

Hair Tonics and Conditioners

Introduction

No toilet preparation has aroused such derision as the so-called hair 'tonic'; the use of the word 'tonic' is unfortunate in this respect since even in therapeutics it is viewed with grave suspicion. Much of this scepticism is the result of the claims made in the past by the manufacturers of such preparations—widely based on old recipes inspired by 'Nature'—coupled with the lack of success experienced by the user.

However, there are many purposes for which a lotion provides an ideal vehicle and the increasing success of modern rinses and conditioners is outstanding evidence of this.

Two categories of hair 'tonic' should, in fact, be distinguished: medicated products which deal with specific problems of the hair and scalp—greasy hair, dandruff, loss of hair—and the so-called conditioners, used primarily by women, which aim at improving, restoring and maintaining the condition of the hair. To this class should be added rinses which, as their name does not make clear, are usually followed by a water rinse, and which aim to combat tangles and to render combing easier. Rinses and conditioners look similar to the older type of women's hair dressings and mostly take the form of a clear lotion or a liquid cream. The border between rinses and conditioners tends to become ever vaguer owing to the development of clearer rinses with increased conditioning properties, warranting the name of clear rinse-conditioner. However, the main requirement is to provide the conditioning effect.

MEDICATED PRODUCTS

The objective of medicated products is to cure, to reduce, to restrain or to offset the unaesthetic phenomena or disabilities resulting from some abnormality in the functioning of the scalp. Although in the past use was often made of irritant, keratolytic, rubefacient compounds, the present trend is that the treatment should rather bring about a return to a normal state, promote balance and alleviate and restore the disturbed substrate. The main conditions with which medicated products should deal are dandruff, seborrhea and hair loss.

Dandruff

Dandruff results from an excessive scaling of the scalp, without clinical signs of inflammation.¹ Rare among children and the elderly, it usually reaches a peak in winter and eases off in summer. Although a relationship may exist with the general state of health (nervous, digestive or metabolic factors, state of tiredness), the causes of this scaling are still not clear. Dandruff has been noticed

to be very often accompanied by a proliferation of some micro-organisms, and more particularly a sporulating yeast, *Pityrosporum ovale*, once considered to be responsible for the condition. The scalp is a lush environment for the growth of micro-organisms and high scaling conditions increase their niches and the nutrients beneficial to their development. Indeed, the scalp flora appears to be ubiquitous, but only one micro-organism experiences a dramatic increase in the dandruff condition: the prevalent resident, *P. ovale*—75 per cent of the population, versus 45 per cent under normal conditions.² However, as stressed by Kligman following investigations with specific germicides,¹ it is generally believed today that the increase in *P. ovale* is not causative but is a secondary effect resulting from increased scaling.

In the absence of knowledge of the cause of dandruff, the trend is to treat the phenomenon; thus the compounds added to antidandruff lotions generally meet two requirements:

- (i) antimicrobial, to prevent proliferation, an aggravating factor of the local disorder;
- (ii) keratolytic or exfoliative, to cleanse the scalp by promoting the elimination of dead skin.

As germicides, quaternary ammonium compounds (such as benzalkonium, cetyltrimethylammonium and cetylpyridinium salts), chlorophenols, PVP-iodine complexes, oxyquinoline and 5,7-dichloro-8-hydroxyquinoline^{3,4} in particular have been used. But the compounds which have gained the dominant position because of their efficacy are the derivatives of 2-pyridine-thiol-N-oxide; according to Kligman these compounds, although strongly antimicrobial, may exert rather a cytostatic activity, depressing the turnover rate of epidermal cells and inducing more complete keratinization.^{5,6} Soluble derivatives⁷⁻¹⁰ are preferred for lotions. Related compounds from pyridazines,¹¹ quinoxalines¹² and quinolines¹³ have been patented.

As keratolytic ingredients, colloidal sulphur, resorcinol, salicylic acid^{14,15} and selenium disulphide have been used most often. The latter, which owing to its toxicity is largely confined to prescription uses, has been shown to act rather as a powerful cytostatic agent.¹⁶ Coal tar is also known to provide good results; it may act similarly by restraining the multiplication of epidermal germinative cells, as will corticosteroids, or affect cohesiveness of desquamating cells.¹ Other patented materials are polyene derivatives¹⁷ and zinc hydroxymethylsulphinate.¹⁸

Antidandruff products can be simple solutions of an antimicrobial agent in a 1:1 aqueous-alcoholic medium or a setting or rinse composition (examples 1-4).

<i>Anti-dandruff lotion</i>	(1) per cent
*Bis(2-pyridyl-1-oxide) disulphide soluble complex	0.15
Camphor	0.10
Menthol	0.05
Ethanol or isopropanol	50.00
Water	q.s. to 100

*Magnesium sulphate or calcium chloride complexes (Olin Mathieson).

<i>Anti-dandruff lotion</i> ¹⁹	(2)
Cationic polymer from epichlorhydrin piperazine	0.5 g
Lauryl isoquinolinium bromide	1.3 g
Lactic acid	q.s. to pH 5.0-5.3
Ethyl alcohol	55 ml
Menthol pantothenate	0.1 g
Perfume	0.3 g
Water	q.s. to 100 g

<i>Anti-dandruff hair-dressing</i> ²⁰	(3)
	per cent
Polypropylene glycol (40) monobutylether	1.75
Polypropylene glycol (33) monobutylether	0.50
Polyoxypropylene (12) polyoxyethylene (16) monobutylether	15.75
Alkyl benzyldimethylammonium saccharinate	0.52
Ethanol	63.05
Perfume	q.s.
Water	q.s. to 100

<i>Clear anti-dandruff rinse</i>	(4)
	per cent
Stearyl dimethylbenzylammonium chloride	5.0
Cetyltrimethylammonium chloride	0.25
Tallow amido propylamine oxide	3.00
Propylene glycol	3.00
Hydroxypropylmethyl cellulose	0.6
Distilled water	to 100

Methods have been developed for quantitative evaluation of anti-dandruff products by counting corneocytes, bacteria and yeasts on the hairy scalp.^{6,21}

Greasy Hair and Scalp

Seborrhea results from an excessive secretion from the sebaceous glands. Discharged into the follicular duct, sebum is then excreted onto the surface of the skin where it may undergo a number of transformations by aerial oxidation and under the action of the resident micro-organisms. The mechanisms which lead to the setting up of a seborrheic state remain largely unknown. In addition to the fact that it may induce a loss of hair, its consequences on the hair are particularly unaesthetic: hair becomes greasy very quickly after shampooing, forms bunches and catches dust, it becomes heavy and the benefits of a setting operation are lost soon afterwards.

The phenomenon of regreasing is itself a source of much controversy.²²⁻²⁵ A method of reducing sebum uptake by hair is to apply an oil-repellent treatment, that is, to deposit a lipophobic ingredient onto the hair; this approach is illustrated by the use of some hydrophobic and lipophobic perfluorinated compounds²⁶⁻²⁹ such as $\text{CF}_3(\text{CF}_2)_x(\text{CH}_2)_y\text{Z}$, where Z is a water- or oil-solubilizing group which may be anionic, cationic, nonionic or amphoteric

($x = 7-11$, $y = 0-4$). These substances^{26,27} are used in 70:20 aqueous-alcoholic lotions at concentrations between 0.05 and 0.2 per cent; commercial compounds are Fluorad (3 M Co.) and Zonad (Du Pont).

The formula given in example 5 has been claimed to retard oil uptake by 85 per cent.

	(5) per cent
Ethanol	30.0
Water	69.7
Polyoxyethylene polymethylsiloxane	0.1
Perfluorononanoic acid	0.1
Perfume	0.1

The use should also be mentioned of oil-adsorbing materials such as finely divided starches³⁰ and silicas to keep hair looking clean for longer periods.

Another approach consists in a topical treatment in order to reduce secretion or excretion of sebum; it has given rise to a multitude of patents describing a large number of possible molecules. Most of the proposed substances are rather indiscriminately recommended for seborrhea and hair growth. Classes of compounds with a seemingly more selective activity are thio-ether or sulphoxide derivatives of cysteine, cysteamine, glutathione, pyridoxine and hydroxylated aminothiols;³¹ some, such as salts of 2-benzylthioethylamine, have been reported to act specifically on lipid synthesis processes,^{32,33} thereby reducing the production of sebum. Other claimed inhibitors of sebum synthesis are thiolanediol derivatives,³⁴ polyunsaturated acids such as eicosa-5:8:11:14-tetraynoic acid^{35,36} and 5-phenylpentadienoic acid,³⁷ as well as N,N'-sebacoyl dimethionine.³⁸ Another more specifically medicated proposal, which tends to counteract androgen-induced sebum secretion, is to apply steroid^{39,40} or non-steroid anti-androgens such as flutamide.⁴¹ However, a local action, that is a non-systemic effect, of such compounds is questionable.

It is also worth mentioning antioxidant-based lotions—for example alkyl gallates, *t*-butyl hydroxyanisole—to prevent peroxidative transformation of sebum on hair and scalp.^{42,43} Antimicrobial agents can be added to reduce or control enzyme (for example, lipase)—releasing bacteria or yeasts. The after-shampoo lotion represents the mode of application offering the best hope of producing activity and somewhat modifying the refatting process. Alcohol content should not be too high; application of 70 per cent isopropyl alcohol as hair tonic has been shown to displace scalp lipids from the scalp on to the hair.⁴⁴

Hair Loss

It remains essentially true that there is no substance known to science which, when applied externally to the human scalp, will cause—in a statistically significant number of cases—the regrowth of normal hair on a bald head.

Causes of hair loss vary widely and are usually complex (see also Chapter 23). It may be more or less profuse, more or less localized; it may be congenital or acquired. It may present an acute state or be a transient event resulting from an affective disturbance, a trauma, an infectious disease, the effect of some

medicines, endocrinological troubles, anaemia or an ionizing radiation treatment. It may be shown to be progressive, chronic, ineluctable, linked or unlinked to seborrhea or to a hormonal imbalance. The tensions of modern life and the evolution of societies with high living standards are the reasons that hair loss appears increasingly among women and with psychological, even social significance, so that the resort to tonics may have little promise of success.

Many points raised by earlier reviewers^{45,46} remain to be explained; knowledge is lacking for the understanding of the processes and the biological factors that elicit or aggravate hair loss. In this field the problems of investigation lie in the time needed to collect statistically significant data; the development of trichogram and macrophotographic studies should help to collate observations on the mystery of evolving hair. Chase⁴⁷ suggested five methods by which hair growth might be increased, but concluded that only the last offered any real hope of practical realization:

1. Increase of the anagen growth of hair.
2. Production of new follicles or more multiple follicles.
3. Lengthening of the anagen stage or shortening of the telogen stage.
4. Prevention or delay of telogen.
5. Initiation of anagen in follicles in the telogen state.

In normal male-pattern baldness, it is known that there is a shortening of the hair cycle and a progressive thinning until what is called 'club hair' remains. In alopecia areata, in contrast, most of the hair roots are in the anagen state; the hair falls out for a variety of reasons during anagen phase and the scalp is left bald during the period corresponding to catagen and telogen, and then more hair grows during the next anagen period. If the disease has passed off during the bald period these new hairs will be completely healthy. If not, they will be stunted and thin, and will again fall out during anagen. Alopecia areata is considered today to be an autoimmune disease which may be due to a deficiency of T-cells; in support of this is the success of treatment with a solution of the potent sensitizer chlorodinitrobenzene in acetone.^{48,49}

Hair loss has long been held to be linked to poor 'irrigation' of the scalp and a number of preparations recommended as 'anti-loss' were based on the use of irritating, rubefacient, 'exciting' substances to provoke an abundant blood supply of growth-promoting nutrients. It now appears that blood circulation does not play a determinant role and it may be preferable to reduce the flow rate in an already well vascularized region. The development of hypoxic conditions has been favourably noted for the reduction of a seborrheic alopecia.³⁹

Evidence suggests that the process of loss more probably involves a lack of balance in the growth and division of germinative cells of the hair; this imbalance may be due to a deficiency of some nutrients and to the influence of certain hormonal factors. The role played by a metabolite of testosterone—the 5- α -dihydrotestosterone—is highly suspect, and treatments based on anti-androgen^{40,50,51} or on some quinones and phenols⁵² have been recommended, which should inhibit the production of the 'guilty' metabolite by the enzyme α -reductase.

Aristotle pointed out that eunuchs do not go bald, and in general this is true. Though there is no clear-cut relationship between the incidence of baldness and

the quantity of circulating male hormones in normal subjects,⁵³ it is significant that the removal of any one of several glands (hypophysis, adrenals, pituitary) from rats will have a profound effect on the quantity or quality of their hair, and it seems most likely that a similarly complex system governs hair growth in humans.

It still seems to be true that the only sure preventative for baldness is the proper choice of parents.

Formulation of Medicated Hair Tonics

A number of completely unrelated compounds have been recommended for use in hair tonics and some of the formulae, both old and new, are given below.

To build up a good tonic, it seems sensible to incorporate the following ingredients:

Nutrients necessary to the biosynthesis of keratin (vitamins, sulphur-containing amino acids).

Regulating factors for the secretion from sebaceous glands.

Antiseptics to control scalp conditions which may interfere with hair growth.

Soothing ingredients (to reduce itching).

The main adversary for a tonic is the time required before an effect other than that attributable to placebo may be detected. Considering the relative slowness of the process of rejecting mature hair, it is most likely that the application of a product is perceived as an increase of loss of hair at first; possible effects may not be identifiable before two months. To encourage persistence in use it may be desirable to add to the active ingredients elements offering preliminary benefits such as compatible additives which impart a healthy look, sheen and volume.

'Stimulating Agents'

Most of the compounds used as stimulants have been drawn from nature, being irritant agents which supposedly have stimulating effects on the growth of hair. The compounds mostly used have been cantharides tinctures (which contain a very irritating lactone, cantharidin); capsicum tinctures (containing a pungent principle, capsaicin); jaborandi tinctures with pilocarpine as the active agent; and miscellaneous, arnica and red quinquina tinctures, *Urginea maritima*,⁵⁴ rhubarb extract,⁵⁵ camphor, β -naphthol, pilocarpine, quinine salts, turpentine oil. Esters and salts of nicotinic acid, notably ethyl and tetrahydrofurfuryl esters and pyridoxine nicotinate, have also been claimed as rubefacient and penetrating agents, and brassidic acid and 1-citronellol have been claimed as acanthogens.⁵⁶

Sulphur Derivatives

The use of topically applied amino acids in hair growth has been investigated by Edwards.⁵⁷ He applied radio-labelled methionine (S^{35}) to the skin of guinea pigs and found a 1 per cent incorporation of sulphur in the hair, but when the methionine was fed to the guinea pigs, 2.5 times as much sulphur was incorporated. Graul *et al.*⁵⁸ applied radio-labelled sulphur, methionine and

methionine esters (S³⁵) to the skin of guinea pigs and found that the uptake of sulphur was greatest for elemental sulphur. These results indicated the importance of sulphur and sulphur-containing amino acids in hair growth, and a number of patents have appeared claiming the use of such materials in topically applied preparations. Cysteine itself, although very important in normal growth, is not a very stable compound and attempts have been made to overcome this drawback. Magnesium cysteinate in conjunction with magnesium dehydrocholate and magnesium salts of unsaturated fatty acids have been claimed⁵⁹ to stimulate growth of hair, nails and skin. Various derivatives suitable for topical delivery, with protecting groups thought to release free cysteine *in situ*, have been patented; they include 4-thiazolidine carboxylic acid,⁶⁰ and S-alkyl and S-carboxymethyl cysteines,⁶¹ the latter having in addition been shown to be efficient in reducing the greasy condition of the scalp.

Tars

Vegetable tars resulting from the carbonization of specific woods (pine tar oil, cade, cedar and birch oils) have proved to be of interest in cases of seborrhea, dandruff and dry scalp. Antiseptic and astringent, they are complex mixtures of polyphenols, high molecular weight acids or alcohols, waxes, ketones, etc.

Vitamins

The topical action of vitamins is controversial but numerous compositions are based on their use. Group B vitamins (B₁, B₂, B₆, and B₁₂), vitamins A and E, extracts of wheat germ which contain a cocktail of vitamins, the so-called vitamin F composed of essential (unsaturated) fatty acids, biotin, and vitaminic factors such as *p*-amino-benzoic acid, pantothenic acid and the related alcohol panthenol,⁶² are widely used. They aim at stimulating cellular synthesis.

The use of amniotic liquid⁶³ and placenta extracts^{64,65} also tends to provide nutrients and stimulating elements that are necessary to keratinization.

Miscellaneous Materials

Sericine (silk glue) is a complex serine-rich protein that has been noted to provide an interesting tonic and anti-seborrheic effect.

Among other miscellaneous substances recommended as hair growth promoters are egg yolk, ginseng,⁶⁶ snake serum,⁶⁷ ferulic acid,⁶⁸ cholic acids,⁶⁹ 4-iodo-3,5-dimethyl-2-cyclohexylphenol,⁷⁰ steroids,⁷¹ hydroperoxides⁷² and an organic silicon compound—chloromethyl silatrane.⁷³

Examples of Formulae

<i>Cinchona lotion</i>	(6)
	<i>per cent</i>
Tincture of cinchona	2.0
Birch tar oil	0.3
Glycerol	6.0
Resorcinol	0.3
Jamaica rum	15.0
Ethanol	50.0
Perfume, dye	<i>q.s.</i>
Water	<i>q.s. to 100</i>

<i>Quinine-based lotion</i>	(7)
	<i>per cent</i>
Quinine sulphate	0.01-0.2
Alcohol	30.0
Water	69.0
Perfume, colour	<i>q.s.</i>

<i>Cantharidin lotion</i>	(8)
	<i>per cent</i>
Cantharidin	0.002
Alcohol	30.000
Malic acid	0.500
Water	<i>q.s. to 100</i>

<i>Jaborandi hair tonic</i>	(9)
	<i>per cent</i>
Tincture of jaborandi	0.5
Tincture of capsicum	0.5
Isopropyl alcohol	60.0
Salicylic acid	0.1
Panthenol	0.2
Distilled water	38.7

<i>Vitamin lotion</i> ⁷⁴	(10)
	<i>per cent</i>
Vitamin E nicotinic acid ester	0.1
Isopropyl myristate	3.0
1-Menthol	1.0
Calcium pantothenate	0.05
Pyridoxine chlorhydrate	0.05
Irgasan DP 300	0.2
Perfume	0.5
Ethanol 95%	80.0
Water	15.1

<i>Vitamin lotion</i>	(11)
	<i>per cent</i>
A Ethanol	50.0
Birch cambium sap	7.5
Boric acid	0.5
Glycerin diacetate	2.0
Water	40.0
B Linoleic acid ethyl ester	10 mg
Arachidonic acid ethylester	10 mg
Ascorbyl palmitate	180 mg
Vitamin D ₃	10 000 I.U.
Calcium pantothenate	10 mg
<i>p</i> -Amino benzoic acid	5 mg
Inositol	10 mg

Procedure: Add B to each litre of product A.

<i>Oily hair lotion</i> ⁷⁵	(12)
	<i>per cent</i>
Benzylthio-2-ethylamine malate	1.0
Benzalkonium chloride	0.8
Ethanol	45.0
Water	<i>q.s.</i> to 100

<i>Anti-loss lotion</i> ³⁰	(13)
	<i>per cent</i>
Amniotic fluid	10
Chlorohydroxy-aluminium allantoinate	10
Glycerol	1
Pine tar	2
Lemon essence	0.1
Ethanol	<i>q.s.</i> to 100

CONDITIONERS

It may be said that conditioners have their origin in the fundamental need of women for attractive and healthy-looking hair. Conditioners should give to hair life, spring, softness, volume, body, sheen, a silky touch, fly-away control and ease of styling.

Today's conditioners are the modern sophisticated and scientific expression of what was looked for earlier in egg yolk and white, marrow and vegetable oils. They may be formulated to be applied either as a pre- or a post-treatment. They are mainly intended for disturbed or weakened hair resulting from chemical treatments such as bleaching or permanent waving, too frequent shampooing, handling abuse (blow-drying, brushing), weathering (severe sun exposure) or internal causes. Such hair types, usually gathered under the description 'dry', tend to look dull and are harsh, porous and brittle, in addition to having increased sensitivity. To make up for a natural deficiency of sebum, a conditioner must smooth, soften, 'texturize', restore the protective sheath, fill in gaps, flatten or tighten cuticle scales, alleviate sensitivity and provide resilience, bounce, control and ease of combing.

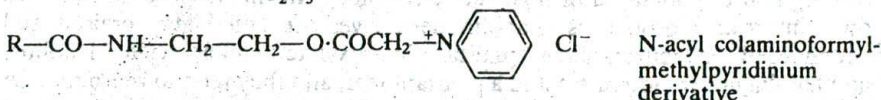
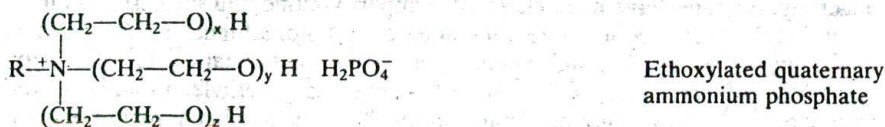
Another reason why conditioners have been one of the fastest growing segments of the hair care market⁷⁶ is the trend towards a more natural hair style. From this arose the need for a clear, water-white agent to be applied after a shampoo, without the need for rinsing as after conventional cream rinses, while imparting a better mix of the above mentioned characteristics of a healthy hair, and obviously accompanied by a natural appearance.

To a great extent, conditioning is based on the concept of substantivity, that is the sorption of adequate ingredients to modify surface properties and perhaps hair texture. Generally speaking, substantivity is higher when hair is more damaged or more porous. Keratin is an anionic resin, and therefore it shows preferential affinity for cationic substances. Some treatments, such as bleaching, markedly enhance this feature by creating strongly anionic sulphonic acid sites; long-term exposure to sun and the environmental atmosphere have similar effects, though to a lesser extent.

Thus, not surprisingly, the conditioners first marketed in 1945 were based on

the use of a cationic surfactant, cetyltrimethylammonium chloride; it is still used. Then followed alkyl-dimethylbenzylammonium, alkylisoquinolinium and alkylpyridinium halides. The best conditioning properties were shown to be contributed by the longer-chain alkyl compounds.⁷⁷ In small amounts these quaternary ammonium derivatives⁷⁸ improve manageability, prevent fly-away by neutralizing negative charges in the scalp and, to some extent, promote 'body'.

A wide variety of other cationic surfactants (see Chapter 24) have since been proposed and introduced into conditioners. The emphasis is usually on a lower irritancy (or 'non-irritancy') for hair and skin compared with the earlier surfactants; they also offer greater flexibility in formulation and impart particular properties—enhanced body, softness, volume and spring—to hair. Examples are ethoxylated quaternary ammonium phosphates⁷⁹ (for example, Dehyquart SP—Henkel), quaternized fatty acid amino-amides derived from lanolic acids^{80–82} (Lanoquats—Emery) and mink oil,⁸³ and N-acyl colaminoformyl-methylpyridinium derivatives (Emcol E607S—Witco):



Non-quaternized fatty acid amino amides salts, for example stearyl-amidopropyl-dimethylamine lactate, have been said not to differ substantially from related quaternary ammoniums in respect of conditioning properties and to have the additional advantage of creating no build-up.⁸⁴ More recently, similar salts whose anionic part is also a surfactant have been patented.⁸⁵

Some cationic polymers have been proposed (see Chapter 24—conditioning agents in shampoos) to provide clear formulations yielding high conditioning effects; among them are cationic cellulose derivatives (Polymer JR), vinylpyrrolidone-quaternized dimethylaminoethyl methacrylate copolymer (Gafquats),⁸⁶ 'polyazonia' compounds,^{87–90} epichlorhydrin cross-linked adipic acid-diethylenetriamine polymers,⁹¹ polyethyleneimines, piperazine copolymers⁹² and cationic silicones.⁹³ The high substantivity of these polymeric materials, however, leads to some problems—such as excessive build-up—and they need careful control. Sodium chloride may help to reduce the substantivity.⁹⁴

Another class of compounds long used in conditioners to protect, enrich or repair hair fibres is that of partially or totally hydrolysed proteins, particularly hydrolysates of collagen, ichthyocolla, keratin (horn, horsehair, hoof, hair), and milk casein. The sorption of enzyme-hydrolysed collagen has been widely studied,^{95,96} virgin hair takes up only low levels of protein, and maximally at pH

9-11; waved hair absorbs very high levels, which can penetrate deeply into the cortex. Generally speaking, sorption is higher and is obtained at lower pH when the hair is more damaged (pH 6 for strongly bleached hair). Sorption is controlled by ionic equilibrium phenomena and therefore is highly sensitive to pH modifications;⁹⁷ it seems to increase rapidly with concentration up to a value of about 5 per cent.⁹⁸ Highest substantivity is obtained with polypeptidic fractions of average molecular weight 1000.⁹⁹

Evidence of the restorative and healing effects on the hair shaft may be found in the 95 per cent improvement in split ends obtained with a leave-on protein conditioner;¹⁰⁰ similarly a cream rinse formulation containing 5 per cent hydrolysed animal protein (Lexein X-250—Inolex Group) has been shown to repair 50 per cent of split ends versus 25 per cent for the same rinse without protein.¹⁰⁰

New hydrolysates are now available in which free amino groups have been quaternized^{102,103} to increase protein substantivity. Combined elastin and collagen hydrolysates have been claimed to impart volume and softness to hair.¹⁰⁴ Oleic acid-protein condensate and abietic acid homologue have been said respectively to improve wet combing and to thicken hair.⁹⁹ Condensation products of proteins with amines—such as diethylenetriamine—and epoxide,^{105,106} and protamines from fish milt¹⁰⁷ have also been mentioned.

Oily materials are the third type of ingredient classically used to improve hair condition. Since antiquity they have been used to supply lubrication and lustre. They help to reduce fibre friction and the abrasive effects of handling, and they improve the condition of hair either by levelling out the scaly surface or by coating it with a material of high refractive index. In this respect, silicone oils offer interesting properties. Lanolin derivatives are still highly praised and widely used for their emollient qualities; hydroxylated and acetylated lanolins, and lanolin esters, add lustre and a pleasant feel, and they tend to reproduce on dry hair the beneficial effect of sebum on healthy hair. Other fatty compounds used with this aim include fatty alcohols, natural waxes (beeswax, spermaceti), ethoxylated alcohols, fatty acids and waxes, fatty acid esters, partially sulphated fatty alcohols such as lanette wax, polyethyleneglycols, lecithins, and some oils (almond, avocado pear, mink, castor, wheat germ). Fatty acid lactylates have been suggested as efficient restoring agents for damaged hair.¹⁰⁸

A new approach to the lubrication of hair has recently been proposed: it is based on the use of perfluorocarbon resins such as tetrafluoroethylene and hexafluoropropylene polymers.¹⁰⁹

Products for mending damaged hair have been more specifically dealt with in Chapter 28, but it is relevant to mention here the association of quaternized vinylpyrrolidone, cationic surfactant, hydrolysed collagen and a calcium salt to restore strength and elasticity to bleached hair.¹¹⁰

Examples of Formulae

Conditioner to be applied without rinsing	(14) per cent
Gafquat 734	0.5
Cetyl trimethyl ammonium chloride	0.3
Ethanol	10.0
Water	q.s. to 100.0

<i>Conditioner to be applied without rinsing</i>	(15)
	<i>per cent</i>
PVP-VA S630	1.0
Cetyldimethyl(hydroxyethyl)ammonium chloride	0.5
Silicone oil	0.3
Ethanol	25.0
Water	<i>q.s. to</i> 100.0

<i>Old-fashioned cream for care and restoration of dry or damaged hair</i> ¹¹¹	(16)
	<i>per cent</i>
Beef marrow	35
Almond oil	40
Mink oil	15
Deodorized castor oil	10

<i>Thick creamy hair conditioner</i> ¹¹²	(17)
	<i>per cent</i>
A Glycerol stearate	5.0
Cetyl alcohol	3.0
Lanolin quaternary (50% active)	5.0
Synthetic beeswax	2.0
*PEG 75—Lanolin and hydrolysed animal protein	3.5
Propylene glycol	2.5
Sesame oil	1.5
Stearic acid	1.5
Lecithin	1.0
Hydroxypropyl cellulose (2% aqueous solution)	7.5
Methyl paraben	0.1
Propyl paraben	0.2
B Demineralized water	67.2

*Protolate WS (Malmstrom).

Procedure: Heat A to 75°C and B to 60°C. Add A to B with constant agitation until homogeneous. Cool to room temperature with gentle mixing.

<i>Hair conditioning lotion</i> ¹¹²	(18)
	<i>per cent</i>
A Propylene glycol	5.0
Glyceryl stearate	3.0
Sorbitan stearate	1.5
Polysorbate 20	2.5
Mineral oil, 70 visc.	3.5
Cetyl alcohol	3.0
Stearic acid	1.5
B Lanolin quaternary	5.0
PEG 75 lanolin oil hydrolysed animal protein	5.0
Propyl paraben	0.1
Methyl paraben	0.2
C Demineralized water	69.7

Procedure: Heat A and B separately to 75°C. Add B to A with stirring then add C (preheated to 60°C). Continue mixing while cooling to room temperature.

<i>Conditioner for fine, thin, limp hair</i> ¹¹³		(19)
		per cent
Water phase		
*PPG 20 methylglucose ether		2.0
Water		60.0
Hydroxyethylacetamide		15.0
Hydrolysed animal protein		5.0
Oil phase		
Glyceryl stearate		3.0
PEG 100 stearate		5.0
Triton X 400		5.0
Cetyl alcohol		2.0
Stearyl alcohol		1.0
Acetylated lanolin alcohol		2.0
Perfume, preservative, colour		q.s.
*Glucam-P20 (Amerchol).		

<i>Rapid-acting conditioner to impart body, elasticity and lustre</i> ¹¹³		(20)
		per cent
Water phase		
Water		89.8
Cetyltrimethylammonium chloride		1.5
Alumina		0.5
Oil phase		
Petrolatum		1.5
Glyceryl stearate		0.2
Acetylated lanolin alcohol		2.0
Lanolin alcohol		2.0
Stearyl alcohol		2.5

<i>Flowing emulsion conditioner (manageability, appearance)</i> ¹¹³		(21)
		per cent
Water		54.7
Propylene glycol		7.5
Alcohol		6.0
Triton X 400		4.8
Stearic diethanolamide		5.0
Lauric diethanolamide		4.0
Hydrolysed animal protein		2.0
PPG 20 methylglucose ether		1.5
Polyethoxylated (16) lanolin alcohol		2.0
Sorbitan sesquioleate		5.0
Polyethoxylated (4) dodecyl alcohol		5.0
Sorbitan stearate		1.5
Polysorbate 40		1.0
Perfume, dye, preservatives		q.s.

<i>Protein conditioner</i> ⁸⁴	(22) per cent
Stearylamidopropyldimethylamine	1.5
Cetyl alcohol	2.0
Stearyl stearate	1.0
Lactic acid (88%)	0.7
Sodium chloride	0.5
Hydrolysed animal protein	1.5
Methyl paraben	0.15
Propyl paraben	0.05
2-Bromo-2-nitro-1,3-propanediol	0.05
Perfume, dye	q.s.
Water	q.s. to 100

Procedure: Dissolve sodium chloride in water, add remaining components except dye and perfume and heat to 70°–75°C. Stir until homogeneous and cool. Add dye and perfume at 45°C and cool. Fill batch at 30°C.

<i>Balsam conditioner</i> ⁸⁴	(23) per cent
Stearylamidopropyldimethylamine	1.60
Cetyl alcohol	1.80
Phosphoric acid (85%)	0.90
Sodium chloride	0.30
Preservatives	q.s.
Perfume CS 18479 (Albert Verley)	q.s.
Water	q.s. to 100

<i>Lotion hair conditioner, balsam type</i> ⁸³	(24) per cent
Cetyl lactate	2.0
Isopropyl linoleate	2.0
Glyceryl stearate	4.0
PEG 40 stearate	1.0
*Cetyl stearyl alcohol and its polyethoxylated (20) derivative	2.0
Cetyl alcohol	1.0
Deionized water	83.8
Ethyl cellulose	0.3
Quaternium 22†	1.0
Quaternium 26†	2.5
Lactic acid	0.3
BTC 2125 M†	0.1
Colour, perfume oil (V-2374/2)	q.s.

*Promulgen D (Robinson-Wagner).

†See also under 'Rinses' for the use of quaternary compounds.

<i>Pretreatment of hair before anionic shampoo</i> ¹¹⁴		(25)
		<i>per cent</i>
Stearyl dimethylbenzylammonium		
or N-lauroylcolamino formylmethyl pyridinium chloride		2.5
N-ethanol acetamide		15.0
Polyethyleneimine (60 000 HW)		
(40% active)		1.5
Nonionic emulsifier		2.0
Formic acid (90% active)		1.4
Hydroxyethyl cellulose		0.37
Methylparaben		0.1
Perfume		<i>q.s.</i>
Water		<i>q.s. to 100</i>

An original mode of application has been suggested according to which conditioning polymer is delivered from a moulded comb, composed of the water-soluble polymer, for example, cationic Polymer JR, and a water-insoluble carrier polymer, for example, high-density polyethylene.¹¹⁵

Evaluation of Conditioning

The objective evaluation of hair conditioning properties is difficult. The relation of sensory perception of hair condition factors to quantifiable physical properties remains a problem that requires a great deal of inventiveness to develop appropriate experimental techniques. A good review of this issue has been published by Breuer *et al.*¹¹⁶ A powerful tool now available to provide precise data on hair condition in relation to treatment is the scanning electron microscope (SEM).

Hair Thickeners

Hair thickeners are a variant of conditioners designed to give a temporary appearance of thicker and more full-bodied hair.¹¹⁷ These preparations are usually oil-in-water emulsions which combine synthetic or natural polymers used in hair sprays or setting lotions and various ingredients described above, together with bulking agents (Veegum, Bentonite) and thickening agents (Carbopol resins). Cationic polymers are more particularly used (such as Merquats, Gafquats and Polymer JR) to deposit a substantive and stiffening film coating which thickens the hair and imparts body.

The formula in example 26 has been proposed.

		(26)
		<i>per cent</i>
A	Deionized water	44.00
	Methyl paraben	0.20
	Carbopol 940	1.00
	Triethanolamine	2.00

B	Deionized water	25.20
	Merquat 550	5.00
	Ucon HB 660	8.00
	Propyl paraben	0.10
	PVP K90	1.50
	Titanium dioxide	0.50
	Carbowax 6000	7.00
	Polyethoxylated (5) lanolin alcohol	3.00
C	Dowicil 200 (10%)	2.00
D	Perfume	0.50

Procedure: Sprinkle Carbopol into rapidly agitated water. Heat to 70°C and add triethanolamine. In a separate vessel, combine all ingredients of B and heat to 70°C. Add B to A and vacuum mix until 25°C. Add C and D.

RINSES

If the development of rinses is a comparatively recent phenomenon, the idea and the need were evident long ago. The forebears of rinses are nothing more than the vinegar and lemon juice used by women to remove the 'lime soap scum' left on the hair by the rough soaps used in the early days. In addition to the dissociation of calcium salt, acidic rinsing brings the pH of hair nearer to the isoelectric point and helps to maintain its integrity; hydroxyacids have been widely used in this respect. However, modern rinses came to life with the use of a cationic surfactant, stearyldimethylbenzylammonium chloride, combined with fatty alcohols; the best known compound is Triton X-400 (Rohm and Haas), an aqueous solution containing 20 per cent of stearyldimethylbenzylammonium chloride and 5 per cent stearyl alcohol. This combination improves hair manageability and wet and dry combability, and gives a smooth feel to hair. The rinse was formulated as a cream not for technical reasons but with a view to marketing, that is, because of the need to cope with emollience and give the impression that the hair was 'creamed'. The first formulations generally consisted of 3 per cent stearyldimethylbenzylammonium chloride diluted about ten times when applied to the hair.

	(27)
	per cent
Triton X-400	12.5
OPE-1 (octylphenoxyethanol)	1.0
Perfume, colour	q.s.
Water	q.s. to 100

Procedure: Mix thoroughly the OPE-1 and warmed X-400. Heat the water to 70°C and add to the paste with thorough stirring. Cool to 50°C, add perfume and colour. Viscosity can be adjusted by 0.1-0.2 per cent sodium chloride; pH can be adjusted as desired by citric acid.

Good creamy emulsions are obtained with various nonionic emulsifiers such as glycerol, glycol or diethyleneglycol stearates, polyethoxylated fatty alcohols,

polyethoxylated sorbitan esters, methyl glucoside esters and ethoxylates. In addition to fatty alcohols, the most popular additives to promote feel and lustre are lanolin derivatives and silicone oils, some of which are interesting because they are more soluble in cold water than in hot water and so resist rinsing; hydroxyalkylcelluloses and perfluorinated compounds^{26,27} have also been suggested.

Other basic cationics for rinses are N-stearyl colaminoformylmethylpyridinium (Emcol E607S—Witco), ethoxylated quaternary ammonium (Dehyquart—Henkel) and quaternized fatty amidoalkyldialkylamides. The last-named, as non-quaternized tertiary amines, offer the advantage of possible neutralization into salts by the choice of the most suitable mineral or organic acid.

Rinse balsam (to disentangle, and give smoothness and sheen)

	(28)
	per cent
Stearyldimethylbenzylammonium chloride	1.5
Stearyl alcohol	0.75
Cetyl alcohol	0.75
Polawax GP200 (Croda)	3.0
Oleyl alcohol	1.0
Preservatives, perfume	q.s.
Citric acid	q.s. to pH 4-5
Deionized water	q.s. to 100

Procedure: Heat the first five ingredients to 80°–85°C, then add water with stirring. After cooling to 45°C, add perfume and preservatives under thorough stirring. When the temperature reaches 30°C, add citric acid to adjust to pH. A fluid cream of 500 cS viscosity is obtained, to which protein hydrolysate may be added at a concentration of 0.5–1.0 per cent.

*Pearly cream rinse*⁸⁴

	(29)
	per cent
Stearamido propyldimethylamine	1.5
Cetyl alcohol	1.0
Sodium chloride	0.5
Lactic acid 88%	0.5
Water	to 100.0
Dye, perfume, preservative	q.s.

Procedure: Add components, except dye and perfume, to water and heat to 65°–70°C. Blend until homogeneous. Add dye and perfume at 45°C and fill at 35°C or less.

*Pearlescent rinse*¹¹⁸

	(30)
	per cent
Stearyldimethylamine oxide (25% active)	7.5
HCl 36%, 1:1 dilution in water	0.23
Colour, perfume, preservative	q.s.
Water	92.27

Procedure: Heat together amine oxide and water and mix thoroughly. Add HCl in small increments until pH 5.5. Mix for 15 min, then cool gradually with moderate agitation.

<i>Pearlescent repairing rinse (with cationic polymer)</i> ¹¹⁹		(31)
		<i>per cent</i>
Stearyldimethylbenzylammonium chloride (25% active)		5.0
Cetyl alcohol		0.3
Glyceryl monostearate		0.5
Cationic cellulose derivative (Quaternium 19)		1.0
Preservative		0.1
Water		93.1

<i>Hair rinse-conditioner</i> ¹²⁰		(32)
		<i>per cent</i>
A	Arlacel 165	4.0
	Emcol E 607S	2.5
	Stearyl alcohol	2.0
	PPG 30 lanolin ether	2.5
	2-Ethylhexyloxystearate	0.5
	Propyl paraben	0.1
B	Demineralized water	87.75
	Methyl paraben	0.15
	Glucose glutamate	0.5
C	Perfume, colour	<i>q.s.</i>

Procedure: Heat separately phases A and B to 75°–80°C. Slowly add A to B at 75°–80° using high-speed mechanical agitation for approximately 15 minutes. Begin to cool and continue agitation. Add perfume and colour at 40°–45°C. Continue mixing until temperature reaches 35°–40°C and then fill containers.

<i>Foaming cream rinse</i> ¹²¹		(33)
		<i>per cent</i>
	Ammonium lauryl sulphate	15.00
	Cocoamido betaine	10.00
	Lauric diethanolamide	2.00
	*PPG 5 Ceteth-10-phosphate	2.00
	Stearyl alcohol, polyethoxylated	
	(10) and (20) stearyl alcohol	2.50
	Sucrose cocoate	12.00
	Stearyldimethylammonium hydrolysed animal protein	3.00
	Magnesium silicate	0.45
	Fragrance, preservatives	<i>q.s.</i>
	Water	53.05

*CTFA name; Complex mixture of phosphoric esters of polyoxypropylene (5) polyoxyethylene (10) ether of cetyl alcohol.

<i>Rinse-conditioner</i> ⁸³		(34)
		<i>per cent</i>
A	Hydroxyethylcellulose (Cellosize QP 30.000)	0.3
	Water, deionized	92.5
B	*Quaternium 26	2.5
	Ethanol (anhydrous)	2.5
	Standapol OLP	1.0
	Perfume	<i>q.s.</i>

	(34) per cent
C †Quaternium 22	1.0
Citric acid (30% aq)	0.1
BTC 2125 M	0.1

*CTFA name (Ceraphyl 65—Van Dyk).

†CTFA name (Ceraphyl 60—Van Dyk).

A great improvement in the field of rinses was the incorporation of quaternary ammonium compounds with two fatty chains, as exemplified by distearyl dimethylammonium chloride. These compounds, such as commercial products known under the name Arquad-2C, 2T, 2HT and 2S, are very efficient against tangles and rather less irritant.

<i>Cream rinse with di fatty-chained 'quat'</i>	(35) per cent
Distearyl dimethylammonium chloride	3.0
Cetyl alcohol	1.0
Partly acetylated ethoxylated lanolin alcohols	0.1
PEG 600 distearate	1.0
Water	q.s. to 100.0
Perfume, colour, preservative	q.s.

<i>Cream rinse (to be left on the hair)²⁷</i>	(36) per cent
Water	83.20
A Anti-foam AF	0.05
B Arquad 2HT (10% active)	15.50
C Arquad S50	0.10
D Perfluorinated hydrophobic-lipophobic compound	1.00
Perfume	0.15

Procedure: Disperse A in the water with stirring and then add B. Mix the perfume with C and add to the previous mixture. Add D slowly with stirring over a period of about 20 minutes.

The development of conditioners led to the evolution of rinses in a water-white form and to the promotion of a clear hair rinse-conditioner; it was argued that an oil-free composition should lead to a non-oily feeling on the hair. For this purpose clear soluble 'quats' are used, such as cetyltrimethylammonium and benzalkonium chlorides; an oleyldimethylbenzylammonium salt was designed with this specific aim.¹²²

Interesting complements to these formulations are amine oxides, giving the benefit of cationic properties at low pH. They are said to contribute to manageability, to reduce fly-away and to impart a soft feel to hair. The search for conditioning properties explains the introduction into rinses of a wide variety

of other ingredients such as proteins (whose concentration should be comparatively high to comply with 'instant' action as required in the rinse concept), cationic polymers such as Gafquats, Polymer JR (bearing in mind that body and lubrication are often antagonistic characteristics), sterols, ethoxylated cholesterols, lipoaminoacids,^{123,124} polyethyleneimines, silicones, Ucon fluids and anti-dandruff compounds.

<i>Clear rinse</i> ¹²²	(37)
	<i>per cent</i>
Oleyl dimethylbenzylammonium chloride	4.0
Hydroxyethyl cellulose (3% aqueous soln)	40.0
Ethoxylated (10) lanolin acetate	0.5
Distilled water	<i>q.s.</i> to 100

<i>Clear protein rinse</i>	(38)
	<i>per cent</i>
Stearyldimethylbenzylammonium chloride	5.0
Hydrolysed animal protein	5.0
Ethoxylated cetyl alcohol	0.5
Ethanol 90%	5.0
Water	<i>q.s.</i> to 100

<i>Clear rinse</i> ⁸⁴	(39)
	<i>per cent</i>
A Castor oil amidopropyldimethylamine	1.0
B Cocodiethanolamide	0.3
C Hydroxyethyl cellulose	0.8
Citric acid	0.3
Perfume	0.1
Deionized water	<i>q.s.</i> to 100
Preservative, dye	<i>q.s.</i>

Procedure: Disperse C in water, heat to 50°C and stir for 20 min. Add A, B, citric acid, and cool. Adjust to pH 5.0–5.5. Preservative, dye and perfume can be added as desired.

<i>Clear rinse</i> ¹¹²	(40)
	<i>per cent</i>
*Quaternium 33	1.5
Hydroxypropylethyl cellulose	1.0
Polyoxyethylene 20 sorbitan monolaurate (Polysorbate 20)	1.0
Methyl paraben	0.2
Deminerlized water	96.3

*CTFA name (Lanoquat DES—Malmstrom)

Procedure: Dissolve methyl paraben in water with heat. Disperse the cellulose gum and mix until clear. Then add the quaternary and Polysorbate 20.

Clear conditioner, to be rinsed (gives volume, sheen, spring, untangling, smoothness)	(41)
Hydroxyethyl cellulose (Cellosize QP 4400 H)	per cent
Oleyldimethylbenzylammonium chloride	1.0
Gafquat 755	2.5
Protein Q	1.0
Parabens, water-soluble perfume	0.6
Water	q.s.
	q.s. to 100.0

Procedure: Dissolve Cellosize in water and warm. Then add the other ingredients and adjust the pH to 5.0.

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Hair Colorants

Introduction

The colouring of hair is one of the most important acts of adornment among those made by men and women since the origins of man. The quest for a change of external appearance has found expression in various ways in all civilizations. This desire, far from being a secondary and futile activity, as it is sometimes considered today, can be linked to a whole series of fundamental attitudes in the life of the individual and can even be linked to the sexual instinct of the species and thus reflect its inevitable presence.

Leaving on one side the most ancient attempts and the empirical formulae used, the matter has now entered the phase of a major industrial development, in that since World War II there has been a great advance in the discovery and utilization of a series of new synthetic colorants for hair. Indeed, it is estimated that today 30–40 per cent of women in the industrialized countries are users of colouring products, either in the home or at the hairdresser.

The usual reasons for colouring the hair are the following: to change the natural colour, to colour the white hairs which begin to appear with age, or to change the colour of the hair temporarily on a particular occasion. To satisfy all these purposes it is necessary to use a range of colorants with varying composition and behaviour which will be described later. First, in order to provide a more complete picture, the various hair colouring systems, the characteristics of an ideal hair colorant and the various practical hair colouring processes are described.

HAIR COLOURING SYSTEMS

Modern systems of hair colouring may be divided into three categories in terms of the duration of the presence of the colour on the hair after the operation has been carried out.

Temporary Colouring

These are fugitive colours which can be removed at the first shampooing. One finds in this category the commercial products commonly designated 'colour rinses'. These products utilize colours of a high molecular weight which are in effect deposited on the surface of the hair without being able to penetrate into the cortex.

Semi-permanent Colouring

These are colours which resist several shampoos (three to six), but whose fastness is poorer than that of permanent colours. The colours used in this case are direct dyes of low molecular weight, having a good affinity for hair keratin. Because of this, they are capable of penetrating the cortex.

Permanent Colouring

As the name indicates, this category provides effectively permanent coloration, resistant to shampooing and other external factors such as brushing, friction, light, etc. This is the process most widely used and represents at least 80 per cent of the total colourings effected.

In this system, uncoloured intermediates are used, which then by a series of chemical reactions produce *in situ* in the hair the desired colour. The process is one of oxidation (almost always effected by hydrogen peroxide), followed by coupling and further oxidations, as will be examined in detail later.

CHARACTERISTICS OF AN IDEAL HAIR COLORANT

The ideal hair colorant should possess the following properties:

Harmlessness

- (a) It should be non-injurious to the hair shaft, but should colour the hair without impairing the natural texture and gloss.
- (b) It should possess no primary irritant action and be free from sensitizing properties, i.e. it should not be a dermatitic agent.
- (c) It should produce no toxic effect when it comes in contact with the skin.

As regards points (a) and (b), thanks to the steady improvement in the purity of raw materials used (dyestuffs, surfactants, polymers, etc.) and thanks to systems of formulation which permit rapid reaction and elimination of the intermediate products possibly responsible for various dermatological consequences, colorants in fact no longer pose a major problem. On the other hand, the question of systemic toxicity has recently been raised, taking account of the small quantities of some ingredients which can penetrate across the skin to the interior of the body.¹⁻⁶

Thus the problem of evaluating the potential degree of risk to health which hair colorants could present can be seen as a part of the much more general problem of the possible danger to health presented by introducing chemical substances into man's environment. The specific problem may be represented in terms of the three following possible effects of chemicals:

Mutagenicity—the risk pertaining to future generations

Carcinogenicity—the lifetime risk to the individual

Teratogenicity—the risk linked to conception

The relation of these risks to that of hair colorants is currently a matter of considerable discussion and a conclusion has not yet been reached. Major work is in hand in various research institutes and groups, as well as in the hair products industry.

Very briefly summarized, one can say that inconsistent results have been obtained across the experimental variables:

- (a) of methods used and their significance;
- (b) of operating variables (concentrations, methods of application, duration etc.);
- (c) of biological system used (bacteria, yeasts, animals);
- (d) of the different research workers themselves.

A similar situation is found with the epidemiological studies carried out.

In our opinion, these inconsistencies, imprecisions and contradictions demonstrate that hair colorants do not present a real danger to health. Of course, no chemical product can be shown to be completely non-toxic to man. But whenever a product does possess real toxicity, this has been recognized by science rapidly and without any doubt. This is not the case for hair colorants.

Adequate Physical and Chemical Stability on the Hair

The colour of the dyed hair should be stable to air, sunlight, friction (rubbing, brushing) and sweat.

Compatibility with Other Hair Treatments

It should not change colour, nor bleach out, on the application of toilet preparations such as brilliantines, setting lotions, hair lacquers, hair waving preparations, soaps or shampoos.

Stability in Solution

Colorants should be stable over time in the aqueous solutions and formulated products in the forms in which they are sold and used.

Absence of Selectivity

Because it is always necessary to use a mixture of dyestuffs, the phenomenon of selectivity assumes a very great importance. More precisely we are concerned with hairs to be tinted that are very heterogeneous both individually and in their 'history' (the ends damaged by air and sun, previous perms or other treatments, roots compared with shaft, etc.) and thus trying to avoid:

- (a) different coloration on different parts of the same hair;
- (b) different fastness over time of different dyestuffs on the hair *vis-à-vis* external agents.

The problem of selectivity plays a most important part in the technology of hair colorants. One can try to avoid it by utilizing dyestuffs belonging to more or less the same chemical class from the point of view of their physicochemical behaviour. It is necessary to check the solutions by preliminary tests on swatches in the laboratory, and then, and above all, by tests on hair on the head.

Affinity for Hair Keratin

The physicochemical characteristics of affinity, in conjunction with the penetration of the dyestuff into the hair shaft, can be seen to be very important when

account is taken of the technical limitations controlling the dyeing of hair, such as: temperature not greater than 40°C; short time of contact of hair with the dye, up to say 40 minutes; very weak dye solutions, etc.

The problem is tackled by the use of dyes with small molecular dimensions or by making use of formulation techniques such as use of solvents, swelling agents, alkalis, etc., with the object of improving penetration or of modifying the partition coefficient between water and hair.

Much scientific research has been devoted to studying the mechanism of hair dyeing, in conjunction with the much greater volume of work on wool and on the structure of hair keratin. Thus Evans⁷ pointed out that X-ray measurements of the keratin lattice structure indicate that molecules much larger than ethylene glycol penetrate keratin slowly if at all. The interatomic and interchain distances in hair can be altered by causing hair to swell in aqueous solutions at high pH values. Such swelling will promote absorption and diffusion of solute molecules into the hair shaft. But the degree of reversible swelling that may be resorted to without damage to the hair is limited and therefore the molecular size of the dyestuff that can diffuse within is also limited. Alexander⁸ has reviewed the information available on the effect of molecular size on the suitability of a molecule for dyeing hair. He concludes that the smaller the dye molecule the less critically does the penetration depend on the molecular size.

Holmes⁹ has discussed the theoretical aspects of the diffusion of dye molecules into hair and fibres and concludes that the mechanism can be explained in terms of passage of a molecule across a barrier which contains holes. Thus molecules below a certain critical size can pass through rapidly, whereas larger molecules pass through slowly or not at all. He also notes that size is by no means the only critical factor and that the basicity of the dye is also of vital importance.

It is interesting to note that in the most successful dyeing systems the majority of the ingredients, including ammonia, water, hydroxyl ion, hydrogen peroxide, *p*-phenylenediamine and resorcinol, are all small molecules and can penetrate the hair shaft readily.

Zviak¹⁰ has discussed the effect of solvents on the penetration of molecules into hair. He concludes that the presence of solvents which swell hair results in the penetration of molecules of much larger size. Thus for dry hair the largest molecule that can enter the hair has an apparent diameter of 5 Å (0.5 nm). In the presence of water the diameter is increased to 40 Å (4.0 nm) and in the presence of polar solvents molecules of still larger diameter can enter the hair. This accounts in part for the fact that many colorant systems contain solvents which help the dyes to penetrate the hair shaft.

Considerable information is available on the dyeing of textile fibres and Walker¹¹ has discussed the theory of hair dyeing in relation to the theories of wool dyeing. However, such information is only of limited value, since the dyeing of human hair differs in a number of important aspects from wool dyeing.¹²

THE PROCESS OF HAIR COLOURING

Hair colorants provide a range of commercial products, capable of colouring the hair in various shades and tints, ranging from very light blonde to black, passing

through a range of tones: golden, ash, reddish, mahogany, violets, etc. The number of shades constituting such a range can exceed sixty.

All these products use and are based on strictly limited technical factors, of which a summary follows.

Commercial Products are Mixtures

The dyeing solutions contain mixtures of several single dyestuffs, say 3 to 10. In fact each particular colour is the overall result of the superposition of individual colorations (red, yellow, violet, blue, etc.) supplied by each of the dyestuffs in the commercial mixture.

Concentrations of Dyestuffs

The total quantity of all the dyestuffs used to obtain a shade is small and limited. It can range between 0.01 and 5 per cent by weight of the tinting medium applied to the head. The concentration is a function both of the dyestuffs used and of the procedure involved.

Duration of Colouring Process

The time of contact of the dyeing solution with the scalp and the hair is of the order of 5 to 40 minutes.

Quantity of Solution Applied

The amount of dyeing solution applied to a female head varies between 15 and 100 ml.

Frequency of Application

For temporary colorants, this is of the order of once a week. On the other hand, for more permanent colorants, it is about once a month. In fact this is controlled by the regrowth rate of hair, which is about 1 cm per month.

Treatment after Coloration

Colorants must be conceived and formulated so as to avoid to the maximum extent the staining of the scalp. This is, moreover, assisted by abundant rinsing with water which is obligatory after every application of permanent dye and above all by carrying out one or more shampoos, which will lift the greater part of the dye which has not been absorbed by the hair.

These details of the colouring process have been cited over and above the description of the procedure itself, because they are elements that must be considered in designing toxicological protocols so as to extrapolate the findings to a true appreciation of their significance to the human being. Indeed, colorants have for some time been investigated more and more under conditions in which these procedures are 'forgotten' by the experimenters, and could thus yield results which are erroneous or unrealistic.

Uptake of Dyestuff by the Scalp

Semi-permanent and Temporary Dyes. In order to achieve the desired colour, it is sufficient to place on the head a maximum of about 60 g of dye solution. This quantity is spread over a total surface of 700 to 1000 cm² of scalp and about

50 000 cm² representing the surface of the hair. (Normally the number of hairs is given as 150 000, with a mean diameter of 60 μ m and a typical length of 20 cm.) One can thus easily calculate that 1.2 mg of solution is applied per square centimetre of scalp or hair. Referring back to the dyestuffs themselves and for a concentration of 2 per cent dyestuffs in the solution, that is 24 μ g cm⁻² with which the scalp or hair comes in contact. In other words, the scalp in its totality comes in contact with 1.2 g of solution or with 24 mg of dyestuff.

Taking as the mean percentage for passage of a dyestuff across the scalp the figure of 0.2 per cent normally quoted,^{1,5} one finds an actual transfer of 0.05 μ g cm⁻² (50 ng cm⁻²) of dyestuff or otherwise a total transport of 50 μ g for the whole scalp and hence the body.

Permanent Colours (Oxidation). The numerical data remain unaltered, but there is one difference to note: it concerns the first stage of about 10 to 15 minutes, during which half the quantity of product is applied to the roots of the hair, the first 2 cm, close to the scalp, before applying the remainder to the rest of the hair and leaving in contact for a further 15 minutes.

TEMPORARY HAIR DYES

Dyestuffs

The dyestuffs used are generally basic dyes, acid dyes, disperse dyes, pigments or metallized dyes, belonging largely to the chemical classes: azo, anthraquinone, triphenylmethane, phenazinic, xanthenic or benzoquinoneimine. A list of some 145 dyes capable of being used for this purpose has been submitted by the European manufacturers of hair colorants to the European Economic Community authorities with the object of their acceptance in the appropriate directives.

Table 27.1 lists dyestuffs according to category together with the Colour Index Number where known. This list is obviously not exhaustive. Thus one could add a whole series of certified dyestuffs such as may be found in the examples of formulation given by Daniels.¹³ Furthermore, many basic dyes may also be used

Table 27.1 Dyestuffs used in Temporary Hair Dyes

Chemical class	Colour	Colour Index Number
ACID DYES		
Azo	Yellow	13 065
	Yellow	19 140
	Red	14 720
	Red	15 620
	Red	16 185
	Red	16 250
	Red	17 200
	Orange	15 575
	Orange	16 230
	Brown	14 805

Table 27.1 (cont.)

Chemical class	Colour	Colour Index Number
Triphenylmethane	Green 22	42 170
	Violet acid 49	42 640
	Acid blue	42 735
Xanthene	Acid violet	45 190
Azine	Nigrosines (violet)	50 420
Anthraquinone	Acid violet 43	60 730
	Blue 62	62 045
BASIC DYES		
Azo	Yellow 57	12 719
	Orange	11 270
	Orange	11 320
	Red 76	12 245
	Brown 16	12 250
Triphenylmethane	Basic blue 5	42 140
	Violet 14	42 510
	Violet 3	42 555
Azine	Red	50 240
Indoaniline	L'Oreal ¹⁴⁻²²	
Indophenol	L'Oreal ²³⁻²⁵	
Indamine	L'Oreal ²⁶⁻³²	
DISPERSE DYES		
Azo	Yellow	11 885
	Orange solvent 45	11 700
	Orange solvent 9	11 005
	Disperse red 17	11 210
Anthraquinone	Orange 11	60 700
	Red 15	60 710
	Violet	60 725
	Blue 3	61 505
	Blue	62 500
	Black acetoquinone	—
	Black celliton	—
METALLIZED DYES		
Azo	Cibalane blue F.B.N.	—
	Solvent yellow 90	—
	Solvent brown 43	—
	etc.	

in the form of their leuco-derivatives, in which form they penetrate the hair better and develop their colour later by aerial oxidation.³³⁻⁴¹

Types of Commercial Temporary Product and their Formulation

Temporary hair colouring can be achieved by two principal types of product: rinses and coloured setting lotions.

In rinses the dyestuffs are used in the form of simple aqueous or aqueous-alcoholic solutions. In order to increase the substantivity to hair, various assistants (organic acids, special solvents) are added¹⁰ or the hair may be pretreated with cationic compounds.⁴²⁻⁴³ It should be noted that such tinting solutions may be sold as ready for use or alternatively be prepared by the user from concentrated products by simple dilution in water.

The second approach, that of coloured setting lotions, consists in applying the dyestuffs to the hair through the medium of solutions containing transparent polymers, and following the technical requirements of hair sprays and setting lotions. Such a medium can be produced by dissolving 3 per cent polyvinylpyrrolidone (K30 grade) in water (or aqueous alcohol for quicker drying). Any innocuous dyestuff may be added to this base.

Alternatively such a product may be packed in an aerosol can. In this case the use of any water in the product is not advisable in view of possible corrosion of the can (see Chapter 40 on aerosols), and care should be taken that no solid matter precipitates which could block the valve.

The main problem in using such polymer sprays is the tendency of the polymer to flake off the hair, carrying the dyestuffs with it into pillows, towels and clothes. Interested readers should experiment with other hair spray materials, such as ethylcellulose, and PVP-VA copolymers. It has been suggested that such problems might be overcome by grafting the dye on to a polymer skeleton.⁴⁴⁻⁵⁴

Crayons have been used from time to time for temporary colouring, and are employed like mascara—either rubbed direct on to the wet hair or transferred to the hair with a brush. They can be formulated with soaps and waxes, so as to give a product rather like a lipstick (example 1).

	(1) per cent
Stearic acid	15.0
Triethanolamine	7.5
Glyceryl monostearate	4.0
Beeswax	46.0
Paraffin wax	10.0
Microcrystalline wax	10.0
Coconut diethanolamide	7.5
Colour	q.s.

SEMI-PERMANENT COLORANTS

Dyestuffs

These dyes occupy an important place in formulation practice, not only because they permit the creation of this important class of hair colorants, but also

because their presence is often indispensable in the formulation of the permanent colours, the oxidation dyes. Certain of these dyes are capable of providing hair shades ranging from yellow to orange, shades which, in terms of efficacy, are practically impossible to obtain with oxidation dyes and whose contribution is necessary to provide the complete range of shades such as the copper tones.

The great majority of these dyes belong to the following chemical classes:

Nitrophenylenediamines

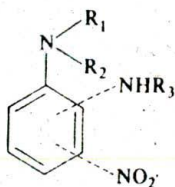
Nitroaminophenols

Aminoanthraquinones

A list of some 50 dyes which could be used has been submitted by the European manufacturers to the EEC authorities for approval. In making the selection, consideration has been given to a great number of physiological criteria. It should be noted that it is also possible to utilize a certain number of the dyestuffs already quoted for temporary dyes such as some nitroazo dyes and some basic dyes.

Nitrophenylenediamines

Nitrophenylenediamines can be described by the general formula:



where R_1 , R_2 and R_3 may be the same or different, and represent H or substituted or non-substituted alkyl groups such as $-\text{CH}_3$, $-\text{CH}_2\text{CH}_2\text{OH}$, $-\text{CH}_2\text{CH}_2\text{NH}_2$, $-\text{CH}_2\text{COOH}$, $-\text{CH}_2\text{CONH}_2$, etc. According to the position occupied by the $-\text{NO}_2$ and $-\text{NHR}_3$ groups these dyes can be regarded as derivatives of 4-nitro-*o*-phenylenediamine, 2-nitro-*p*-phenylenediamine or 4-nitro-*m*-phenylenediamine.

By successive alkylations (R_1 , R_2 , R_3), starting from these nitrophenylenediamines which are themselves excellent dyes, one arrives at interesting increases in depth of colour and thus enriches the range.⁵⁵⁻⁶⁶ Examples are given in Table 27.2. Note also that this class of substitute nitranilines can be enriched:

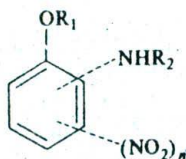
- by using other substituted derivatives in the aromatic ring, by weak electron donors such as $-\text{CH}_3$ or $-\text{OCH}_3$.⁶⁷⁻⁶⁸
- by using some derivatives of nitrodiphenylamine⁶⁹⁻⁷⁰ such as:
 - 4[*bis*-(2-hydroxyethyl)]amino-3-nitro-4'-methylamino-diphenylamine (blue)
 - disperse yellow 1 (Colour Index No. 10385)
 - 2-nitro-4-[*bis*-(2-hydroxyethyl)]amino-diphenylamine
 - 2-nitro-4-methoxy-diphenylamine
 - 2-nitro-4-amino-diphenylamine

Table 27.2 Shades Produced by some Nitrophenylenediamine Compounds

Compound	Shade
nitro- <i>p</i> -phenylene diamine	Orange red
4-amino-3-nitro-N-methylaniline	Purple
4-amino-3-nitro-N-(2-hydroxyethyl)aniline	Violet red
4-(2-hydroxyethyl)amino-3-nitro-aniline	Violet red
4-(2-hydroxyethyl)amino-3-nitro-N-(2-hydroxyethyl)aniline	Violet
4-(2-hydroxyethyl)amino-3-nitro-N,N-[bis(2-hydroxyethyl)]aniline	Blue violet
4-methylamino-3-nitro-N,N-[bis(2-hydroxyethyl)]aniline	Violet blue
4-methylamino-3-nitro-N-methyl-N-(2-hydroxyethyl) aniline	Blue violet
4-nitro- <i>o</i> -phenylene diamine	Orange yellow
2-amino-4-nitro-N-(2-hydroxyethyl)aniline	Orange
2-(2-hydroxyethyl)amino-4-nitro-N-(2-hydroxyethyl)-aniline	Orange
2-amino-4-nitro-N-[tris-(hydroxymethyl)]methyl aniline	Orange
4-nitro- <i>m</i> -phenylene diamine	Yellow

Nitroaminophenols

Dyes of this class can be represented by the general formula:



in which R_1 and R_2 may be the same or different and represent $-H$ or a lower alkyl group, substituted or not, such as $-CH_3$, $-CH_2CH_2OH$, and where n is 1 or 2.

According to the positions of the nitro and amino groups, a series of dyes can be produced, of which the most important are given in Table 27.3. Other derivatives with different substituents have also been synthesized.⁷¹⁻⁷⁵

Aminoanthraquinones

Aminoanthraquinones form a whole range of dyes based on amino- and hydroxy-anthraquinones with various substituents.⁷⁶⁻⁸³ Examples of interesting dyes in this range include the following:

1-amino-4-methylamino anthraquinone (disperse violet 4/solvent violet 12/Colour Index No.61105)

Table 27.3 Shades Produced by some Nitroaminophenol Compounds

Compound	Shade
2-amino-4-nitro-phenol	Orange
2-amino-4,6-dinitro-phenol (picramic acid)	Deep orange
2-amino-5-nitro-phenol	Orange yellow
2-(2-hydroxyethyl)amino-5-nitro-phenol methyl ether	Yellow'
2-(2-hydroxyethyl)amino-5-nitro-phenol-2-hydroxyethyl ether	Yellow
4-amino-2-nitro-phenol	Salmon pink
4-methylamino-2-nitro-phenol	Rose
4-methylamino-2,6-dinitrophenol (isopicramic acid)	Rose
4-amino-3-nitro-phenol	Deep orange
4-(2-hydroxyethyl)amino-3-nitro-phenol	Red
4-(2-hydroxyethyl)amino-3-nitro-phenol methyl ether	Orange
4-amino-3-nitro-phenol-2-hydroxyethyl ether	Orange

1,4-diamino-5-nitro anthraquinone (disperse violet 8/Colour Index No.62030)

1,4,5,8-tetra amino anthraquinone (disperse blue 1/solvent blue 18/Colour Index No.64500)

1-methylamino-4-(2-hydroxyethyl)amino anthraquinone

1-hydroxy-2,4-diamino anthraquinone

Various Dyes

Numerous other dyes can be used in formulating semi-permanent colorants, in general as auxiliaries serving to modify the shade: for example, *heterocyclic azo-derivatives*,⁸⁴⁻⁸⁵ also derivatives of *diazamercyanines*⁸⁶⁻⁸⁷ and *quaternary derivatives of aminophenoxazinium*.⁸⁸⁻⁸⁹

Reactive Dyes. The use of reactive dyes has been a relatively new approach in the field of textile dyeing. These include materials such as dichlorotriazines (for example Procion dyes *ex* ICI), monochlorotriazines (for example Procion dyes *ex* ICI and Cibacron dyes *ex* Ciba) and trichloropyrimidines (Reactone dyes *ex* Geigy, Drimaren dyes *ex* Sandoz). These dyes work by actually reacting with the fibre and thus the dye part of the molecule is firmly held by the fibre.

Broadbent⁹⁰ has discussed the possibility of using reactive dyes for the colouring of human hair. Shansky⁹¹ has reviewed the mode of action of such dyes and also considers their application to human hair. However, he concludes that considerable modification is required before they are as acceptable for human hair as the more conventional oxidation dyes. Patents⁹²⁻⁹⁴ have appeared describing the use of reactive dyes, but little practical experience of their use is available.

Other types of reactive dye have been developed recently:

- (a) after a pretreatment of the hair with a reducing agent, a reactive dye of the class—C—S—R is applied;⁹⁵



- (b) after pretreatment with a dialdehyde, various amino-aromatic compounds can be applied, such as aminonitrophenols, *p*-amino-diphenylamine, etc.⁹⁶⁻⁹⁷
- (c) a mixture of dihydroxyacetone and aliphatic or aromatic amines.⁹⁸

The use of reactive dyestuffs for the dyeing of hair is not as revolutionary an idea as it may at first seem. In fact it is now believed that conventional oxidation dyes such as *p*-phenylenediamine develop their final colour by interacting with reactive sites in the hair. Oxidation dyestuffs may thus be regarded as being a particular type of reactive dyestuff.

Metallized Dyes. The preparation of such dyes may be based on the formation of complexes *in situ* in the hair by means of nickel or cobalt ions and various complexing agents.⁹⁹⁻¹⁰¹ In addition, one may use the metallized dyes already offered for wool dyeing, such as the Neolans, Irgalans, Cibalans, etc.¹⁰

Azo dyes Obtained by Coupling on the Hair. Diazonium salts, together with various coupling agents, may be applied to the hair, as described in a series of patents.¹⁰²⁻¹⁰⁵

Commercial Semi-permanent Products and their Formulation

Semi-permanent colorants can be presented either in the form of foaming lotions (anionic, cationic or nonionic) or as anionic or cationic shampoos. According to the type of medium chosen and the product performance sought, various approaches to formulation have been developed, all having the goal of promoting the penetration of the dyes into the hair. The great number of patents describing various procedures and compositions may be classified as five types:

1. Procedures based on the simultaneous or successive use of thiols and particularly thioglycolic acid.¹⁰⁶⁻¹⁰⁹
2. Procedures based on the use of various solvents: work at Leeds University and elsewhere has shown the possibility of cold dyeing of textiles by using metallized acid dyes (such as the Cibalan and Neolan ranges) in the presence of a solvent such as butanol, which is small enough to penetrate the fibre and which will set up a partition of dyestuff between water and itself. A patent¹¹⁰ describes a similar process and its application to hair, where the dyestuffs are selected from almost every class and the recommended solvents cover a number of different alcohols. A number of other patents have appeared on the use of solvent-assisted dyeing systems and these have been described in a *Schimmel Brief*.¹¹¹ In addition Alexander⁸ and Heald¹¹² have reviewed the patent literature. The work of Peters and Stevens^{113, 114} is of particular importance in the development of solvent-assisted dyeing systems and its application to the colouring of hair at low temperatures, and is worthy of special note.

In a US patent¹¹⁵ the use of boosters for anionic direct dyestuffs has been suggested.

Many other solvents or mixtures have been put forward. Suggestions include

Aryl ethers of the formula $\text{Ar}(\text{OCH}_2\text{CH}_2)_{1-4}\text{OH}$ ¹¹⁶

N-substituted formamides¹¹⁷

Phenoxyethanol¹¹⁸

Phenoxyethanol and ethylene glycol acetate¹¹⁹

N,N-dimethylamides of monocarboxylic acids C₅₋₉ and N,N-N',N'-tetramethylamides of dicarboxylic acids C₉₋₁₉ or linoleic acid dimer¹²⁰

Alkyl glycol ethers¹²¹

Benzyl alcohol and its lower carboxylic acid esters or cyclohexanol¹²²

A mixture of urea and benzyl alcohol¹²³ or benzyl alcohol and N-alkyl pyrrolidone¹²⁴

3. The selection of a range of shades for a semi-permanent dye product depends largely on the market in question. It is usually sufficient to provide brown shades for light and dark brown hair with adequate intensity to cover up 10 per cent grey hair, and a small range of decorative shades such as auburn, chestnut, copper, burgundy, etc.¹²⁵ Greys for levelling the colour of hair which is more than 90 per cent white can also be included. It is essential to note, however, that such products should have a bluish-violet tone, as natural grey hair has a yellowish tint and application of a natural or blue-grey will result in a pale green colour.

4. A popular medium for such dyes is a colour shampoo, formulated as a cream or liquid cream product containing the solubilized dyestuffs¹²⁶⁻¹³² (see Chapter 24 on shampoos for suitable formulations). However, it must be remembered that the inclusion of detergents increases the affinity of the dyestuffs for the medium and hence decreases the amount of 'active' dyestuff available to colour the hair. The concentration of dyestuffs should be higher in a colour shampoo than in a plain aqueous solution. Testing of such products can only be carried out on actual hair, preferably on the head. If wigmaker's hair is used, care should be taken not to use white hair that has been bleached with sulphur dioxide, as this hardly behaves like hair at all.

5. Finally, so-called anionic-cationic complexes may be used, that is to say the formation of a complex from acid dyes, for example azo or azinic, and a quaternary surfactant, followed by solution in a, generally, nonionic surfactant.¹³³⁻¹³⁵

PERMANENT HAIR DYES

Permanent hair dyes are based almost exclusively on the use of oxidation dyes, the so-called *para*-dyes, which are substances that are colourless at the time of their application to the head (the precursors) and are transformed into a coloured material *in situ* on the hair as a consequence of chemical reactions set in motion by the execution of the coloration.

The precursors can be classified into two categories: the compounds called oxidation bases or primary intermediates and those called couplers or modifiers.

The chemical reactions in the formation of dyes are oxidation reactions and couplings or condensations, effected at alkaline pH (essentially due to the presence of ammonia) by the action of an oxidizing agent, almost exclusively hydrogen peroxide or one of its solid derivatives—urea peroxide¹³⁶ or

melamine peroxide.¹³⁷ The choice of hydrogen peroxide is justified not only by its action on the precursors, but also by its ability to promote the simultaneous decoloration of the hair to be tinted.

In fact, the hydrogen peroxide, which is used for this purpose in quantities much greater than are necessary to effect the oxidation of the precursors, is capable of acting on a part of the melanin pigments of the hair, which are the origin of the natural colour, by oxidizing and so solubilizing them—that is to say, decolorizing the hair.

This bleaching, which occurs simultaneously with but independent of the dyeing, results in the hair being rendered lighter and so permits it, in accordance with the aesthetic goal, to be given new shades with the help of the new pigments which this system of dyeing is capable of creating in an almost infinite variety. It can thus be seen why this system of coloration is unique and irreplaceable; this explains its widespread use and its name of colour lightening ('teinture éclaircisante').

To sum up, in order to create colour by this process it is necessary to have three types of reactive chemical:

Base or primary intermediates

Couplers or modifiers

Oxidizing agent, almost always hydrogen peroxide

The chemical nature of the bases and the couplers and the possible mechanism of the formation of colours and pigments are now considered.

Bases

The bases are aromatic compounds, almost exclusively benzene derivatives, substituted by at least two 'electron-donor groups, such as NH_2 and/or OH , these being *para* or *ortho* to each other; this confers the property of easy oxidation.

The most important compounds of this class are thus *p*-phenylenediamine and *p*-aminophenol, and *o*-phenylenediamine and *o*-amino phenol, to which one could add the *p*- and *o*-dihydroxybenzenes.

Starting from these basic compounds and proceeding by various substitutions or by drawing on other aromatic systems, chemists have been able to enlarge considerably the number of 'bases' usable in oxidation dyes. The field is so vast that only recent references can be given, such as the following:

- proceeding from alkylation of the $-\text{NH}_2$ and its transformation into $-\text{NR}_1\text{R}_2$ (where R_1, R_2 are the same or different, and are H or lower alkyls) one such enlargement of the number of bases is obtained.¹³⁸⁻¹³⁹
- Another increase arises from substitutions in the benzene ring by weak electron donors such as $-\text{OCH}_3$, $-\text{CH}_3$, $-\text{NHCOCH}_3$, etc., which can produce bases having special or different properties.¹⁴⁰⁻¹⁴⁵
- Also other aromatic rings can be used, such as pyridine, pyrimidine, quinoline, indole, pyrazolone, benzimidazole, etc., giving rise to a new series of oxidation bases.¹⁴⁶⁻¹⁶⁰

In fact the most important oxidation 'bases' are:

- p*-phenylenediamine
- p*-toluenediamine (2,5-toluenediamine, sometimes called *p*-toluenediamine or *p*-tolylenediamine)
- p*-aminodiphenylamine
- p*-aminophenol
- p*-diaminoanisole
- o*-phenylenediamine
- o*-aminophenol

Couplers or Modifiers

Couplers or modifiers are aromatic compounds, almost exclusively benzene derivatives, substituted by the same groups (—NH_2 and —OH) as the 'bases', but this time in *meta* position to each other. In this position it should be noted that the couplers do not have the property of easy oxidation by H_2O_2 .

The range of couplers can also be enlarged:

- (a) by introducing weak electron donors such as —OCH_3 , —NHCOCH_3 , etc., with or without various alkylations of the OH and NH_2 groups by alkyls and hydroxyalkyls.¹⁶¹⁻¹⁷⁸
- (b) by using heterocyclic rings, such as pyridine, quinoline, indazole, benzimidazole, benzoxazine, pyrazolone.¹⁷⁹⁻¹⁸⁸

The most usual couplers are among the following:

- m*-phenylenediamine
- 2,4-diaminoanisole
- resorcinol
- m*-chlororesorcinol
- m*-aminophenol
- 1,5-dihydroxynaphthalene
- 6-methyl-3-aminophenol
- 2-methylresorcinol

Formation of Colours in the Hair

A very large amount of work has been devoted to elucidating the mechanism of oxidation dyeing and to the structure of the dyes. But all is not yet clear.

In fact, the number of parameters affecting the overall process is very great. For example, consider the influence of pH on the speed of reaction, the presence of the hair keratin itself which can affect the orientation of reactions, the complexity of the reaction mixtures (it is not unusual to use up to 10 couplers and bases), the possible hydrolyses of intermediate products, etc. All these variables make it practically impossible to specify exactly all the compounds which could potentially be formed. Thus empiricism in formulation still plays a very important part in the technology of oxidation dyeing, and no mean effort is required to arrive in practice at a formula that gives commercially reproducible performance.

Be that as it may, the general picture of formation of colours lies in a series of oxidation and coupling reactions in which one can schematically distinguish the three following stages:

(i) *Formation of Quinoneimines.* This phase consists of the oxidation of the bases under the action of alkaline H_2O_2 with the formation of quinone monoimines from *p*- and *o*-aminophenols, and quinone diimines from *p*- and *o*-phenylenediamines.

These reactions can be typified by the scheme for *p*-phenylenediamine and *p*-aminophenol shown in Figure 27.1a. In the same manner the structures of other quinone immonium cations, derived from other bases, can be represented.

(ii) *Formation of Diphenylamines.* The quinone immonium cations formed in the first stage readily undergo a Michael-type conjugate addition with the pseudo-carbanions of the couplers, to give an N-substituted *p*-phenylenediamine: in other words, a differently substituted diphenylamine.

Nucleophilic compound structures capable of addition at the $-NH$ of the quinone imines by attacking the nitrogen atom not only include the *meta*-structure couplers but also the original *para*-bases not yet oxidized and which then function as couplers for their own imines. As an example, consider the formation of diphenylamines from the reaction of *p*-phenylenediamine with *m*-phenylenediamine in its carbanion form (Figure 27.1b).

In the same way, a whole series of variously substituted diphenylamines can be obtained starting from the quinoneimines of other *para*-bases and reacting with other non-oxidized bases.

(iii) *Formation of Colour.* The previously formed transitory diphenylamines can be seen in their turn as new oxidation bases, in which one of the benzene rings is at least trisubstituted (in positions 1, 2, 4 or 1, 2, 5) by electron donor groups. By virtue of this, they possess the same two reaction potentialities as the original *para*-base from which they derive, namely oxidizability and ability to couple—and this to an enhanced degree.

Thus, either they go to be oxidized and transformed into the appropriate indoamines, indoanilines or indophenols—in fact into a first group of dyes—or they act themselves as couplers and are involved in an attack on the quinoneimines from the original *para*-bases, which continue to be formed in the reaction medium, thus leading to a 'double' phenylamine. These new compounds, easily oxidized in their turn, give rise in their oxidized form to a new group of dyes with three benzene rings.

This process of addition of the initial quinoneimines on to the transitory aromatic forms of compounds which are more and more condensed, followed by further oxidations, can lead to still new dyes with more than three benzene rings. Because these dyes have other reaction capabilities, such as intramolecular cyclization or partial hydrolysis, they can partially change into azines or oxazines, that is to yet more dyestuffs.

All these dyes and pigments, of which all the structures are not yet completely elucidated, make up the third group of dyes formed in the hair.

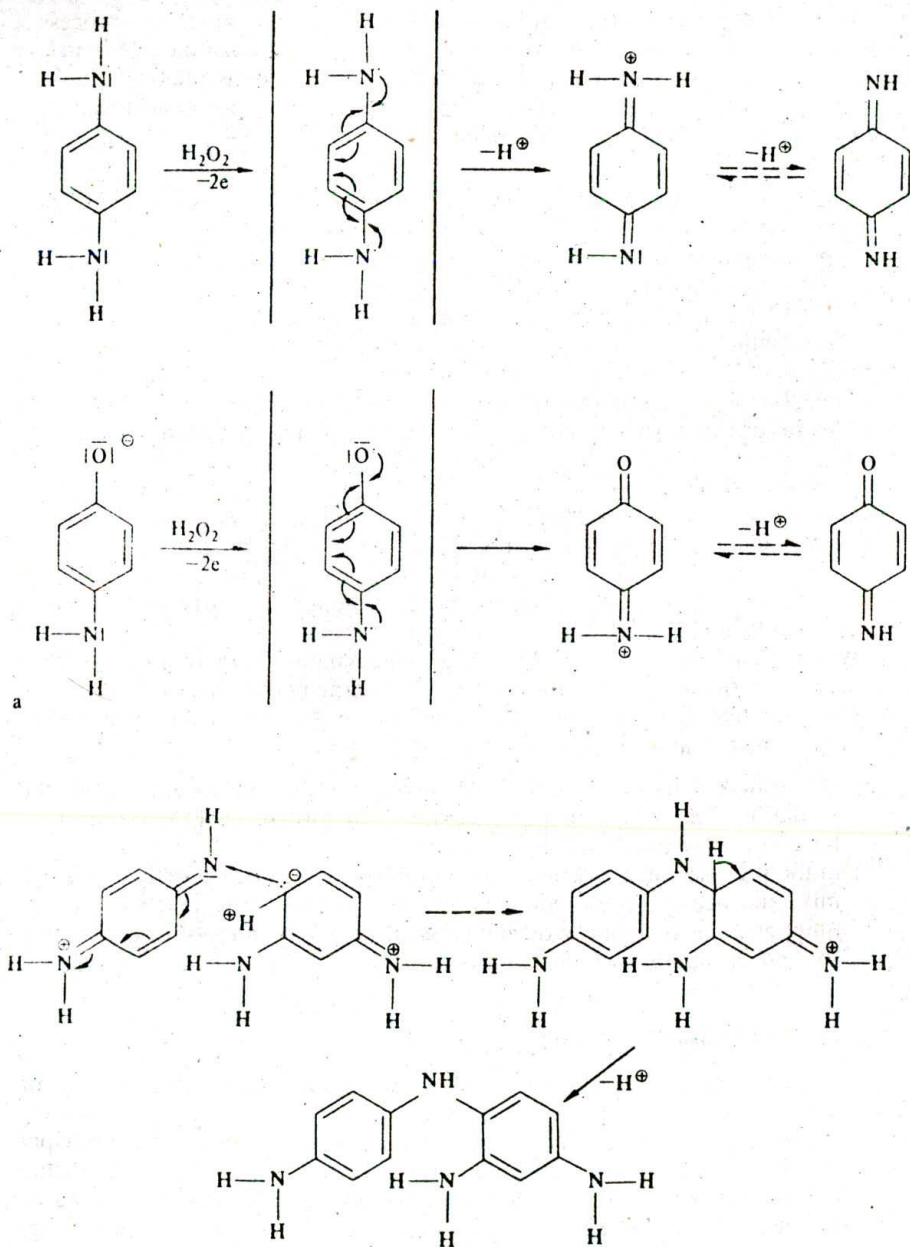


Figure 27.1 *a* Formation of quinoneimines from *p*-phenylene diamine and *p*-aminophenol

b Formation of 4,2',4'-triaminodiphenylamine

It should thus be restated that hair colouring by the permanent dye process is the result of a competition between, on the one hand, indoamine dyes and, on the other hand, dyes originating in a cascade of condensations and oxidations far remote from the primary reactions. Examples of colours to be achieved with various couplers and *p*-phenylenediamines include:

<i>Coupler</i>	<i>Colour obtained</i>
resorcinol	green/brown
<i>m</i> -aminophenol	magenta/brown
2,4-diaminoanisole and <i>m</i> -phenylenediamine	blue
1-naphthol	purple-blue

The structures of a number of these dyes have been studied,¹⁸⁹⁻¹⁹¹ but within the scope of this text it is not possible to discuss this subject in depth.

Bandrowski Bases

The problem of Bandrowski bases should be examined briefly in order to clarify not only their formation from *p*-phenylenediamine and their presence in the colorant mixture, which have given rise to some confusion, but also their toxicological properties which have, by extension, been attributed to *para*-phenylenediamine.¹⁹²⁻¹⁹³

At one time these trimers of *p*-phenylenediamine were thought to be a principal intermediate in the formation of the permanent dyes, but it should be made clear that in hair-dyeing conditions, i.e. *in the presence of hair* and in a process of oxidation of the order of 30-45 minutes:

- Bandrowski's base is not formed to any appreciable extent during the oxidation of *para* by hydrogen peroxide—the formation of the Bandrowski base is a slow process;
- in the presence of the various couplers which accompany *para* in a hair dye mix, and because these couplers are considerably more reactive towards quinoneimine than the oxidized *para* itself, no Bandrowski base is ever formed in quantities detectable by analysis.¹⁹⁴⁻¹⁹⁷

Toxicity and Dangers of Para Dyes

There are two problem areas, that of skin irritation or sensitization and that of systemic toxicity.

p-Phenylenediamine, and also *p*-toluylenediamine, which are the principal components of an oxidation dye, are known to be sensitizers capable of causing contact dermatitis. Because of this, many countries have introduced laws or regulations requiring users to carry out prophetic patch tests before dyeing, specifying limits to concentrations of ingredients in the formulae, etc.

For example, in the UK the Pharmacy and Poisons Act (1933) stipulated that all hair dyes containing phenylenediamines or tolylenediamines or other alkylated benzene diamines or their salts must be labelled with the words: 'Caution. This preparation may cause serious inflammation of the skin in certain persons

and should be used only in accordance with expert advice.' The required labelling was repeated in the Poisons Rules, 1970.

In the USA, Sections 601 (a) and 902 (a) of the Food, Drug and Cosmetic Act require, among other things, that a coal tar hair dye which may be injurious to users shall bear the statement: 'Caution. This product contains ingredients which may cause skin irritation on certain individuals, and a preliminary test according to the accompanying directions should first be made. This product must not be used for dyeing the eyelashes or eyebrows; to do so may cause blindness.'

Section 602 (c) requires that the caution statement appear on the label in a prominent and conspicuous place. This requirement is met if the caution statement appears conspicuously in a colour that contrasts with the background and the remainder of the printed matter. The caution statement should appear on the main panel of the label with the name of the product.

In a notice to 'Manufacturers of Hair Dye Preparations', dated 17 October 1937, the Food and Drug Administration of the US Department of Agriculture, Washington, DC, states: 'It is necessary, as provided in the caution statement, that all such hair dyes bear labelling prescribing adequate preliminary tests. For the benefit and guidance of those interested, there are published herewith directions which, in the light of present knowledge and information, are regarded as acceptable. This information is given merely as a guide and does not mean that other tests may not be acceptable' (see Table 27.4).

Table 27.4 Directions for Making Skin Test (US FDA Recommendations)

1. The hair dye contained in this package must never be used for dyeing the hair unless a preliminary skin test has been made. The skin test must be made each and every time before the hair is to be dyed, regardless of whether or not a skin test has been made at some time previously.
2. The dye used for the preliminary test must be a portion of the article intended to be used for dyeing the hair.
3. The sample of dye to be used for the preliminary skin test should be mixed and prepared in exactly the same manner and according to the directions applicable to the actual use of the hair dye itself.
4. By means of a suitable applicator (clean camel's hair brush, cotton-tipped applicator or other applicator) a streak of dye not less than a quarter of an inch wide and at least one-half inch long is made on the skin and scalp behind one ear. It is important that the streak of dye extend into the hair portions of the scalp as well as that portion of the skin that is hairless.
5. The streak of dye should be permitted to remain for 24 hours. The test should be read between 24 and 48 hours after application. The test area should not be covered with any type of dressing and contact with hats, spectacles or any other object should be avoided.
6. Warning: If redness or burning, or itching, or small blisters, or any type of eruption appears in the general area used for the skin test during the first 24 hours the individual is sensitive to the dye, and under no circumstances should it be used for dyeing the hair. Hair dyes should not be used when there is any disease or eruption present anywhere on the skin or on the scalp.

Even if all these precautions are necessary and desirable, it should just the same be noted that the technology of hair dyes has, with time, made considerable progress, with the result that cases of allergy or dermatitis have become very rare. Thus in 1969, the Committee of Cutaneous Health and Cosmetics of the American Medical Association¹⁹⁸ estimated that 'allergic dermatitis due to PPD in hair dyes would be one reaction in every 50 000 applications'. Dermatologists themselves consider that the level of these incidents has been decreasing over the years.

On the basis of their statistics, the producers estimate that the level of allergic incidents lies at one case of allergy per 1 million units of dye applied.

The improvements in dermatological behaviour of dyes since the beginning of their use can be found in the purity of raw materials used in the formulations, in the improvement in the nature of products formed and, finally, in the associated use of shampoos which remove all remaining substances at the end of the dyeing process.

As to systemic toxicity, a large series of toxicological and epidemiological studies is now in progress. Final conclusions cannot yet be drawn, although a number of indications are beginning to appear.¹⁻⁶

Formulation of Permanent Hair Dyes

Cook,²⁰¹ while noting that in practice they are never used alone, has listed the colours obtainable from the main oxidation bases and coupling agents (Table 27.5).

Brown,¹⁹⁹ Cook²⁰⁰⁻²⁰¹ and Zviak¹⁰ have reviewed the main factors which have to be considered in developing suitable formulations, and note that the following are critical:

1. The formulation base: solution, emulsion, gel, shampoo or powder.
2. The selection of the dye components: the oxidation base, the coupling agent or the addition of a direct colorant.
3. The selection of an alkali: ammonia is usually used.
4. Antioxidants: usually a sulphite or ammonium thioglycollate is used to prevent oxidation of the dye before the product is to be used.
5. The pack: required to be attractive and convenient in use.

Considerable work has been carried out on selection of components but the other major approach is to improve the formulation base so as to achieve more efficient and more convenient colouring.

The most convenient medium for colouring the hair is a shampoo. The system consists of a solution of the dye precursors together with an ammonium oleate soap or other surfactant, to which is added at the time of use another solution of stabilized hydrogen peroxide contained in a separate vessel. This mixture is applied direct to the hair and left in contact for 20 to 40 minutes. Afterwards the hair is rinsed with water and then washed again.

By use of various other additives, such as fatty alcohol sulphates, fatty acid dialkanolamides, nonionic or amphoteric surfactants, fatty alcohols, amine oxides, fatty amines and cationic surfactants, a whole range of emulsions can be

formulated in order to produce the dyes in the form of creams, gels, shampoos, etc.

The use of antioxidants is necessary to protect the system²³ from aerial oxidation during manufacture and packing and also to retard this oxidation during the preparative procedures and the application of the colouring mixture with hydrogen peroxide. Sodium sulphite or thioglycollic acid with or without hydroquinone can be used as antioxidant. The use of ascorbic acid has also been recommended²⁰²⁻²⁰³ as has that of pyrazolones.²⁰⁴

The hydrogen peroxide, essential to the reaction as already detailed, can be used in various procedures. At one time it was common practice among hairdressers to ensure evenness of oxidation dyeing by bleaching the hair first with a mixture of hydrogen peroxide and ammonia and then applying the dyeing solution in mixture with a new minimum quantity of peroxide. This technique is now rarely used.

The modern version of this process is the combined bleach and dye, in which oxidation dyes are used in the presence of enough hydrogen peroxide to bleach the hair while the dyes are penetrating. In this way, dark mousy hair can be dyed to a warm blonde colour several shades lighter than the original colour, yet not apparently bleached. The difficulties found with early formulae have been overcome and suitable products are now available for both home and professional use.

The formulae which may be used are similar to those used for conventional oxidation dyeing, except that more alkali and hydrogen peroxide are used. The degree of lightening depends on the concentration of hydrogen peroxide and ammonia. Thus, for example, if 15 per cent ammonia and 20 per cent hydrogen peroxide are used a lightening of one shade may be achieved (say from black to brown), while if 15 per cent ammonia and 30 per cent hydrogen peroxide (20 vol) are used, then much greater effects can be produced (for example, dark auburn to blonde).

Research has been conducted over many years into the details of final formulation and additives, the objects being improvement in technical performance of the dye mixes themselves and also a widening of the role of the product, which is more and more devoted to functions additional to dyeing. In fact, those skilled in the art now concern themselves not only with the synthesis of higher-performance colorants, obtaining a wider range of colours, greater stability and less risk of skin or systemic toxicity, but also with the preparation, evaluation and manufacture of formulations which provide an almost ideal medium for the dyestuffs, increasing the advantages and reducing the inconveniences to a minimum. This preoccupation, already noticeable in the years 1950-60 in the use of better surfactants, emollients, alkalis and solvents and hair-conditioning agents, has become marked since 1970. Thus the number of hair colorants containing various additives has grown considerably.

One can identify two endpoints of this work on formulation:

1. *The improvement of essential dyeing properties:*
 - Storage stability
 - Ease of application
 - Shortening of time of application

Increased covering power and penetration, fixation in the hair
 Reduction in potential for skin damage
 Protection against eventual hair damage

2. *The conferring of new properties on the hair colorant:*

Protection of hair structure

Improvement of aesthetic quality of the hair, brightness, bulk, combability, general appearance

Addition of antiseptics, antidandruff agents, antiseborrhea agents for the scalp, deodorants, etc.

Addition of substances specific to operations other than dyeing, for example, film-formers, etc.

Some details of various types of these improvements are given below.

The classic permanent hair dye formulations demand a strong basicity; this has generally been obtained by addition of ammonia, which has the disadvantage of strong odour and is aggressive. It is proposed therefore to replace it partially or totally by alkalis that are less injurious and more pleasant in use. Eugene-Gallia replaces the ammonia by an alkali metal or ammonium carbonate, or an amino acid associated with an organic base (morpholine, mono-, di-, or tri-ethanolamine).²⁰⁵ Bristol-Myers propose the addition of an aminohydroxyl compound such as the lower alkanolamines, tris-hydroxymethyl-aminoethane etc.²⁰⁶ Procter and Gamble propose guanidine or arginine derivatives or peptides rich in arginine together with a NaH_2PO_4 - Na_2HPO_4 buffer.²⁰⁷

Another type of improvement concerns the increase of the light stability of a toluenediamine-resorcinol preparation by addition of diamino-1,2- or 1,3-benzene substituted in positions 4,5 or 4,6 by identical groups that are not proton-donors (F or CH_3),²⁰⁸ or further addition to the dye mix of a UV-filter such as benzylidene-camphor²⁰⁹ or mixtures of the isomeric branched-chain dodecyl benzotriazoles.²¹⁰

Additives designed to inhibit premature oxidation of *para* dye bases include indazolone sulphonic acid and its salts,²¹¹ sodium sulphite or dithionite, or ascorbic acid.²¹² The use of enzymes as additives has been known for a long time; recently Procter and Gamble have extended the range in covering the use of a whole series of oxidases.²¹³ In the same area, L'Oreal have proposed the incorporation of peroxide dismutase in oxidation hair colorants.²¹⁴

In the surfactant field, an extension has been proposed to the number of agents used by the employment of surface-active oligomers of the polyhydroxylated polyether type as colouring vehicle.²¹⁵

It is well known that some of the necessary conditions for achieving a good permanent wave, a good dyeing or bleaching can cause damage in the long run to the structural integrity of the hair. Thus strong alkalinity and use of oxidizing agents can attack the hair shaft. To inhibit eventual damage or to restore damaged hair, the following substances have been proposed for incorporation in hair dyes: keratin hydrolysates,²¹⁶ keratose obtained by hot treatment of keratinous materials with aqueous bases,²¹⁷ methylol derivatives,²¹⁸ an alkyl imidazolone associated with an amidobetaine or with Miranol,²¹⁹ polyesters of polycarboxylic cycloaliphatic or aromatic acids and of polyalkylene oxides.²²⁰

The application has also been proposed of an after-dye lotion containing

alkoxymethyl esters of carboxylic acids²²¹ or an oxazolidine²²²⁻²²³ in order to improve the structure of damaged hair.

Another line of formulation has as its goal not only the protection and/or restoration of damaged hair, but at the same time improvement of the aesthetic qualities (combability, lustre, bulk, general appearance). For this purpose, such formulae contain conditioning agents. Accordingly there are proposals for the incorporation of: quaternary ammonium compounds on their own,²²⁴ or together with polyethoxylated fatty amides²²⁵ or a film-former such as polyvinyl pyrrolidone (PVP); formaldehyde-dimethyl hydantoin resin,²²⁶ or a whole series of cationic polymers, among which may be mentioned the quaternized copolymers of N-vinyl pyrrolidone-dimethylaminoethylmethacrylate-polyethylene glycol;²²⁷ quaternary polymers of the ionene type;²²⁸⁻²³¹ cationic cellulose ethers; piperazine polycondensates,²³²⁻²³³ cyclopolymers of diallyldimethylammonium and its copolymers with acrylamide and diacetone acrylamide.²³⁴⁻²³⁶

A special type of formulation has been developed to permit cosmetic operations other than dyeing to be carried out by means of specific additions. As example can be quoted compositions in the form of aqueous creams or gels containing direct and/or oxidation dyes together with film-formers such as PVP, acrylic resins, PVP-vinyl acetate, basic polymers of acrylates and methacrylates.²³⁷ Also there are those intended for colouring and defrizzing which contain lithium, sodium or potassium hydroxide for the softening of the keratin.²³⁸

It has been further envisaged that additives could be incorporated with the object of reducing the concentration of active matter in cosmetic preparations (including colorants). A little before use an addition is made of 1-10 per cent by weight of organic compounds which dissociate in alkaline media and possess ester groups and/or halogens, and which can form an acid on dissociation (ethyl acetate, ethyl lactate, chloracetamide).²³⁹

OTHER DYES FOR HAIR

Considerable work has been reported on the development of oxidation dyes which can be used under ambient conditions and which do not require chemical oxidation. A large number of different materials have been examined and these can be classified according to their basic chemical structures.

Aromatic Polyhydroxy Compounds

Aromatic polyhydroxy compounds include trihydric phenols such as 1,2,4-trihydroxybenzene, 2,4,5-trihydroxytoluene and 1,2,4-trihydroxy-5-chlorobenzene. A British patent²⁴⁰ describes the use of such materials in a formula which includes sulphite or mercaptan reducing agent. The use of compositions free from sulphites or other reducing agents is described in two later patents;^{241,242} the polyhydric phenols are used in conjunction with short-chain aliphatic amines. A range of shades from blonde through reddish-brown and auburn to chestnut and bluish-black is available.²⁴³⁻²⁴⁵

There has been, for some time, an interest in the use of 3,4-dihydroxyphenylalanine as an oxidation dye, mainly because it is the precursor

of melanin, the natural pigment of hair. The use of the next material in the chain, 5,6-dihydroxyindole has been described in a British patent,²⁴⁶ but it appears that the melanocyte does a better job in producing a satisfactory colour. Light shades ranging from light ash to blonde have been reported^{247,248} and are based on the use of methyl derivatives of 5,6-dihydroxyindole. The use of 3,4-dihydroxyphenylalanine in admixture with other phenols such as hydroquinone is described in a US patent,²⁴⁹ but the colours produced are again rather pale. Other dihydroxybenzene derivatives have also been reported as being suitable. Thus *ortho*-dihydroxybenzenes (i.e. catechol and some of its derivatives),²⁵⁰ dihydroxyaminobenzenes^{251,252} and N-substituted 2,4-dihydroxyaminobenzenes²⁵³ have been reported as giving colours ranging from brown and auburn to grey and black.

Vegetable Hair Dyes

Henna

Of the vegetable hair dyes, only henna is of any real importance today. It consists of the dried powdered leaves of *Lawsonia alba*, *Lawsonia spinosa* and *Lawsonia inermis*, which are removed from the plants prior to flowering.

Henna owes its hair-dyeing properties to the presence of 2-hydroxy-1,4-naphthaquinone, often termed *lawsone*, which is soluble in hot water and is, in acid solution, a substantive dye for keratin. In dyeing hair with henna, a paste of the powdered henna and hot water, slightly acidified with citric, adipic or other suitable acids to an optimum pH of about 5.5, is applied to the washed hair.

This 'henna pack', which is kept in place by means of a towel, is allowed to remain on the head for the required time, which may vary from five to sixty minutes, after which the hair is thoroughly shampooed, rinsed and dried. The treatment time depends upon the shade desired, the texture and condition of the hair, the activity of the henna, the acidity of the paste and the temperature at which the pack is applied.

Henna has the advantage that it is neither a primary irritant nor a sensitizer and possesses no local or systemic toxicity. The colour obtained is relatively stable and is deposited in the hair shaft, whereas metallic dyes coat the hair shaft. Unfortunately it suffers from a number of disadvantages—in particular, that it is messy to use, and the range of colours produced is limited to reddish auburn shades. Contact with the finger-nails must be avoided or the keratin of the nails will also be stained. Repeated dyeing with henna tends to spoil some of the effect and produces a somewhat hard auburn colour.

In addition to its use as a hair dye, henna extract is incorporated in certain acidic rinses. The difficulty here lies in the fact that any rinse strong enough to tint the hair is equally likely to tint the nails during application unless they have been previously protected.

Henna Reng

By the addition of other substances to henna, shades other than auburn may be obtained; for example, a mixture of powdered indigo leaves and henna produces blue-black shades and such mixtures are known as *henna renga*s.

Chamomile

Of the various species of chamomile, only *Anthemis nobilis* (Roman chamomile) and *Matricaria chamomillae* (German chamomile) have a cosmetic use; they appear to be equally useful in tinting hair. The active ingredient in these flowers is 1,3,4-trihydroxyflavone, known also as apigenin. Either an aqueous extract or a paste of the ground flower heads may be used. To lighten the hair, a paste consisting of 2 parts chamomile and 1-2 parts kaolin mixed to a thin cream with hot water is applied to the head for a period varying from 15 minutes to 60 minutes depending on the shade required.

Chamomile is also used as a constituent of hair-brightening rinses and shampoos. Some doubt has arisen as to whether chamomile is really effective. The point is that at least 5 per cent chamomile, or its equivalent in extract, must be present to produce any effect at all, but the azulene also present in chamomile probably contributes to the brightening effect.

Metallic Hair Dyes

In metallic dyes, compounds of lead are the most frequently used; compounds of silver, copper, iron, nickel and cobalt are sometimes employed, and less frequently salts of bismuth.

It is not quite certain whether the colours produced by such compounds are due to sulphides formed by a reaction between the sulphur in the keratin and the metallic salts, or to metallic oxides formed by the keratin reducing the metal salts. It is possible that both reactions occur to some extent. Whatever the mode of action, the result obtained is the deposition of a coloured film along the hair shaft which, eventually, gives the hair a characteristic dull metallic appearance, renders the hair brittle and diminishes the efficiency of a subsequent permanent wave.

Lead Dyes

The active ingredient in these dyes is usually lead acetate together with some precipitated sulphur, glycerin and water. Example 2 is a typical formula. Sodium thiosulphate may be incorporated in place of precipitated sulphur. Such preparations have poor stability.

	(2) per cent
Precipitated sulphur	1.3
Lead acetate	1.6
Glycerin	9.6
Rose-water	87.5

The action of lead dyes is slow and progressive, and the shades produced in grey hair usually pass from yellow through brown to black. The shades achieved depend upon the concentration of lead salts in the preparation, the number of applications, the original colour of the hair and the time during which the colour has been allowed to develop.

Probably because of interaction with skin proteins, such lead solutions are relatively non-toxic under normal conditions of use. However, it must be

remembered that these preparations are usually sold for home use and systemic effects may follow if lead remains on the hands and contaminates food. The ingestion by children might be fatal and preparations containing lead should carry adequate precautionary notices.

Other Metallic Dyes

Other metallic hair dyes, such as bismuth, silver, copper, nickel and cobalt salts, have been proposed, but pose important problems of toxicity and of necessary precautions.²⁵⁴⁻²⁵⁶

HAIR DYE REMOVERS

The removal of hair dyes is sometimes necessary either because of a mistake or because the user wishes to have a lighter shade. In the case of metallic dyes it is usually dangerous to remove the dye by chemical means since the metals catalyse many reactions and may cause a violent production of heat which will probably damage both hair and scalp. The only remedy for an unwanted metallic dye is to let the hair grow.

Oxidation dyes can be removed, more or less successfully, by treating the hair with reducing agents such as sodium hydrosulphite or sodium formaldehyde sulphoxylate, usually at a concentration of 5 per cent. The use of formamidine sulphinic acid has also been described²⁵⁷ and a formula²⁵⁸ has been quoted as follows:

	(3) per cent
Formamidine sulphinic acid	1.5
Polyvinylpyrrolidone	5.0
Ethylene glycol monobutyl ether	5.0
Ammonium carbonate	1.0
Ammonia (25%)	0.5
Carboxymethylcellulose	2.5
Water	to 100.0

Semi-permanent dyes can often be removed by vigorous washing with shampoos, particularly if a little ammonia is added. Some dyestuffs, however, prove very resistant and a mixture of shampoo, reducing agent and bleach in the proportions 1:1:2 has been recommended for such cases.²⁵⁹

BLEACHING AND LIGHTENING

Obviously no description of hair dyes would be complete without reference to the method of producing blonde shades. This is accomplished by bleaching the hair in the usual manner to the palest possible shade of blonde with ammonia and hydrogen peroxide. The hair is afterwards given a rinse with a blue rinse containing about 1:100 000 of methylene blue (Ext. D&C Blue No. 1), or other suitable blue certified colour. The addition of the blue colour is necessary since

the human eye considers a substrate which is very slightly blue in colour as whiter than white.

Bleaching of the hair must be thorough or the combination of a deep yellow hair shaft and a blue rinse may give the hair a distinctly greenish appearance.

Cook²⁶⁰ has reviewed the bleaching treatments available for human hair and discusses the effects of factors such as controlled oxygen release and the use of additives to help overcome the damage caused to the hair by such treatments. He particularly recommends the use of substantive proteins either added to the oxidant or used before treatment.

To obtain better control in the application of peroxide to the hair, and extend the bleaching time, powder products have been introduced. These powders vary from inert materials such as kaolin or magnesium carbonate, used with peroxide and ammonia, to powders which themselves provide ammonia and some form of active oxygen, when wetted with water or hydrogen peroxide. These powders were at one time called 'white henna', which was misleading because they contained no henna, but was convenient because it indicated their method of use. Typical early formulae contained up to one-third of sodium perborate or percarbonate, the balance being kaolin and/or magnesium carbonate. More complex formulae are given in examples 4 and 5.

	(4) per cent	(5) per cent
Ammonium persulphate	3.0	—
Potassium persulphate	—	8.0
Potassium hydrogen tartrate	3.0	—
Potassium hydrogen oxalate	—	8.0
Sodium carbonate	3.0	13.0
Surfactant	1.0	1.0
Thickener	5.0	—
Magnesium hydroxide and/or aluminium hydroxide	to 100.0	to 100.0

Procedure: Mix the powder to a paste with hydrogen peroxide (10–40 vol) before use, and spread evenly over those parts of the hair which it is wished to bleach.

All the preparation types described above are essentially for the professional hairdresser because of the degree of skill and care required to get satisfactory colour results with a minimum amount of damage.

For home use, products are formulated on much more simple lines. A suitable two-bottle pack would be:

	(6) per cent
A Hydrogen peroxide 20 vol	98.6
Tartaric acid	0.8
Sodium stannate	0.6
B Ammonia	4.5
Surfactant, e.g. ammonium soap	3.0
Water	92.5

Procedure: Mix equal volumes of A and B before use.

Even more simple products, popular in the 1950s, were known as hair lighteners or brighteners. These were often simple solutions of hydrogen peroxide at concentrations between 1 and 3 per cent (3–10 vol) stabilized as solution A in example 6. The solution is combed through the hair and left to react slowly. Since the reaction does not take place in alkaline conditions, and there is no ammonia present, the solutions cause very little damage to the hair, and no red or brassy off-shades.

A bleaching composition for human hair described in US patent²⁶¹ is particularly intended for localized bleaching, e.g. bleaching new hair growth close to the scalp without damaging any previously bleached hair and without skin irritation. The bleaching composition described is prepared by combining a dry mixture of an anhydrous silicate, an alkali or ammonium salt of a peracid, for example a persulphate, with hydrogen peroxide and a liquid alkaline ammonium soap within a pH range of 9.3 to 10.0, when this mixture will gel. By mixing hydrogen peroxide with a constant amount of the liquid ammonium soap but different amounts of the dry powder mix, it is possible to produce a range of bleaching compositions of different strengths in which the pH value remains within a desired narrow range. The function of the soap is to contribute to the alkalinity of the compound, to help in attaining the desired consistency of the gel and to function as a shampoo in the removal of the bleach. The peracid salts, preferably a mixture of potassium and ammonium persulphate, assist by virtue of their oxidizing action in the bleaching process and thus permit less hydrogen peroxide to be used. Together with the sodium meta-silicate and the ammonium soap, they are claimed to buffer the bleaching composition within the desired pH range throughout the bleaching operation, and to produce a gel of the desired consistency.

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Permanent Waving and Hair Strengtheners

Introduction

From the time the earliest Egyptian woman curled her hair by means of wet mud, and through the Roman and Grecian era up to the present day, the desire of all women has been to possess an attractive and beautiful coiffure. In general, even allowing for the vicissitudes of fashion, curly, or at least wavy, hair is more attractive than straight hair, and at the same time provides more opportunities for rearrangement in suitable and fashionable styles. Hence any process by which curls or waves could be introduced into hair was bound to affect to a very marked degree the trend of modern hairdressing.

Suter¹ has pointed out that '... until around 1910, hair was always curled by means of a curling iron or by boiling it in water. This, however, never resulted in a lasting wave . . . Three pioneers, Charles Nessler, E. Frederics and Eugene Suter, each working independently, found that the addition of chemicals such as borax to the boiling water would curl hair so that it would survive several washings. Around 1924 ammonium hydroxide first came into use in connection with borax . . .'

Subsequently chemical methods of heating and the cold wave have been developed; these are discussed later in this chapter.

The statement that naturally curly hair is observed to be oval or flattened when examined microscopically while straight hair is usually circular is incorrect. Many naturally curly hairs are oval, but many others cannot be differentiated from ordinary straight hair. Kneberg² has shown that hairs of widely varying cross-sectional form may or may not curl, while Danforth³ states that there would seem to be no reason why a shaft that is uniform in structure should curl merely because its cross-section is elliptical. If, however, the upper and lower sides of the shaft were of different density or if the transverse axis did not bisect the vertical, a differential would be provided which might be expected to form curls readily.

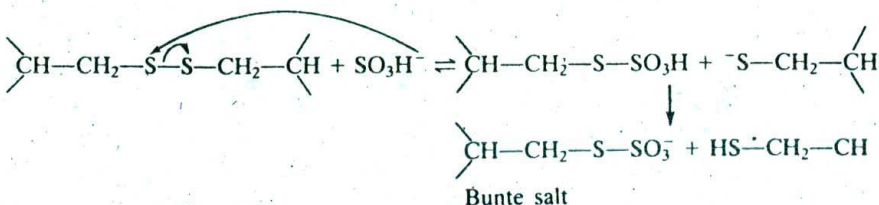
The natural shape of the hair is determined during the keratinization stage, as the almost fluid cells produced by the papilla are shaped by the follicle wall and converted into keratin. The shape of the hair is thus a very deep-seated structural characteristic, not easily altered by subsequent treatments of the fully keratinized shaft. Hence all the processes described in this chapter, although they are called 'permanent' are subject to gradual relaxation, as the hair returns to its normal straightness or kinkiness. The time taken for this relaxation varies

Reducing Agents

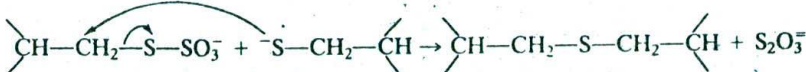
In normal hot waving practice, the reducing agent is invariably a sulphite; in cold waving it is usually a thiol compound, more particularly thioglycollic acid, which since it was introduced in 1940 has remained in favour with the user.

The reaction of sulphites with disulphide bonds is not simple because of the reversibility of the basic processes involved and its high sensitivity to pH. The maximum reductive action of sulphite ranges between pH 3 and 6²¹ but there may in fact be two maxima, one at pH 3.25-3.50 and the other about pH 5.²² In practice, an acidic medium is not often used because of the instability of sulphites under these conditions; pH ≥ 6 is generally used, and at pH 7 (30 minutes, 30°C) about 15 per cent of hair disulphide bonds are reduced. To increase the reduction rate the equilibrium should be displaced, which is achieved by heating.

The sulphite reaction seems to involve a typical nucleophilic reaction:^{23,24}

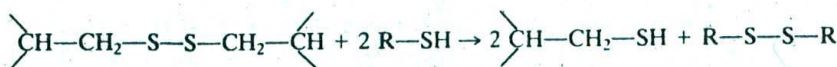


In alkaline medium the keratocysteine formed is ionized and the formation of lanthionine is promoted:



The displacement of the previous equilibrium towards the right should be improved by this reaction but the excess of negative charges prevails against sulphitolysis.

Thiol is, beyond any doubt, the best reactive agent for cold reduction of disulphide bonds through the reaction:



This reaction is ruled by a number of equilibria which depend on several parameters (pH, stress during treatment, swelling, protein charge, concentration, time, etc.) but the overriding factor controlling the equilibrium cleavage level of keratin disulphide is the pK of the thiol relative to the keratin pK. 9.8:^{21,25} in other words, the relative concentration of thiolate ions RS^- in relation to pH. If the relative pK of the thiol is above 9.8, the cleavage level will be optimal at alkaline pH; if it is below 9.8, the optimal cleavage rate will be reached at neutral or even acidic pH.

The main body of the studies refers to the action of thioglycollic acid, with its high pK of 10.4, or more precisely to its ammonium salt.²⁶ The first step of the reaction leads to the formation of a mixed disulphide (A) which was first proved

The nature of the thiol compound, mainly expressed by the pK, is therefore critical to the rate at which the above equilibria are established and to the competitive reactions which could occur according to the pH.

Formulae of thiol compounds mentioned below are given in Table 28.1. Those containing carboxylic acid functions have necessarily a high pK because the carboxylate anion prevents the ionization of the thio-group, as for β -mercapto propionic acid, thiolactic acid, cysteine and its N-acylated derivatives,^{32,33} dimercapto adipic acid and thiomalic acid, which is a diacid monothiol.

All these thiol compounds are rather less efficient than thioglycolic acid, but their use is claimed to be more suitable for hair that has already been damaged by previous treatments, and with regard to odour.^{25,34,35}

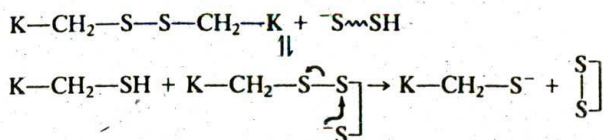
The blocking of carboxylic acidity by esterification or amidification significantly lowers the pK (10.4 \rightarrow 7.8) and allows very effective reductions at neutral pH,^{25,34,36} for example with glycol thioglycollate, glycerol thioglycollate and thioglycollamides.

Table 28.1 Formulae and pK Values of Some Thiol Compounds

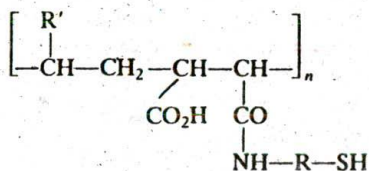
		pK value
Thioglycolic acid	HS—CH ₂ —CO ₂ H	10.4
β -Mercapto propionic acid	HS—CH ₂ —CH ₂ —CO ₂ H	10.4
Thiolactic acid	HS—CH—CO ₂ H CH ₃	10.4
Cysteine	HS—CH ₂ —CH— / \ CO ₂ H NH ₂	{ 8.3 10.8
Dimercapto adipic acid	HS—CH—(CH ₂) ₂ —CH—HS CO ₂ H CO ₂ H	
Thiomalic acid	HS—CH—CH ₂ —CO ₂ H CO ₂ H	
Thioglycollamides	{ HS—CH ₂ —CONH ₂ HS—CH ₂ —CONH—NH ₂	{ 8.4 8.0
Glycol thioglycollate	HS—CH ₂ —COOCH ₂ —CH ₂ OH	7.8
Glycerol thioglycollate	HS—CH ₂ —COOCH ₂ —CHOH—CH ₂ OH	7.8

Unfortunately, in addition to the problem of hydrolysis with time, which may alter the efficiency of the compounds, there seems to be some inverse relationship between the potential irritation to the scalp and the pK of the thiol compound.³⁴ Conditions and very specific associations had therefore to be investigated, but their possible development was limited.³⁷ Despite its disadvantages (odour, only average efficacy, alkali pH for activity), thioglycolic acid remains a reliable 'partner' since it offers an excellent compromise between activity and tolerance. However, it is not necessarily irreplaceable: among a

number of new proposals are some dithiol compounds³⁸ which may be used at low concentration and at neutral or even acidic pH; they have only faint odour and limited aggressiveness. Their efficacy is linked to their ability to yield a cyclic disulphide by oxidation, which results in a complete displacement of the equilibrium thiol-disulphide towards formation of keratocysteine through an internal thiol-disulphide exchange reaction on the mixed disulphide:



Other interesting thiol compounds have been patented for permanent waving:³⁹ the polythiolated polymers obtained by addition of an aminothioliol compound to a maleic anhydric-vinyl ether copolymer:



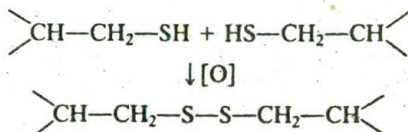
They may reduce keratinic disulphides, thereby being oxidized to an insoluble disulphide polymer with various degrees of cross-linkage. By setting within the keratinic structure, the polymer is believed to strengthen hair and setting and to protect them from environmental effects, particularly those of water. Furthermore, these compounds are expected to give a much better skin tolerance than monomeric thiol compounds.

Use of enzymes has also been suggested for disrupting the disulphide bonds of keratin, particularly transhydrogenases and reductases,⁴⁰ but thiol compounds are usually required as hydrogen donors.

Many other reducing agents have been proposed, such as thioglycerol, hydrosulphide,⁴¹ formamidine sulphinic acid or thiourea dioxide,⁴² dithiocarbamates,⁴³ esters of trithiocarbonic acid,⁴⁴ borohydrides,⁴⁵ phosphinic derivatives,⁴⁶ chlorothioformates,⁴⁷ 2-aminoethanol and the so-called keratein, that is, reduced keratein.⁴⁸

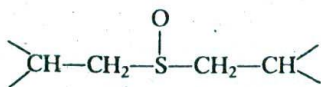
Re-oxidation Step

The oxidation of hair after any of these reducing treatments is a necessary stage in hardening the structure into the new imposed shape (straightened, curled or waved). The basic process is a simple re-oxidation of keratocysteine into keratocysteine but at the same time it should induce the formation of cross-linked fibres and restore the former mechanophysical properties of hair:

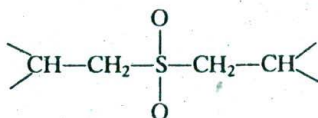


It means that pairs of keratocysteine groups happen to be in a favourable position to re-establish a disulphide bridge under the action of oxygen—otherwise keratocysteine may undergo peroxidation to the stage of sulphinic or sulphonic acid. Similarly, side compounds formed during the reducing step may evolve into different oxidation levels. So, in fact, the oxidation process is no simpler than the reduction process considered above, the more so because it is operated with an excess of oxidant (H_2O_2 , bromate, iodate, etc.).

A number of studies have been carried out to explain the various possible reactions involved,^{26,29,49} but they were often biased because of analytical artefacts. For example, a certain amount of cysteic acid was said to appear; it is now known that, although this degree of oxidation may be reached to some extent with continued treatments,³⁰ it is usually produced during the analytical process²⁸ as a result of acidic hydrolysis of lanthionine oxidation species. The studies of Boré²⁸ have cleared up most of the mystery and settled some of the earlier proposals, by giving a consistent assessment of the two phases in cold waving process: under mild conditions of setting (20 minutes, 25°C) transformation of keratocysteine into disulphide is optimal (96–99 per cent) without prejudicial keratolytic effect either with '6 volume' hydrogen peroxide at pH 3 or with 18 per cent sodium bromate solution at pH 5. The lanthionine formed during the reduction phase—which may represent 30 per cent of the hair cysteine—is oxidized, at least 70 per cent, to sulphoxide and sulphone (the same applies to the hair methionine):



sulphoxide



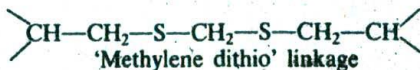
sulphone

On the whole, permanent wave processing with thioglycollic acid shows a loss of 10–30 per cent of cysteine transformed into lanthionine and its oxidation derivatives.

As to whether lanthionine may form bridges between the chains or contribute to the quality of permanent wave, discussion is still open, although the considerable decrease of solubility in urea-bisulphite medium when lanthionine increases favours the cross-linkage theory.

Sulphite-reduced hair is usually hardened through the same procedure: the thiosulphate and the thiol groups are transformed into disulphide by hydrogen peroxide, but by a much slower reaction process and therefore not completely.

Cross-linking of reduced hair may be effected by other means than through peroxides, which may involve a risk of lightening the hair; thus polythionates⁵⁰ allow the rebuilding of keratocysteine without the side-effects mentioned with the former compounds. A formaldehyde-producing agent such as hexamethylene tetramine may lead to another kind of cross-linkage: 'methylene dithio' linkage. Azadioxabicyclooctane derived from tris(hydromethyl) aminomethane and formaldehyde is recommended for this purpose.⁵¹



Alkylene dihalides⁵² also yield dithioether compounds but the conditions of the reaction and the potential skin irritancy of these alkylating substances seem to be hardly compatible with human use. The use of particular salts has been claimed for cross-linking: triethanolamine titanate,⁵³ the zirconium salt of an organic hydroxy acid,⁵⁴ barium salts⁵⁵ which produce S—Ba—S linkages, divalent metal mercaptide of N-methylol thioglycolamide with double cross-linking potentialities,⁵⁶ sulphinamides were also described as suitable neutralizers.⁵⁷ More recently, acylthiosulphates⁵⁸ were proposed as cross-linking or alkylating agents, as well as unsaturated compounds such as maleates.⁵⁹

Another patent⁶⁰ reports the insertion of polymers into the keratinic structure by polymerization *in situ* of a vinylic monomer by a catalyser in reduced hair.

More recently a rather different chemical reaction was patented to wave hair⁶¹ whereby hair undergoes oxidation, for example by alkaline monopersulphate, without prior reduction. This reaction, better performed with chelating agents (EDTA or its salts), is believed to modify hair without yielding visible discoloration.

In addition, in spite of the theoretical and practical reasons for using sulphites in hot waving and thio-compounds in cold waving, successful cold products for the achievement of 'soft' permanent waves are now available which employ sulphite at high pH (about pH 10) and hydrogen peroxide neutralization. Such products have been discussed by Markland.⁶²

Evaluation of Permanent Waving

It may be understood from the foregoing that the chemistry of the waving process is extremely complicated and therefore the investigative method, however sophisticated, cannot encompass all the physicochemical modifications involved, particularly the state of hair after treatment. As with the other hair processes, permanent waving may only be assessed *in vivo*.

A number of techniques *in vitro* may, however, give some valuable information on the evolution of the mechanophysical properties during and after the process. They thus help in the screening of potential agents.

The instrument most commonly used to investigate the mechanical properties of hair is the extensometer, which allows a graph to be drawn relating the extension of the hair to the load applied. Typical curves obtained in this way are shown in Figure 28.1. It may be seen that there is a sharp change in the slope of the extension curve at A. The yield point corresponds to an extension of slightly less than 2 per cent and section OA represents an elastic-like response. Beyond A, hair is seen to stretch easily with a plastic-like response up to an extension of almost 25 per cent (B). Beyond B there is a new change in the slope of the curve which shows increasing resistance to stretching. C corresponds to the disruption point.

The precise physical interpretation of the various sections of the curve is still controversial, particularly in relation to the contribution of amorphous and crystalline regions of the hair. Speakman,⁶³ studying wool, demonstrated that salt links had no effect on these properties. Hamburger and Morgan⁶⁴ attributed the OA portion of the curve to the breaking of hydrogen bonds and unfolding of keratin spirals and stated that the main effect of permanent waving agents was to

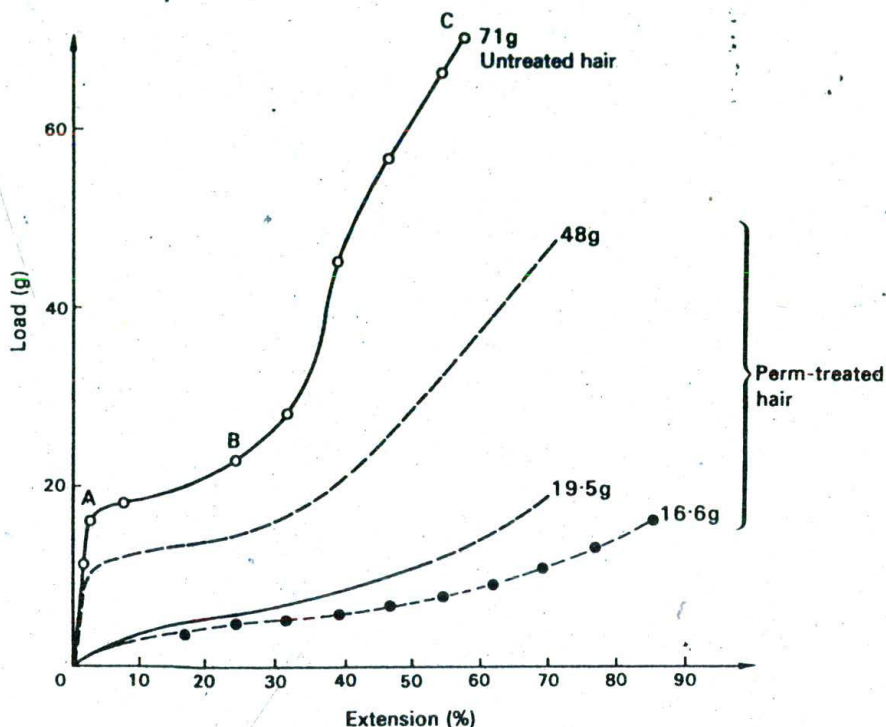


Figure 28.1 Percentage extension of hair related to load applied

lower the slope of the BC section, which is said to represent the resistance of disulphide bonds to extension.

Patterson *et al.*⁶⁵ showed that the total work of extension to 30 per cent was lowered to 65 per cent of its original value after reduction with thioglycollic acid and could be brought back to its former value either by oxidation or by substituting bulky groups on to the cysteine residues, but this appears to be a somewhat idealized picture.

These studies, more or less adapted from investigations into wool, may not adequately explain the effect of a process performed on hair which, although of similar structure, is of different composition and sensitivity. The most suitable extension conditions for studying the setting of hair cover the range of the mechanical strain usually set up in hair, that is 0–10 per cent; in setting, the strain ranges from 0 to 1.5 per cent and in permanent waving it lies around 2 per cent. The plastic region (Figure 28.2) is thus suitable; the rates of reduction and of setting and a mechanical overall assessment well correlated with analysis²⁸ are obtained by comparing the stresses necessary to effect a given extension. It is noticed that in the end the permanent waving process always leads to a notable loss of mechanical properties;³⁰ the oxidative step restores only part of the initial strength of the hair fibre. However, owing to a lack of systematic studies a direct relationship with loss of keratocystine has not been established.

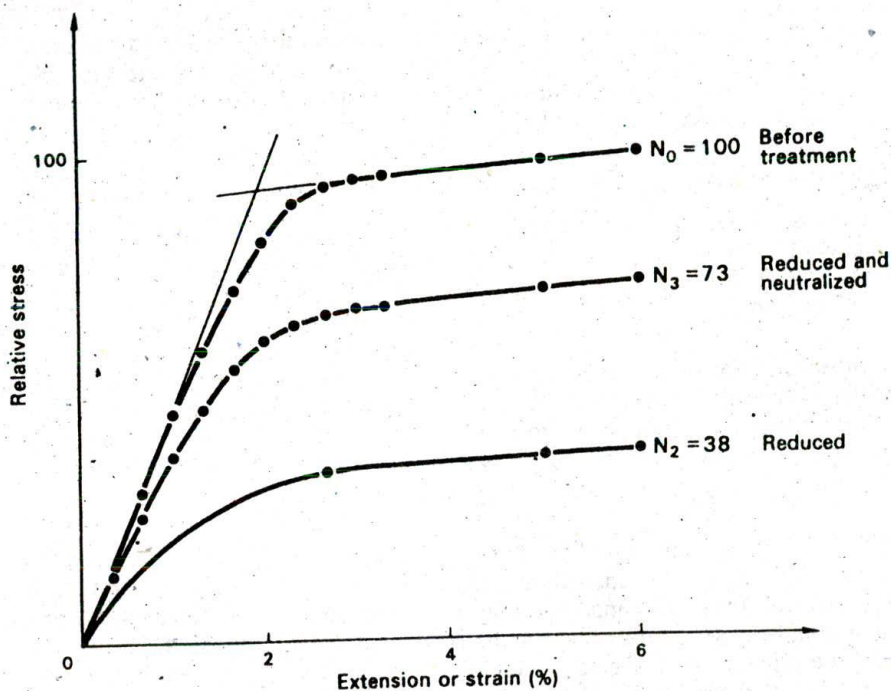


Figure 28.2 Relative stress, N , for a 6 per cent strain at stages of the permanent waving process; $N_0 = 100$ for untreated hair

Formation of lanthionine may contribute to weakening of the mechanical properties of the fibre but it is most likely that intra-keratinic chain cystine links may be formed in the neutralizing step, which reduces the level of cross-linking, that is, the rebuilding.

Other techniques for evaluation *in vitro* are the following:

Measurement of disruption loads, extension at disruption point and disruption energy (point C of curve 1, Figure 28.1).

Examination of curve of extension at constant load, hair being immersed in the reducing solutions to be compared.

Evaluation of perming efficacy, that is the ratio of diameters between curlers and final curl.³⁷

Measurement of fibre swelling during reducing step.

The effect of permanent waving on the surface of hair can be studied by scanning electron microscopy.

However, the final evaluation lies in the hands of the 'man of the art', whose sensitivity supersedes any other means of assessment. Permanent waving is a meticulous operation in which a number of parameters must be taken into account in practical trials. Any variation in one of these can result in significant

changes in the tightness and permanence of the resulting wave, and the usual precautions must be taken in carrying out comparison work to make sure that observed variations are really due to the factor under investigation (for example, the strength of the lotion) and not to an artefact.

Main Factors Leading to Variations in Permanent Waving

Choice of Lotion. This is the most significant factor; it is independent of the degree of curling desired but depends on the quality and structure of the hair to be treated. It may even be chosen according to whether it is applied to the root or to the tip of the hair (bleached hair).

Temperature Variation. The ambient temperature in the salon has a considerable effect on the cold waving process. This factor will be nullified if tests are carried out on either side of the same head, but other sources of variation such as the heat of the hair and possible heat loss by evaporation can be quite significant if the lotions being examined are vastly different in type.

Processing Time. This should be short, since if it is extended the result may be excess softening of the hair without further efficacy of the treatment. In hot or tepid waving the processing time may be reckoned to begin either when the apparatus is switched on or when the heating pads are activated.

In the usual method of cold waving, the hair is wetted with lotion before and after winding the curls. A salon operator cannot wind a head of hair in much less than 30 minutes, and the home user may take as long as 90 minutes. In view of this time interval between the application of lotion to the first and last curls, the so-called processing time after rewetting becomes far less significant.

The equilibrium between cystine in the hair and thiols in the lotion is reached after about four minutes when the hair is immersed in a large volume of lotion, but this process is probably slower on an actual head. Most of the lotions are studied at setting times, after winding on natural hair, varying between 10 and 20 minutes.

Some manufacturers (see example 5 below) suggest that the lotions applied before and after winding should be of different strengths. Others recommend a modified process in which the hair is wetted with water only before winding, then treated with lotion from the outside of each curl. This, of course, raises in an acute form the problem of penetration, but it is often of use for the treatment of bleached or otherwise damaged hair, as it allows the use of a really short processing time entirely within the control of the user.

Penetration Rate. This depends not only on the presence or absence of wetting agents, etc., but also on the nature of the hair to be waved. Fine hair will obviously be penetrated more rapidly than coarse hair, but there may also be differences in the porosity of the hair. After bleaching, for instance, the hair has usually lost a good many cross-linkages and will swell very much more rapidly than normal hair, thus taking up the waving lotion more completely. Washing the hair with a shampoo beforehand removes sebum which might hinder penetration but some detergents are strongly absorbed on the fibre and may be

capable of changing the permeability. This point should not be overlooked when adding detergents to the lotion itself—cationic detergents, for instance, show a definite inhibiting effect when present at concentrations as low as 1 per cent.

Choice of Curlers. The curl diameter obviously depends on the diameter of the curler. Some methods make use of very large diameter curlers or rollers, and some depend on making a pincurl with the aid of a waving lotion. Another factor is the amount of hair on each curler, which depends on the number of curlers per head and the amount of hair on the head, as the outside layer of hair has a curl diameter equal to the curler diameter plus the thickness of hair.

Neutralizing Step. This is a rather important operation since it determines the set of the permanent waving and the rebuilding of keratin. Hair must be very carefully rinsed beforehand to eliminate reducing lotions. Then the setting lotion must be applied in two separate stages: first, two-thirds of the lotion are applied to the wound hair, impregnating each curl for 5 minutes and left for 5 minutes; then, after the hair has been unwound without stretching, the remaining lotion is applied to the tips and left for 5 minutes before being carefully rinsed out.

Hot Waving Processes

The procedure adopted by the professional hairdresser in hair waving is as follows:

1. Any grease is removed from the hair by shampooing.
2. The hair is then divided and wound around a suitable roller under slight tension.
3. A sachet or absorbent strip dipped in a suitable solution is wound over the hair and the whole encased in an electric heater, and the hair is steamed for the required period.

It must be understood that the above method is modified somewhat according to whether *sachet* waving or *oil* waving is being employed and according to the particular type of wave desired. Usually heat is supplied to the rollers by means of an electric current; in the wireless system the heaters are preheated and allowed to cool for the desired period. Chemical heating methods are also used, in which moisture from the wrapper induces an exothermic chemical reaction when in contact with a suitable mixture. The advantages claimed for this latter system are that there is no risk of electric shock and the individual has freedom of head movement.

Permanent waving demands, in addition to suitable reagents, considerable professional skill and experience. The selection of suitable methods of winding and of strengths and types of reagents, times of steaming, etc. (according to the type and condition of hair treated) is of paramount importance.

It has been claimed by hairdressers that the success of permanent waves can be affected by the state of health of the subject. Thus after pregnancy, after an operation involving an anaesthetic or during periods of the menstrual cycle the effectiveness is reported to be reduced. In view of our lack of knowledge of the changes occurring in the skin and hair during menstruation and pregnancy and

following parturition and surgical operations, there is no definite proof either way.

Goodman⁶⁶ considers that hair which has been keratinized and has erupted beyond the limits of the hair follicle is outside the sphere of influence of anything taking place inside the body. Only the freshly growing part of the hair within the follicle—the part not yet keratinized—is under the influence of the body. He points out that hairdressers have successful salons in hospitals and that the actual causes of failure of permanent waving are:

- Taking too large a section of hair
- Taking too small a section of the hair
- Too much or too little alkali
- Too tight or too loose winding
- Too short or too long steaming time

Goodman suggests that reasons other than these provide excuses for the careless hairdresser, the hurried technician and the cut-rate operators who do not make a test curl.

Permanent Waving Solutions

Permanent waving solutions are almost invariably strongly alkaline in reaction, since the presence of alkalis considerably shortens the time necessary to produce a satisfactory wave. Those recommended for such purposes include lithium hydroxide; sodium, potassium, ammonium carbonates, borax, ethanolamine or neutral or alkaline solutions of sulphites (sodium, ammonium, mono- or triethanolamine, morpholine sulphites).

The following formulae give good results on average hair in about 10 minutes steaming times (this being adjusted to suit the type of hair):

	(1) <i>per cent</i>
Monoethanolamine	6.0
Potassium sulphite	1.5
Potassium carbonate	1.5
Ammonium carbonate	2.5
Borax	0.5
Sulphonated castor oil	1.0
Distilled water	87.0

	(2) <i>per cent</i>
Ammonium hydroxide (s.g. 0.88)	20.0
Sodium carbonate	4.0
Potassium sulphite	2.0
Water	74.0

	(3) <i>per cent</i>
Monoethanolamine or ammonium hydroxide (s.g. 0.88)	14.0
Borax	4.0
Potassium sulphite	2.0
Water	80.0

The use of agents that activate the lanthionization (NaCl, sulphates, cationic surfactants) and of boosters (urea, amides, lithium bromide) helps to reduce the concentration and lower the pH.⁴

A gel to be applied at 40° for 30 minutes is given in example 4. However, hot waving, because it is aggressive to the hair and uncertain in its results, is not much used nowadays.

	(4) per cent
Hydroxyethyl cellulose WP 4400	4.0
Lithium hydroxide, LiOH.H ₂ O	2.0
Sodium chloride	17.5
Water	q.s. to 100.0

Chemical Heating Methods (Heating Packages)

Chemical heating methods have been introduced, in which the heat required for the normal waving process is obtained without the aid of electricity. Such methods depend upon heat evolved by the reaction of an exothermic material with a moistening medium as a result of one of the following:

- Oxidation and reduction
- Hydration
- Neutralization

This method originated in England in 1923⁶⁷ with the use of quicklime to generate the heat. Combining ammonia sulphate, agar or ammonia with the moistening agent was shown to delay further the development of heat.

Since that time numerous chemical mixtures have been recommended and patented, including as active agents aluminium and its chloride and sulphate, ammonium salts of various organic acids, barium salts, copper carbonate or nitrate, iron filings and other salts, etc.⁶⁸

Cold Waving Processes

Cold waving has to a large extent replaced the older hot waving process, particularly in the more sophisticated parts of the world where the replacement is total. The operation is performed at room temperature without input of heat energy. The hair is shampooed thoroughly, and divided into sections for ease of handling. Locks of hair of such size as to give 35–50 curlers (6–14 mm diameter) per head are moistened with the waving lotion, and then wound on to croquignole curlers. Because the nape hair needs a good curl to stop it 'wisping' and because it also seems rather resistant to perming, it is usual to start at the nape and work forward.

When winding is complete, the hair is left to 'process' for 10–40 minutes. Some manufacturers recommend set times for various types of hair, while others advise the examination of a test curl by the user, who then decides how much longer to leave on the lotion. Hairdressers usually use the test-curl method. The complications of the home perm have brought about an interesting social situation, in that about 60 per cent of UK users have someone to help them with the process. After the processing with reducing agents, the hair is rinsed and

neutralized by application of an oxidizing solution to the wound curls. After 5–10 minutes the curls are unwound and usually a further application of neutralizer is made. The hair is then rinsed and set into the desired style.

The Reducer in Cold Waving

As explained above, most permanent waving formulations are based on thioglycollic acid. The simplest lotions are ammonium thioglycollate at pH 9.2–9.8. The curve shown in Figure 28.3 represents solutions with the same curling potential (average lotion for normal hair).³⁷

In practice, pH 9.3–9.5 is used for concentrations of thioglycollic acid between 7.5 and 11 per cent, but the strength of the lotion is essentially dictated by the quality of the hair to be waved; the average concentrations for use in a salon are as follows:³⁷

	<i>Thioglycollic acid</i> per cent
Difficult natural hair	8–9
Medium and easy natural hair	7
Slightly bleached hair	5
Medium bleached hair	3
Heavily bleached hair	1

For use at home, concentrations should be decreased by about one-third.

The use of bases other than ammonia has been much discussed. Sodium and potassium hydroxides have been said to render the hair too soft to take a good wave;⁶⁹ ammonia and organic amines have been proved to hydrolyse peptide less than alkali. In the event, only monoethanolamine seems to be as good as ammonia, and this is used together with ammonia to reduce the odour.

The main problem is to maintain the reducing activity of the thiol during the whole softening phase—that is, to maintain pH despite the volatility of

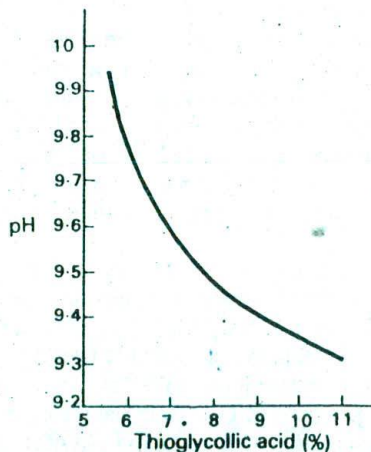


Figure 28.3 Solutions of thioglycollic acid with the same curling potential

ammonia; to achieve this, buffering with ammonium carbonate, sesquicarbonate or bicarbonate is often employed, and this also allows the use of a lower pH (<9).

Another ingenious method of ensuring the base supply and obtaining more regular curling and reduced aggressiveness is to generate ammonia *in situ* under controlled conditions by introducing urea and the enzyme urease which, in the presence of water, transforms urea into ammonia.⁷⁰

Other bases have been suggested: basic amino acids such as arginine,⁷¹ carbonates of alkali amino acid salts such as sodium glycinate carbonate,⁷² alkanolamines 'specific for bleached hair',⁷³ and guanidine or its carbonate^{74,75} which, in addition, contribute to the swelling of the hair by disrupting hydrogen bonds, although the problem of safety has to be dealt with.

In order to maintain the reducing activity during the stretching and shaping process it has also been proposed to introduce reducing agents in two phases, the second lotion containing a more potent reducer (ester of thioglycollic acid) which can give stronger bonds,⁷⁶ at the same time lowering the pH to reduce damage to keratin (example 5):

(5)	
Parts by weight	
Ammonium mercaptoacetate (50% aqueous)	9.4
Ammonium bicarbonate	4.2
Ammonium carbonate	0.5
Urea	3
Perfume	0.4
Oleic acid pentaerythritol polyglycol ether	0.4
Water	62.1

Procedure: 40 g of this lotion is applied to the hair. Another 40 g is mixed with 4 g mono mercaptoacetic glycerol ester and the hair is treated for 10–15 minutes, then washed with water and fixed with hydrogen peroxide.

Many other ingredients may be used in permanent waving lotions: for example, hardening agents to reduce the necessary thioglycollic acid concentration and pH, and boosters such as urea, lithium bromide or 2-imidazolidinone (ethyleneurea) which penetrate by breaking hydrogen bonds. Example 6 using such a booster,⁷⁷ has a pH value of 8.

(6)	
Parts by weight	
Ammonium thioglycollate (50% aqueous)	18
2-Imidazolidinone	4
Ammonium bicarbonate	4
Perfume	0.3
Polyoxyethylene octylphenol	0.5
Water	73.2

Other ingredients include:

Alcohols (ethanol and isopropanol) and sodium sulphite to strengthen the lotions.

Wetting or foaming agents.

Softening agents: animal and vegetable oils, protein hydrolysates, lanolin derivatives.

Complexing agents, mostly for iron which colours and also catalyses the formation of hydrogen sulphide.

Opacifiers, to give an impression of softness and gentleness through their milkiness—acrylic, vinyl and styrene polymers have been claimed as opacifiers;⁷⁸ stable emulsions of ammonium thioglycollate have been reported,⁷⁹ but a cream formulation makes rinsing difficult.

The application of permanent waving products as a quick-breaking foam from an aerosol dispenser has been described⁸⁰ and such preparations have been marketed.

More recently, cationic compounds and, chiefly, resins have been introduced so as to impart improved strength, body or elasticity to the waved hair. They are cationic PVP-VA polymers,⁷⁶ polyamide-epichlorhydrin resins,⁸¹ quaternary ammonium salts⁸² and protein hydrolysates.

For hair which has been weakened by previous treatments, particularly by bleaching and tinting, less potent reducers may be used such as thiomalic or thiolactic acids⁸³ or the so-called 'acid permanent waving' formulations (pH between 5.5 and 7) said to 'protect' hair,⁸⁴ and which today enjoy some popularity. Following this trend, glycerol monothioglycollate has undergone some revival.

The Neutralizer in Cold Waving

Most hairdressers use hydrogen peroxide as neutralizer because it is not expensive and is easy to handle. It can be obtained as a concentrated solution to be diluted or as a ready-to-use solution. In either case it is acidified by adding citric, tartaric or lactic acid for stability. Usually agents such as polyoxyethylene fatty alcohols or cationic compounds are added to improve wetting, together with softening agents (self-emulsifying waxes, lanolin derivatives).

To speed up the neutralizing step, activators of the decomposition of inorganic percompounds have been suggested.⁸⁵ Self-warming systems have also been proposed—for instance, the addition to hydrogen peroxide of either sulphite or thiourea,⁸⁶ or anhydrous calcium chloride or magnesium sulphate,⁸⁷ elicits an exothermic reaction, producing an available oxidizing bath of about 40°–45°C.

Catalase⁸⁸ was suggested to degrade the potential hair-decoloring excess of hydrogen peroxide. As in the reducing stage, cationic polymers and surfactants are added to enhance the setting.^{89,90}

For home use, dry powdered sodium perborate or percarbonate is often used in the UK and sodium or potassium bromate in the USA. The bromates have the advantage that stable solutions in water can be made and stored, but they are extremely toxic and should be labelled 'Poison'. These persalts should be used at a neutral pH; bicarbonate, monosodium phosphate or carbonate is added to settle the pH after solution is made, together with foaming agents.

It used to be claimed that the neutralizing step could be achieved without the intervention of a chemical agent, by merely leaving the hair in curlers for more than 6 hours and trusting the air oxygen to do the job; this process is obviously

only suitable for home use. Evidence now exists to show that this does not work and a still more convincing proof is that a hair switch, previously reduced under standard conditions by thioglycollate, was not significantly reoxidized even after more than a year of atmospheric exposure!⁹¹

Formulae of both setting lotion and neutralizer for home and professional use, quoted by Shansky,⁷⁵ are given in examples 7 and 8.

(7)

<i>Setting lotion (pH 9.4-9.5)</i>			
Ammonium thioglycollate (52%)	17	US gal	64.3 litres
Caustic soda (76%)	20	lb	9.0 kg
Ammonia (28%)	6.4	lb	2.9 kg
Nonionic detergent	3.0	lb	1.4 kg
Resin cloud	3.0	US gal	11.3 litres
Water	150	US gal	568 litres
<i>Neutralizer</i>			
Hydrogen peroxide	158.5	lb	72 kg
Citric acid	6.75	lb	3.0 kg
Polyoxyethylene lauryl ether	16.75	lb	7.6 kg
Resin opacifier	2.5	lb	1.1 kg
Water	400	US gal	1514 litres

(8)

<i>Setting lotion (pH 8.7)</i>			
Ammonium thioglycollate (52%)	15	US gal	56.8 litres
Ammonium hydroxide (28%)	8.0	lb	3.6 kg
Ammonium carbonate	8.0	lb	3.6 kg
Resin opacifier	2.0	US gal	7.6 litres
Nonionic detergent	1.8	lb	0.8 kg
Water	100	US gal	378.5 litres
<i>Neutralizer</i>			
Sodium bromate	200	lb	90.7 kg
Polyglycol 400 laurate	50	lb	22.7 kg
Diglycol stearate	10	lb	4.5 kg
Glyceryl monostearate	10	lb	4.5 kg
Sodium cetyl sulphate	25	lb	11.3 kg
Polyglycol 400	5	lb	2.25 kg
Water	700	US gal	2650 litres

Single-operation Waving

A method has also been patented for hair waving or straightening in a single operation.^{39,92} It had not previously been possible to effect permanent deformation in a single phase, because one process involves reduction of the hair and the other oxidation: if both active agents were to be combined, they would interact and their separate effects would be inhibited. The process for the permanent deformation of hair by a single stage entails subjecting the hair to the action of a mixture of a thiol and a disulphide for 20-30 minutes at ambient temperature, after which the hair is rinsed and the curlers are removed. The optimum molar ratio of disulphide to thiol is a function of the pK value of the thiol used. The pH

value of the applied composition should preferably lie within a range of 8.5-9.5 in order to permit the disulphide present to act as an oxidizing agent.

It is believed that when hair keratin, itself a disulphide of a complex nature, is brought into contact with the mixture of thiol and disulphide (the latter at a higher concentration), part of the thiol reduces part of the keratin, resulting in the formation of the corresponding disulphide, thereby increasing the concentration of disulphide in relation to the thiol and bringing the reduced keratin into contact with the disulphide. The disulphide then regenerates the original keratin, the corresponding thiol being formed at the same time. In other words, it is a cascade reaction—disulphide breakage and rebuilding—based on an alternated displacement of chemical equilibria and thereby allowing a smooth styling of the hair.

New conditioning systems for permanent waving agents have been proposed, including strips, squares, or continuous rolls from which the agents may be released by wetting,⁹³ and microcapsules soluble in appropriate solvents,⁹⁴ which might in the future constitute a means of applying hydrogen peroxide, reducing agents and ammonium salts all together.

Tepid 'Warm Air' Wave

Thioglycollates have been used at slightly elevated temperatures to obtain a better result with less active material, either employing a special version of the standard electric apparatus or using hood dryers. Cold waving lotions are usually diluted by 30 per cent and sodium sulphite is often added so as to reduce thiol concentration even more. However, this technique may be regarded as obsolete nowadays.

Roller and Pin Permanent Waves

Ordinary permanent waves are normally intended to remain in curl for 4-6 months, and may therefore start with the hair much more tightly curled than is desirable. After the process the hairdresser has to set the hair in a looser style by water waving. This resetting takes a good deal of salon time, which accounts for most of the cost of a professional permanent wave.

It is possible, of course, to set the hair in looser styles while still using a permanent waving process, as long as the client does not expect the curls to last more than 6-8 weeks, and this is, in fact, done with roller and pin permanent waves.

The first method uses large-diameter curlers ($1\frac{1}{2}$ in or 64 mm), while the second employs ordinary hairpins to make flat curls about 1 in (25 mm) in diameter. A reducing lotion is applied as usual, the hair is processed and neutralized and the client then goes straight under the dryer, and needs only brushing to complete the set when her hair is dry.

Some manufacturers recommend a further saving by drying the hair immediately after the waving lotion is rinsed out, but this tends to produce waves that fall out as soon as moisture is present. It is doubtful whether this process, carried out every 6 to 8 weeks, is good for the hair and furthermore these soft waves require constant attention at the expert hands of the hairdresser.

Instant Permanent Waves

Instant permanent waves are not really different from those that are chemically neutralized in the ordinary way, except that the 'processing time' after winding is nil. The hair is first wetted with the reducing lotion, then wound onto the curlers; as soon as winding is finished, setting is carried out without processing time. It saves time but the loss of efficacy must be compensated by the use of a stronger lotion; as a result, the waving is often uneven and the quality of the hair suffers.

Perfuming of Thioglycollate Lotions

An extremely good review of this subject is given by Sagarin and Balsam,⁹⁵ who list the results of their own tests with over 200 materials. Unfortunately it is impossible to mask the smell of thiols completely, particularly during the application stages when they are spread over the whole head, and the inherent smell of the thiol is enhanced by the odour of the reduced hair. Another difficulty is to choose perfumes that can be stable in ammoniacal reducing medium. The cosmetic industry and the public are still awaiting new methods of permanent waving using completely odourless materials;⁹⁶ a significant reduction in odour is claimed for the cold 'soft perms' which use sulphite as the reducing agent.⁶²

Toxicity

The toxicity of permanent waving lotions has been reviewed in considerable detail by Norris.⁹⁷ It must be accepted that, owing to the pH of use and in view of the mode of action on hair, compounds such as thioglycollate will be toxic if they get into eyes, or irritant if they are left on the skin for a considerable period of time. The inclusion in the reducing lotion of anti-irritation agents such as antihistaminic imidazoles⁹⁸ or thiamine⁹⁹ has been claimed to be effective. In all cases care must be taken to prevent contact of such lotions with eyes and skin.

Hair Strengthening Preparations

Weakened hair, which may result from sensitization due to hair treatment or overprocessing or from environmental or internal causes, usually lacks bulk, tensile strength, lubricity, sheen, body and a barrier to penetration. It is often stringy, oversensitive to moisture, or even flimsy and, as a result, difficult to handle. The prevailing factor in the weakening of hair is the breaking of too many disulphide links, as may be the case with hair that is too frequently and excessively waved, bleached or dyed.

A process was proposed in 1967¹⁰⁰ for improving the strength and-elasticity of weakened hair, which entailed treatment of the hair with solutions or dispersions of dimethylol urea or dimethylol thiourea for 15 minutes at a temperature of 30°-40°C in the presence of an acid catalyst (for example, glycerophosphoric acid) in an organic or aqueous medium at a pH between 1.5 and 6.0. These compounds react with the free amino groups of hair keratin, producing cross-links between the hair fibres, and polymerize in the presence of the acid

catalyst to form a resin within the hair fibres. The resin strengthens the hair and is said to make the hair virtually insoluble in water and various organic solvents.

It has been found, however, that these compounds when used alone are markedly unstable and can release a certain amount of formaldehyde while in solution or in contact with the hair and, to some extent, even during storage. In many countries legislation restricts the amount of free formaldehyde that may be applied to the scalp, and thus the commercial use of such compounds. The release of free formaldehyde has subsequently been shown to be efficiently reduced by the inclusion of stabilizing compounds such as urea, dicyandiamide, melamine or ethylene urea in the methylol compositions; improved compositions for strengthening damaged or weakened hair¹⁰¹ contain, more specifically, monomethylol dicyandiamide and its methyl ether, methylolethylenethiourea, and methylolated melamines as well as the 'methylols' previously used.

Further compositions for strengthening degraded hair, which comprise at least one alkylated compound, were claimed to be so stable that virtually no formaldehyde was released during application. The methylol ether compounds proposed include mono- and dialkoxymethylureas or ethyleneureas and corresponding thioureas, tris(alkoxymethyl) melamines, N-alkoxymethylcarbamates or adipamides.

Other stable, easily obtainable yet more water-soluble compounds are condensation products of the former linear or cyclic methylolated substances with secondary amines such as N,N'-bis-(morpholinomethyl) urea or N,N'-bis-(ureidomethyl) piperazine¹⁰² and methylol derivatives of glyoxalurea or thiourea condensation products.¹⁰³

Lastly, addition of fairly small quantities of sulphites to any of the previous compounds has been claimed to prevent almost any occurrence of free formaldehyde.¹⁰⁴

The amount of methylolated compound included in strengthening preparations—preferably between 1 and 4 per cent by weight—will depend on the product used and on its water solubility, as well as on the type of hair to be treated. Hydroxylated acids, acetic, phosphoric and hydrochloric acids (or salts thereof, such as acid phosphates) may be used as polymerization catalyst. The remarkable strengthening effect given by these compositions is confirmed by the notable reduction they produce on the solubility of hair in alkali, which has been suggested as a criterion for evaluating physical and chemical changes in the human hair.¹⁰⁵

Many new compounds have been proposed to enrich hair, enhance its protection against subsequent hair treatments, impart more body and bulk, eliminate a slimy feel on wetting and add lubricity, at the same time restoring it. Particularly interesting are, on the one hand, cationic resins with methylol groups¹⁰⁶ and, on the other hand, methylolated compounds or derivatives with functional groups that may be transferred into the hair or onto its surface so as to modify its sensitivity to chemicals. The above-mentioned functional groups are disulphides^{102,107}—such as in N,N'-bis(hydroxymethyl)dithiodiglycolamide and 2,2'-dithiodiethyl-bis-(morpholinomethylurea); tertiary amines—such as in diethylaminoethylurea and methylimino-bis-(3-propylurea)methylols; and quaternary ammonium compounds—such as in alkyl dimethylammonium acetamide chloride and diethyl(ureido ethyl) ammonium acetamide chloride

methylols.^{102-105,107,108} Dicarbonyl compounds such as glyoxal,¹⁰⁹ glutaraldehyde, quinone, etc.¹¹⁰ and amino-dialdehydes¹¹¹ have also been claimed to have strengthening properties.

Repetitive bleaching or retinting will also cause non-uniform porosity of hair with an adverse effect during subsequent treatments. A process for uniform waving of damaged hair¹¹² entails pretreatment of the damaged hair with an aqueous acidic oxidizing agent, before it is subjected to the action of an aqueous alkaline thioglycollate.

In permanent waving the degree to which the hair is waved will depend on the amount of waving lotion that gets into the hair, and this in turn is governed by the porosity of the hair. The more porous the hair, the more waving lotion has to be applied. This will cause end sections to be well waved while root sections will only be weakly waved. If waving solutions are then applied that are strong enough to wave root sections of, for example, bleached hair, they may cause damage and break the more porous end sections of the hair. However, by using a pre-neutralizing agent, it is possible to apply a waving solution of average strength to obtain a uniform wave irrespective of the variations in the porosity of the treated hair, that is the degree of damage. This will be mainly absorbed at the most porous end section of hair, as with cold waving lotion, and will inactivate it by oxidation, simultaneously reducing its pH and thereby blocking its action. The concentration of the pre-neutralizing agent, which is generally an acidic persulphate, for example, potassium or ammonium persulphate, may vary over a wide range. In the majority of cases proposed formulations contain between 0.5 and 5.0 per cent of active oxygen and have a pH value of between 3.5 and 7.0. Treatment time is preferably about 10 minutes. The cold waving solution is subsequently applied for a further 10 minutes, whereupon the hair is rinsed and neutralized.

More recently, a number of pre-treatments with cationic compounds or resins have been recommended for protection of the weakened hair shafts by preventing penetration and excessive softening by the reducing lotions.

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Hair Straighteners

Introduction

Hair straighteners are a need for several types of consumer, some of whom want tightly curled hair made straight or very gently waved, while others want essentially kinky hair opened up and made more controllable.

The idea held at one time that curly or kinky hair is elliptical in cross-section whereas straight hair is circular is now completely discarded. According to recent work there are two forms of keratin which make up the orthocortex and paracortex of the hair shaft (see Figure 23.1); Negro hair appears to have a much higher proportion of the reactive and highly differentiated orthocortex.

There are several types of hair straightening preparation on the market:

Hot comb-pressing oil methods

Caustic emulsion

Methods entailing the use of keratin reducing agents

Hot Comb Method

In the hot comb method, hair is straightened by the use of petroleum jelly and a hot metal comb. This procedure is referred to as 'hot pressing'. Alternatively a mixture of petrolatum and paraffin may be used, in which petrolatum is the major component, acting as a heat transfer agent between the comb and hair, lubricating the latter to allow the comb to slide through it without drag. The hair is washed and dried before the pressing oil is applied and the heated metallic comb is used to straighten the hair.

Quite apart from the fact that considerable stress is applied to the hair, causing a high incidence of breakage, the set is not very permanent and tends to be destroyed by rain or even by perspiration so that the hair reverts to its original state. Silicone-containing sprays have been marketed as barriers against moisture, but they did not appear to bring any really significant improvement.

Caustic Preparations

Caustic alkali preparations, usually in cream form, are the second type of hair straightening preparation still fairly widely employed. The use of caustic lye involves risks such as irritation of the scalp and even accidental eye damage.

The viscosity of these products varies according to the softening and melting points of the cream base. The amount of active constituent employed is between 2 and 9 per cent; it is frequently about 4-5 per cent. The more alkali present, the more rapid the action but at the same time the greater the risk of hair solubilization and the care required in using the product.

The addition of activators of lanthionization helps to reduce the temperature, the time and the pH value of treatment¹ (cf. permanent waving).

The selection of ingredients for the cream base to act as vehicle for the caustic obviously requires considerable care if incompatibility is to be avoided. The emulsifier should be neither an acid nor an ester, nor should it be an anionic of a type that would be salted out by the caustic alkali, such as soap. The fatty phase, too, should be neither an acid nor an ester and is best formulated from waxes, more particularly from fatty alcohols, with mineral oils and petroleum jelly as protecting agents and polyoxyalkylated lanolin as emollient.² Generally, the cream base also contains sodium lauryl sulphate or lauryl ether sulphate as wetting agent and emulsifier.

A typical composition is given in example 1.³ This paste is applied by combing and allowed to remain on the hair for 30 minutes. The hair is then washed well with water to remove all the paste.

		(1)
		parts by weight
A	Gum tragacanth	2
	Boric acid	1
	Water	40
B	Sodium carbonate	1
	Potassium hydroxide	1
	Glycerin	2
	Water	8

Procedure: Unify A as a paste and then stir it into the previously dissolved B.

The straightener with activator given in example 2¹ is applied to the hair for 30 minutes at a temperature of 40°C.

		(2)
		grammes
	Hydroxyethylcellulose WP 4400	4.0
	Lithium hydroxide	2.0
	Sodium chloride	17.5
	Water	to 100.0

The simple lye straighteners described above are mainly designed for people who want their hair straightened, not styled. There are, however, more complicated multi-component straighteners on the market which provide a more sophisticated process that is more beneficial to the scalp and hair and the final styling.

Multi-component lye straighteners conform to a general pattern of five components:

- (i) A soft pomade based on mineral oil-jelly-wax applied to the scalp as a protective pretreatment.
- (ii) The 'relaxer', which consists of an oil-in-water emulsion containing about 3 per cent caustic-soda and about 40 per cent fatty material on the same general lines as the simple straighteners described above.

- (iii) A cream shampoo which is used to follow the relaxer. The constitution is usually 12 per cent alkyl sulphate, 2 per cent fatty acid diethanolamide, together with some unspecified emulsified fatty material.
- (iv) A dilute oil-in-water emulsion containing about 2 per cent fatty esters and a cationic wetting agent referred to as the 'neutralizer', preferably slightly acid.
- (v) A stiffer pomade containing petroleum jelly, fatty ester and lanolin to provide the final set and dressing.

It has also been recommended to follow the alkaline treatment by an application of an alkaline solution or suspension containing an alkaline earth metal, particularly calcium as in quicklime, so as to form chelates of this metal with keratin and thus firmly set in the new hair shape; keratin may then be released from the chelates by means of a complexing agent (EDTA) and a surfactant.⁴

Compositions that are both straightening and colouring have been patented; they consist of alkali at pH 12–13.8, dyestuffs together with shading agents in a vehicle containing cetyl stearyl alcohol, sodium lauryl sulphate and a carboxyvinyl polymer.⁵

Chemical Hair Reducing Agents

Hair straightening preparations of the third type contain a chemical keratin-reducing agent as the 'relaxer' which effects the softening and straightening of the hair. The active agents are frequently thioglycollates, that is, the same compounds which are used in the opposite process of permanent waving but usually at a slightly lower concentration.

Unlike permanent waving, where the hair is kept in curlers throughout the treatment, in hair straightening the hair is free and kept in shape while combing by virtue of the high viscosity of the product. As a result, a cream-like formulation is no longer a disadvantage but becomes highly desirable, so that the majority of the preparations are oil-in-water emulsions, gels or thickened liquids.

This type of straightener is sold in two containers, one holding the 'relaxer', the other the 'neutralizer', although, just as with 'home perms' there are preparations that dispense with the neutralizer and rely on supposed 'aerial oxidation'.

Relaxer

In most existing examples, the relaxer is an ammoniacal thioglycollate and the pH value of the product is adjusted to 9.0–9.5. Organic bases such as monoethanolamine and an alkali carbonate of an amino acid⁶ may partly replace ammonia. Cream products are based on glycerol, glycol stearates, or on cetyl and cetyl stearic alcohols emulsified in water by polyoxyethylated (usually 20 to 25 ethylene oxide) cetyl or oleyl alcohols. Gels or viscous liquids are obtained by means of carboxyvinyl polymer or copolymers. In example 3,⁶ imidazoline is included with the aim of speeding up straightening.

	(3) per cent
Emulsion base:	
Demineralized water	to 100.0
Cetyl alcohol emulsified by oxyethylated cetyl alcohol	22.0
Demineralized water	30.0
Sodium carbonate glycinate	5.0
Ammonium thioglycollate or thiolactate (50% aqueous soln)	12.0
EDTA (disodium salt)	0.3
Sodium <i>p</i> -hydroxybenzoate methyl ester	0.05
Monoethanolamine	2.0
Imidazoline	0.2
Perfume	0.2

Neutralizer

Neutralizers are the usual materials, either sodium perborate or hydrogen peroxide. It is important to remember that hair which has already been damaged during hot combing treatment or by the use of lye straighteners should not be subjected to a thioglycollate straightener until several weeks have elapsed. The thioglycollate cream is applied liberally to the hair, which is then combed rapidly until the hair no longer has a tendency to curl. When the hair is sufficiently straight the cream is rinsed off and the neutralizer is applied to give a permanent set. Care should be taken to ensure complete neutralization so as to avoid hair damage. Again a cream-like composition is preferentially used to weight down the hair and improve the maintenance of a straightened shape.

To avoid irreversible damage, due in particular to the solubilizing action of thioglycollic acid on the keratin in highly alkaline medium and on already treated hair, different systems have been proposed. The first—rather complicated—consists in introducing the basicity usually required at a late stage in the action of the reducer and entails a series of four applications:

- (i) A cream containing 3–8 per cent of thioglycollic acid in an oil-in-water ointment base adjusted to pH 7.0–8.6 with ammonium hydroxide (28 per cent): this can be left on the hair for 45–90 minutes.
- (ii) A cream containing ammonium hydroxide or ethanolamine or ethanolamine carbonate in an oil-in-water base adjusted to pH 10–12.5, designed to help straighten the hair: the amount to be applied depends on the thickness and the degree of frizziness of the hair.
- (iii) The hair is then washed and treated with an aqueous composition comprising an oxidizing agent, for example potassium bromate or sodium perborate and a buffering agent, for example gelatin (included to ensure that the hair is kept firmly stretched for about 15–20 minutes during the reoxidation process, while the buffering agent maintains the pH of the solution during the treatment).
- (iv) The hair is then washed and rinsed with an acid rinse of maleic acid to neutralize any residual alkali. Unlike citric, tartaric and boric acids which have been found to cause curling-up of straightened hair, maleic acid helps to maintain the hair in a straightened condition.

Another technique, based on the use of less potent reducers such as sulphites and bisulphite of ammonium or alkaline metals, offers the advantage of being effective between pH 6.5 and 8.5. In addition, such preparations contain alkali or ammonium carbonate, wetting or jellifying agents (sodium lauryl sulphate, Carbopol) and hair swelling agents. They may also contain a chelating agent to complex metals which could prevent the action of sulphites or, as in example 4, a soap which is said to prevent discoloration and embrittlement of the hair.⁷

	(4) per cent
Ammonium carbonate	4.5
Sodium bisulphite	2.2
Sodium lauryl sulphate	4.2
Tallow soap	5.6
Oleic acid	1.0
Water	82.5

These compositions are said to be mild towards scalp and skin and less damaging for hair.^{8,9}

Another suggested process derives profit from the delayed use of swelling agents to complete and to enhance the straightening action, thereby reducing the contact time to the minimum with a highly alkaline medium. The so-called swelling agents are compounds such as urea and its derivatives, thiourea, formamide, lithium bromide, lower aliphatic alcohols, benzyl alcohol, sulphoxide and sulphone, which are thought to break hydrogen bonds and/or weaken hydrophobe interactions, penetrating keratin easily and thereby dramatically altering the network of non-electrostatic interactions.

The proposed process consists in applying the keratin-softening agent (alkali, sulphite or thioglycollate) to the hair, and, when the action is substantially complete, in combing out surplus agent; then, in a second step, exposing the hair to a swelling agent and smoothing the hair with repeated combing, and lastly fixing or neutralizing the hair.¹¹ A formulation for this two-step process is given in example 5.¹¹

	(5) grammes
A Thioglycollic acid	8.0
Cetyl alcohol	5.4
Paraffin oil	1.8
Adduct of oleyl alcohol and 20 EO units	3.9
Colloidal silicic acid	1.5
Ammonia 25%	12.3
Water	67.1
B Cetyl stearyl alcohol	17.0
Sodium lauryl sulphate	2.0
Water	59.0
Thiourea	7.0
Sulpholan	15.0

Procedure: Apply Cream A (pH 9.6), strand by strand, on the previously shampooed hair and distribute uniformly. After 5 minutes reaction time,

carefully comb out the agent; then apply Cream B for 5-7 minutes with repeated combing. Thoroughly rinse the hair with water and fix in the usual way with 100 ml 2 per cent hydrogen peroxide solution.

Example 6 gives another two-stage composition, in gel form, of which cream A is left for a 15 minute action period on the hair.

	(6) grammes
A Ammonium sulphite 35% aqueous soln (22.7 g SO ₂ per 100 ml)	36.5
Carbopol 960 (ammonium salt of a carboxyvinyl polymer)	3.5
Water	60.0
B Carbopol 960 (Goodrich)	0.5
Water	69.5
Urea	3.5
2,2-dimethyl-1,3-propanediol	10.5
Isopropyl alcohol	15.0

Straightening is still a delicate process and should be carried out with great care, taking into account the nature of the hair so as to avoid dryness, degradation and breaking of hair.

The addition of natural polymers has been patented to promote the setting of the straightened shape; they include soluble proteins, corn or rice starch,¹² fruit galactomannan.¹³ More recently, the application of vinyl polymers used for wave sets¹⁴ has been claimed.

Lastly, it is to be noted that another chemical straightening process, entailing an oxidation by alkaline monopersulphates ('oxone') is said to alter the shape of natural hair without appreciably modifying its colour.¹⁵

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PART FOUR

The Teeth and Dental Products

The Tooth and Oral Health

Introduction

The function of the cosmetic chemist is that of maintaining or enhancing the appearance of the external surface of the body. The emphasis changes when the human mouth is considered. In civilized communities the prevalence of tooth decay and other oral diseases has come to be accepted as normal. Oral preparations are therefore much more orientated to the prevention and control of oral diseases such as caries and gum disorders. This situation has arisen in the last 30 years as developments in oral biochemistry have increased the understanding of the problems.

THE TOOTH AND ITS SURROUNDINGS

The field of oral hygiene is concerned not only with the tooth, but with the whole of its environment. This involves an understanding of the biochemistry of the whole mouth.

Structure of the Tooth

The tooth is distinguished macroscopically by the *crown* (that portion of the tooth above the gum) and the *root* (the portion embedded in the gum); the constricted portion separating these is termed the *neck*.

Enamel

The outer surface of the crown of the tooth is composed of enamel, a hard tissue, thickest at the apex of the tooth and thinner at the neck. The root is protected by a thin layer of cementum.

Enamel is the hardest tissue in the body. It is composed chiefly of hydroxyapatite ($3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2$) which accounts for about 98 per cent of the composition, the rest being keratin and water. Hydroxyapatite is capable of ion exchange, and anions such as F^- and CO_3^{2-} may replace the OH^- group, while cations such as Zn^{2+} and Mg^{2+} may replace Ca^{2+} . Caries susceptibility may be influenced by this ion exchange and, for example, the extent to which OH^- has been replaced by F^- has an effect on the vulnerability of the enamel.

Enamel in fact contains a wide variety of other elements which are present systemically or by ion exchange. In addition to those mentioned sulphur (270 ppm), chlorine (4400 ppm), potassium (370 ppm) and strontium (56 ppm)

are all present at levels above 10 ppm together with a host of other elements at levels below this. Their biological significance is not known.¹

The hydroxyapatite of which enamel is largely composed is present in the form of crystallites which make up rods orientated at right angles to the surface. The theoretical Ca:P molar ratio for pure hydroxyapatite is 1.67, but biological apatites such as enamel are frequently below this level. This departure from stoichiometry has stimulated speculation, but the subject is still not completely resolved. Adsorption of ions which are too large to enter the crystal lattice or which have an inappropriate charge, and ionic exchange, are two mechanisms which may account for non-stoichiometry. A summary of the current position is given by Jenkins.²

Dentine

The layer of material beneath tooth enamel is the dentine. It, too is composed of hydroxyapatite to the extent of about 70 per cent, the remainder being collagen and water. The dentine matrix is perforated by a number of tiny canals which radiate from the pulp cavity to the surface. These are the *dentine tubules*.

The apatite of dentine may also contain a variety of other elements and these must of course be of systemic origin since dentine is not exposed to oral fluids. The most remarkable element present is fluorine—remarkable because its content varies with the fluoride content of the water supply and because it is higher than the level in enamel.³

	Fluoride concentration (ppm)		
Water supply	0.0-0.3	1.1-1.2	2.5-5.0
Enamel	100	130	340
Dentine	240	360	760

(The enamel figures are average for bulk enamel—the fluoride concentration at the surface of the enamel may be as much as 10 times the average figure.) Thus the softer and more vulnerable tissue, dentine, has a much higher fluoride content than enamel and this fluoride must be of systemic origin. The significance of these facts will be discussed later in this chapter.

The major differences between enamel and dentine are set out in Table 30.1.

Table 30.1 Major Differences between Dentine and Enamel⁴

	Dentine	Enamel
Hardness		
Knoop's scale	55-60	250-300
Moh's scale	2	4
Specific gravity	2.14	2.9-3.0
Inorganic matter (%)	68	96
Phosphorus (%)	11.5	16.5
Calcium (%)	24	35
Fluorine (ppm)	240	100
Protein (%)	20	1
Protein type	Collagen	Keratin

Saliva

Saliva is part of the environment of the tooth and is a major factor in the maintenance of a healthy mouth. Since saliva is continuously being produced, the tooth environment is dynamic not static and this complicates the study of the chemistry of the mouth.

Saliva is produced by three pairs of large glands and the smaller glands of the oral mucosa (labial, lingual, buccal and palatal). The secretions differ from one another in composition and may differ themselves according to the rate of flow, time of day, etc. There are also differences between individuals. It is impossible, therefore, to give any meaningful figures for the composition of saliva; tables of published data are probably the best guide.⁵

Saliva contains bacteria, mucopolysaccharides, proteins, enzymes and inorganic materials such as calcium, sodium, potassium, chloride and phosphate ions.

The organic constituents of saliva are thought to be responsible for the development of acquired pellicle and plaque. The presence of calcium phosphate is believed to be important both in the control of dental caries and in calculus formation. An inadequate flow of saliva has been associated with increased caries susceptibility, probably because of the poor removal of food debris, a loss of buffering capacity and a reduction in Ca^{2+} and PO_4^{3-} concentration. The complexities of saliva composition are fully discussed by Jenkins.⁶

Acquired Integuments of the Tooth

Leach⁷ has drawn attention to the confusion in dental literature over the nomenclature of the various acquired integuments of human dentition. If a tooth surface, either *in vivo* or *in vitro*, is thoroughly cleaned with a toothbrush and toothpaste it is possible to remove the various integuments until the individual crystallites of the surface enamel are exposed. If this surface, again either *in vivo* or *in vitro*, is exposed to saliva for an order of time measured in minutes, an acellular, bacteria-free layer is deposited on the tooth surface.⁸ This is defined as the 'acquired pellicle' or 'pellicle' and must be derived from the saliva. In the course of time, now measured in hours, bacteria begin to become deposited on the surface of the pellicle, at the same time surrounding themselves with a matrix that is distinctly different from the acquired pellicle. This aggregation of bacteria and its surrounding matrix, once it is present in sufficient quantity to be recognized, is defined as 'dental plaque'. The electron microscope is able to detect this material at an earlier stage of formation than can histological staining which, in turn, is more sensitive than ordinary visible detection as observed clinically. In certain areas of the mouth, crystals of various calcium phosphates begin to appear in localized areas both in the acquired pellicle and in the extracellular matrix of the dental plaque. The order of time for this material to form is measured in days, and it is clinically recognizable as 'calculus' when sufficient of it forms for the individual crystals to be sufficiently closely packed together for the aggregates to become resistant to deformation. The electron microscope reveals the initial stages of calculus formation considerably in advance of this condition⁹ at a stage before the crystals become closely packed

together, and is able to differentiate between the initial calcification of the matrix and the subsequent intracellular calcification of the plaque bacteria.¹⁰

The nomenclature of the various integuments and their nature have been clearly tabulated by Jenkins.¹¹

Acquired Pellicle

There is ample evidence that there is a physical film on the surface of the teeth and this is the acquired pellicle. This layer is usually 1–3 μm thick and is free from bacteria. It also has staining reactions different from those shown by plaque.

The pellicle film can be removed from the surface of an extracted tooth by dissolving the surface layer of the underlying enamel in 2–5 per cent HCl Material which has been removed in this way has been found to consist of protein high in glutamic acid and alanine and low in S-containing amino acids. It also contains carbohydrates and muramic acid which is a constituent of bacterial cell walls.¹²

It would appear that pellicle is formed by the selective adsorption of some of the salivary proteins by the apatite of the enamel.

It has been suggested^{13,14} that pellicle has some protective action against the attack of acids on the enamel surface but this is by no means certain.

Plaque

On all parts of the teeth other than those cleaned by erosion, i.e. the biting surfaces, there is a mucous coating of varying thickness and this is known as dental plaque. Plaque is now considered to be the prime etiological factor in the development of caries;¹⁵ it is also implicated in periodontal disease.

The amount of plaque formed is very variable, but 10–20 mg per day is typical. It is now believed to consist of salivary proteins, perhaps modified by bacterial enzymes, with varying quantities of polysaccharide of bacterial origin. The composition may vary not only among individuals, but also in different parts of the mouth, but typically it contains about 82 per cent water. Other components are:

	<i>% dry weight</i>
Protein	40–50
Carbohydrate	13–17
Lipid	10–14
Ash	10
	<i>$\mu\text{g}/\text{mg}$ dry weight</i>
Calcium	8
Phosphorus	16
	<i>ppm dry weight</i>
Fluorine ¹⁶	20–100

Perhaps the most interesting and significant of these components is the fluorine which, at a typical level of 50 ppm on dry weight, is at a higher concentration than in any food or drink passing through the mouth.

The carbohydrate present is most likely to arise from the dietary intake of sugars. These may be partly metabolized by plaque bacteria to produce extracellular polysaccharides such as dextran and levan.^{17,18} This sugar is also metabolized to form acids which it is believed are the initial cause of caries. This effect—the production of acid in plaque—can be easily demonstrated by measuring the fall in plaque pH after a sugar mouth rinse.^{19,20} It is of great significance in the study of caries.

Calculus

The term *tartar* was commonly used to describe the mineralized deposits formed on neglected teeth. The origin of the term was of course the crystalline deposits formed in wine.

The deposit is now more correctly called *calculus*. It may occur both above (supragingival) and below (subgingival) the gum. The two forms differ in properties and are possibly of different origin. Supragingival calculus is certainly of salivary origin and occurs near the orifices of the main salivary ducts.

Calculus varies in composition but always contains about 80 per cent of inorganic material containing calcium, magnesium, phosphorus and other elements. The calcium and phosphorus are present in early plaque as Brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) and octacalcium phosphate ($\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4$). Whitlockite ($\text{Ca}_3(\text{PO}_4)_2$) may also be found, but the ultimate stage is probably apatite ($3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2$). This transition is helped by the presence of fluorine which is present to the extent of about 400 ppm.^{21,22}

The remaining 20 per cent of calculus is an organic matrix containing carbohydrate, protein, lipid and bacteria. Typical total compositions^{23,24} of supragingival calculus are:

Density	1.09–1.33
Organic matter (%)	11–20
CO_2 (%)	2.0–3.7
Calcium (%)	26.9–28.0
Phosphorus (%)	14.9–16.0
Sodium (%)	2.09–2.58

Calculus is first observed when the plaque on the enamel surface begins to mineralize. There are a number of theories of calculus formation. One of the earliest was that loss of CO_2 from the saliva caused a rise in pH and a consequent precipitation of calcium phosphates. A change in pH may also be caused by ammonia formation. Phosphatase concentration in the plaque has also been proposed as a calculus controlling mechanism. Today, the most generally accepted explanation is that calculus is formed by a seeding mechanism, but this does not explain differences between individuals which are often considerable. The role of bacteria cannot be disregarded, but calculus can form in germ-free animals. The subject is thoroughly discussed by Jenkins.²⁵

It has been recognized for some time that there is an association between the presence of calculus and the incidence of periodontal disease. The commonly accepted theory is that calculus irritates the gingivae and encourages the

formation of a pocket between tooth and gingivae, in which food debris and bacteria may lodge.

An inverse relationship between calculus and caries has also been noticed²⁶ and this would seem logical since calculus should only be deposited under non-acidic conditions.

Mechanical treatment by a dental hygienist is the only means of removing calculus, and until recently there has been no means of preventing its formation. Within the last few years, however, a number of patents have claimed to prevent calculus formation.²⁷

The secret of preventing calculus formation must surely be in preventing plaque deposition, since it is from plaque that calculus is precipitated. Regular brushing will, of course, help to reduce plaque and there are now claims that certain toothpaste or mouthwash additives will reduce plaque formation. Among compounds suggested probably most work has been done on chlorhexidine.²⁸

Food Debris and Materia Alba

Food debris, unless impacted between the teeth, is usually easily removed by a stream of water. *Materia alba* is a white, diffuse, loosely attached layer which is also easy to remove. It is usually a mixture of bacteria with a high proportion of extracellular polysaccharide.

Since normal oral hygiene removes these deposits easily, they are not thought to have any significant effect on oral disease. They may, of course, contribute to mouth odours.

MAJOR PROBLEMS OF ORAL HEALTH

Magnitude of the Problem

Dental diseases are primarily diseases of civilization and the incidence in Western communities is appalling. Surveys conducted by the UK Department of Health and Social Security^{29,30} give a complete and depressing picture of the dental health of the population. Among adults the proportion edentulous (that is, without natural teeth) was found to be as given in Table 30.2. Although an improvement is evident between 1968 and 1978, the proportion of the UK population with no natural teeth is still high. Among children the picture is equally depressing (Table 30.3). It has been estimated that 4 tons of teeth are extracted from British children each year, which corresponds to about 4 million lost teeth. In the USA it is estimated that the adult population (111 million) has the staggering total of 2.25 billion (2.25×10^9) decayed, missing and filled teeth, and that at any one time there is a backlog of 700 million teeth awaiting treatment.³¹

Teeth which are not extracted because of caries may later be attacked by periodontal disease, which is the major cause of tooth loss after the age of 35 (see Figure 30.1).³²

Despite these appalling statistics, serious research into the causes of dental disease has only been undertaken in the last 30 years. This is all the more

Table 30.2 Edentulous Adult Population of England and Wales²⁹

Age group	Percent edentulous	
	1968	1978
16-24	1	—
25-34	7	3
35-44	22	12
45-54	41	29
55-64	64	48
65-74	79	74
75+	88	87

Table 30.3 Active Decay in Children's Teeth, England and Wales³⁰

Age	Per cent with decayed teeth
5	63
6	69
7	73
8	78
9	76
10	69
11	66
12	61
13	61
14	62
15	57

surprising since the probable cause of caries was described as long ago as 1890 by an American dentist who first showed the relationship between dietary sugar and caries.³³ A recognition that the primary cause of caries was biochemical stimulated research by chemists and the last 30 years has seen a massive research input both in university dental schools and in the laboratories of commercial companies. This research has now reached the stage where the cause of caries and the mechanism of its development are fairly well understood and accepted. The clinical treatment of disease is no part of the cosmetic chemist's function—the prevention of disease is, and in order to be able to formulate prophylactic products it is necessary for him to understand the disease that he is trying to prevent.

Dental Caries

A conference held at the University of Michigan in 1947 to evaluate and correlate all available information on the aetiology and control of dental caries,

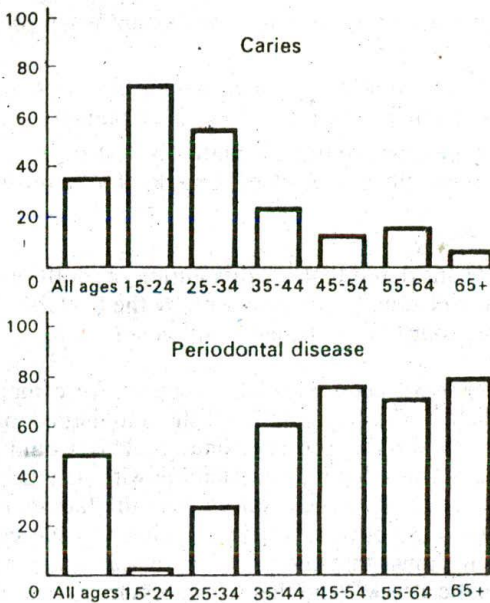


Figure 30.1 Teeth extracted because of caries and periodontal disease

unanimously adopted the following definition:³⁴

... Dental caries is a disease of the calcified tissues of the teeth. It is caused by acids resulting from the action of micro-organisms on carbohydrates, is characterized by a decalcification of the inorganic portion and is accompanied or followed by a disintegration of the organic substance of the tooth. The lesions of the disease predominantly occur in particular regions of the tooth and their type is determined by the morphological nature of the tissue in which they appear ...

The following general observations may be used to describe the process:

- Cariou lesions are localized, generally beginning in a small circumscribed area. They are found most frequently in pits and fissures of occlusal surfaces.
- Demineralization begins with the enamel, usually beneath an intact enamel layer. This demineralization is often accompanied either by a discoloration or a change in the opacity of the enamel, that is, development of a so-called 'white spot'.
- The demineralization penetrates deeper into the tissue and spreads within it, roughly assuming the shape of a cone with its apex orientated towards the dentino-enamel border and the base still below the enamel surface. At this stage of the process there still may be no visible break or cavitation evident on the enamel surface. It is generally accepted that the dentine begins to demineralize or soften before an actual cavity becomes visible. Gradually,

the tissue softens sufficiently so that it 'breaks up' when pressure is applied with a dental probe.

- (d) The decay process continues and the enamel develops a lesion which is visible. The cavitation is often discoloured or pigmented.
- (e) During the decay process the organic matrix is destroyed. The exact step at which this occurs is still a subject of considerable controversy.

Theories of Dental Caries

In the 1890s Miller³³ considered that the dissolution of tooth substance was due to the action of acids which had been produced by the bacterial fermentation of carbohydrates in the mouth. This theory is still generally accepted as the basic cause of caries.³⁴

Alternative theories have been postulated such as, for example, the proteolytic theory of Gottlieb.³⁵ This suggested that the initial effect on enamel might be a proteolytic attack on the protein content. This would be even more important if the caries proceeded into the dentine with its much higher protein content. This theory appeared to be supported by the fact that carious lesions are pigmented and the only obvious source of colouring matter is the protein. However, it has been shown that the presence of Ca^{2+} salts actually protects dentine from proteolytic attack³⁶ and that it is necessary to demineralize dentine with acid before proteolysis can occur.

Schatz and his colleagues³⁷ have postulated a 'proteolysis-chelation' theory which suggests that some of the products of the action of oral bacteria on saliva, food debris, enamel and dentine may be capable of forming complexes with calcium.

It is now generally accepted that the acid theory is most probably correct and that the initial step in the carious process is the presence of fermentable carbohydrate in the diet. It is important to recognize that caries is a step-wise process:

*Bacteria in the mouth release
enzymes which attack
fermentable carbohydrates releasing
acids which attack
enamel thus producing a
carious lesion*

This is a simplified statement of the series of events which lead to the development of caries.

Control of Caries

In the light of the above discussion it is possible to suggest methods for the control of caries:

Reduction of Fermentable Carbohydrate Intake. There is a mass of clinical evidence to support the association of dietary sugar with caries. In separate papers Marthaler³⁸ and König³⁹ have reviewed the evidence for this association.

The improved dental health of Norwegian school children during World War II⁴⁰ was attributed to the reduction of dietary sugar. The dental health of the natives of Tristan da Cunha fell rapidly when they were exposed to Western diet.⁴¹ The World Health Organization⁴² has now accepted the fact that sucrose plays a dominant role in the development of caries.

It is impracticable to prevent fermentable carbohydrate intake, as sugar has become an important part of the Western dietary habit. Nevertheless, there is an excellent case for reducing sugar intake, particularly when it is taken between meals, for example in the form of sweets (candy).

Removal of Fermentable Debris from the Mouth. There is ample evidence that the removal of food debris from the mouth reduces the incidence of caries. Fosdick⁴³ found a 50 per cent reduction by after-meal tooth brushing. Certain foods such as apples, carrots, nuts, etc., help in the removal of debris by mechanical means and by stimulation of salivary flow, which additionally buffers plaque acids resulting from previously eaten sugary foods (Figure 30.2).⁴⁴

Brushing the teeth after eating is not always practicable and a twice-a-day routine is more realistic. Clark *et al.*⁴⁵ developed a tooth cleaning tablet which stimulated salivary flow and was shown to be as effective as tooth brushing with water. Slack *et al.*⁴⁶ showed a small but significant benefit in children using the tablets as an adjunct to tooth brushing.

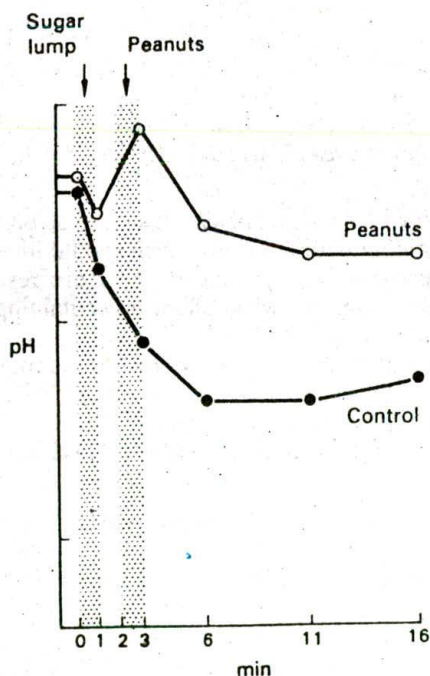


Figure 30.2 Effect on plaque pH of eating peanuts after consumption of sugar

Reduction in Bacterial Activity. Bacteria present in the mouths of most human subjects will promote fermentation in dilute sugar solutions causing a pH drop to a level of about 5.3. This fall in pH is the classical 'Stephan curve'⁴⁷ which can be reproduced *in vitro* and *in vivo*. Certain organisms have been identified as specific causative agents and these include *Lactobacillus acidophilus* and *Streptococcus mutans*. This immediately suggests that it should be possible to produce a vaccine which would confer caries immunity on subjects. A considerable volume of work has been done on this assumption and though vaccination of monkeys has produced positive effects, the results are not as spectacular as was hoped. Bowen *et al.*⁴⁸ and Lehner⁴⁹ have used this technique on monkeys with some success.

An obvious technique for reducing the bacterial population of the mouth would be to use an antibiotic in a mouthwash or in a toothpaste. This method was tried by Zander⁵⁰ using penicillin. Although this technique appeared to cause a reduction in the incidence of caries it is potentially harmful. It could lead, for example, to the development of penicillin-resistant organisms and it might sensitize significant numbers of the population to penicillin. For these reasons it is unlikely that antibiotics will ever be components in routine prophylactic oral products.

It is, of course, possible to reduce the bacterial population of the mouth by the regular use of chemical bacteriostats. There is some evidence that this may be effective in preventing caries.⁵¹

Interference with Enzyme System. A further obvious method of interrupting the step-wise development of the carious process would be to inhibit the enzymes responsible for the glycolytic breakdown of sugars to acids. This approach was used by Fosdick who showed that sodium N-lauroyl sarcosinate specifically inhibited the enzyme *hexokinase*. This subject is dealt with in a later section.

Decrease of Susceptibility of Tooth to Attack. It should be possible to strengthen enamel by topical treatment with fluorides which should ion-exchange with the hydroxyl group in hydroxyapatite, producing the more resistant fluorapatite. This may be the mechanism by which fluoride-containing toothpastes and mouthwashes exert their effect.

Alternatively, a physical barrier may be applied to the tooth surface; this has been explored by Irwin, Walsh and Leaver⁵² and others.⁵³ Films polymerized by UV radiation appear to be particularly effective.⁵⁴ The use of these polymers as fissure sealants has been found useful in reducing occlusal caries.⁵⁵

Fluoridation of Water Supplies. In 1952 it was established in the USA that there was an inverse relationship between the incidence of caries in children and the fluoride content of the local water supply (Dean⁵⁶ and see Figure 30.3). Weaver⁵⁷ confirmed these findings in Britain. An investigation sponsored by the Government showed beyond doubt that the American findings were valid. Experimental fluoridation in Great Britain was started and after eleven years' experience it was concluded that the addition of 1 ppm of fluorine to water supplies was a safe and effective way of reducing dental decay.⁵⁸

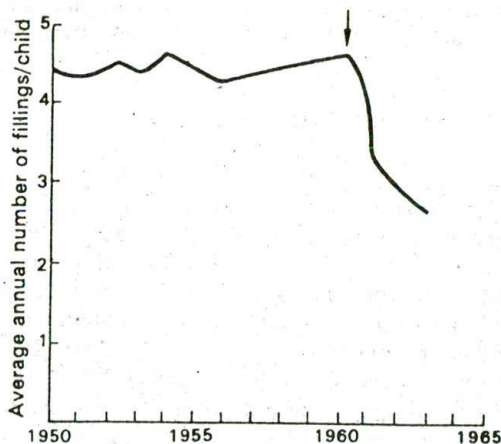


Figure 30.3 Average number of fillings per child per year, School Dental Service, Gothenburg, Sweden. Fluoride rinsing was started in 1960

The two aspects of effectiveness and safety have been further emphasized by the World Health Organization⁵⁹ and by the Royal College of Physicians.⁶⁰ No scientist can deny the validity of the conclusions reached by these bodies. It could be argued indeed that the artificial fluoridation of water is merely reinforcing the natural situation where both the enamel and dentine of human teeth collect and retain fluorine and thereby increase their resistance to attack.³

The effect of the fluoridation of water in Sweden is shown dramatically by Figure 30.3 which plots the incidence of fillings in children's teeth before and after fluoridation. It was originally thought that this benefit only accrued to children born in the area of fluoridated water—in which case the fluoride content of teeth would be of systemic origin. Later studies indicate that adults may benefit also—presumably by a topical effect.⁶¹

The whole subject of the caries mechanism has been summarized by Jenkins⁶² and by Grenby.⁶³ The vast accumulation of knowledge on this subject has reached the stage at which it can be stated that caries is a preventable disease, or at the worst, its incidence can be enormously reduced.

Periodontal Disease

Teeth are attached to the basal bones of the jaw through the periodontal tissues. There are many abnormalities of these tissues which can be regarded as periodontal diseases. The World Health Organization (1961) has divided periodontal diseases into three broad classes: inflammatory processes, degenerative processes and neoplastic processes. Periodontal diseases involving inflammation are by far the most common and they are the easiest to prevent and to treat.

Gingivitis is an inflammation of the gums and is rapidly caused by poor oral hygiene. It appears to be caused by substances produced in plaque which irritate the gum membranes. Periodontitis in addition to gum inflammation is

manifested by a pocket formation and destruction of the collagen fibres of the periodontal ligaments. It is encouraged by calculus at the gum margin.

USE OF PROPHYLACTIC TOOTHPASTES

The review of the mechanism of the caries process indicates that toothpastes and mouthwashes may play a part in the prevention of oral diseases. The primary function of a toothpaste as a cosmetic for cleaning and polishing the teeth has now been extended. A toothpaste in fact is an ideal vehicle for conveying prophylactic ingredients to the tooth surface. Most modern dentifrices have accordingly changed their emphasis and are formulated with the object of controlling caries and improving oral hygiene. A properly organized clinical trial thus becomes an essential preliminary to the marketing of such a product.

Advertising claims for prophylactic oral products must be substantiated by clinical evidence that is acceptable to dental authorities. It is worth noting that if such claims are made to dental practitioners the product must come within the scope of the Medicines Act in the UK or corresponding regulations such as those of the US Food and Drugs Administration.

Active Ingredients

Chlorophyll

Earlier editions of this work devoted considerable space to chlorophyll which was once popular as a toothpaste ingredient. It is perhaps indicative of the increased knowledge of the chemistry of the mouth and the volume of clinical research performed, that chlorophyll has almost disappeared as a toothpaste ingredient.

Bacteriostats

Although it would seem obvious to prevent caries by destroying the bacteria in the mouth, the ideal bacteriostat has yet to be found. Such a compound should be adsorbed strongly onto mucous membranes and should continue to exert its influence for some time; it should be non-toxic and non-irritant. Among compounds which have been used in toothpastes and mouthwashes are hexachlorophene (G11), benzethonium chloride and other cationics and, most recently, chlorhexidine (Hibitane, ICI). Probably most research has been done on this last compound as it has been shown to be effective in reducing plaque and hence in improving gingival health. It may also be expected to have an effect on the incidence of caries. Unfortunately, chlorhexidine (in common with many other cationics of the same type) produces a slight brown staining of the teeth. A symposium devoted to the subject⁶⁴ presents a very clear picture of the whole subject.

Enzyme Inhibitors

Another obvious route to preventing or reducing the production of acid from sugar breakdown is to inhibit the enzymes concerned with glycolysis. Fosdick⁶⁵ proposed the use of sodium N-lauroyl sarcosinate ($C_{11}H_{23}CO \cdot N(CH_3)$

$\text{CH}_2 \cdot \text{COONa}$) which is an excellent inhibitor of the enzyme hexokinase. This was found to be clinically effective in reducing caries but this has not been confirmed. More recently Mühlemann⁶⁶ has shown that this substance prevents the reduction of plaque pH to the danger level and Tomlinson⁵¹ has shown it to be effective in a mouthwash.

Sodium N-lauroyl sarcosinate has mild detergent properties and its use in dentifrices is described in a number of patents.⁶⁷

Enzymes

In contrast to the use of enzyme inhibitors, some workers have proposed that enzymes are added to toothpastes to assist in the breakdown of proteins, starch and lipids. Patents exist for oral products containing such enzymes.⁶⁸

Dextrans and levans are gummy metabolic products of bacterial attack on carbohydrates and the presence of these substances in plaque is thought to play a part in maintaining the plaque film on teeth. It is not surprising therefore to find that it has been suggested that dextranases should be added to toothpastes.⁶⁹

Leach⁷⁰ has reviewed the relationship between dextrans in the plaque and caries. It is unlikely that this route would lead to a dramatic solution to the problem.

Ammonium (Salt)/Urea

Dentifrices containing an ammonium ion and urea have been proposed⁷¹ on the grounds that these compounds might neutralize acids produced in dental plaque or inhibit their formation. Clinical trials have not established this approach as valid⁷² and Peterson⁷³ does not believe that these compounds have a future in prophylactic dentifrices.

Fluorides

It is now well established that the fluoridation of water supplies is an excellent public health measure since it is effective, safe and economical. It is an obvious step therefore to add fluorine-containing compounds to toothpastes and thus convert the social habit of toothbrushing into a prophylactic treatment. Among compounds which have been used for this purpose are sodium fluoride, stannous fluoride, sodium monofluorophosphate and amine fluorides.

The addition of compounds containing the F^- ion to dentifrices is difficult. Most toothpaste abrasives are calcium salts and calcium fluoride is one of the most insoluble substances known. Loss of fluoride ion on aging is therefore one of the great problems of fluoride-containing dentifrices. It has been overcome by the use of highly insoluble abrasives (calcium pyrophosphate), by the use of non-calcium-containing abrasives (silica, plastics, insoluble sodium metaphosphate) and by the use of sodium monofluorophosphate (Na_2FPO_3) which does not release free F^- ions except after hydrolysis.

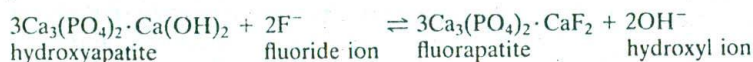
Since the introduction and widespread use of fluoride toothpastes in the 1950s the Council on Dental Therapeutics of the American Dental Association has included certain fluoride-containing toothpastes in 'Accepted Dental Therapeutics'. In order to qualify for acceptance products have to show evidence of clinical effectiveness. A similar position has been taken by the British Dental

Association which will endorse fluoride-containing toothpastes of which the clinical effectiveness can be demonstrated.

Thus, in a period of less than 25 years, toothpastes have moved from the position of being cosmetic products to the current position in which many of them have been professionally endorsed because of their clinically-proven prophylactic effect.

Simple Inorganic Fluorides

The two simple inorganic fluorides commonly used are sodium fluoride and stannous fluoride. Provided the problems of inactivation can be overcome, both these compounds have shown clinical effectiveness in reducing the incidence of caries. The mechanism is thought to be that the free F^- ion reacts with the hydroxyapatite present in tooth enamel, thus converting it to the less soluble fluorapatite:



Such a reaction would be favoured by acid conditions and the first stannous fluoride toothpaste produced in 1955 had a pH value well below neutrality.

This and other fluoride dentifrices have been extensively tested clinically. Reductions of 20–30 per cent in the incidence of caries in children are commonly reached and, though this is by no means a solution to the problem, it is a step in the right direction.

The volume of clinical testing done is so enormous that no single reference is adequate. Duckworth⁷⁴ has reviewed the mechanism of clinical trials and Von de Fehr and Møller⁷⁵ have recently reviewed caries-preventive fluoride dentifrices.

Dentifrices containing inorganic fluorides normally contain about 0.4 per cent of SnF_2 or 0.2 per cent of NaF . Both these levels correspond to about 1000 ppm of F in the toothpaste. At this concentration one of the inevitable consequences of use is that CaF_2 will be precipitated in the plaque or on the surface of the tooth. This should itself resist acid attack and may produce a very low F^- ion concentration near the surface of the tooth. This condition is known to promote the remineralization of early carious lesions⁷⁶ and it may be that some of the clinical effect is due to this.

Low concentrations of F^- ion are also known to have effects on enzymes and it may be that acid-producing enzymes in the plaque are inhibited by F^- ions present.

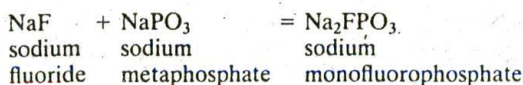
Thus the reasons for the clinical effectiveness of F-containing toothpastes are not fully understood. It may be that improvements in clinical efficiency still await the fuller understanding of the caries preventive mechanism.

Sodium Monofluorophosphate

Sodium monofluorophosphate (Na_2FPO_3) has the advantage over sodium and stannous fluorides in that it ionizes to give not the F^- ion, which will immediately precipitate in the presence of calcium ions, but the FPO_3^{2-} ion of which the calcium salt is soluble. It was this thought which prompted Ericsson to propose the use of sodium monofluorophosphate in a calcium carbonate

dentifrice.⁷⁷ Subsequent clinical trials showed this substance to have an anti-caries effect.⁷⁸ Patents on various formulation combinations are well known.⁷⁹

The mechanism of the protective action of sodium monofluorophosphate is not fully understood. The commercial material is made by the fusion of NaF and NaPO₃:



This reaction yields a product about 95 per cent pure and consequently the commercial material is always contaminated by up to 2 per cent NaF. It is not possible therefore to say with certainty which component is responsible for the clinical effect, particularly since it is known that low F⁻ concentrations may have a significant effect.

Ingram⁸⁰ suggested that the FPO₃²⁻ ion exchanged with the HPO₄²⁻ ion in the apatite lattice of calcium-deficient enamel, thus rendering it more resistant to acid. Duff⁸¹ suggested that the FPO₃²⁻ ion exchanged with HPO₄²⁻ on the enamel surface and that the subsequent dissolution of this under acid conditions favoured the precipitation of fluorohydroxyapatite.

Pearce and More⁸² showed that only free F⁻ is taken up by the enamel and that this arises only from the free F⁻ impurity and by hydrolysis of Na₂FPO₃. Tomlinson⁵¹ showed that purified Na₂FPO₃ (that is, free of F⁻) did have a clinical effect and that the mechanisms involving the whole FPO₃²⁻ ion were therefore possible.

Whatever the mechanism, there is no doubt of the clinical effectiveness of sodium monofluorophosphate when incorporated in a dentifrice.

It is not possible to be dogmatic about the relative effects of stannous fluoride and sodium monofluorophosphate. Both have about the same level of effectiveness and both appear to show their greatest effect on teeth which erupt during the course of a clinical trial, that is on teeth which have been exposed to a fluorine-containing compound from the moment of eruption. A review of a number of trials is given in a special issue of the British Dental Journal.⁸³ Duckworth⁷⁴ states that the clinical evidence obtained from UK trials supports the view that 'certain fluoride-containing dentifrices can be of value when used in a conscientiously applied programme of oral hygiene and regular professional care'.

Organic Fluorides

Work by Mühlemann and Marthaler in Zurich suggested that certain amine fluorides had more protective action against caries in rats than had sodium fluoride. Subsequent clinical trials on children⁸⁴ showed a substantial reduction in the incidence of caries. Compounds of this type would be expected to adsorb onto tooth and mucous membrane surfaces and thus retain an effect in the mouth for some time. They will, of course, present many problems in toothpaste formulation. A number of patents exist for compounds of this type.⁸⁵

Other Fluorides

A number of other metallic fluorides have been proposed as toothpaste components and their use is protected by patents. These include ferric and

zirconium fluorides, stannous and indium fluoro-zirconates, manganese fluoride and aluminium fluoride.⁸⁶ The fluoride and monofluorophosphate salts of chlorhexidine (Hibitane, ICI) have also been patented. So far as is known, none of these compounds is in commercial use at the present time.

Other Metal Compounds

A number of metals have been proposed as toothpaste additives for various purposes.

Thus water-soluble indium salts are said to increase the activity of fluorides in toothpastes.⁸⁷ Organo-tin compounds have been patented as bactericides.⁸⁸ Aluminium salts are astringent and are claimed to have some effect on gum health.⁸⁹ Zinc salts have also been used for this purpose and have some clinical evidence to support the claim.⁹⁰

The presence of molybdenum in water supplies in concentrations as low as 0.1 ppm appears to have an effect in reducing caries and this has been confirmed in animal experiments. The mechanism is not understood; the whole subject has been well reviewed by Jenkins.⁹¹

Strontium in the form of strontium chloride has been used to reduce the sensitivity of exposed dentine, for example because of gum recession in older subjects. Reports vary on the clinical effectiveness of this procedure;⁹² nevertheless, patents exist for this additive and it has been used commercially.⁹³

Anticalculus Ingredients

Although there has been no large-scale promotion of an anticalculus toothpaste there has been a considerable volume of work on this subject.

Dissolution of existing calculus is a problem because of its chemical similarity to tooth substance. For this reason sequestering agents of the EDTA type cannot be used. Research has concentrated instead on means to inhibit crystal growth and means of preventing adhesion to the teeth. Patent literature is a particularly useful source of information on developments in this field.⁹⁴

Sturzenberger⁹⁵ has shown that disodium etidronate (a diphosphonate) inhibits crystal growth of apatites, and zinc salts are also claimed to have a similar effect.

Organic titanates⁹⁶ are also claimed to prevent the adherence of calculus to tooth surfaces.

Remineralizing Ingredients

Within recent years it has become clear that early carious lesions may become repaired by a process which has been termed remineralization. The effect has been described by Levine⁷⁶ and the phase conditions necessary for remineralization to occur have been worked out by Duff.⁹⁷ It is not surprising, therefore, that the concept of remineralization has become part of toothpaste formulation; indeed it is possible that the clinical effect of some existing fluoride toothpastes is due, in fact, to their remineralizing effect.

Remineralization requires the presence of very low concentrations of F^- , PO_4^{3-} and Ca^{2+} ions; because these components would precipitate, it is customary to have a two-component system.

The patent literature is a valuable source of information⁹⁸ but so far no commercial product has been promoted with a strong remineralization claim.

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