concentrations of the additive only serve to increase the viscosity without improving the lather or the condition of the hair.

The diethanolamides are sold as liquid products (up to myristic diethanolamide) or low-melting solids.

It is worth noting the amides of the Kritchevsky type, obtained by heating one mole of a fatty acid with at least two moles of diethanolamine (DEA), and the superamides prepared by a 1:1 molar ratio reaction between the methyl ester of a fatty acid (usually coconut or lauric acid) and DEA. The superamides, which largely outsell the other compounds, are mainly the amides $R—CO—N[CH_2—CH_2OH]_2$ but the first class of compounds—Kritchevsky type—are complex products also containing esters of DEA such as $R—COOCH_2—CH_2—NH—CH_2—CH_2OH$ and mixed ester amides.[27]

Diethanolamides are quite useful as shampoo additives although their thickening and lather synergist qualities may not be so great as those of the corresponding monoethanolamides; however, they offer better solubility—oleic diethanolamide is an emulsifier. Care should be taken with commercial products of the Kritchevsky condensation type as they usually have a high soap content and free DEA, and may thus lead to an alkaline reaction. There is also danger of the formation of toxic nitrosamines.

The lather-improving qualities of these compounds have not been adequately explained, but it is likely that they form complexes with lauryl sulphate ions at the air–water interface, perhaps through weak ionic attraction between the sulphate ions and the slightly cationic amide group. Fatty alcohols also form surface complexes of this type, but their influence on the lather is not nearly as pronounced as that of the amides. Goddard and Kung[28] have discussed the effect of adding long-chain polar materials to ionized surfactants.

Polyalkoxylated Derivatives. Though they may not be much used as main surfactant, mostly because of their low foaming power, these compounds nevertheless constitute an important class of auxiliaries for shampoos. They are obtained by polyaddition of an alkylene oxide to a hydrophobic compound containing a labile hydrogen atom, such as an alcohol, thiol or phenol.

Both ethylene oxide and propylene oxide may be used as polyadditive reagents. The oxyethylene unit imparts hydrophilic properties: for a given hydrophobic chain R, the number of oxyethylene units added will determine the water solubility, which gives wide freedom in adjusting the properties according to the hydrophobic chain and the rate of polyalkoxylation.

The compounds obtained may be wetting, emulsifying, dispersing or foaming agents, or detergents. The following have been used in shampoos:

Ethoxylated fatty alcohols, $R(OCH_2—CH_2)_nOH$: very stable whatever the pH, they bring stabilizing, emulsifying and opacifying characteristics.

Ethoxylated alkylphenols (mostly nonylphenol): low cost and very stable products; their use is limited by their high irritating tendency for eye mucosa.

Ethoxylated fatty amines and *fatty acid amides*.

Block polymers known as 'pluronics' (CTFA: poloxamers): they are polycondensates of ethylene oxide and propylene oxide, of general formula:

$$HOCH_2—CH_2(CH_2—CH_2O)_a—(\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_2O)_b—(CH_2—CH_2O)_c—H$$

Propylene oxide brings some hydrophobic properties. In these compounds the fatty chain R is replaced by a propylene oxide polyadduct, the hydrophilic properties being given by the adjunction to each end of a number of oxyethylene units (usually $a + c = 100$ to 200 ethylene oxide and $b = 15$ to 50 propylene oxide units).

The pluronics are very mild detergents imparting a good rinsability, and they may be used in high percentages in shampoos.

Sorbitol esters: the polyethoxylated sorbitol monoesters, known as Tweens, are excellent solubilizers and emulsifiers. Moreover, they are remarkably mild compounds. The laurate (Tween 20) is claimed to give neither irritation nor stinging. These compounds are therefore extensively used in non-irritating shampoos.

Highly ethoxylated (30–78 ethylene oxide moles per mole) *mono-* and *diglyceryl fatty acid esters* have been proposed within the same field of low irritation shampoo formulation.[29]

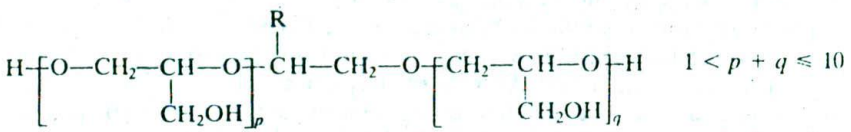
Polyglyceryl ethers: an important new class of nonionics has arisen in the last few years, characterized by the replacement of the usual 'oxyalkylene' units by hydroxylated units, thereby leading to considerable improvement in foam-generating capability in addition to mildness.

Two types of telomer have been patented; they derive from polyaddition of epichlorhydrin or glycidol on a compound containing labile hydrogen.

The first type is composed of hydroxymethylated oxyethylene units condensed on a fatty alcohol[30] (which may be polyethoxylated):

$$R—O\left[CH_2—\underset{\displaystyle CH_2OH}{\underset{|}{CH}}—O\right]_n—H \qquad n = 1 \text{ to } 10$$

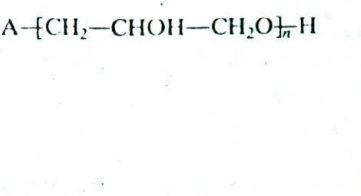
or on an α-diol:[31]



$1 < p + q \leq 10$

The hydroxymethyl group may be replaced by a thioether or an α-hydroxylated sulphoxide[32] such as in the dihydroxypropylsulphinylmethyl group. Besides having foaming properties, these compounds are devoid of aggressiveness to the eye mucosa, even when mixed with cationic surfactants.

The second type of polyglycerylether is obtained through polyaddition of glycidol, either pure or prepared *in situ*[33] by acidic[34] or alkaline[35] catalysis, on thiols,[36] α-diols or alkanolamides with a hydrophobic chain:[37]



$n \leq 10$

A = R—S(O)$_m$—

or R—CHOH—CH$_2$O—

or R—CON(—(CH$_2$—CH$_2$O)$_p$—)—

R = C_{12-14}

These nonionics offer such remarkable foaming properties that they may be used as main surfactants; they are also devoid of irritancy to skin and eye.

Amine Oxides. The third group of nonionics is often referred to as polar nonionic surfactants since they have a highly polarized link N → O; they may even take on a true cationic character at low pH values. They have found use as foam boosters and antistatic agents.[38–39] Preferred are coconut and dodecyl dimethyl amine oxides, which are said to be more effective foam boosters than alkanolamides. Antistatic properties are only shown at relatively low pH values. They are often associated with ampholytics.

Amphoteric Surfactants

These surfactants are very fashionable in the development of mild shampoos. Their compatibility with other detergents, their ionic equilibrium together with anionic/cationic potentialities (depending on pH), allow for a large flexibility of use; in addition they may contribute to the conditioning effect on hair.

They can be classified into three groups:

Long-chain N-substituted amino acids

Long-chain betaines

Long-chain imidazoline derivatives

N-alkyl Amino Acids. These mainly consist of two types:

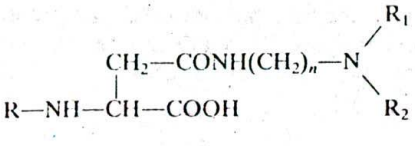
(i) β-amino acid derivatives, known as Deriphats (from General Mills—CTFA: sodium cocaminopropionate); these are products of the substitution of fatty amines with 1 or 2 carboxyalkyl residues, for example:

N-alkyl-β-amino propionates	RNH—CH$_2$—CH$_2$—COOH
N-alkyl-β-imino propionates	RN(CH$_2$—CH$_2$—COOH)$_2$

Their isoelectric point, which corresponds to the zwitterion state ($-N^+ \sim\sim COO^-$), lies in the region of pH 4·3.

Best foaming properties are exhibited in slightly alkaline pH range where they display the anionic character of a carboxylic salt. On the other hand, cationic properties are assumed at lower pH values, provided by either a secondary or tertiary amino group; the optimum contribution to hair manageability is found at an acidic pH. Therefore a compromise must be found between foaming and conditioning properties, as required, by adjusting the pH value. Most often used is the coconut fatty acid derivative (Deriphat 151) at pH 5·5.

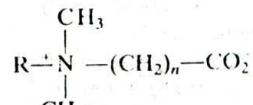
(ii) Asparagine derivatives.[40] These surfactants show good foaming, cleansing and conditioning properties:



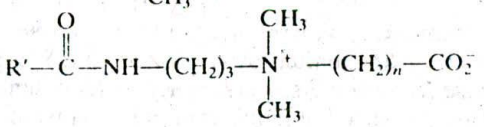
R_1 and $R_2 \leq 4$ carbon atoms
$n = 2$ or 3

Their added cationic valence imparts hair substantivity and easy untangling, while their ampholytic nature makes them compatible with both anionic and cationic surfactants.

Betaines



(A)



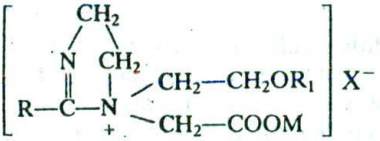
(B)

This generic term refers to zwitterionic compounds derived from trimethylglycine ($R = CH_3$, $n = 1$), known as betaine, one methyl group being replaced by a fatty C_{12-18} radical (**A**), or a fatty amido alkyl radical (**B**).

Cationic in acidic and anionic in alkaline solutions, and substantive to hair, these surfactants are mild and effective cleansers with high foaming properties, comparable to alkyl sulphates for flash foam characteristics. Moreover, foam performances are unaffected by any pH variation. Betaines are compatible with cationics, anionics and nonionics, and display additional interesting thickening properties, and therefore offer a wide range of use.

Amidobetaines are somewhat milder and therefore find a current surge of interest, more particularly the already widely developed cocoamidopropylbetaine. Other available betaines are sulphobetaines (or sultaines) in which the carboxylic group is replaced by a sulphonic analogue (with $n = 3$), thereby resulting in further improved mildness for skin and eye with the same range of properties.

Alkyl imidazolines are also known as cycloimidates (CTFA: Amphoterics 1–20):



R_1 = H, Na or CH_2COOM

X^- = OH or a carboxylate (acid salt) or a sulphate (or sulphonate) anion from anionic surfactant.

They are obtained by condensing fatty acids with aminoethylcolamines and subsequent ring closure and quaternization;[41] these compounds have lately made a formidable gain related and directed to the formulation of fast-growing mild shampoos. First known under the trade name Miranol,[42] they are stable within a wide range of pH (2 to 12) and are present in most low-irritation and baby shampoos.

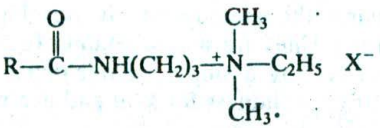
They exhibit fair foaming properties but they can be combined with practically all surfactants as well as with many electrolytes. They are reputed to improve foam stability while being quite innocuous to the eye mucosa.

Cationic Surfactants

Generally speaking, the cleaning and foaming properties of cationic surfactants are considerably inferior to those of anionics. Furthermore, their strong affinity for proteins such as keratin may induce the redeposition of dirt on the fibre during shampooing. As already mentioned, another drawback lies in a potential weighing-down effect on hair. Since in addition they are generally aggressive to the eye, above all with nonionics, and as they have gained a reputation of non-compatibility with anionics, their use has been limited to the beneficial development of their wet and dry combing, antistatic and lubricating properties as additives in small amounts (largely below 5 per cent). The most used compounds have been alkyl (C_{14-16}) trimethylammonium, stearyl-dimethylbenzyl ammonium, cetylpyridinium salts, and the less irritating double fatty-chained quaternary ammonium salts, which gained popularity with the development of rinse–conditioners, particularly distearyldimethyl ammonium (CTFA: Quaternium 5), dicetyldimethyl ammonium (Quaternium 31) and di-(hydrogenated tallow) dimethyl ammonium chlorides (Quaternium 18).

By and large, this class of surfactants has been kept for a long time in the background on account of their ill-famed properties. More recently, some very interesting breakthroughs have taken place in this field: compatibility with anionic surfactants has been shown to be possible and foam depression to be avoidable by proper formulation and suitable choice of cationics.[43]

Under the pressure of a need for extra effects in anionic shampoos, and despite (or thanks to) the rise of anionic-compatible cationic polymers, new cationics for anionic bases have flourished on the market. Examples include quaternized fatty acid amides:



derived from isostearic acid (Schercoquat—Scher Chemicals Inc.) and lanolin acid (Lanoquat—Malmstrom)[44] and proposed to impart body and softness; polyoxypropylene methyldiethyl ammonium chlorides (Witco—CTFA: Quaternium 6, 20, 21) with antistatic and foam stabilizing properties; N-stearoylcolaminoformylmethyl pyridinium chloride (Emcol 607 S, Witco—CTFA: Quaternium 7); and benzalkonium saccharinates, cyclamates and phthalimidates.[45]

On the other hand, adequate combinations of cationics with ampholytics and nonionics have been shown to alleviate aggressiveness while providing effective conditioning effects. The insertion of polar connecting groups between the fatty chain and the cationic end has also helped to diminish considerably the potential for causing irritation; typical examples are fatty acid monoesters of quaternized aminopropane diol, which are claimed to be particularly well tolerated by eye mucosa while providing greater beneficial effects in manageability, feel and appearance of the hair.[46]

More recently, new polyglycerolated cationics have been patented which seem to offer the ideal characteristics of a surfactant for shampoo, that is good foaming, cleansing and conditioning properties with a fairly low risk of irritation.[47]

Additives

Numerous materials other than detergents are incorporated in shampoos to complete the formula or to impart specific properties. Some play a prominent part in the composition, others are optional adjuncts.

Conditioning Agents

Conditioning agents have been a main focus of study in recent years. Besides specifically designed surfactants, these agents include a wide variety of materials such as fatty materials (lanolin, mineral oil), natural products (polypeptides, herbal additives, egg derivatives) and synthetic resins. They are intended to influence favourably manageability, feel and lustre of the hair, covering the whole range of magnitudes according to the nature of the hair, its condition, various compatibilities and the particular expectations of the consumer (including the quality–cost ratio). As seen above in reviewing surfactants, everything points to cationics and more precisely to quaternary ammonium compounds as conditioning agents. The great improvement in recent years has been the introduction into shampoos of cationic compounds, the hydrophilic functional groups of which are no longer at the end of a fatty chain but inserted within a polymeric structure, whereby potential for irritation is far reduced as compared with conventional products. Such resins, formerly used in setting lotions for their hair-holding properties, can be combined with amphoteric and nonionic surfactants and some show remarkable compatibility with anionics, which is the most required property both for good foaming and cleaning power and for economic reasons.

The first resin to be introduced into an anionic shampoo in 1972 was a strongly cationic cellulose derivative known as 'Polymer JR' (CTFA: Quaternium 19) from Union Carbide.[48] It is obtained by reaction of hydroxyethylcellulose with

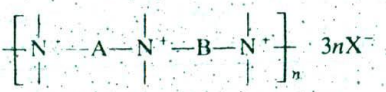
epichlorhydrin followed by quaternization by trimethylamine.[49] The average molecular weight of JR resins is between 250 000 and 600 000; they display strong affinity for keratin. Hairs treated with shampoos containing such a resin and then rinsed have been shown to be uniformly coated by it.[50]

Subsequently a number of other highly substantive resins have been successfully introduced into shampoos to impart wave-retention properties, as well as manageability and combability. Thus dimethylsulphate quaternized poly(diethylaminoethylmethacrylate)[51] and water-soluble phosphate salts of either polyacrylic acid aminoethylester or a copolymer of the latter with hydroxypropylacrylate, or the terpolymer aminoethylacrylate–hydroxypropylacrylate–acrylamide[52] have been reported in amphoteric shampoos. Similarly, condensation products of polyamines, bifunctional polyalkyleneglycol derivatives and epichlorhydrin[53] have been used in anionic-based shampoos. Cationic polymers derived from piperazine,[54] added to anionic, nonionic or ampholytic bases, have been claimed to increase body and set-retention qualities.

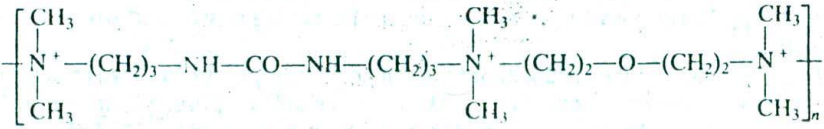
Other conditioning resins specifically claimed to provide easy wet combing are a dimethylsulphate quaternized copolymer of vinylpyrrolidone and dimethylaminoethyl methacrylate, known as Gafquat 755 resin (from General Aniline—CTFA: Quaternium-23),[55] quaternized[56] or cross-linked[57] polyaminoamides, and diallyl dimethylammonium chloride cyclopolymers[58] known as Merquat resins (from Merck Co.). To avoid excessive build-up on the hair with subsequent shampoos, less substantive resins have been proposed; examples are a cationic polymer grafted on the end of a cellulosic chain (Product 78-4329, National Starch & Chemical Corp.), which has been found highly efficient in dissipating static charges generated by combing and brushing, and a highly conductive interpolymer aminoethylacrylate phosphate–acrylic acid (Catrex, National Starch & Chemical Corp.).[1]

Another class of interesting compounds for these various purposes comprises polyquaternaryammonium (that is 'polyazonia') chains; the simplest elements correspond to completely quaternized substituted polyalkyleneimines such as poly(dimethylbutenylammonium chloride)-α,ω-*bis*(triethanolamine chloride) (Millmaster Onyx Corp: Onamer).[59]

A great variety of patterns and combinations within the following general structure has been patented, which may provide a wide scope of extra effects and modulation possibilities:[60]



A typical newly available product is the proprietary Mirapol A-15 (from Miranol Co.):



Its average molecular weight is 2260 (about six repeated units); it is compatible with anionic surfactants and is thought to absorb on the hair and link with the surfactants, whereby the hair becomes tangle-free, smooth, shiny and antistatic.

Another compound on the borderline between surfactants and polyquaternary compounds, stearylpentamethylpropylenediammonium dichloride, has been claimed to enhance the mechanical properties of hair when used at a concentration of 1 per cent in an anionic shampoo.[61]

However, the issue of conditioning is not limited to polyammonium (or azonia) compounds or resins which, furthermore, are not easy to manage and to adjust so as to monitor the deposition on the hair. Thus, alkylated[62] and partly formylated[63] polyethyleneimines have been claimed to impart softness and combability. Water-soluble proteins, preferably hydrolysed collagen (average molecular weight 500–10 000), and quaternized derivatives have been proposed for improving curl retention and wet combing, as well as for protective and synergistic mildness effects. The more damaged the hair the higher the protein absorption onto hair and the lower the pH at which it occurs. Virgin hair absorbs little, with a maximum at pH 9–11; waved hair absorbs the most, followed by bleached hair with a maximum uptake at pH 9 → 6, decreasing with increased level of bleaching. The polypeptidic fraction with average molecular weight of 1000 shows highest substantivity.[21,64]

More recently, a serum containing antibodies ('hair anti-serum') has been claimed to display similar properties with improved substantivity.[65] A mixture of proteins and polysaccharides from waste liquid beer sludges has been patented as conferring body,[66] as have natural wood resins.[67]

All these 'texturizers' more or less help to improve the feel and appearance of hair after shampooing. Another compound, the triethanolamine salt of alginic acid, added to anionic base, has been claimed to give more specifically a 'feel of a velvety nature'.[68] Smoothness and gloss can be obtained by including so-called superfatting agents, that is, oily materials such as ethoxylated lanolin derivatives, silicones, Ucon fluids (PEG and PPG alkylethers), PEG-modified polysiloxanes,[69] mineral oil, mink oil, sesame oil, jojoba oil, or other vegetable or animal oils, which deposit onto the keratin fibre during shampooing and lubricate it. Benzyl and phenethyl alcohols have also been claimed to impart extra effects when added to anionic–amphoteric systems.[70]

Addition of honey has been patented as a lubricating agent.[71] Lustre performance may also be enhanced by depositing a specific resin or resin–oil film on the hair surface, as suggested by different patents; thus, some data have been given on the beneficial incorporation in anionic shampoos of water-soluble anionic linear polymers—such as polymethacrylic acid (MW 10 000–100 000) or hydrolysed copolymers of ethylene (or methyl vinyl ether)–maleic anhydride[72]—or of various resins either combined with mineral oil[73] or coacervated with dimethylpolysiloxane.[74]

Miscellaneous Additives

Among the parameters susceptible to influence by specific additives, the drying time should also be mentioned; it usually increases with the state of damage of the hair. Apart from aluminium soaps,[75] the introduction of particular water-repellent film-forming fluorinated polymers in low amounts (0·003 per cent) has

been claimed to reduce significantly the time needed for drying;[76] a typical resin is the copolymer of N,N-diethyl aminoethylmethacrylate and hexafluoroisopropyl (or perfluoro-octyl) methacrylate. Similar fluorinated compounds[77] have been shown to be efficient in delaying migration of sebum on the hair and therefore checking the subsequent greasy relaxation of set hair.

Another approach to preventing the hair from regreasing too rapidly has been patented, using thiocompounds such as cysteine, glutathione and aminoalkanethiol derivatives.[78–83]

Lastly, it is worth noting the use of compounds—notably antioxidants—to prevent the production of unpleasant odours arising from sebum maturation on the hair and scalp.[84–86]

Viscosity Modifiers

Thickening of a shampoo may be achieved by inclusion of various types of compound, such as:

(a) electrolytes: 1–4 per cent (w/w) ammonium or sodium chloride in alkylether sulphates increases the viscosity steadily;
(b) natural gums (karaya, tragacanth), alginates;
(c) cellulose derivatives (hydroxyethyl, hydroxypropyl, carboxymethyl) which protect the hair against redeposition and soften foam;
(d) carboxyvinyl polymers (Carbopol 934 and 941 from Goodrich—CTFA: Carbomer) which in addition promote stability of the shampoo.

However, attention must be paid to the temperature and concentration dependence of most of these effects.

Ethoxylated fatty acid diesters (for cream shampoos), phosphate esters, amidoamine oxides, TEA soaps, polyvinyl pyrrolidones and polyvinylalcohols and the previously mentioned alkanolamides are other thickeners.

Reduction in viscosity may be obtained through the addition of small amounts of solvents (alcohols), or polyoxyalkylene compounds or of sodium xylene sulphonate, which also provides clarity.

Opacifying and Clarifying Agents

Opacity or pearlescence is provided by:

(a) alkanolamides of higher fatty acids (stearic, behenic);
(b) glycol mono- and distearates, propyleneglycol and glycerol monostearates and palmitates;
(c) fatty alcohols (cetyl, stearyl), which also contribute smoothness;
(d) milky emulsions of vinyl polymers and latexes;
(e) insoluble salts—for example, magnesium, calcium or zinc—of stearic acid;
(f) finely dispersed zinc oxide or titanium dioxide;
(g) magnesium aluminium silicate (for example, Veegum—Vanderbilt Co.), which also prevents sedimentation in the product.

Pearl-like effects depend on the size, shape, distribution and reflectance of the opacifier crystals included.

Transparency may be improved and stabilized by addition of solubilizing alcohols (for instance, ethanol, isopropanol, propyleneglycol, hexylene glycol and dimethyloctyne diol—Surfynol 82: Air Products), phosphates, or nonionic solubilizers (for example, polyethoxylated alcohols and esters).

Sequestering Agents

The function of these compounds is to prevent the formation and deposition onto the hair of Ca and Mg soaps when rinsing with hard water. Ethylene diaminetetra-acetic (EDTA) salts or polyphosphates are mostly used. Nonionic surfactants may also display efficacy by peptizing Ca salts.

Preservatives

Preservation is an extremely important aspect of shampoo formulation. The early soap shampoos were not hospitable media for moulds and bacteria, but as products became milder in their action on the skin, they became milder in their action on bacteria. The introduction of nonionic surfactants and more recently of some 'natural additives' has appreciably increased the risk of microbial contamination.[87] Most modern shampoo materials are liable to mould attack unless preserved with agents such as the hydroxybenzoate esters (see Chapter 36 on preservatives).

More serious in many ways is the growth of bacteria in shampoos, since they can lead to the breakdown of the detergent and discoloration of the product. Many shampoo surfactants will support the growth of Gram-negative organisms of the *Pseudomonas* type, and in fact it seems likely that these widespread bacteria have adapted themselves to prolific growth in unpreserved shampoo solutions, where they can produce off-odours (especially in diluted solutions) and cloudiness as a result of the production of mycelium.

The question of preservatives for toilet preparation in general is discussed in Chapter 36, but it may be said here that the surface-active agents in shampoos tend to interfere with the activity of germicides—thus it was shown that the bactericidal action of quaternary ammonium surfactants was markedly reduced in the presence of nonionics[88]—so that higher concentrations of a preservative are often necessary in a shampoo compared with that in simple solutions.

The preservation of shampoos is therefore a specialized subject and its peculiar aspects have been reviewed by various authors.[87,89] The most simple broad-spectrum germicide, that is formaldehyde, is about the most effective, together with phenyl mercuric salts. Although formaldehyde is unaffected by surfactants and is efficient in amounts of 0·1–0·15 per cent, it is however not compatible with certain ingredients, particularly protein hydrolysates, which furthermore present problems of preservation.[90] Esters of *p*-hydroxy benzoic acid are quite effective against moulds, but inactive against *Pseudomonas* and inactived by nonionics. Other recommended preservatives are 5-bromo-5-nitrodioxan, known as Bronidox,[91] and a formaldehyde-releasing quaternary ammonium compound known as Dowicil 200,[87] neither of which is adversely affected by anionic or nonionic surfactants.[92,93] Dimethyloldimethylhydantoin also releases formaldehyde and is of interest because of its efficiency and compatibility.

Perfumes

Long considered as an incidental additive, perfume is becoming an important feature for sales appeal with the increasing impact of the 'back to nature' concept. Simple descriptive odours—herbal, fruity, floral—are increasingly sought to provide the evocative whiff of natural freshness.[94] Some believe that fragrance will play an increasing functional role of quality-communication,[95] with higher levels of concentration and a thrust towards 'substantive odours' (residual notes for long-lasting fixatives).

Shampoo fragrance must first comply with basic technical requirements such as solubility, compatibility—that is, no effect on viscosity and stability—non-discoloration of formula (or hair), and non-irritation. Moreover, the introduction of conditioning agents into shampoos has increased possible interactions and often added to the need for a blend of covering fragrances.[96]

FORMULATION OF SHAMPOOS

Many of the detergents available for shampoos have already been described. The examples of shampoos given below are not exhaustive, but represent the various types of formulae. Where a formula is based on some particular detergent, it may usually be assumed that other detergents or mixtures can be used in its place, allowing for such matters as solubility, foaming capacity, etc. By this means the simple formulae quoted may be used as bases for further formulation.

The principles involved in formulating shampoos (see also Cook[97] and Mannheim[98]) have been reviewed by Zviak[10] and Markland;[99] an excellent survey of materials and formulations has been published by Alexander[38] (see also Kass[100a] and Donaldson and Messenger[100b]).

It is important to note that consumers in different countries have different ideas of the ideal concentration for a shampoo. In the UK, for instance, most people prefer to use a shampoo of medium concentration, whereas in some other countries the consumer expects a shampoo to have high active level. This difference in social habits and requirements makes it difficult to recommend detergent levels that will be universally suitable. Formulators should make themselves aware of the requirements of the market they are working for. Most of the formulae that follow comply with the UK pattern of 12–20 ml per head.

Many shampoos are available in three types: for normal, dry and oily hair. Those for oily hair often have a higher percentage of surfactant or a blend that is more active in emulsifying sebum out of hair; those for dry hair usually contain a higher level of conditioner.

The main types of shampoo on the market are the following:

Clear liquid shampoos
Liquid cream shampoos
Solid cream shampoos
Oil shampoos
Powder shampoos
Aerosol foam shampoos
Dry shampoos

Alternatively, shampoos may be classified according to function, more particularly:

Conditioning shampoos
Anti-dandruff shampoos
Baby shampoos
Acid-balanced shampoos

Clear Liquid Shampoos

This is at present the most popular type, and is subject to the greatest variety of formulation and presentation. While there is no very clear picture of what members of the public expect from a clear liquid shampoo, it seems that the formulae can be divided roughly into those bought largely on the grounds of their cleansing power for greasy hair (which can be categorized as 'cleansing shampoos') and those bought because, along with their promise of cleansing, they carry the suggestion that the hair will still be left in good condition after shampooing. Predominantly transparent or translucent, the latter are popular among consumers, particularly women with dry or normal hair, and are often called 'cosmetic shampoos'.

The 'cleansing' type are easily formulated, as they required only a suitably presented solution of a detergent, such as triethanolamine (TEA) lauryl sulphate or a lauryl ether sulphate, providing a low cloud point and therefore ensuring clarity even at low temperature; TEA lauryl sulphate is usually sold as 30–33 per cent solution, and 50 parts of this, perfume, colour, and water to 100 parts will make a mobile, clear solution with good foaming power. For a more viscous product, the ether sulphate may be used as in example 1.

	(1) *per cent*
Sodium lauryl ether sulphate 30%	45·0
Sodium chloride (according to the viscosity required)	2·0–4·0
Perfume, colour, water, preservative	to 100·0

The 'cosmetic' type of liquid shampoo can be formulated by selecting those detergents recommended for their good after-effects, such as methyl taurides, amphoterics, etc., in admixture with lauryl sulphate and alkanolamide additives:

	(2) *per cent*
Triethanolamine lauryl sulphate (33%)	45·0
Coconut monoethanolamide	2·0
Perfume, colour, water	to 100·0

	(3) *per cent*
Lauryl amino propionic acid (Deriphat 170 C)	10·0
Triethanolamine lauryl sulphate (33%)	25·0
Coconut diethanolamide	2·5
Lactic acid to give pH 4·5–5·0	*q.s.*
Preservative	*q.s.*
Fragrance, colour, deionized water	to 100·0

Dry hair shampoo (Alcolac Inc.[87])	(4) *per cent*
TEA lauryl sulphate	49·0
TEA oleate (50%)	9·8
Propylene glycol	2·0
Oleyl alcohol	1·0
Water	38·2

High quality low-cost shampoo base (Witco Chemical Corp.[87])	(5) *per cent*
Sodium C_{14-16} olefin sulphonate	25·0
Coconut monoethanolamide	3·0
Conditioners, fragrance, preservative	*q.s.*
Water	to 100·0

Liquid Cream or Lotion Shampoos

Liquid cream shampoos really form an extension to the class of 'cosmetic' shampoos, since users expect them to be very mild in their action on the hair. The appearance of the liquid creams is calculated to suggest emollience, though it is unwise to include very much fatty material in such a product, or the hair will become greasy again very soon after use. Example 6, from the American Alcolac Corporation, is typical.

	(6) *per cent*
Sodium lauryl sulphate 30%	25·0
Polyethylene glycol 400 distearate	5·0
Magnesium stearate	2·0
Distilled water	68·0
Fatty acid alkanolamide (for thickening)	*q.s.*
Oleyl alcohol (for conditioning)	*q.s.*
Perfume	*q.s.*

The opacifier used in this example to convert clear liquid shampoo into liquid cream shampoo is a glycol distearate. The addition of insoluble magnesium stearate is desirable because the glycol esters tend to redissolve in the shampoo in hot weather, thus leaving the shampoo only hazy instead of creamy.

DeNavarre[101] has discussed the formulation of liquid cream shampoos and notes that the fatty alcohol sulphates are the best foaming agents, and are usually used at concentrations of 25–45 per cent of the finished shampoo. He recommends the use of an opacifier such as magnesium stearate in admixture with a mucilaginous thickener such as a solution of polyvinyl alcohol, methyl cellulose, solubilized methacrylate, alginate, Irish moss or carboxymethyl cellulose at a concentration of about 0·5 per cent. He notes that higher alcohols or alcohol esters can also be used for opacifying purposes, and lanolin and glycol or glyceryl laurate at a level of 1 or 2 per cent will further opacify and thicken the

emulsion. Pantaleoni *et al.*[102] quote a formula based on the above principles:

	(7) *per cent*
Fatty alcohol sulphate paste	30·0
Magnesium stearate	1·0
Polyvinyl alcohol, 10% solution	20·5
Methyl cellulose, 3% solution	9·0
Water	38·0
Lanolin	0·5
Glyceryl monolaurate	1·0

Procedure: Mix the magnesium stearate with the fatty alcohol sulphate, then add the polyvinyl alcohol, methyl cellulose and water, each separately, to make the water phase. Agitate the mixture while heating to 71°C. Bring the oil phase to the same temperature and add the water phase with agitation.

In this class fall most of the shampoos described as containing egg, milk, cream, coconut, and other 'magic' ingredients. The oldest and still the most popular additive is egg. Eggs can, of course, be used to clean the hair; after rinsing (with cold water!) they will have removed a surprising amount of dirt and leave the hair with a smooth, albeit rather greasy, appearance. The action is mainly suspension by the albumen acting as a protective colloid followed by the absorption of the cationic phosphatide lecithin from the egg-yolk. All this is a far cry from the extravagant claims made for minimal amounts of egg-yolk churned up in an excessive amount of detergent, as in most modern 'egg' shampoos. However, if these are made, it is better to avoid the egg-white, which is liable to solidify, and use dried or frozen yolk. The dried material can often be dispersed easily if it is first slurried with a little nonionic detergent or with perfume.

Egg shampoo (Clintwood Chemical Co.)	(8) *per cent*
Sodium lauryl sulphate 30%	20·0
Coconut diethanolamide	5·0
Glycol stearate	1·0
Preservative:	
Methyl *p*-hydroxybenzoate	0·1
Formaldehyde	0·1
Sodium benzoate	0·1
Phosphoric acid to pH 7·5–8·0	*q.s.*
Sodium chloride	0·25
Yellow dye	*q.s.*
Perfume	*q.s.*
Egg, powdered (or whole)	2·0
Water	to 100·0

Solid Cream and Gel Shampoos

Solid cream and gel shampoos are usually intended for use from jars or collapsible tubes, and should therefore be of a suitable consistency to stay in an

open tube without running out of the nozzle. They are traditionally made with sodium lauryl sulphate pastes, or other detergents with a low solubility at room temperature but a higher solubility slightly above room temperature, gelled up with a little sodium stearate or other soap.

	(9) *per cent*
Sodium lauryl sulphate (100%)	20·0
Coconut monoethanolamide	1·0
Propyleneglycol monostearate	2·0
Stearic acid	5·0
Sodium hydroxide	0·75
Water, perfume, colour if desired	to 100·0

		(10) *per cent*
A	Sodium lauryl sulphate (90%)	20·0
	Sodium lauryl ether sulphate (27–30%)	20·0
	Coconut diethanolamide	0·6
	Anhydrous lanolin	0·6
	Sodium chloride	1·2
B	Stearic acid	4·0
C	Sodium hydroxide	2·12
	Colour, perfume, preservative	*q.s.*
	Water	to 100·0

Procedure: Dissolve A and C in the water and heat to 70°C. Melt B and add at the same temperature with agitation. Cool the mixture and add the perfume.

The major trouble with these pastes is the effect of temperature. The consistency depends on a mass of crystals, and in warm weather a large proportion of these may dissolve, making the product runny and translucent. When the product recrystallizes, the new crystals may be large and cause either lumps or fibrous characteristics in the shampoo. Similar considerations apply to all cream shampoos in which the opacity or the consistency depends on the detergents forming a paste of incompletely dissolved material. Since the 1950s cream paste shampoos have receded to a minor position except for some medicated forms in the anti-dandruff field.

Clear gel shampoos gained some popularity in concentrated form, notably in beauty shops, but the interest has largely declined. These may be formulated using detergents alone or in admixture with soaps. By varying the amounts of triethanolamine–coconut soap, triethanolamine lauryl sulphate and sodium lauryl sulphate, preparations of different consistencies and textures may be obtained. By variation in the type and amount of sequestrant the properties of this gel may be modified. Gelation can also be achieved by thickening a conventional clear liquid shampoo with hydroxyalkyl or methyl cellulose ethers or alkanolamides, or by combining anionic and amphoteric surfactants.

Clear gel shampoo	(11) *per cent*
Miranol C2M conc.	15·0
Triethanolamine lauryl sulphate (40%)	25·0
Coconut diethanolamide	10·0
Methocel (hydroxypropylmethyl cellulose)	1·0
Water	to 100·0
Colour, perfume, preservative, etc.	*q.s.*

Oil Shampoos

The development of sulphonated oils (that is, oils which have been treated with sulphuric acid or other sulphonating agents under the influence of heat and then neutralized with alkali) led to their introduction many years ago as hair shampoos. They are effective detergents in that they remove soil and oil from the hair, but they are nearly devoid of foaming properties. For this reason, they never really successfully competed with the more conventional surfactants which were becoming available at the time. However, there has been a tendency to use them in the formulation of 'oil shampoos' in which the head is treated with a mixture of sulphonated oils (mainly castor and olive oil) which is allowed to remain on the head for a short time and then rinsed off. Example 12 is representative (see also Alexander[38]).

	(12) *per cent*
Sulphonated olive oil	16·0
Sulphonated castor oil	16·0
Water	68·0
Colour, perfume	*q.s.*

The modern version of an oil shampoo is a two-phase separable shampoo in which the upper layer consists of an oily material, while the lower layer is a conventional shampoo. The product is shaken before use to give an unstable oil-in-water emulsion.[103,104]

Powder Shampoos

Powder shampoos have fallen out of favour, partly because of the trouble involved in using them, but mainly because they tend to leave the hair in poor condition.

They consist of a detergent powder extended with easily soluble non-hygroscopic substances. Sodium and magnesium lauryl sulphates are suitable materials for such cheap shampoos, and about 3–4 g is sufficient per head.

As diluent, sodium pyrophosphate or bicarbonate or, more generally, sulphate is used (example 13).

	(13) *per cent*
Sodium lauryl sulphate	25
Sarcoside	5
Sodium bicarbonate	10
Sodium sulphate	60

Aerosol Shampoos

Aerosol shampoos are not a special type of formulation but represent an alternative way of applying the product. The only extra condition that such products must satisfy is that they must be stable in the presence of the propellant gas; it is usual to use a clear liquid shampoo of medium viscosity so as to allow easy mixing with the propellant, while maintaining it in an emulsified form long enough for use after shaking. Expensive, and having more drawbacks than advantages, they never achieved much success.

Dry Shampoos

Dry shampoos are powder compositions which allow the hair to be cleaned simply by sprinkling absorbent powder onto the greasy hair, leaving it for about 10 minutes and then brushing it off. Their main attraction is that they do not involve the use of water. There is no fear that the process of shampooing will remove the set, and there is no loss of curl.

However, powder shampoos are not very efficient, because it is mechanically difficult to get the particles of the powder into contact with the grease. It is also difficult to brush the powder out of the hair, with the result that a hasty dry shampoo treatment can leave the hair dirtier than it was before. Consequently these shampoos are useful only for hair that tends to become rapidly weighed down with sebum, for those who have no time to set and dry wet hair and for use in times of acute water shortage.

They consist of a mixture of absorbent materials, such as starch, borax and silicas. A powder composition modified to retain or impart 'bounce' and gloss might be based on the following mixture:[105]

	(14) *per cent*
Insolubilized rice starch (tetramethyl acetylendiurea reaction product)	30
Boric acid	7
Finely divided silica	25
Starch	23
Talc	15
Perfume oil	*q.s.*

Dry shampoos can also be based on solvents such as white spirit, isopropyl alcohol, ethylene dichloride, etc. They are efficient at dissolving the grease, but the main difficulty is to find some effective and aesthetic way of removing the solution from the hair. Another problem is the hazardous nature of most of the good organic solvents—the alcohols, etc., are flammable, and the chlorinated solvents are usually narcotic and sometimes extremely toxic.

An alternative approach has been to combine the two methods and to use a powder as a carrier for the organic solvents, preferably fluorinated hydrocarbons applied from an aerosol dispenser. This mixture gives adequate cleaning and products of this type have achieved limited popularity.

Another formulation, based on powdered chitin as a suspension in a volatile liquid carrier such as ethyl alcohol, has been shown to be efficient in removing sebum.[106]

Conditioning Shampoos

As pointed out by Gerstein,[107] the distinction is not always obvious between what are generally called 'conditioning shampoos' and 'shampoo conditioners', particularly since they are similar in application. However, the former are intended primarily to cleanse and secondarily to improve manageability and promote desired feel and appearance; the latter are mainly designed to enhance untangling of wet hair and improve manageability of both wet and dry hair.

The development of shampoo–conditioners is mainly the result of exploiting the benefits and optimizing the properties of synthetic cationic polymers, of which the efficacy is linked to the characteristics and amount of film deposited on the hair.

Their main drawback, the counterpart of their substantivity, is the excessive build-up on the hair which may occur following successive applications and which may lead to an unexpected behaviour of the hair after other treatments. However, the adsorption of some cationic polymers on hair has been demonstrated to be notably reducible by addition of small amounts of electrolytes (such as sodium chloride) which may also partially desorb the absorbed polymer.[108]

The ways in which conditioners act, as well as the effects obtained, are various; it should always be borne in mind that they involve a number of extremely complex interactions, both among the compounds themselves—which in most cases are statistical mixtures—and with the hair. As a consequence, the adjustment and the control of these effects—stiffening, softening, untangling, combability, body, springback, antistatic, etc.—require a careful and skilled development according to the type of hair concerned and the surfactant system used.

Examples are given below—see also Kass.[100] In example 16, mildness and foaming properties are given by the mixture of ethoxylated nonionics with amphoteric and anionic surfactants. Conditioning properties and thickening are given by cationic cellulose.

Shampoo leaving hair soft and combable, both wet and dry[63]	(15)
	per cent
Sodium lauryl sulphate or lauryl sarcosinate	10·0
Lauric diethanolamide	5·0
Hexylene glycol	3·0
Methyl *p*-hydroxy benzoate	0·1
Boric acid	1·0
Sodium chloride	2·0
Polyethyleneimine-ethylformate polyamide	2·5
Ethyl alcohol	15·0
Water	to 100·0

Mild, thickened shampoo with conditioning properties[109] (16)

	per cent
Coconut amidopropyl-3-dimethylamino betaine	5·4
Sodium lauryl sarcosinate	5·2
Ethoxylated tridecyl alcohol (20 EO)	14·0
Cationic cellulose (Polymer JR: Union Carbide)	0·5
Water	to 100·0

Conditioning clear shampoo giving easy wet combing (Sandoz) (17)

	per cent
Ammonium lauryl ether sulphate	25·00
Cocoamino betaine 31–32%	25·00
*Sandopan TFL conc. 48%	4·20
Adipic acid/dimethylamino hydroxypropyl diethylenetriamine copolymer (Cartaretine F4)	3·33
Citric acid anhydrous	0·98
Water	*q.s.* to 100·0

*Sandoz—CTFA: Amphoteric 7 (sulphoamidobetaine)

One-step shampoo-creme rinse[45] (18)

	per cent
Potassium cocoylhydrolysed protein (Maypon 4C)	25·0
Lauraminopropionic acid (Deriphat 170C)	15·0
Laurylmonoethanolamide	3·0
Stearyldimethylbenzylammonium saccharinate	0·3
Ethanol	3·0
Quaternary polymer of vinyl pyrrolidone/di (lower alkyl) aminoacrylate (Gafquat 755, MW = 1 000 000)	1·0
Colour, perfume	*q.s.*
Water	to 100·0

Shampoo conditioner[110] (19)

	per cent
Polymer JR 30 M (CTFA: Quaternium 19) (MW = 30 000)	1·5
Miranol C2MSF (CTFA: Amphoteric 2) 70%	11·0
Sandopan DTC acid (CTFA: Trideceth-7-carboxylic acid) 90%	15·0
Ethyleneglycol distearate	2·0
Methyl *p*-hydroxybenzoate	0·2
Propyl *p*-hydroxybenzoate	0·05
Protein hydrolysate	0·5
Perfume oil	0·3
Water	to 100·0

Some conditioning shampoos incorporate oil to improve the quality of the deposit on hair: thus a single-phase formula uses 1·5 per cent olive oil, 0·5 per cent extra light mineral oil, together with an amide, an amine oxide, an

amphoteric surfactant, and a quaternary ammonium such as 'tallow' amidopropyl dimethyl hydroxyethylammonium chloride;[105] a two-phase shampoo combines hydrocarbon oil, giving a creamy emulsion top layer, and a mixture of cationic and amphoteric surfactants as a clear aqueous alcoholic lower layer.[111]

Among a number of patented compositions, it may be worth mentioning high-lathering conditioning shampoos that combine tertiary amine oxides, alkyl sulphobetaines, and triethanolamine soaps,[112] and also the use of triethanolamine salts of 'lipoproteins' with anionic and amphoteric surfactants to provide shampoos effective in repairing split ends of hair,[113] which has been identified as a significant problem of young women with long hair.

Baby Shampoos

In baby shampoos the overriding requirement of blandness towards eye, skin and hair (and even towards the digestive tract if they are accidentally ingested) fully warrants some sacrifice in foaming and cleaning performance. Their implicit safety and innocuity explain the increasing favour they encounter among adults, and also contribute to their liberal and frequent—if not daily—use.

Mildness is provided by choosing non-irritating surfactants that produce limited detergency—most commonly amphoteric imidazoline derivatives and the fatty sulphosuccinate esters and amides, which are known to be almost irritation-free and to exhibit anti-irritant properties when associated with laurylsulphate.[16] Imidazolines are usually combined with ethoxylated sorbitan or mannitan esters to give sting-free compositions. This association was the basis of the success achieved by Johnson and Johnson who, in the 1950s, initiated baby shampoos: for 'no more tears', Tween 20 was combined with a complex obtained from tridecyltriethoxysulphate and N-(2-cocoamidoethyl) diethanolamine.[114] It has recently been shown that foam stability may be improved with no loss of mildness by changing the last compound for betaines or sulphobetaines and by increasing the number of ethylene oxide moieties in sodium tridecylether sulphate (to 4·4) and in sorbitan ester (over 20).

A typical composition is given in example 20.[115]

	(20)
	per cent
3-Cocoamidopropyldimethyl betaine 30%	17·1
Tridecylether sulphate salt 4·4 EtO 65%	8·3
Polyoxyethylene (100) sorbitan monolaurate	7·5
Preservatives, perfume, dye	*q.s.*
Water	to 100·0

Generally speaking, a high ethoxyl value is recommended to provide mildness; thus the association of 20 per cent lauryl ether sulphate with 12 moles of oxyethylene and 8 per cent imidazoline—both as 100 per cent active bases—has been claimed to produce an exceptionally low level of ocular irritation while providing good foaming characteristics.[116]

Anti-dandruff and Medicated Shampoos

Any of the types of product described above is suitable as the basis for the preparation of medicated or anti-dandruff shampoos; the most popular are clear liquids and opaque lotions.

Whatever the etiology of the dandruff disease (defined as a chronic, non-inflammatory scaling of the scalp), the problem remains of removing the scurf produced by a cutaneous medium in poor condition; an efficient but mild and non-drying shampoo is required. As dandruff is commonly associated with a marked microbial proliferation it is usually recommended to add a germicide (with particular effect against *Pityrosporum ovale*) as active controlling agent. As the shampoo remains on the scalp and hair for only a very short time, the germicide must be of the substantive type so that it is left behind on the scalp to exercise its action.

Various agents have been used for this purpose, such as quaternary ammonium surfactants, thymol, chlorinated phenols, trichlorocarbanilide, halogenated salicylanilides, 5,7-dichloro 8-hydroxyquinoline,[117] zinc undecylenate, undecylenic acid ethanolamides, polyvinyl pyrrolidone–iodine complex and Captan.[118]

A typical formula is given in example 21.

	(21) *per cent*
Triethanolamine lauryl sulphate	15·0
Lauric diethanolamide or mixture of lauric and myristic diethanolamide	3
Germicide	0·5–10·0
Colour, perfume	*q.s.*
Water	to 100·0

In recent years the greatest developments have been in the derivatives of 2-pyridinethiol-N-oxide; the first to be introduced into a shampoo was the highly insoluble zinc salt, used in the early 1960s at a 2 per cent concentration in the very successful 'Head and Shoulders' shampoo. Its high acceptance and efficiency[119] led to a number of studies and patents concerning the best conditions of formulation and covering the range of compounds of the same family. Attention was particularly focused on substantivity and tolerance. One of the great advantages of this type of substance lies in its great affinity for the hair. The absorption of zinc salt has been shown to reach a maximum at a concentration of about 1 per cent in shampoo,[120] but the nature of the vehicle may notably affect the absorption rate as well as the bactericidal activity. Thus, polyethylene glycol 400 laurate was shown markedly to reinforce activity, but not polyethoxylated lanolin alcohols.[121]

Another interesting observation was the enhancing effect of cationic resins and particularly polyethyleneimine resins (antimicrobial *per se*[122]) on particulate deposition onto the hair, whereby the concentration of zinc pyridinethiol-oxide (ZPTO) may be reduced and efficiency maintained longer.[123] ZPTO has been found to cause severe irritation of the scalp in some cases, and it has been claimed that the conditioning agent stearyl dimethylamine oxide exerts a strong counter-irritant effect when added to sodium lauryl sulphate–ZPTO systems.[124]

With regard to other 2-pyridinethiol-1-oxide salts, the use should be mentioned of the corresponding disulphide which, when combined with metal salts such as $CaCl_2$ and $MgSO_4$, is soluble in water, allowing the formulation of clear products of comparable efficiency.[125]

Among other patented compounds for anti-dandruff shampoos are the following: the chemically related 2-mercapto-quinoxaline-1-oxide,[126] 2-mercapto-quinoline-1-oxide[127] and polyene derivatives related to vitamin A.[128]

Details of other germicidal additives, including soluble and insoluble materials, are given in Chapter 23 (The Hair) and Chapter 35 (Antiseptic Materials).

Acid-balanced Shampoos

Among proposals to minimize damage to the hair and the skin, there should be mentioned a trend to promote shampoos of lower pH, the so-called acid-balanced shampoos. Mild acidity prevents swelling and promotes the tight flattening of scales against the hair shaft, thereby reducing penetration and inducing sheen. It offers favourable conditions for the display and use of conditioning properties of cationics, amine oxides and amphoterics, but is detrimental to foaming and cleansing performance.

Moreover, acidic pH often entails instability for surfactants, which may result in changes of viscosity of shampoo with time. These disadvantages may be overcome either by the use of surfactants unaffected by pH values between 5 and 7—such as ammonium lauryl sulphate and lauryl ether sulphate—or by the development of synergistic associations including amphoterics and nonionics, or the addition of fair amounts of foam boosters. Examples 22 and 23 illustrate acid-balanced shampoos.

	(22) *per cent*
Miranol C2M (Amphoteric 2)	20
Cocamidopropylamine oxide	5
Lauric diethanolamide	2·5
Polyethoxylated lauryl alcohol	8
Lactic acid	*q.s.* to pH 6
Water	to 100

	(23) *per cent*
Ammonium lauryl sulphate	40
Cocamidopropyl betaine	15
Lauric diethanolamide	4
*PPG 5 Ceteth 10 Phosphate	3
Hydrolysed animal protein	1·5
Perfume, preservatives, dyes	*q.s.*
Citric acid	*q.s.* to pH 5·4
Deionized water	to 100

*CTFA name.

SAFETY OF SHAMPOOS

The question of the dermatological safety of shampoos is extremely important. Shampoos need to be safe to the skin and eyes as well as being generally non-toxic. The evaluation of products for dermatological safety is discussed in Chapter 2, while the evaluation of general detergent toxicity is dealt with in Chapter 33. The subject of eye safety will be discussed in detail here.

In the process of shampooing the hair it is not unusual for some of the shampoo to trickle down the face and gain access to the eyes. When the shampoo is diluted adequately this is not usually harmful, but in some cases it has, in fact, been found that contact of any of the undiluted shampoo with the eyeball may (depending upon the type of detergent employed, its concentration and the formulation) involve a very serious hazard and even lead to scarring and opacity of the cornea of the eye.

The first shampoo to be recognized as hazardous to the eyes consisted of a nonionic detergent, described as a polyethylene oxide alkyl-phenol ether in combination with a quaternary ammonium salt, which caused clouding of the cornea and impaired vision. Eckermann and Gessner[129] reported cases of eye damage caused by cosmetics including some egg shampoos; the damage was reversible.

Smyth *et al.*[130] tested the effects of some synthetic surfactants on the eyes of rabbits, any damage to the cornea being observed by staining with fluorescein.

The basic technique of evaluating eye safety is that described by Draize *et al.*[131] In this method a 0·1 ml portion of the preparation under test is instilled into the conjunctival sac of an albino rabbit with the left eye being allowed to serve as a normal control. After a 4 second period of contact, both the treated and control eyes are flushed with 25–30 cm^3 of physiological saline to remove the test solution. Observations for pathological symptoms are made 1 hour after instillation, again after 2 hours, and thence daily for 35 days.

Draize and Kelley[132] examined a number of cationic, anionic and nonionic surface-active agents used in cosmetic preparations, for eye irritation. The 'maximal tolerated concentrations' (Table 24.1) are those that produced no corneal or iris lesions which lasted 7 days.

Martin, Draize and Kelley[133] pointed out in a later publication that a number of detergents are capable of causing anaesthesia of the eye and this permits increased pain levels to be tolerated. If these detergents also damage the eye then this is extremely dangerous. Such materials included polyoxyethylene condensates and fatty acid amine condensates, and formulations containing these compounds must be assessed with extreme care. Numerous variations and modifications of the Draize test have been reported and it is best to examine these in a historical order. The method described in a BIBRA bulletin[134] recommends the original test[135] to be changed from 9 rabbits' eyes with 3 rinsed after 2 seconds, 4 rinsed after 4 seconds and the remainder not rinsed, to 6 rabbits' eyes with none being rinsed.

One of the major difficulties with the test is the variability of the results. This can be overcome to some extent by modifying the scoring system, but this is not completely satisfactory. Weltman *et al.*[136] attempted to overcome this by using large numbers of rabbits, but this is a somewhat lengthy and expensive

Table 24.1 Eye Irritation Studies with Surface-active Agents

Trade name	Chemical designation	Maximal tolerated concentrations of active ingredients (%)
A. CATIONICS		
BTC®	Lauryldimethylbenzylammonium chloride	0·5
Hyamine 1622®	*p*-Diisobutylphenoxyethoxyethyldimethyl-benzylammonium chloride	0·5
Roccal®	Alkyldimethylbenzylammonium chloride	0·5
Isothan Q–15®	Laurylisoquinolinium bromide	0·8
Ethyl Cetab®	Cetylethyldimethylammonium bromide	1·0
Triton X–400®	Stearyldimethylbenzylammonium chloride	1·0
B. ANIONICS		
Nacconol NRSF®	Alkylaryl sulphonate	5·0
Miranol SM®	Capryl imidazoline derivative	10·0
Aerosol OT®	Dioctylester of sodium sulphosuccinic acid	15·0
Duponol WA®	Sodium lauryl sulphate	20·0
Orvus WA®	Sodium lauryl sulphate	20·0
Triton X–200®	Sodium salt of alkylated aryl polyether sulphate	28·0
C. NONIONICS		
Triton X–100®	Alkylated aryl polyether alcohol	5·0
Nonic 218®	Polyethylene glycol *tert*dodecyl thioether	10·0
Alrosol®	Fatty acid amide condensate	10·0
Neutronyx 600®	Aromatic polyglycol ether condensate	15·0
Detergent 1011®	Secondary amide of lauric acid	15·0
Ninol 2012®	Fatty acid alkanolamine condensate	20·0
Span 20®	Sorbitan monolaurate	100·0
Tween 20®	Sorbitan monolaurate polyoxyethylene derivative	100·0
Span 80®	Sorbitan mono-oleate	100·0
Tween 80®	Sorbitan mono-oleate polyoxyethylene derivative	100·0
Arlacel A®	Mannide mono-oleate	100·0

procedure. A special application device was described by Battista and McSweeney[137] and its use results in a reduction of the variability of the results.

Gaunt and Harper[138] pointed out that there is poor correlation between rabbits and man, and they have found that 10 shampoos available to the public with no deleterious effects caused irritation to rabbits. Bonfield and Scala[139] reported similar results on 13 brands of shampoo. Regarding animal species, an interesting study was carried out by Gershbein and McDonald[140] who tested commercial shampoos and surfactants, according to the standard Draize method, on rabbits, guinea-pigs, rats, mice, hamsters, dogs, cats, monkeys, and chickens. In all cases, albino rabbits and mice yielded much higher corneal irritation scores than the other species, while cats, monkeys and chickens exhibited the best resistance to corneal involvement.

The whole subject of the evaluation of eye safety has been reviewed by Beckley,[141] Alexander[142] and more recently in a comprehensive analysis by McDonald and Shadduck[143] who concluded that assessment methods in eye irritation testing are still to be improved. Later, reviewing objective methods for the assessment of eye irritation—that is, slit lamp examination, corneal thickness, intra-ocular pressure, corneal curvature, conjunctival and corneal weight, histological studies—Heywood and James[144] were led to conclude that the eye test system is subject to such wide variations that precise measurements are most unlikely to be achieved. Consequently they consider that the most satisfactory evaluation is provided by the subjective Draize clinical appraisal, supplemented by measurement of corneal thickness and of intra-ocular pressure, for which applanation tonometry[145] seems best suited.[146]

Over a period of time a wide variety of materials has been tested using the rabbit's eye test and for some time it has been realized that, in general, the eye irritancy potential of surface-active agents follows the order of cationics > anionics > nonionics. There are, however, exceptions to this order which suggest that factors other than this classification by chemical nature may be involved, or that there may be a correlation between eye irritation and some more specific properties of these agents. With this in mind, certain physical and chemical properties were studied by Hazleton[147] for correlation with capacity to produce eye injury, as well as potency in such activity.

To confine the survey to general trends, Hazleton made no attempt to review the minimum exposures required to produce injury. In turn, injury was interpreted broadly rather than specifically and included generalized erythema, oedema, necrosis, vascularization of the sclera and/or cornea, and opacity. Also, injury could vary in onset, severity and duration. For quantitative comparison the maximum concentration (percentage of active ingredient in aqueous solution) that would produce only moderate irritation was used, if available. The capacity to induce injury was the irritant potential for a specific material. Potentials of 1–10 per cent were considered as severe irritants, 10–20 per cent as moderate and above 20 per cent as mild.

A good supporting example is that of the imidazoline amphoteric surfactants of 'Miranol' type, which are rather severe irritants *per se* in high concentrations and display super-mildness and anti-irritant properties when neutralized and diluted below 20 per cent w/w.[16,148]

The compounds used in Hazleton's study are given in Table 24.2 and the results of the physical measurements and irritation studies in Table 24.3, and summarized below.

Surface Activity at 10 per cent

Of the materials included in the report, the maximum variation in surface tension of the 1 per cent solution was from 27 to 46 dyne/cm. Determinations were made on the Cenco-duNouy Tensiometer at 25°C. In view of the wide variations in irritant potential there appears to be very little possibility of a correlation between this and surface activity.

pH at 10 per cent

The pH of aqueous solution of the surface-active agent is not necessarily characteristic of the compound, but is influenced by manufacturing process.

Table 24.2 Chemical Nature of Cationics, Anionics and Nonionics

Commercial name or Laboratory No.	per cent active	Chemical nature
CATIONICS		
G–271®	35	*N*-soya-*N*-ethyl morpholinium ethosulphate
Hyamine 1622®	100	Di-isobutyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride
Ceepryn®	100	Cetylpyridinium chloride
Emcol E607®	100	*N*(acyl colamino formyl-methyl) pyridinium chloride
Roccal®	50	Mixture of high-molecular-weight alkyl dimethyl benzyl ammonium chlorides
Hyamine 2389®	50–52	Alkyl (C_9H_{19} to $C_{15}H_{31}$) tolyl methyl trimethyl ammonium chlorides
Isothan Q–15®	20	Lauryl isoquinolinium bromide
ANIONICS		
Duponol WAT®	50	Triethanolamine salt of lauryl sulphate
Ultrawet 60L®	60	Triethanolamine salt of alkyl aryl sulphonate
Armour's 600 KOP Soap®	100	Potassium coconut oil soap
Ivory Soap®	100	
NONIONICS		
Span 20®	100	Sorbitan monolaurate
Span 80®	100	Sorbitan mono-oleate
Tween 20®	100	Polyoxyethylene sorbitan monolaurate
Tween 40®	100	Polyoxyethylene sorbitan monopalmitate
Tween 60®	100	Polyoxyethylene sorbitan monostearate
Tween 65®	100	Polyoxyethylene sorbitan tristearate
Tween 80®	100	Polyoxyethylene sorbitan mono-oleate
G–7569J®	100	Polyoxyethylene sorbitan monolaurate
Myrj 45®	100	Polyoxyethylene monostearate
Myrj 52®	100	Polyoxyethylene monostearate
Brij 30®	100	Polyoxyethylene lauryl ether
Brij 35®	100	Polyoxyethylene lauryl ether
G–2132®	100	Polyoxyethylene lauryl ether
G–3721®	100	Polyoxyethylene 2-butyl octanol
Renex®	100	Polyoxyethylene esters of mixed resin and fatty acids
G–1690®	100	Polyoxyethylene ether of alkyl phenol
G–1790®	100	Polyoxyethylene lanolin condensate
G–1441®	100	Polyoxyethylene sorbitol lanolin derivative

The pH of the various solutions tested was determined on a Beckman Model G pH meter. The range of the pH was from 3·93 to 9·52, with most of the values falling in the range pH 6·0 to 7·0; there appeared to be little correlation between pH and irritancy.

Wetting Power (Draves Method) at 0·1 per cent

Within the group of materials tested, six were moderately good wetting agents with values below 51 seconds, and the balance were 85 or above; there appeared to be very poor correlation between wetting power and irritation.

Table 24.3 Surface-active Agents and their Physical Properties
Wetting power was determined by the Draves method and foam height by the Ross-Miles method

Trade name	pH at 10%	Surface tension at 10% (dyne/cm)	Wetting power at 0·1% (s)	Foam height at 1·0% (mm)	Irritation potential
CATIONICS					
G–271®	7·11	33	>300	217	1
Hyamine 1622®	7·01	36	142	268	1
Ceepryn®	4·79	41	258	240	1
Emcol E607®	3·48	37	300	213	1
Roccal®	7·28	33	234	110	1
Hyamine 2389®	7·30	31	85	292	1
Isothan Q–15®	3·93	34	300	150	1
ANIONICS					
Duponol WAT®	7·11	32	31	273	20
Ultrawet 60L®	7·10	30	10	302	10
Armour's 600 KOP Soap®	9·52	27	>300	375	10
Ivory Soap®					>10
NONIONICS					
Span 20®		28	>300	14	100
Span 80®		30	>300	13	100
Tween 20®	6·81	36	203	173	100
Tween 40®		40	>300	87	100
Tween 60®		43	>300	81	100
Tween 65®		31	>300	27	100
Tween 80®	6·46	40	>300	59	100
G–7596J®		33	203	162	100
Myrj 45®		33	>300	15	100
Myrj 52®		44	>300	26	100
Brij 30®	4·70	28	51	18	20
Brij 35®	6·02	42	174	220	
G–2132®	5·98	28	13	247	20
G–3721®	4·39	27	7	287	<20
Renex®	6·95	39	>300	77	100
G–1690®		31	8	235	<10
G–1790®	5·83	46	>300	23	100

However, among the nonionics there did appear to be some correlation between the wetting properties and irritant potential. None of the group having a value of 174 seconds or longer exhibited irritation either undiluted or in solution. Four of the nonionics had values of 51 seconds or less, and each was rated for irritation at 20 per cent or less. No similar correlation could be established within either the limited anionic or cationic groups studied.

Foaming Power (Ross-Miles Test) at 1·0 per cent
Foam heights for non-injurious undiluted materials ranged from 13 to 220 mm, and even higher for materials with an irritant potential rating of 20 per cent or above. There is thus some evidence that most of the irritant chemicals are good foamers but, fortunately for the formulator, the converse that good foamers are irritants is not true.

Wetting and Foaming
Since it is indicated that there may be some slight correlation between wetting power or foaming power and eye irritation, the combination of these two properties is obviously suggested. The data here suggest that good wetting plus good foaming may be an irritant combination; for example:

	Wetting (s)	*Foaming* (mm)	*Irritant potential* (%)
Alkyl aryl sulphonate	10	302	10·0
G–3721®	7	287	<20·0
G–1690®	8	235	<10·0

That these two properties are not essential to highly irritant material is shown by the following:

	Wetting (s)	*Foaming* (mm)	*Irritant potential* %
Hyamine 1662®	142	268	1·0
G–271®	>300	217	1·0

Hopper *et al.*[149] tested a number of commercial detergents for corneal irritation in rabbits. However, these investigators used solutions of 1 per cent concentration only, that is, very much weaker than those which might enter the eye during shampooing. Nevertheless, according to these investigators, butyl diphenyl sodium sulphonate, dodecyl benzene sodium sulphonate and decyl benzene sodium sulphonate produced severe inflammation of the cornea.

Bellows and Gutman[150] found solutions containing 1 per cent or less of Aerosol OS (sodium isopropyl naphthalene sulphonate) harmless to the conjunctiva and cornea but 2 per cent solutions produced inflammation. In concluding the above brief discussion of the potential hazards of detergent solutions to the eyes, attention should be drawn to the warning of the Division of Pharmacology of the US Food and Drug Administration that mixtures of surface-active agents may be more irritating to the eyes than could be predicted from the ocular toxicity of the individual components. However, the reverse is

also true[16] and a number of compounds have been shown to reduce considerably the damaging effects of irritant surfactants when adequately combined, for example N-hydroxyethylacetamide with sodium lauryl sulphate.

The only way to ensure the safety of a given shampoo formulation is to have the finished formulation, including any antiseptics, perfumes, etc., tested for corneal irritation by instillation into the eye of animals in the way recommended for the Draize tests. Most shampoos on the market today are irritant to the eyes, in the sense that they produce stinging or even acute pain if the undiluted shampoo enters the eye; most of them produce some inflammation of the eyelid. While this is undesirable, it can at least be considered as normal, and a hazard not confined to shampoos—alcohol, for instance, would have the same effect.

What must be guarded against is the use of materials which, even if misused grossly, could produce corneal opacity of any sustained duration.

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Chapter Twenty-five

Hair Setting Lotions, Sprays and Dressings

Use and Purpose of Hair Dressings

The main aims of hair dressings, whether they are for men or women, are to improve the control and manageability of hair, to impart some lustre, and to maintain a hairstyle in spite of the movement involved in daily activities and despite the various environmental conditions to which hair is submitted (wind, humidity, dryness, cold, heat, sun, etc.).

The relative importance of these factors varies from one country to another, from age to age, and according to the state of the hair. It also differs notably between male and female users: men generally consider adequate control as the prime requisite for a hair dressing, with gloss as secondary, and as such men's products have been classically based on the use of oleaginous materials. Women first look for products that give a pleasing appearance to the hair, but at the same time they require good hold; they do not want products which render hair heavy and which tend to make it lank or greasy.

Because of the different demands of men and women, and in spite of the fact that the evolution of hair styles and a common desire for a 'natural look' have brought them closer during the last few years, hair dressing products will be considered separately in this chapter according to the sex for which they are designed.

The trend in women's fashions for softer and freer styles and the increasing use of the brushing technique have led to an increase in the demand for products that enhance disentangling and a greater need for products that protect, strengthen and/or improve the condition of the hair; this has occurred at the same time as the extraordinary development of conditioners. Though there may exist some overlap for some new compounds intended to impart set, manageability and sheen, products which more specifically treat the condition of hair will be dealt with in the next chapter, 'Hair Tonics and Conditioners'. The present chapter discusses products that are intended to set and maintain the hair style.

WOMEN'S HAIR DRESSINGS

Setting Lotions

Setting lotions are intended to strengthen and maintain for an extended period a temporary deformation imparted by waving. An important characteristic of

these lotions is that they are applied to wet hair. They differ from permanent waving compositions in that they do not affect in general the internal structure of the hair; although a number of hydrogen bonds and ionic sites in the hair may be involved, the lotions mainly provide a mechanical means of holding the set and a means of restraining water uptake. The principle is to deposit on the shampooed hair a solution of a polymeric material which after setting and drying leaves a flexible film that ensures the cohesiveness and hold of the hair style and protects it from the effects of humidity.

The oldest products of this type were simple aqueous or hydroalcoholic solutions of natural polymers, including tragacanth, karaya gum, arabic gum, shellac, etc. The lotions based on these mucilages are now obsolete. They work by sticking the hairs together and present major disadvantages; they yield dull, brittle films, which crumble into dust and become sticky in humid air because they are very hygroscopic.

They have been replaced by lotions based on synthetic polymers which are soluble in hydroalcoholic solutions. The first resin to be used was polyvinylpyrrolidone (PVP) which, owing to its solubility in many solvents including water, and to its non-ionic character, offered a wide range of use.

Two product types have appeared: the clear lotion and the aerated gel. Both product types represent a considerable advance over the older gum-based products; they form clear, non-greasy and quite glossy films while considerably improving the set retention of the hair. Their mode of action is somewhat different from that of the gum-based products in that, instead of just sticking the hair together, they tend to form a plastic sheath round each individual hair so that the setting effect is not completely lost on combing out the hair. Formulating a setting lotion, though simple in principle, is complex in reality. The film formed on the hair has to withstand, without breaking or flaking, repetitive combing and brushing while maintaining good adhesion in order to preserve the set.

The setting product should be compatible with the wetness of the hair at the time of application and be waterproof after drying, while remaining flexible. It should be easily shampooed out, and should not be sticky or 'cardboard-like'. The flexibility of the film and its resilience to extensive handling are imparted by adding amounts of plasticizers.

Generally speaking, a setting lotion contains, in a hydroalcoholic solution, film-forming polymers, plasticizers for these polymers, perfumes, colorants, and additives to enhance sheen, softness and disentangling. Example 1 gives a clear lotion, and example 2 an aerated gel.

	(1) *per cent*	(2) *per cent*
PVP K.30	4·0	0·8
Polyethyleneglycol	2·0	1·5
Carboxyvinyl polymer	—	1·5
Diisopropanolamine or triethanolamine	—	1·5
Alcohol	40·0	—
Water	54·0	94·7
Colour, perfume	*q.s.*	*q.s.*

PVP is too hygroscopic, however, and has been replaced by vinylpyrrolidone–vinyl acetate copolymers; the higher the proportion of vinyl acetate, the higher the resistance to water, but the hardness of the film increases concurrently and the addition of plasticizer is necessary. The ratios of vinylpyrrolidone to vinyl acetate and of water to alcohol, and the amount of plasticizer, are chosen in relation to the desired physical properties of the film. Plasticizers are polyethyleneglycols, lanolin derivatives, silicones, esters, and polysiloxanes, which modify the hardness and flexibility of films as well as the water resistance.

	(3) *per cent*
PVP–VA (60:40)	2·5
Alcohol	50·0
PEG 40 castor oil	0·3
Water	to 100·0
Perfume	*q.s.*

A number of patents have appeared describing the use of a wide range of water-soluble or alcohol-soluble polymers for use in hair setting. The majority of these materials have been claimed for use in aerosol sprays; they are used in lower concentrations in setting lotions. Examples are resins with carboxylic groups such as copolymers of vinyl acetate and crotonic acid[1,2] or copolymers of alkylvinylethers[3,4] or vinylesters[5,6] and maleic acid hemiesters. Representative commercial resins are Resyn 28-1310, Resyn 28-2930 and Luviset CE 5055 for the former, Gantrez ES 225 and ES 425 for the latter. Typical formulae are given in examples 4–6.

	(4) *per cent*
Resyn 28-2930	3·00
2-Amino-2-methylpropanol (AMP)	0·25
Carbowax 1000 (PEG 20)	0·80
Ethanol	47·95
Distilled water	48·00
Perfume	*q.s.*

	(5) *per cent*
Luviset CE 5055	2·50
AMP (80% neutralization)	0·21
Ethanol or Isopropanol	50·00
Distilled water	47·29
Perfume	*q.s.*

	(6) *per cent*
Gantrez ES.255 or ES.425	4·2
Alcohol	21·2
Water	74·0
PEG.40 castor oil	0·3
2-Amino-2-methyl-1,3-propanediol (AMPD)	0·3
Perfume	*q.s.*

More recently, sulphonated polystyrenes, which are strongly anionic polymers, have been proposed.[7]

The addition to the setting lotions of various ingredients (quaternary ammonium compounds, proteins, panthenol, etc.) that are not rinsed off, which more or less blend with the film and interact during drying and heating, yields 'body' and lubrication. The advent of cationic polymers was revolutionary for hair dressings; these compounds are substantive to keratin and when added to setting lotions they improve the appearance of the hair and promote disentangling. Such products are copolymers of quaternized dialkylaminoalkylacrylate and polyvinylpyrrolidone[8,9] such as Gafquat 755, as well as Polymer JR resins which are esters of hydroxyethylcellulose and 2-hydroxypropyltrimethylammonium chloride; they permit the formulation of setting strengtheners–conditioners which provide at the same time hold, manageability and sheen. The following formula has been cited:

Lotion with holding and grooming properties[10]	(7) *per cent*
Polymer JR 400	0·30
Carbowax 400	4·00
Diisopropyl adipate	1·00
Dipropyleneglycol	0·70
Benzethonium chloride	0·10
Perfume	0·40
Colour	0·37
Ethanol	50·00
Water	43·13

Polymers with dipolar aminimide[11] and betaine-type groups[12] have also been claimed as effective setting–conditioning compounds. Polyamide epichlorhydrin resin added to PVP has been said to impart stronger resistance to moisture attack.[13,14] Other additives specified in patents are finely divided silica or aluminium oxide,[15] silicates[16] and perfluorinated polymers, the hydrophobic and oleophobic properties of which are used to render styling longer lasting.[17–21]

Heated Curlers and Blow Drying

The major difficulty with the use of setting lotions is that, since the products contain water, the hair has to be dried after use. This problem can be avoided by the use of aerosol sprays, but this introduces its own problems.

One of the earliest methods of introducing waves into hair was the use of a heated comb or tongs. Such treatments gave the hair a very good set but, since it was easy to overheat the hair, were often damaging. The heat applied was such that the hair was modified chemically and this accounted both for the good set and for much of the damage. For further details on the theory of setting see Chapter 28.

The possibility of using a controlled heating system, which would not change the hair chemically but would only affect the water set of the hair, has been considered for some time and a number of different types of heated curlers have appeared. The majority of these are heated electrically, and are usually fitted

with some form of control device to prevent overheating. However, many of the models currently available are somewhat cumbersome in use and are rather expensive.

The trend of fashion towards softer, freer, loosely moving hair styles found expression in the brushing technique which combines mechanical action for shaping the hair with thermal blowing for setting. The desire and skill of women to style their hair themselves induced the development of an array of appropriate devices (blow combs and brushes). These new techniques have also required the availability of specific products—in the field of conditioners—to promote disentangling and manageability of hair when blow drying.

The following formula has been given:[22]

	(8) *per cent*
Quaternized VP–dimethyl amino ethyl methacrylate (CTFA—Quaternium 23)	3·50
Castor oil amidopropyldimethylamine	0·40
Citric acid monohydrate	0·10
Perfume	0·20
Hydrolysed animal protein	1·00
2-Bromo-2-nitro-1,3-propanediol	0·10
Water, dye	to 100·0

Procedure: Combine all ingredients except perfume, heat to 40°C with stirring until dissolved. Add perfume to batch at 40°C. Stir and cool batch to 30°C, add water to make up evaporation loss, and fill at 30°C.

A novel proposal in this line is a colloidal aqueous suspension of fibrillatable polytetrafluorethylene resin particles, said to generate on brushing a random network of microscopic fibres which holds the hair in a natural set.[23]

Hair Sprays

Hair sprays meet the requirement for a quick-dry preparation which imparts just sufficient rigidity to the set to keep it in place and control loose ends during the day, while not detracting from the natural sheen of the hair.

The early sprays were not entirely satisfactory because the spray units gave little control over the spread of the product. The advent of the pressurized container changed the situation radically. The fine spray and easy control obtained from pressurized packs made uniform coverage of the hair possible. As a consequence, the popularity of hair setting sprays of all kinds experienced a phenomenal increase and they were developed until they became the most important hair setting product, if not indeed the most important hair product. However, the success reached its peak around 1970 when the sales started to level off and decline with the growing fashion among young people for soft and free hair.

A further marked decline was seen in 1975 when Rowland and Molina proposed that the amount of stratospheric ozone (a shield against UV radiation) was progressively reduced by the action of the chlorinated propellants released from aerosols. A widely-publicized campaign against the use of these propellants culminated in 1979 with the banning by the US Food and Drug Administration

of the chlorofluorocarbons currently used in aerosols. Most European countries have not followed the FDA recommendation, particularly because the theory about the depletion of ozone has not yet been confirmed and is the subject of controversy amongst scientists. However, the trend in European countries is setting towards a limitation of the concentration of fluorocarbons. These battles and threats against propellants have compelled investigators to consider new formulations and technology for aerosols and to find acceptable alternatives.

The objective of a hair spray (when combing is finished and a hair style established) is to deposit onto the dry hair an invisible film to protect it against all external agents that are likely to change its desirable features. Requirements for such a product are stringent and numerous:

(a) The spray must be very fine.

(b) The force of the spray should be gentle; it should not be wet, which means that the characteristics of the spray should allow it to be of a fineness not to wet the hair but also not to dry before reaching the hair.

(c) It should spread over a wide area in a short period and dry quickly.

(d) The film should be relatively flexible to follow movement of the hair without breaking.

(e) The film should be substantive to the hair but should be easy to eliminate without becoming powdery under a mere brushing. Any accumulation would render hair heavy and dirty.

(f) It should be soluble enough to be shampooed off easily.

(g) The film should not be sticky nor tacky to the touch and should hold the hair, but at the same time leave it free to move.

A good hair spray should be a compromise between adhesion and elimination, tightness and lightness. Building a hair spray is a matter of careful adjustment depending on technological qualities both of the spraying system and of the formulation. The new restraints imposed for propellants have further increased the difficulties of such an adjustment.

Hair Spray Resins

The earliest material used in hair lacquers was shellac, a natural resin composed of polyhydroxy acids and esters. Alcoholic solutions (8–15 per cent) were sprayed onto the hair out of soft plastic containers. Shellac produced hard and insoluble films. To make the shellac more water-soluble and therefore able to be shampooed away, an alkali such as borax or ammonia solution was used to form a salt. The following formula and procedure have been quoted:[24]

	(9)
	parts by wt
Shellac (bleached, dewaxed)	3·5
Ammonium hydroxide (28%)	0·5
Water	32·0

Procedure: Add the ammonia and about half the water to the shellac and warm with constant stirring until solution is obtained. Add the rest of the water (the

solution should be clear; if it is not, more ammonia should be added); filter and cool. This solubilized shellac may then be diluted for use.

As early as 1948 a hairdresser thought of applying the aerosol technique to an alcoholic solution of shellac by adding to the solution chlorofluorocarbon propellants 11 and 12, and by packaging it in an aerosol can to obtain a spray that was much improved compared with the current sprays.

The use of anhydrous alcohol to prevent hydrolysis of propellants and the use of purified shellac helped in the formulation of aerosol sprays with good holding properties,[25] but the films formed after drying were hard, brittle and sticky, and rendered the hair rather harsh; furthermore they were so insoluble in water that they could not be shampooed off. The addition of lanolin, isopropyl myristate and other plasticizers to soften the film generally had the effect of making the film greasy. The first significant improvement in formulating hair sprays was achieved in 1953 with the use of a polyvinylpyrrolidone, a synthetic resin that is soluble in water and easily shampooed off. It shows some substantivity for keratin and yields clear and flexible films which, however, are deficient in hardness and therefore in holding power. Its main drawback is its hygroscopicity, which tends to make the film rather tacky in a highly humid atmosphere. A remedy is to add some hydrophobic materials or a resin less sensitive to moisture. PVP K.30 (MW 40 000) is now the most commonly used grade.

At about the same time the dimethylhydantoin formaldehyde resin (DMHF) was proposed; it yields a film of low hygroscopicity but which has a low holding power and is easily powdered.

In order to overcome the hygroscopicity of the PVP films, copolymer resins of vinylpyrrolidone and vinyl acetate (PVP–VA) were developed. They provide good clear films with good hair-holding properties. As mentioned above, the higher the ratio of vinyl acetate, the less susceptible to atmospheric humidity and the harder the film, but consequently it is less easily shampooed off. The copolymers used contain between 30 and 70 per cent PVP. These resins became very popular and nearly superseded PVP, but their use has somewhat declined with the development of resins with free carboxylic groups which give harder films and better adhesion, with a higher moisture resistance.

The advance brought about by carboxylated resins lies, above all, in the flexibility they provide in their neutralization, allowing the building of a variety of formulations adapted to multiple-hold requirements. By controlling the degree of neutralization of the free acid groups, the hardness, solubility and hygroscopicity of the films may be closely monitored. The earliest polymer of this type was Dicrylan 325, which is a polymer of acrylic acid and esters. But the most favoured resin was the copolymer of vinyl acetate and crotonic acid with the brand name Resyn 28-1310. To solubilize it in alcohol, a hydroxylated amine should first be added, such as 2-amino-2-methyl-1,3-propanediol (AMPD) to partially neutralize the acidic groups. Another resin, derived from 28-1310, was proposed later; it offered the advantage of being soluble in a hydroalcoholic medium without previous neutralization. This is Resyn 28-2930, which is a terpolymer of vinylacetate (75 per cent), crotonic acid (10 per cent) and vinyl pivalate (15 per cent). This resin, in addition to improved solubility, brings a better curl-retention under varying humidity.

More recently, another copolymer of vinyl acetate and crotonic acid called Luviset CE 5055 has been proposed; its characteristic is a lack of odour which may be advantageous compared with some earlier compounds which could involve problems of perfuming. Another category of carboxylic polymers developed for hair sprays is the Gantrez series, which are copolymers of methylvinylether and alcoholized maleic anhydride, and particularly the ethyl and butyl hemiesters called ES 225 and ES 425; they are poorly soluble in water even when neutralized, and they yield films with firm hold.

Other marketed resins include a terpolymer of polyvinylpyrrolidone–methylmethacrylate–methacrylic acid, sold under the name 'Stepanhold R-1', the VEM resin which is a carboxylic acrylic resin, and a complex resin called Quadramer which results from the copolymerization of four different monomers (acrylamide–N-t-butyl acrylamid–acrylic acid–vinylpyrrolidone) and which contains fewer free acid groups than the others (about half as many as Resyn 28-2930 and seven times less than Gantrez ES 425).

The preferred neutralizers for these carboxylic resins are 2-amino-2-methyl propanol (AMP), the above cited AMPD, and triisopropanolamine (TIPA). In addition to controlling solubility and hardness, the neutralizers act as internal plasticizers, thus preventing the film from scaling and imparting to it homogeneity and softness; they also help to compensate for a possible sensitivity to non-volatile additives in the preparation.[26]

Another resin, launched later, is Amphomer, an amphoteric acrylic resin which possesses both carboxylic and cationic groups; it is described as offering, through a three-dimensional matrix, a higher hold than conventional carboxylic resins, and thus it can be used in lower concentration to provide a soft and natural hold.[26]

Many more than 100 patents have been published since 1966 which claim an array of polymers to be used in hair sprays. Only the most notable commercial proposals have been cited above. In addition to resins, formulation of hair sprays requires the use of plasticizers, softening agents, glossing agents, perfumes, solvents, and propellants. Plasticizers are mainly aimed at making the film more flexible, at modifying the adhesion and preventing brittleness. Introduced at an average of 5 per cent compared with the weight of the resin, they may be derivatives of lanolin, silicones (which also exert a lubricating effect and bring sheen), esters (isopropyl myristate, diacid esters), polyols (glycerol, polyglycols) and glycol ethers. Other much used additives are protein hydrolysates.[27–29] Polysiloxanes[30] and more recently fluorinated polymers[31] have also been suggested.

Solvents have an important role in the spreading of the film, the rate of drying and the compatibility of the ingredients. The best of all is ethanol, which is highly taxed in Europe, so that for reasons of cost either the alcohol phase is reduced (and thus the resin concentration increased) or isopropanol is substituted where this is permitted (as in Germany and Switzerland).

The common ratio between Freon propellant and solution for a spray is 40–70 propellant to 60–30 solution.

Perfumes should be unobtrusive and just covering because they are enhanced by spraying.

Typical formulae are given in examples 10–13.

	(10) *per cent*
PVP K.30	1·25
Lanolin	0·20
Silicone	0·10
Perfume	0·20
Alcohol	28·25
Propellants 12/11 (35:65)	70·00

	(11) *per cent*
PVP–VA 70/30	1·50
Lanolin derivative	0·05
Silicone	0·10
Isopropyl myristate	0·05
Perfume	0·10
Alcohol	28·20
Propellants 12/11 (35:65)	70·00

Source: Baudelin[31]

	(12) *per cent*
Resyn 28-1310	3·45
AMP	0·38
Lanolin derivative	0·10
Isopropyl myristate	0·40
Dipropyleneglycol	0·10
Perfume	0.10
Ethanol	95·57
Concentrate	35·00
Propellants 11/12 (65:35)	65·00

	(13) *per cent*
Amphomer	0·75
AMP	0·123
Perfume	0·075
Ethanol	39·052
Propellants 12/11 (40:60)	60·00

New Spraying Systems

Fluorinated propellants may be considered the ideal means of dispensing minute droplets onto and into the hair, thereby inducing a good hold of the hair by welding individual hairs together through quick drying.

The FDA ban on chlorofluorocarbons created critical issues from a technological point of view. Three alternatives were developed: hydrocarbon aerosols, pump sprays, and carbon dioxide aerosols.

Pumps. In addition to the price, which is about two or three times higher than that of an aerosol, pumps are encumbered with a number of disadvantages such as a spray that is too wet, clogging, leakage, manual dependence, which render them unsuitable for dispensing a spray of quality.

Carbon Dioxide. The main problem with the use of this propellant is the wetting effect of the spray dispensed. Essentially it is a technological issue since it requires extremely small holes at the valve together with a device to prevent clogging.

Hydrocarbons. As liquefiable and compressible gases, propellants which came forward to replace fluorocarbons were mixtures of propane, butane and isobutane. However, comparatively, they exhibit a number of drawbacks:

(i) They are not such good solvents for components of sprays, which means that the ratio of propellant has to be reduced and other solvents have to be introduced, such as methylene chloride and water.
(ii) They are inflammable, which demands the use of special valves[32] to limit the rate of delivery of the product and means increasing the relative amount of methylene chloride and water to cut down flammability.
(iii) Sprays are more wetting because they carry more solvent, which necessitates the incorporation of break-up spray actuators and an additional gas inlet to obtain a better spray pattern and finer droplets for fast drying.

Moreover, these changes in the spray device and the ratios between propellants and solvents entail their own drawbacks and incompatibilities. It is extremely difficult with these new systems to regain the quality of sprays propelled by fluorocarbons.

Among the proposed alternatives to fluorocarbons it is also worth noting dimethyloxide (dimethyl ether) which is, apparently, comparable with regard to toxicity and flame propagation when it is adequately formulated.[33] Aerosol products containing dimethyl ether are sold in several countries.

The use of alternative spraying systems is discussed further in Chapter 40.

A number of resins cannot be adjusted to these new systems of dispensing; however, at least PVP–VA, PVP K.30, Gantrez ES, Amphomer, Stepanhold, Luviset, and Resyns 28-2930 and 28-1310 can be formulated according to the three systems. Owing to its higher solubility in a hydroalcoholic medium, Resyn 28-2930 is more adaptable than Resyn 28-1310 in the new types of hair spray. Hard resins such as Gantrez and Amphomer allow the concentration of film-forming agent to be reduced and give less sticky and less tacky films, which can be more easily eliminated and which leave the hair softer.

Typical formulations are given in examples 14 and 15,[32] 16 and 17[34] and 18.[35] The solvent in examples 14 and 16 is anhydrous ethanol, or ethanol/water (90:10), or ethanol/methylene chloride (80:20). It should be noted that each propellant system requires specific adjustment of perfume.

	(14)
	per cent
Gantrez ES 225 or ES 425	4·00
AMP	0·08
Polyethoxylated (75 EO) lanolin	0·10
Perfume oil	0·10
Solvents	75·72
Isobutane/propane (90:10)	20·00

Concentrate for carbon dioxide	(15) *per cent*
Gantrez ES 225 or ES 425	8·00
AMP	0·40
Dioctyl sebacate	0·50
Perfume	0·10
Ethanol	91·00

	(16) *per cent*
PVP–VA	4·00
Benzyl alcohol	0·10
*Dimethicone copolyol	0·05
Perfume	0·10
Solvents	75·75
Isobutane/propane (90:10)	20·00

*CTFA; polymer of dimethylsiloxane with polyoxyethylene and/or polyoxypropylene side-chains.

	(17) *per cent*
Resyn 28-2930	2·25
AMP	0·18
*Dimethicone copolyol	0·12
Perfume	0·10
Methylene chloride	20·00
Ethanol	72·85
Carbon dioxide	4·50

*CTFA; polymer of dimethylsiloxane with polyoxyethylene and/or polyoxypropylene side-chains.

	(18) *per cent*
Resyn 28-2930	1·50
AMPD	0·38
Alcohol-soluble lanolin	0·90
Isopropyl myristate	0·40
Dipropyleneglycol	0·10
Perfume oil	0·35
Ethanol	96·37
Concentrate	75
Isobutane/propane (90:10)	25

Evaluation of Hair Sprays

The great number of resins and formulations used entails the development of techniques for their evaluation and selection. The following properties need to be measured.

(a) for the film, *in vitro:* hardness, clarity, stickiness, tackiness, flaking, gloss, solubility, ability to be shampooed off, moisture uptake;
(b) on hair: hold, ease of combing (softness, disentangling), powdering, sheen, stickiness, tackiness, harshness.

Procedures have been described for measuring the more important properties[36,37] as follows:

Hardness	Walker Steel Swinging Beam Apparatus or Sward Hardness Rocker
Clarity	Visual assessment
Curl retention	Curl height determined under controlled humidity conditions
Moisture uptake	Weight gain under different controlled humidity conditions

A schedule[38] for the evaluation of hair sprays at a number of important development stages is given in Table 25.1

Table 25.1 Tests to Evaluate Hair Sprays[38]

Purpose	Test
Screening of new resin	Hardness Tackiness and stickiness Switch test to evaluate affinity for hair
Evaluation of modified propellant and solvent systems	Compatibility in transparent glass aerosol Blow-about Headspace pressure Spray pattern
Evaluation of new components e.g. valves and actuators	Spray pattern Cone angle
New formulae	Spray on glass plates and hair pieces Curl-retention Salon and home user tests
Routine assessment	Spray pattern Blow-about Curl-retention Plate testing to determine tack and moisture resistance

Another important factor to be considered concerning non-fluorinated propellants is the necessity to comply with official flammability standards. Two techniques are commonly used: the flame extension test and the closed drum test.

A review of the recent methods for assessment of aerosols (flammability, particle size, corrosion, conservation and spray pattern) is given by Whyte.[39]

Toxicity of Hair Sprays

The question of potential toxicity of sprays has given rise to numerous studies and kept many controversies alive, mainly linked to particular conditions of

exposure and new toxicological risks due to dispensing as an aerosol. Three important issues were successively raised:

The toxicity of the resins *per se*
The size of the sprayed particles in relation to the potential penetration by inhalation
The toxicity of propellants

The first doubt against resins was raised in 1943 when Schwartz[40] drew attention to the fact that, when certain resins were substituted for shellac, cases of dermatitis were noted. These resins contained maleic anhydride. Patch tests confirmed that sprays containing the resins were the cause of dermatitis which was apparently due to sensitization (rather than to primary irritation) caused by a residual monomer. Since then, reactions to sprays based on synthetic resins have been extremely rare. However, before any new resin is incorporated in a hair spray, it should be tested for both primary irritation and sensitization.

A major dispute started in 1960 about the potential hazard of inhaling particles of resin emitted by a spray. It was initiated by the report of two cases of thesaurosis ascribed to hair sprays, and by the statement by Bergmann *et al.* that the inhalation of solid PVP formulation could induce the formation of foreign-body granulomatous inflammation in the lungs.[41] These results, supported by others,[42–44] led to a number of works—of which 70 were published mainly between 1962 and 1966—trying to demonstrate whether there is a correlation between thesaurosis and hairsprays.[45] Cambridge has given a very good review on these studies.[46]

The analysis of clinical findings suggests that the quoted cases could be due to an abuse, over a long period, of sprays.[47–49] The cause of the observed affections could not be convincingly established. Epidemiological studies dealt with two small samples of population of high exposure level (hairdressers, cosmetologists) to provide useful data.[47,50–56] Experimental inhalation studies carried out on various animal species by numerous authors and under multiple conditions have failed to demonstrate that prolonged exposure to hair spray aerosol could cause granuloma.[57–60] Even under extreme exposure conditions involving deposition of resin in tissues, it has not been possible to provoke pulmonary lesions.[61]

Brunner *et al.*[62] submitted animals to large exposure of aerosols based on copolymers PVP–VA, VA–crotonic acid and vinyl alkyl ether–maleic ester; they concluded that it was impossible to repeat the 'syndrome of granulomatosis' as alleged in human cases. Kinkel and Eder[63] failed to find evidence of thesaurosis in the monkey, the rabbit or the hamster when submitted to excessive dosage for 70 to 100 days; they noted that inhaled PVP–VA resins were eliminated from the lungs within five days by phagocytosis. In another study carried out on guinea pigs which were exposed for a year to repeated sprays of an aerosol dispensing particles of about 1 μm size, Cambridge[46] could not evince any histological alteration of the pulmonary tract.

From these investigations, it appears that the likely risk of thesaurosis by aerosol sprays is low if not nil. However, it does not preclude the risk, by inhalation, of exciting or even enhancing pre-existing disturbances, particularly in cases of allergic background;[64,65] therefore, taking into account the large surface area of the lungs (25 times that of the skin), it appears highly necessary to

include tests of toxicity by inhalation in the evaluation of safety of aerosol hair sprays. A good review on inhalation testing, including preliminary screening methods, the precautions to be taken as well as the criteria used to assess toxicity, is given by Wells.[66] An important factor to consider in trying to reduce a potential ill-effect is the particle size distribution of the spray;[67] it is commonly admitted that particles above 10 μm are unlikely to reach the pulmonary tract.[46,69] If the particles have a low probability of penetrating, there is little risk that a particular toxicity will appear after inhalation.

A number of devices allow assessment of the portion of the spray said to be 'respirable', that is, having a high risk of penetrating into the lungs.

In the early 1970s, another cause for concern arose when propellants were believed to be responsible for cardiac attacks following the use of aerosol bronchodilators.[70,71] Since then propellants, on their own or in formulated products, have been subjected to thorough toxicological studies.[72–75] Although no signs of alteration were observed in the lungs,[76–78] it appeared that chlorofluorinated hydrocarbons, at very high dosage, could have untoward effects, notably cardiac arrhythmia. However, in view of the quantities concerned, it may be considered that their use in aerosol sprays does not offer any risk, even under extreme conditions as experienced in a salon.[79,80] Potential adverse effects of alternative propellants were also studied closely, both individually and in mixtures.[81–83] Potentially beneficial (detoxifying) interactions of ethanol or isopropanol with methylene chloride and hydrocarbon propellants have been noted.[84]

MEN'S HAIR DRESSINGS

Hair dressings are used by men firstly to keep their hair in order and secondly to enhance its lustre. Adequate control of the hair, so important for men's grooming, requires two properties from a product—initial setting and long-term control.

The initial set requires a temporary softening of the hair, and for this there is no better ingredient than water. Water exerts a reversible plasticizing effect on hair which allows the early morning tousle to be brushed into shape, but this effect is only transient and disappears when water evaporates. It can be helped to remain longer by adding so-called moisturizing agents which fix water, thereby protecting the hair against drying. However, these do not provide durable control of the hair.

Alternatively, the hair may be loaded with oil or grease to secure the initial set. This method has the disadvantage that much more oil is needed to get the hair in order than is needed to maintain the set during the day. Once distributed over the hair, oil helps the comb to slide, but initially the oil spreads badly and does not plasticize the hair, so that combing is rather difficult. Because of this, many users of solid brilliantines and similar products wet their hair before applying the dressing.

Another approach is to apply a mixture of oil and water—such as an emulsion—so that first water is partially absorbed by the hair, facilitating combing, control and the setting of hair, and the style is then maintained by the

film of oil left on the hair shaft after the water has evaporated. But this requires that the emulsion deposits a continuous film when applied, in order to reduce efficiently the loss of bound water. Oil is enough to ensure the control throughout the day. Adequately chosen, it yields desirable sheen, provides reasonable fixative action, lubricates and protects the hair.

Gum-based products have become less popular because their effect is destroyed when the hair is combed, owing to flaking off of the gum film.

For these reasons, most of the popular hairdressings consist of combinations of oil and water in various forms or, for the less sophisticated market, simple presentations of oil or grease.

Formulation

Initially, vegetable and animal oils were used but, because of their susceptibility to oxidation, they have been replaced by mineral oils which are colourless, odourless, stable and available in a wide range of viscosities. Since antioxidants are now available to overcome rancidity, vegetable and animal oils, the constitution of which is nearer to human sebum, have regained some favour; they are generally thought to have a less greasy feel. Those most commonly used are olive, sesame, peanut, almond, apricot, avocado, peach kernel, and sunflower seed oils. The greater the viscosity of the oil, the better the grooming properties but the more difficult it is to spread the oil thinly and uniformly. The mixture of oils should be carefully chosen and dosed according to the qualities of adhesion, spreading, hold, sheen and combability desired.

Deodorized kerosene is sometimes added to improve spreading. Other main ingredients used to obtain good grooming properties are film-formers such as resins (PVP and copolymers), rosins, and various waxes because of their adhesive and fixative effects, together with substances intended to enhance compatibility and to produce emollience, lubricity, pleasant feel and sheen; such compounds are lanolin and its derivatives (esters, acids, alcohols, acetylated derivatives),[85,86] glycerides, fatty alcohols (cetyl, oleyl, isostearyl), ethoxylated and propoxylated fatty alcohols or esters, fatty alcohol lactates, and dialkyl sebacates and adipates. More conditioning attributes are imparted by fatty acidamides, protein derivatives and cationic compounds.

Some hairdressing compositions described as 'hair foods' also contain vitamins, lecithins and other 'natural' ingredients, so that they should be considered more as hair tonics (see Chapter 26). The idea of a non-greasy product is attractive and many attempts at formulation have been made by partially or totally replacing mineral oil by polyethylene or polypropylene glycols or by blends of branched chain esters—such as 2-ethylhexyl hydroxystearate and palmitate[87]—thereby reducing greasiness and replacing an excessively lustrous appearance by a more natural sheen.

Brilliantines

Non-aqueous Semi-solid Fats

Brilliantines are probably the oldest type of hair dressing and have been in use for hundreds if not thousands of years. They have virtually passed into history,

leaving only such memories as 'bear's grease', and the name 'antimacassar' for the cloth used to protect upholstered chairs from the macassar oil used in hairdressings in Victorian days. Coconut oil is still used in some of the less sophisticated parts of the world.

Solid Brilliantines (Pomades)

Pomades usually consist of suitably thickened, tinted and perfumed mineral or vegetable oil. Stiffening to the desired consistency may be obtained through waxes such as paraffin wax, ozokerite, spermaceti, beeswax, ceresin, carnauba wax and microcrystalline waxes. According to what is sought, consistency may vary from relatively hard wax to butter-type cream; the pomade may be greasy, rapidly absorbed or stringy to the touch.[88]

A simple mixture which is satisfactory is given in example 19, and slightly more complex mixtures in examples 20, 21,[88] 22[87] and 23.[31]

	(19) *per cent*
Petroleum jelly	90·0
Paraffin wax (uncrystallizable)	10·0
Colour, perfume	*q.s.*

	(20) *per cent*
Carnauba wax	5·0
Paraffin wax	5·0
Petroleum jelly	70·0
Mineral oil	20·0

	(21) *per cent*
Petroleum jelly	87·0
Paraffin wax	3·0
Lanolin, anhydrous	2·0
Lanolin alcohol	3·0
Mineral oil 65/75	5·0
Perfume	*q.s.*

	(22) *per cent*
Petrolatum	65·0
2-Ethylhexyl palmitate or isostearate	25·0
Arachidyl propionate	5·0
Myristyl myristate	5·0

	(23) *per cent*
Castor oil	20·0
Almond oil	2·0
Isopropyl myristate	8·0
Petrolatum	46·0
Lanolin, anhydrous	12·0
Alcohol	12·0

Solid brilliantines can also be made with mixtures of mineral oil and 12-hydroxy stearic acid (from hardened castor oil fatty acids). This acid sets the oil to a crystalline mass which is liable to syneresis; this property can be corrected by the addition of a small proportion of wax, such as paraffin or microcrystalline wax. A suitable formula is given in example 24.

	(24) *per cent*
Mineral oil	90·0
12-Hydroxy stearic acid	3·0
Microcrystalline wax	7·0
Colour, perfume	*q.s.*

Procedure: Melt the materials together and stir until the mixture is homogeneous.

Transparent solid brilliantines can be made by gelling mineral oil with a suitable agent. The earliest materials were certain metallic soaps[89] particularly those of lithium and aluminium. Such a composition is as follows:

	(25) *per cent*
Aluminium tristearate or isostearate	5
Paraffin oil	95
Castor oil, perfume, etc.	*q.s.*

Procedure: Heat the mixture to 130°C and stir until homogeneous. Then the optimum method of cooling is to allow the temperature to fall from 130° to 50°C over 1 h.

A number of other materials have been described which are suitable for gelling mineral oil: these include derivatives of glyceryl tris-12-hydroxy stearate,[90] dialkylamino propionic acids[91] and polyethylene.[92] Thau and Fox[93] state that, whereas high molecular weight (about 20 000) polyethylene has previously been recommended for gelling mineral oil, involving heating to about 130°C and a complicated cooling process, more satisfactory gels can be prepared by the use of lower molecular weight (1500–2000) polyethylene wax which is dissolved in about seven times its weight of mineral oil at 90°–95°C. After solution is achieved the solution is mixed with a high shear stirrer while it cools to 65°C (about 10° below the cloud point) after which it is stirred gently without air entrapment down to 45°C, at which temperature it is filled into jars where it finally sets. Products prepared in this way have an improved temperature stability.

Liquid Brilliantines

The day of the heavy brilliantine has passed. The aim today is to secure a glossy sheen and light fixative action without the suggestion that the hair has been plastered down. Formerly it was not possible to incorporate a suitable oil in a volatile mineral base, but by the use of deodorized kerosene, or esters such as isopropyl myristate, a fine film of the oil may now be deposited on the hair shaft.

By the addition of deodorized kerosene the viscosity of light petroleum oil may be further reduced, and such preparations lend themselves to spraying on the hair:

	(26) *per cent*
Light mineral oil	60·0
Deodorized kerosene	40·0
Colour, perfume	*q.s.*

If desired, vegetable oils may replace part of the mineral oil. Because of the tendency of most vegetable oils to rancidity, the addition of a suitable antioxidant is necessary. Alternatively, isopropyl fatty esters may be employed together with, if desired, a small proportion of lanolin, as in examples 27 and 28.[31]

	(27) *per cent*
Isopropyl myristate	24·0
Lanolin	1·0
Light mineral oil	75·0
Colour, perfume	*q.s.*

	(28) *per cent*
Isopropyl palmitate	5
Petrolatum	5
Liquid petrolatum	15
Acetylated lanolin alcohol	15
Benzyl alcohol	24
Propyleneglycol butylether	26
Alcohol, anhydrous	10

Alcoholic Brilliantines

Solutions of oil in alcohol offer the advantage of allowing a good and uniform distribution of oil on the hair. They also give a feeling of freshness and a stimulating effect for the scalp.[31]

Traditionally these were solutions of castor oil in alcohol, suitably coloured and perfumed. These do not possess very marked fixative properties although, if the hair is combed with a damp comb immediately after application, the precipitation of the castor oil in a finely dispersed form gives sufficient body to act as a fixative for hair that is not very dense—examples 29 and 30.[31]

	(29) *per cent*
Castor oil	20·0
Industrial alcohol	80·0
Perfume, colour	*q.s.*

	(30) *parts by wt*
Castor oil	12
Almond oil	4
Polypropyl 40 butyl ether	16
Dihydroabietyl alcohol	5
Isopropyl myristate	15
Butyl stearate	2
Alcohol	44
Water	12

Such a formulation, although not smelling of castor oil when suitably perfumed, has a tendency to develop an odour when castor oil is deposited in the wad of the bottle or along the threads of the bottle neck. In addition, unless the hair is washed frequently, a slight castor oil smell may also develop on the user's head. This may be overcome to some extent by substituting oleyl alcohol for castor oil. Such a preparation will also develop a somewhat fatty odour in time, particularly around the bottle neck and on combs and brushes, but it is not as objectionable as castor oil. An even more satisfying product, as far as odour is concerned, may be obtained by the substitution of isopropyl myristate for castor oil. Unfortunately both oleyl alcohol and isopropyl myristate lack fixative properties though they are useful with suitable additions of perfume and antiseptic in a friction lotion or as a dressing for men with thinning hair.

	(31) *per cent*
Isopropyl myristate	20·0
Cetyl alcohol	2·0
Alcohol	78·0
Colour, perfume	*q.s.*

The next products of this type were those which used hydrophilic derivatives of beeswax and lanolin, for example ethoxylated lanolin. These resemble the alcoholic brilliantines except that they are essentially aqueous. The increased solubility of the fatty material permits more formulation flexibility.

Then came new clear liquid preparations, based on the use of polyethylene or polypropyleneglycols, and esters thereof, which largely superseded previous products. They consist basically of a solution of polyethyleneglycol (10–30 per cent) in water. They may also contain other ingredients including resins (for example PVP) to improve their hair-holding characteristics, and germicides. These products are much less greasy than mineral-oil-based products, but do not give as much gloss. A typical formula is given in example 32.

	(32) *per cent*
Polyethyleneglycol	20·0
Water	20·0
Alcohol	59·0
Resin (PVP)	1·0
Colour, perfume	*q.s.*

Yet another variant on the same theme is the use of the Ucon oils. These are polypropylene–ethylene glycol copolymers, some of which are completely soluble in water. They are much less greasy than mineral oil, but give less gloss. One of the problems with this type of product is the mobility of the liquid. This necessitates the use of a bottle with a narrow orifice. A basic formula is:

	(33) *per cent*
Ucon LB-1715	20·0
Water	20·0
Ethanol	60·0
Colour, perfume	*q.s.*

Separable Brilliantines

Separable preparations are two-layer systems prepared by adding a solution of the desired perfume in the requisite amount of alcohol to non-miscible mineral or vegetable oil. By being vigorously shaken before application the mixture forms a temporary dispersion which may then be spread onto the hair. A drawback is the rapid reversion to the initial state which leads to spreading on the hair of disproportionate amounts of one or the other phase. Adding an emulsifying agent to either phase helps to remedy the problem to some extent. It is usual to tint both the oily and alcoholic layers a similar colour. Formulae are given in examples 34 and 35 (see also Baudelin[31]).

	(34) *per cent*
Industrial alcohol	60
Light mineral oil	40
Spirit-soluble yellow dye	*q.s.*
Oil-soluble yellow dye	*q.s.*
Perfume	*q.s.*

	(35) *per cent*
Sesame oil	32
Olive oil	10
Alcohol, anhydrous	58
Antioxidant, colour, perfume	*q.s.*

The product may be varied by altering the ratio of alcoholic to oily phase, and may be cheapened by using aqueous alcohol provided that the strength is sufficient to dissolve the colour and perfume or alternatively that the perfume is formulated in the oily phase.

Non-oily Fixatives

The oldest type of non-oily fixative was based on the use of mucilages, particularly gum tragacanth. These possess very good fixative properties and do not produce greasy stains. They are particularly effective in controlling unruly hair and they are often preferred to oils to comb into light or grey hair.

However, on brushing the hair the setting characteristics are lost and the particles of gum that flake off tend to accumulate on the scalp and clothes, often giving the impression of dandruff. Moreover, they leave the hair with a harsh feel and a dull appearance, although this disadvantage may sometimes be overcome by adding the proper oil. A typical formula is given in example 36. If desired, about 10 per cent oil may be added to this cream. The addition of a little tincture of benzoin, tolu or styrax assists in increasing the whiteness of the product.

	(36) *per cent*
Gum tragacanth	1·0
Alcohol	6·0
Castor oil	2·0
Water	90·0
Glycerin	1·0
Preservative	*q.s.*

Procedure: Disperse the gum in the alcohol and glycerin and add the perfume and any oils; run in the water with continuous agitation. Allow the cream to stand to thicken, restir, filter through muslin and bottle.

Sodium carboxymethylcellulose,[94] hydroxypropylcellulose[95] and carboxyvinyl polymers and various resins may also be used for such gum-like dressings. Representative formulae are given in examples 37[94] and 38.

	(37) *per cent*
Sodium carboxymethylcellulose 2%	47·85
Alcohol	39·70
Polyethyleneglycol 600 laurate	10·00
Propyleneglycol laurate	2·00
Tincture of capsicum	0·05
Cetyldimethylethyl ammonium bromide	0·10
Perfume	0·30

	(38) *per cent*
Carbopol 940	0·6
Water	55·3
Triethanolamine	0·6
PVP K.30	2·5
Alcohol	28·0
Ethoxylated oleyl alcohol	3·0
Polyethylene glycol	10·0

Aerosols

Aerosol sprays for men tend to fall into two classes: those which contain resins very similar to those used in women's hair sprays, and those which contain only mineral oil. Such products are extremely clean in use, but they do not give such

good initial control as some of the more conventional products and the gloss obtained is often not very good. A further drawback is that men tend to regard aerosol hair sprays as essentially feminine products, and thus before such products become generally accepted there is a need to overcome this inherent prejudice.

Emulsions

Water-in-oil Creams

Water-in-oil creams have achieved considerable popularity, particularly in Western Europe and the USA. It is claimed that they spread easily and offer greater fixatives properties, owing to their oil content and more uniform coating, than do similar creams of the oil-in-water type; moreover they impart a better gloss to hair.

Such creams are usually prepared using mixtures of calcium hydroxide with fatty acids to produce the emulsifying agent. Alternatively, nonionic emulsifiers such as sorbitan esters may be used.

Example 39 is a typical formula of the calcium oleate type. It is convenient to incorporate the calcium hydroxide in the form of limewater which contains approximately 0·14 per cent of calcium hydroxide. By the use of sugar solutions, higher amounts of calcium salts may be rendered soluble in the form of calcium saccharate. If the calcium hydroxide is added in the form of limewater, it should be subjected to a simple titration before use to establish its content of calcium hydroxide.

	(39) *per cent*
Beeswax	1·50
Calcium hydroxide	0·07
Oleic acid	1·00
Mineral oil	40·60
Perfume	1·00
Water	53·83
Magnesium sulphate crystals, 25% aqueous solution	2·00

Procedure: Warm the beeswax, oleic acid, and oil to 70°–75°C and add the limewater with constant stirring. Finally add the magnesium sulphate solution, which helps to stabilize the emulsion, followed by the perfume. The mixture should be kept in continuous agitation until it has cooled down to about 20°C.

It may be added that the manufacture of a stable water-in-oil cream, which is also pourable at ordinary temperatures and suitable for use as a hair dressing, is not easy. Water-in-oil emulsions cannot lose their water, either by evaporation or by absorption into the hair, as rapidly as oil-in-water emulsions, and if emulsion breakage is not rapid the product remains unpleasantly white on the hair after application.

To make a good hair dressing, a water-in-oil emulsion must be formulated as a compromise product. It must have sufficient stability towards temperature changes and transport shocks to possess adequate shelf life, yet it must break easily when submitted to the mechanical action of rubbing it on the hands or

hair. This combination of thermal stability and mechanical instability is best achieved by using an emulsifier which produces a solid interface between the oil and the water—hence the usefulness of calcium soaps. Once such an interface is disturbed mechanically, it is entirely destroyed as a barrier to emulsion breakdown.

The formulator must decide on the balance to be achieved between thermal stability and mechanical instability. If greater stability is required, however, it may be obtained by the addition of wool wax alcohols or cholesterol at a level of 0·1–0·5 per cent, or with such emulsifiers as sorbitan sesquioleate at a similar level. Alternatively, small amounts of soluble soaps may be incorporated. Such a formula is given in example 40.

	(40) *per cent*
Beeswax	2·0
Limewater	59·0
Mineral oil	30·0
Petroleum jelly (short-fibre)	8·0
Stearic acid	0·2
Wool wax alcohols (refined)	0·3
Perfume	0·5

For short (crew cut) hair styles:[86]

	(41) *per cent*
Oil phase	
Petrolatum	40·0
Amerchol CAB (petrolatum and lanolin alcohol)	29·0
Microcrystalline wax	10·0
Sorbitan sesquioleate	6·0
Water phase	
Water	14·0
Tween 81 (Polysorbate)	1·0
Perfume, preservative, colour	*q.s.*

The following formula is based on the use of beeswax–borax as emulsifier, assisted by a nonionic ester in small proportions:

		(42) *per cent*
A	Petroleum jelly	7·5
	Mineral oil 65/75	37·5
	Lanolin, anhydrous	3·0
	Sorbitan sesquioleate	3·0
	Beeswax	2·0
B	Borax	0·5
	Water	46·5

Procedure: Bring A to 75°C. Bring B to 75°C. Add B to A slowly with moderate but thorough agitation. Add perfume at 45°C and agitate until cold.

Oil-in-water Creams

Oil-in-water creams are reputed to give a less greasy feel than water-in-oil creams. This probably arises from the fact that they do not give as much gloss when they are first applied to the hair and that they can be diluted with water.

Stable oil-in-water creams of varying viscosities may be obtained by the use of triethanolamine stearate, together with, if higher viscosity is desired, some fatty alcohol, such as cetyl alcohol. A simple formula is given in example 43; by adding 1–3 per cent cetyl alcohol the viscosity may be increased.

	(43) *per cent*
White mineral oil	45·0
Stearic acid	3·5
Triethanolamine	1·5
Water	50·0
Preservative, perfume	*q.s.*

Examples 44[96] and 45[87] are representative of more complicated formulae; in example 45 mineral oil is replaced by a branched-chain ester.

	(44) *parts*
Mineral oil	33·00
Beeswax	3·00
Stearic acid	0·50
Cetyl alcohol	1·30
Borax	0·25
Triethanolamine	1·85
Water	59·80
Chlorocresol	0·10
Perfume	*q.s.*

Procedure: Melts the oils, fats and waxes at 60°–65°C and add them to the aqueous phase containing the triethanolamine and borax at the same temperature. Stir the cream until cool.

		(45) *per cent*
A	2-Ethylhexyl palmitate	20·00
	Beeswax	10·00
	Cetyl palmitate powder	5·00
	Cetyl alcohol	5·00
	Arlacel 165	8·00
	Propyl paraben	0·15
B	Demineralized water	51·65
	Methyl paraben	0·20

Procedure: Heat A to 70°C. Heat B to 70°–72°C. Slowly add B to A using high-speed mechanical agitation such as homomixer. Mix for approximately 20 min and begin to cool while maintaining agitation. Package at 35°–40°C.

High molecular weight polyacrylamido-sulphonate has been claimed to impart lubricity.[97]

A tendency amongst products of this type has been the inclusion of additives which are intended to give special effects. Thus oil-in-water creams are used as suitable bases for anti-dandruff ingredients. Other additives such as alcohol, which is intended to give a refreshing effect to the scalp, can also be added.

Gels

The semi-solid brilliantines described above have been succeeded by gel products of two types: the micro-gels, which are really transparent oil-in-water emulsions in which the oil droplets are so small that the emulsion appears clear, and the true gels which are based on the use of aqueous polyethylene glycol solutions in conjunction with a cellulosic thickener.

The advantage of the micro-gels is that they are miscible with water and feel much less greasy than conventional creams. Examples 46,[98] 47[99] and 48[100] have been proposed.

		(46) *per cent*
A	Sorbitan monolaurate	12·0
	Deodorized light petroleum distillate	45·0
	Light mineral oil	5·0
B	Mannitol monolaurate (modified)	19·0
	Water	19·0

Procedure: Add B to A. As the aqueous solution is mixed with the oils the mixture becomes first thin and cloudy, then thick and clear.

	(47) *per cent*
Mineral oil 65/75	20·0
Lauric diethanolamide	6·0
Lanolin alcohols	2·7
Water	62·5
Polyoxyethylene (3 EO) lauryl alcohol	4·0
Polyoxyethylene (23 EO) lauryl alcohol	4·8

		(48) *per cent*
A	Polyoxyethylene (10) oleyl ether	15·5
	Polyoxyethylene fatty glyceride	15·5
	Light liquid petrolatum	13·7
	Propylene glycol	8·6
	*Atlas sorbitol solution	6·9
B	Perfume	*q.s.*
C	Water	to 100·0

*Atlas Chemical Company.

Procedure: Heat A to 90°C and C to 95°C. Add C to A with stirring and add B at 70°C. Cool and pour at 55°–60°C. On further cooling a ringing gel of a sparkling clarity is obtained.

The true gels have the same advantages as the micro-gels. A basic formula would consist of polyethylene glycol (30 per cent), alcohol (30 per cent), water

(40 per cent) and a small amount of cellulosic thickener such as isopropyl cellulose. A British patent[101] has described the preparation of transparent hair gels. Such products give good fixative properties and control hair satisfactorily, but they do not give a very good gloss.

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