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## Better Looking (I): Hair, Eyes, Teeth, Nails

A small arrow printed before a word in the main text indicates that there is more information on that topic in the Glossary.

### News from the Future

*Global Times News, 21 March 2025*

#### **Dentist Numbers Fall Again**

For the fifth year running the number of registered dentists in Europe has declined and in some areas people are travelling up to 50 kilometres to obtain their services. The drop in numbers is blamed on the success of the new toothpastes such as LoveSmile that were launched 15 years ago. These not only keep teeth brilliantly white but contain nanoparticles which can penetrate cavities and repair them from the inside, so there is no longer a need for dentists to drill and fill.

“Dental work now mainly consists of fitting braces and occasionally mending broken teeth,” said a leading professor at Rome’s Dental School, adding: “In my early days as a teacher I spent most of my time instructing students on how to repair or replace decayed teeth. Today a call for these services is almost unheard

of. Even cosmetic treatment such as tooth whitening is rarely required.”

Modern toothpastes, first marketed in 2010, have been responsible for young people in Europe today having such wonderful teeth. They contained not only the usual cleaning agents and fluoride but included repairing additives such as nanoparticles of hydroxyapatite, the natural chemical from which tooth enamel is made. It is these which penetrate any tiny cavities and repair them. Products like LoveSmile also contain a whitening agent which prevents staining and, unlike the earlier whitening agents, it does not cause thinning of the outer layer of tooth enamel.

Page 3: Chemicals in toothpaste could cause bone cancer in old age warns dental fillings manufacturer.

Of course there is no such product as LoveSmile toothpaste, at least a search of the Internet failed to reveal one. What the above news item suggests is that a trip to the dentist is likely to become a rare event in the life of children born today, unlike the regular visits to the dentist that most people have had to make in the past if they wanted to keep their teeth in good condition. The new ingredients mentioned in the

news item are already known and we will look at them later in this chapter, the theme of which is improving our looks with the help of various products that chemists have devised, namely hair colorants, hair restorers, contact lenses, tooth whiteners, and artificial fingernails. We begin with hair, regarded by many as their best asset, but it is possible to make it even more attractive.

### **Crowning Glory**

Hair comes in various natural shades and colours, ranging from jet black through brown and auburn to ash blonde, which are produced by varying amounts of two pigments. These are slightly different versions of a biological  $\rightarrow$ polymer called melanin, one is black, and called eumelanin, and the other is blonde, and called pheomelanin. Eumelanin particles predominate in black and brown hair, while pheomelanin particles dominate in fair hair. These melanin pigments are incorporated into the hair as it grows, and the particles are formed in special cells called melanocytes. (When these cease to function then the hair they produce has no colour.) What our genes provide may not be quite what we want, and so we may seek to change the colour of our hair and this option is proving popular with young and old alike. Many will look to a hair stylist for advice, and they in their turn look to chemists to provide the necessary materials to make it possible. We can also purchase packs of these same chemicals and make the change ourselves.

It will come as no surprise to learn that the global market for hair dyes exceeds \$7 billion annually, and it continues to grow, with the US accounting for around a quarter. The first truly permanent hair dye was created by a French chemist, Eugène Schueller in 1907 who founded the French Harmless Hair Dye Company. Today we know it as L'Oréal and it is still the biggest manufacturer of hair dyes with just over a third of world sales. Next comes Procter & Gamble with 13%, followed by Henkel with 11%, Wella with 9%, and Hoya with 6%. Smaller producers account for the remaining 25%.

Hair dyes are of three kinds: temporary, semi-permanent, and permanent. The first kind are easily washed out of the hair, the second will survive several washings but eventually fade, and the third are locked fast within the hair shaft and disappear only as the hair grows

out. What differentiates the various dyes is their chemistry, and it is the permanent type which is the most sophisticated chemically, although some people find this worrying – more of that in a minute. First the good news.

The dyes that are used for temporary colouring can be applied in the form of rinses, gels, mousses, and sprays. They coat the surface of the hair with dye and most of this will be washed away the next time the hair is shampooed. We may want this to occur if we have applied the dye for a special event such as a party, a fun day, or an on-stage performance. A typical temporary hair dye is the →colorant known as FD&C Blue No.1.<sup>1)</sup> This is a large molecule so it cannot penetrate into the hair, and it has three negatively charged groups of atoms which make it highly water soluble so it is easily washed off.

Semi-permanent dyes are smaller molecules and these can pass through the outer layer of the hair, known as the cuticle, and move into the inner cortex, there to remain until they gradually leach out again and are washed away. A combination of dyes is generally required to produce the desired shade and those commonly used are listed in the Glossary.

Chemicals destined to produce permanent hair dyes also penetrate the cuticle but then they become trapped by reacting together to form a much larger molecule which cannot escape. For this to happen the cuticle must be made permeable, which can be achieved by the action of a little ammonia (NH<sub>3</sub>). This causes the hair shaft to swell by raising the →pH to about 10, and this opens up the cuticle scales. Once inside the hair, the molecules react to form the dye molecule which is too large to escape when the scales close again under the action of a final rinse. Permanent hair colorants come as two separate gels which have to be mixed together before application. One contains hydrogen peroxide which serves two functions, one is to bleach away the natural melanins, the other is to activate PPD (short for paraphenylenediamine<sup>2)</sup>) which is then combined with a second molecule, known as a coupler, to form the dye. In fact there may be more than one type of coupler in a hair dye. For example, in L’Oreal’s dye ‘Havana’ there are three couplers<sup>3)</sup> which together generate a pale auburn shade referred to as light amber.

1) FD&C refers to the US Federal Food, Drugs, and Cosmetics Act.

2) Also called 1,4-benzenediamine.

3) These are 4-amino-phenol, 4-amino-2-hydroxy-toluene, and 3-amino-phenol.

That was the good news ... now the bad news:

There is another type of hair colorant which is generally aimed at men who are going grey and is based on lead acetate. Although it is poisonous it is regarded as safe because the metal is not absorbed through the skin. The dye is rubbed on the hair with which it reacts to form a black pigment. With each application the hair gets darker and darker until all the grey hairs have disappeared. Such treatments date back to the days of the Roman Empire, when combs made of lead were used and were dipped in vinegar. The acetic acid of the vinegar dissolved a little of the lead, which was then transferred to the hair. For the past 200 years or so the preferred treatment has been to dab a solution of lead acetate directly onto the hair, and such products are still available. Soon they are to be banned inside the EU on the grounds that lead is inherently dangerous.

More serious perhaps are the charges that permanent hair dyes may cause cancer, they have even killed those who used them. Although PPD has been an ingredient of hair dyes for more than 30 years it has not been without occasional bad publicity due to an allergic reaction in some people. We now know that this type of allergy affects only three women in a million, and it has been traced to a rare genetic susceptibility. Many years ago it was claimed that as many as one woman in a hundred was sensitive to PPD. This turned out to be somewhat of an exaggeration and came from tests in which pure PPD was applied directly to the skin and then covered with a plastic patch. Nevertheless, users of these dyes are warned that a skin allergy test must be carried out. Typically they are told to apply a penny-sized area of the dye to the skin behind the ear. When this has dried, a second coating of dye should be applied, and then left for 48 hours. If the skin becomes inflamed in any way then the dye must not be used.

In May 2001 a Mrs Narinder Devi who lived in Birmingham, England, decided to dye her hair but she skipped the skin test. Sadly she suffered a massive anaphylactic shock from which she died. This was a rare example of a fatality following the use of a hair dye, although what ingredient caused it was never deduced. Other severe cases of allergic reaction continue to occur, although rarely with such a fatal outcome, and while these are widely publicised in the media, they are extremely rare. (Victims invariably settle out of court.) Of women who genuinely do test their skin for sensitivity, around 2% will observe a

slight positive effect and they are informed in the leaflet which comes with the hair dye that they must not use the product.

The 1970s also saw claims that the various chemicals used in hair colorants caused cancers in laboratory animal tests when fed to them in large doses over a long period. Others reported that they caused mutations in bacteria. As a result the suspect ingredients were withdrawn. Although PPD was never implicated in these tests, the EU even introduced limits on PPD to the effect that no more than 6% can be present in hair colorant products. Tests showed that in a typical hair dyeing session a woman would absorb some PPD (at most 36 mg) but in any case this was rapidly excreted in her urine. PPD has been thoroughly tested over many years, but that does not prevent scare stories about its use being circulated.

PPD is manufactured on a large scale by the US chemical giant Du Pont and is mainly used to manufacture resins and polymers. That which is destined for inclusion in hair dyes is specially made by a different process that ensures it is absolutely pure and that it is free from any by-products that could cause adverse effects. What this means is that if there is a risk to health from exposure to PPD then it will be due to the PPD itself and not to some hidden cause. There is an alternative to PPD and that is TDS (short for toluene-2,5-diamine sulfate). This is less skin sensitive but produces shades of brown that are slightly redder.

Hair dyes have come under attack many times from those who thought their use might have long term effects such as causing cancer. In 2001 an epidemiological report linked them to bladder cancer, while another in 2004 linked them to leukaemia. Both reports naturally attracted media interest, and continue to be quoted, despite the fact that similar, and often better conducted, studies found no such links. The leukaemia scare began with a paper in the *American Journal of Epidemiology* which reported a study of 769 adults with acute leukaemia and compared them with 623 adults who did not have leukaemia. The finding was that those who had used older-style permanent hair dyes in the 1980s were more at risk of leukaemia, although that risk was tiny. (There was no extra risk for those who used non-permanent dyes.) The paper attracted worldwide attention although it was a retrospective analysis, and the hair dyes it referred to were phased out more than 20 years ago.

A survey in 2000, carried out in Los Angeles by a group at the University of Southern California School of Medicine, found a link with bladder cancer. It involved 1541 people with this condition and they were compared to 897 people who were not so afflicted. Adjustments were made to take into account smokers, who are liable to be more at risk of this disease in any case, and it found that those who used permanent hair dyes every month had a slightly higher risk of bladder cancer, especially if they had used hair dyes continuously for 15 or more years. Hairdressers had an even higher risk. This revelation prompted the Scientific Committee on Cosmetic Products and Non-Food Products of the EU (SCCNFP) to issue a discussion paper in February 2002. This was followed in December that year by a requirement that manufacturers must submit by July 2005 all their data on hair dyes together with studies to assess their safety in terms of cancer and toxicity. The outcome of this has yet to be published, but it will take the form of an approved list of hair dyes which will be issued in 2007.

In 2004 another epidemiological study was undertaken of 459 cases of bladder cancer in New Hampshire, USA, by the Dartmouth Medical School at Lebanon, and they were matched against 665 people who did not have the disease. This study found that men who used hair dye were *less* likely to suffer bladder cancer, whereas for women there was a slightly higher risk, although in both cases the observations were not statistically significant. Another survey, this time of more than half a million women, and carried out by the American Cancer Society, found no link at all between hair dyes and bladder cancer.

A survey of 608 Connecticut women with breast cancer and 609 women who were free of the disease, was carried out under the auspices of Yale School of Public Health with collaboration from the European Institute of Oncology in Italy, McGill University in Canada, and the US National Cancer Institute. This weighty team of international medics found no evidence that those who used hair dyes of either the temporary or permanent kind were in any way increasing their risk of having breast cancer, and they published their results in the *European Journal of Cancer* in August 2002. In 2003 another study was undertaken by the world-famous Karolinska Institute of Sweden and specifically looked at the incidence of all types of cancer in Swedish hairdressers, the group that was expected to be most at risk.

The medical records of 38,800 women and 6,800 men were consulted stretching back for 40 years and these found that there was a higher risk of cancer in the 1960s but not in subsequent years, and there was no increased incidence of bladder cancer among the hairdressers compared to the rest of the population.

So what should we make of all this? The upshot of all this analysis would appear to be that modern hair dyes present no risk of causing cancer either among those who apply them or those on whose hair they are applied. If you are still not convinced that synthetic chemical dyes are safe, and yet you want to change the colour of your hair or hide any grey then you must perforce turn to the dyes of old – see box – but even some of these should come with test patches and a warning.

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### 'Natural' Hair Dyes

A traditional hair dye is henna which is extracted from a privet-like shrub, *Lawsonia inermis*, which grows in India, Pakistan, and Egypt, and which produces the chemical lawsonone. This acts as the dye molecule and its name is 2-hydroxy-1,4-naphthoquinone and it is also known as natural orange 6. Were it to be produced by a chemical company it would be banned because it would not pass today's stringent health and safety checks; it can cause allergies and asthma in some people. Moreover, as a colorant it gives unpredictable results. Not that this stops those who campaign on behalf of so-called 'green' alternatives from advocating henna as a safe natural dye. Those who recommend henna claim it has other benefits such as prevent-

ing dandruff, killing head lice, and curing ringworm, but these claims are unproven and almost certainly unreliable.

Other 'natural' hair dyes that have been used down the centuries have been indigo (chemical name 2-[1,3-dihydro-3-oxo-2H-indol-2-ylidene]-1,2-dihydro-3H-indol-3-one) extracted from *Indigofera*, a plant of the pea family, and pyrogallol (chemical name 1,2,3-trihydroxybenzene) extracted from walnut shells. This last dye was banned for use in the EU in 1992.

Lemon juice, saffron, cloves, and tea are other plant extracts used to change the colour or tint hair, but they are somewhat unreliable, and may even have no effect at all.

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### Thinning on Top

Few things are more eye-catching than well styled hair, and that is true for both men and women. But while a woman's hair remains a valuable asset to the end of her life, for many men it starts to disap-

pear when they reach 30, and soon their baldness begins to send out a signal which they may not care to broadcast, especially if they still want to be seen as sexually attractive. Not that this should have bothered the Old Testament prophet Elisha but, like many men, he was surprisingly sensitive about his looks. When he was on a journey to Bethel, sometime around 850 BC, he was mocked by a group of young boys on account of his baldness, he was so upset by their remarks that he cursed them. Suddenly two she-bears emerged from a nearby wood and tore into the group, badly savaging 42 of the children – or so it says in the *Bible*.<sup>4)</sup>

Neither cursing, nor praying, is the answer to baldness, whereas chemistry can offer a realistic chance of undoing the ravages of time. The average head has 100,000 follicles from which hair grows at the rate of 0.37 mm per day, amounting to around 14 cm per year (just under 6 inches). Every day we lose about 50 hairs and this is perfectly natural and occurs because a hair follicle enters a resting phase for a few weeks after it has been active for around three years. The old hair then falls out and a new growth phase begins, but the new hair may be somewhat different from the old hair. It may lack melanin so it appears white, or it may be thinner, in which case it is likely to be even thinner after the next resting phase, and eventually it may not even appear at all. Hair cells divide in the bulb at the bottom of the hair follicle and as they migrate upwards they deposit a layer of  $\rightarrow$ keratin to form a tube-like structure. The cells divide about once a day, which is rapid for the human body, and this is why chemotherapy treatment for cancer also affects them. Cancer cells divide as quickly as hair cells, so that drugs designed to prevent cancer cells dividing also stop hair cells from working. When these cannot divide, the follicle behaves as if it is in the resting phase and the existing shaft of hair comes loose.

Male baldness manifests itself on the crown of the head and at the temples, and it will progress until most of the scalp is hairless. This loss of hair has little to do with lifestyle, but partly to do with race; baldness afflicts 50% of white males, 22% of orientals, and 18% of black males. Equally important are the man's genes which govern production of the male hormone testosterone and its conversion to its more active form di-hydro-testosterone<sup>5)</sup> by the enzyme *5- $\alpha$ -reductase* which

4) *The Second Book of the Kings* 2:23.

5) As its name implies this is testosterone with two extra hydrogen atoms attached.

regulates the functioning of several parts of the male body including the genitals and the growth of hair. This enzyme eventually causes the number of active hair follicles to decline, while those that are active spend less time in the growing phase and produce hair that is thinner. One of the paradoxes of dihydrotestosterone is that it reduces the growth of hair on the scalp but promotes growth of hair on the chin, chest, and groin. Men with naturally low levels of *5- $\alpha$ -reductase* do not become bald as they age, and they have much less body hair than normal. Baldness is the legacy inherited from a man's parents and there used to be nothing that he could do about it, that is until the 1980s when something strange began to be reported: the hair of some bald men suddenly started to grow again.

Throughout history there have been those who have sought to exploit men who were losing their hair by selling them expensive cures, none of which worked. Hippocrates in 400 BC recommended applying a poultice of pigeon droppings, horseradish, and nettles. Today many men benefit from two accidental discoveries, or rather from the side effects of two pharmaceutical products that they were prescribed by doctors for very different ailments. Men who were given them reported that the hair on their bald heads was reappearing. These products are now widely available and they are marketed under the names of Regaine (Rogaine in the US) and Propecia.

Propecia is the hair restorer that depends for its effectiveness on the chemical finasteride, which was designed to treat swelling of the prostate, the gland that produces the fluid part of semen. Prostate enlargement results from an excess of dihydrotestosterone, and is a condition that manifests itself in many men over 65. Finasteride was devised by chemists of the drug company Merck Sharp & Dohme and the process for making it was published in 1986 in a paper in the *Journal of Medicinal Chemistry*. This also reported on the way the molecule attached itself to *5- $\alpha$ -reductase* and by blocking this enzyme the level of dihydrotestosterone is reduced. The link between this hormone and an enlarged prostate had been noted more than a century ago, in that castrated males never suffered from an enlarged prostate. As the prostate grows larger it squeezes the urethra, the tube down which urine exits from the bladder and this causes difficulty in urinating and the need to pass water frequently. The prostate may also develop cancer and while this is not a particularly life-threatening cancer it only makes matters worse.

The finasteride molecule has the same shape as testosterone – it has a nitrogen atom in place of a carbon atom – and it can fit into the enzyme’s active site. The upshot is that the enzyme encircles the molecule thinking it has hold of testosterone but finds it cannot carry out the modification which it is supposed to perform. The enzyme clings on to the finasteride in the belief that it has the right molecule and the result is stalemate. Finasteride works mainly on the *5- $\alpha$ -reductase* in the genital region, but it also moderates this hormone in the scalp as well, so that hair begins to grow again. This unexpected side effect eventually led to finasteride being available under two brand names: Proscar, which is prescribed for the treatment of enlarged prostate, and Propecia, which is prescribed to treat baldness. Within a few years Proscar was generating revenues of \$500 million a year in the USA alone, and Propecia was eventually to equal this. Proscar tablets are blue and apple-shaped, and the dose is 5 mg. Propecia tablets are tan coloured and octagonal in shape, and the dose is 1 mg. Those taking finasteride are warned that it must be taken for three months for it to have any effect.

Is Propecia an effective hair-restorer? The answer would appear to be yes, based on comparisons with a placebo, of which only 7% of men taking it said they noticed signs of regrowth, whereas 66% of men who were taking the real thing said there were visible signs of new hair. Interfering with a male hormone might have been expected to have another side effect, namely lowered sex drive. However, only 2% of men taking Propecia reported that this was so. Nevertheless, sexually active men who take Propecia should not risk impregnating their partner because if the fertilized egg is to be male then it may develop into a baby boy with some female characteristics. Finasteride must, of course, only be used by men, which is not the case for the other drug that acts to restore hair, and that is Regaine (Rogaine). This can be used by both men and women.

Regaine is the brand name for minoxidil, a drug produced by the UpJohn Corporation of America, and one that was designed to reduce high blood pressure, which it does very well. As with finasteride, what its users hadn’t expected to experience was a regrowth of the hair on their heads. Minoxidil was patented in 1967 although clinical trials for treating baldness with it were not undertaken until the 1980s. The drug is a vasodilator, in other words it relaxes constricted blood vessels thereby allowing blood to flow more easily round the body. Doses

of between 5 and 50 mg per day can be prescribed, patients generally starting on the lowest dose which is gradually increased.

Minoxidil as a prescription drug is known as Loniten and is taken as a tablet twice a day. It is used when other drugs have failed to control a patient's high blood pressure or when this is rising rapidly. Minoxidil starts to work almost immediately and within an hour the blood pressure will fall markedly. One side effect is fluid retention, most noticeable as a swelling of the ankles, so that a diuretic is prescribed at the same time to enable the body to increase its output of urine. The other side effect, if minoxidil is taken for several weeks, is hair growth around the face, which may explain why some women are reluctant to take the drug even for high blood pressure.

When minoxidil gets into the blood stream it passes a message to the lining of the blood vessels telling them to relax. It does this in several steps, ultimately leading to an opening of the channels that allow potassium ions to move through cell membranes and triggering the desired response. This is no doubt part of the way it works in hair follicles and, by increasing the blood supply there, it revitalises the formation of keratin. Why hair begins to re-grow on the heads of those taking minoxidil is still not truly understood, but it happens, and UpJohn sells the drug as a lotion containing 2% (for women) or 5% (for men).<sup>6)</sup> It is applied directly to the scalp and needs to be used every day. It was the first drug the FDA approved for the treatment of hair loss and that was in the 1980s. Today there are several generic forms on sale, such as Alopexil, Lonolox, Prexidil, etc., and they are available as over-the-counter treatments, but Regaine is the market leader.

Regaine is reputed not only to stop hair loss, which it does for 80% of men using it, but appears even to stimulate re-growth in some cases. Applied twice daily it should begin to produce visible results within three months, although it could take twice as long, and may never work for some. The most noticeable side effect is itchiness, but this will subside after a week or so. In 1985 Regaine was tested at the Glasgow Royal Infirmary hospital in Scotland on 66 volunteers aged between 18 and 50. Half were given Regaine and half were given a placebo to rub on their balding scalps. At first the effects were disap-

6) Minoxidil is a white crystalline solid which melts at 248 °C, and while it is insoluble in water, it is perfectly soluble in

propene glycol, and this is what the lotion contains.

pointing for those using Regaine until it was applied twice daily, and this is now the recommended treatment.

Somewhat perversely, it appears to those who start using Regaine that *more* of their hair is being lost. This is actually a sign that it is working and what they are seeing is hair follicles that have become dormant being activated again and the old hair displaced. Nor should they worry that the new hair is soft and downy; it becomes thicker and stronger as the treatment is continued. However, stop using Regaine and its effects will cease and its benefits will have disappeared within a few weeks. Neither it, nor Propecia, is a permanent cure for baldness but at least they offer men who become prematurely bald some hope of keeping a more youthful appearance.

### **I Can See Clearly Now ...**

“Boys don’t make passes at girls who wear glasses” went the old adage, so what did a young girl do who needed to wear spectacles? She left them at home when she went out looking for a boyfriend. Of course there was always a risk that if she found a boy she really liked, he might reject her when he eventually saw that she needed to wear glasses. Those were the days when young men could pick and choose because they were in short supply, millions having died in two world wars. Today, many men are surplus to requirements and women can be choosy, so men are the ones who don’t want to be seen wearing glasses. In fact there is no need for either sex to wear them; they can wear contact lenses instead.

Contact lenses come in a wide variety: there are soft lenses and hard lenses; there are some you can wear night and day for a month or more, and disposable ones that you need wear only for a day; there are lenses that let your eyes breathe; there are bifocal lenses; and there are even lenses to correct astigmatism, a condition of the lens of the eye which makes everything seem blurred. All are products of years of research by chemical companies like Novartis, Ciba Vision, and Wesley Jessen. There are even coloured lenses that can make blue eyes bluer, and sport lenses that enable tennis players to keep their eye on the ball by enhancing the colour of a yellow tennis ball relative to its surroundings.

The *idea* of contact lenses is not new. Leonardo da Vinci suggested them as long ago as 1508, although he never got around to making any. That did not happen until 1888, when a Dr F.A. Muller of Wiesbaden, Germany, made one from glass and it was worn by a patient of his who had no eyelids. The lens preserved the sight in one eye and he is said to have used it for 20 years. That same year a Dr Adolph Frick at the Ophthalmic Clinic in Zurich fitted six patients with glass contact lenses 1.4 cm in diameter (1/2 inch) and designed to cover the whole eye. They were not successful because he could not make them a perfect fit, though he made plaster casts of the eyes of cadavers, and even of his own eyes, to use as a template. His contact lenses were just too painful to wear.

Despite the efforts of other doctors to make better impressions of eyeballs, there was no major advance in contact lens technology for another 50 years until they could be made of the →polymer PMMA, short for poly(methyl methacrylate), which had been discovered at the laboratories of Rohm & Haas in Germany in the 1920s. They called the new polymer Plexiglas but it remained a curiosity because the chemical from which it was made was too expensive. That changed when chemist John Crawford, working for ICI in England, found a way to make methyl methacrylate cheaply from acetone, and the company named its PMMA Perspex. (In the USA it was called Lucite.) PMMA soon became a most profitable polymer, and it was ideal for all sorts of things such as illuminated signs, hospital incubators, car headlights, and aircraft windows.<sup>7)</sup> It was ideal for contact lenses.

What features should a contact lens have? Clearly it should be as transparent as glass, fit perfectly to the shape of the cornea, and be comfortable to wear. It should not harbour microbes that might cause eye infections, and it should be wearable for days without needing to be changed. It must not block off oxygen because the cornea of the eyeball needs a supply of this vital element. If it is to be disposable, it must be inexpensive. Producing a plastic with all these benefits has almost been achieved, thanks to polymer chemists. PMMA was the first major step forward. It has a refractive index like that of glass, in other words it makes a good lens because it can collect and focus light rays.

7) The Spitfire fighter planes of World War II had Perspex windows. When pilots were injured by splinters from them, surgeons

noted that fragments could remain embedded within the body because this plastic is tolerated by living tissue.

It can be shaped by moulding and, equally important, bacteria find it hard to colonise.

An American, Newton Wesley, set out to make contact lenses from PMMA in 1944, and these were for his own use. He suffered badly from a swelling of the eye, but he was in the right location to do something about it because he was a faculty member of the Monroe College of Optometry at Chicago, Illinois. There he teamed up with a bright student George Jessen, and together they worked in the basement of the boarding house where Wesley lived, using a sewing machine as a lathe to shape pieces of Lucite. His PPMA contact lenses were made to cover the whole eye and they were a success. In 1949, he and Jessen began to teach other lens technicians how to make them, and optometrists how to fit and adjust them. By 1955 their company, Wesley-Jessen, was a success and they were spending \$500,000 a year on advertising. They also engaged in long-term research, regularly checking 350 of their customers who wore their lens. Meanwhile a Kevin Tuohy was working on an even simpler idea: that the contact lens need only cover the cornea of the eye and he patented such a one in June 1960. His lenses were a better fit, were more comfortable to wear and, what was most unexpected, they stayed in place and did not move around the eye ball as one might have expected.

Contact lenses made from PPMA are now history. The reason is that they deprive the cornea of oxygen, which it must get directly from the air because the cornea has no blood vessels, and the lack of oxygen can eventually cause damage. What replaced PPMA was another transparent plastic that was gas permeable and which had been discovered in Prague, Czechoslovakia, in the early 1950s. Polymer chemists Otto Wichterle and Drahoslav Lim had modified PPMA by attaching water-attracting groups to the polymer chain. The new material was called HEMA (short for hydroxyethyl methyl methacrylate) and they had originally intended using the polymer to make artificial blood vessels, but when Wichterle dislodged some which had congealed at the bottom of a test-tube he noticed how like a contact lens it was. He had inadvertently made the first soft lens. HEMA is known as a hydrogel, which means that it is a substance that attracts water and holds it in a framework of polymer molecules.

Although its softness was a real benefit, HEMA still did not allow significantly more oxygen to penetrate through to the cornea. Nevertheless the lenses, marketed by Bausch and Lomb under the brand

name Soflens, were put on the market in 1971 and were an instant hit. The drawback was that they could harbour germs and so they needed to be cleaned every evening, ideally with  $\rightarrow$ hydrogen peroxide, and treated once a week with an enzyme solution of either papain (extracted from pineapple) or pancreatin (from pork) to remove the fat and protein residues which collect from the tears that lubricate and protect the eyes. These residues deposit on the surface of a lens thereby allowing microbes to grow.

Polymer chemists also reformulated HEMA by adding measured amounts of other polymer precursors and then polymerising the mixture to form what is known as a copolymer. Varying ratios of copolymers were tried until a hydrogel was obtained which had all the right features, and in particular a negatively charged surface, so that the contact lens would cling to the film of tears on the surface of the eye. Contact lens wearers now have a choice of improved hydrogel types, and while these are better than the older forms they still rely on water to transport oxygen to the eye. Some have as much as 75% water content and this needs to be high if the lenses are to be worn for extended periods.

The problem of making soft lenses 'breathable' was eventually solved by attaching silicone groups to PPMA polymer. Silicones dissolve oxygen very easily, but add too many silicones and the polymer becomes water-repellent, something we might expect because silicones are often used to make water-proofing materials. These new lenses were patented in 1974 and marketed in 1979. They were referred to as rigid, gas-permeable lenses. The softness and comfort of the older HEMA lenses had been sacrificed in order to prevent long-term damage to the eyes and they had to be custom made for each individual if they were not to be uncomfortable to wear. Softer hydrogel contact lenses, which also incorporated silicone, became available in 1998 and were immediately popular with sales exceeding \$150 million within five years. The trouble was that they sometimes glued themselves to the eyeball because they tended to suck out lipid molecules from the cornea and these acted as an adhesive.

How did the chemists of companies like Johnson & Johnson and Novartis achieve the seemingly impossible task of combining polymers that appear to be irreconcilable? HEMA attracts water but does not take up oxygen very well while silicones repel water but absorb any amount of oxygen gas. At first the combination of silicone and hydro-

gel gave only an opaque material although that was solved by incorporating nanosized components that are smaller than the wavelengths of light so that they appeared transparent. Today there are various silicone-hydrogel materials on the market with water contents ranging from 25–45% and all having excellent oxygen absorption and transmission.<sup>8)</sup> Some contact lenses incorporate a fluoroether, another chemical which is particularly good at absorbing oxygen.

Silicone-hydrogel contact lenses can even be worn when asleep, but there are some drawbacks to them, the main one being that they are stiffer, although one type, Acuvue Advance, is only marginally stiffer and stiffness need not necessarily be a problem because increased rigidity makes handling the lenses easier. Another manufacturer, Johnson & Johnson, has minimised stiffness by reducing the amount of silicone and putting a layer of PVP, short for poly(vinyl pyrrolidone), as a ‘wetting’ agent on to the surface. This PVP layer has been added to overcome one of the major drawbacks of soft lenses which is that they can dry up the eye, as many as half their users reporting this discomfort, which is sufficiently irritating to cause many of them to discontinue wearing them. Another way to counteract dryness is to expose the lenses to a gas plasma which creates a permanent ultrathin layer of silicate on their surface, this being formed from the silicone. The resulting silicate does not attract lipids and has increased wettability.

Acuvue Advance also blocks out ultraviolet rays (UV), filtering out more than 90% of UVA, and 99% of the UVB rays that are more dangerous to the eye. (These lenses are no substitute for protective goggles which some workers wear to screen their eyes from UV light.) Some disposable contact lenses, such as Acuvue-1-day, are meant to be changed every day, while some, such as Focus1–2 week, produced by Ciba Vision, last longer. The daily ritual of cleaning contact lenses puts many off from wearing them but there are some that can safely be left in the eye for a week, and there are some experimental ones that have been left as long as three months. Ted Reid of Texas Tech University Health Science Centre in Lubbock, Texas, has found that this becomes possible if the lenses are coated with a selenium compound, and the coating need only be one molecule thick. The coating binds itself

8) Nathan Ravi of Washington School of Medicine in St Louis, Missouri, has developed a hydrogel that can be injected

into the eye, there to form a new lens to replace a diseased or ageing one. The research is as yet only in its early stages.

chemically to the lens and tests have shown that it can remain in place for as long as two years. These lenses have yet to be approved by the FDA for sale to the public.

## A Gleaming Smile

You may be looking good, thanks to your hair, and seeing better, thanks to contact lenses, but when you smile at the boy or girl of your dreams, are you spoiling your chances by having discoloured teeth? If you suspect that this may be so, then chemistry can help.

Unightly teeth or not, you should think yourself lucky that you are part of this generation. Much earlier generations had a hard time with their teeth as we can see from their remains. A few people in antiquity had the benefit of dental care because we know from mummies that there were dentists in ancient Egypt 4000 years ago. Although they did little more than pull rotten teeth, they sometimes plugged the hole left behind with gold to which they attached a false tooth made of ivory. Their skills were passed on to later civilizations such as the Etruscans and Romans, who developed more sophisticated techniques. Etruscan dentists of the sixth century BC were the first to construct gold bridge-work to which they attached artificial teeth made of bone or ivory to fill the gaps left by extracted teeth. Not only did these look good but they clearly were strong enough to eat with. Dentistry in the West declined in the Dark Ages (500–1000 AD) and did not really emerge again until tooth decay and toothache became a major problem from the 1600s onwards, due mainly to cheap sugar imported from the plantations of the New World. Sugar can be converted to acid by bacteria that breed in plaque, the film of protein that collects on our teeth, and the acid corrodes the tooth enamel forming cavities in which yet more bacteria can thrive.

Dentists did little more than pull out rotten and painful teeth, of which there were many, but they eventually started to make false ones to fill the gaps. Some even used *human* teeth for this purpose and in 1781 a practitioner of Gerard Street, London, was offering to buy real teeth for £2 each, equivalent to something like £400 (approximately €600 or \$700) in today's money, provided they were in good condition. (Such teeth were extracted from newly buried corpses by 'resurrectionists' who dug up bodies to sell to surgeons for their anatomy lec-

tures.) Other dentists fitted imitation teeth made of porcelain but these, first produced in 1774, were brittle and made an irritating squeaking noise when chewing. Across the Atlantic, George Washington had a set of dentures consisting of hippopotamus ivory into which were mounted teeth made from those of horses and donkeys.

The biggest supply of human teeth came as a result of scavengers plundering the bodies of the dead after major battles. The Battle of Waterloo, fought on 18 June 1815, was a particularly fertile hunting ground with around 50,000 casualties to pick from, and dead young men were more likely to have teeth in good condition. Thousands of teeth were extracted and used by dentists in the subsequent years. The dentures made from them were known as Waterloo teeth, and people were proud to be seen wearing them; some were even exported to the US. Later supplies came from the battlefields of the Crimean War of the 1850s, and the American Civil War of the 1860s, although by then it was more common to have dentures made of a stronger type of porcelain which had been invented in London in 1837.

Throughout history, people have tried to preserve their teeth by cleaning them. Back in the 4<sup>th</sup> century BC, Hippocrates suggested doing this with powdered marble, which is calcium carbonate, and indeed this chemical (as chalk) is still used as a mild abrasive in toothpaste. Toothbrushes were invented in China in 1498 and were known in Europe by the 1600s when they were on sale in Paris, as we learn from a letter sent to Sir Ralph Verney in 1649 asking him to buy one while he was visiting that city. They were used in conjunction with tooth powders. More convenient were the early toothpastes, which consisted of powdered chalk, soap, and sugar syrup. Toothpaste was first sold in ceramic pots and then it began to be sold in collapsible tubes that an American artist, John Rand, had invented in 1841 as a way of packaging oil paints.

Modern toothpastes have several components: the scouring agent is likely to be powdered calcium phosphate – or silica if the paste is a transparent gel – and the foaming agent will be sodium lauryl sulfate.<sup>9)</sup> This mild surfactant is added to help disperse the toothpaste in the mouth during the brushing action, thereby solubilising the plaque, and preventing any dislodged debris from re-depositing on the teeth. Toothpaste can have a curious side effect in some people, in that it

9) More about this in Chapter 3.

stimulates the bitter taste receptors on the tongue so that drinks like orange juice become very bitter when drunk immediately after cleaning your teeth. Another major ingredient is the humectant which keeps the toothpaste moist by retaining water and this accounts for about a third of the contents. The ones most commonly used for this purpose are glycerol or PEG (short for polyethylene glycol). The minor ingredients in a typical toothpaste are:

- an artificial sweetener such as saccharin, or the natural sweetener sorbitol;
- a thickening agent such as carboxymethyl cellulose, or sodium alginate, which is a carbohydrate extracted from seaweed;
- sodium benzoate, which prevents bacteria from breeding;
- fluoride, which strengthens the teeth against decay;
- flavouring, such as peppermint, or oil of wintergreen.

The aim of regular brushing is to keep teeth germ-free and looking good. Discolouration, however, comes slowly and cannot be removed by brushing alone.

Teeth have a transparent outer layer of enamel which is about 2 mm thick, and an inner layer of white dentine which surrounds the innermost pulp cavity where the nerves are located. Both the enamel and the dentine are calcium phosphate, a mineral that can exist in various forms, that of the enamel layer being hydroxyapatite, which is one of the hardest naturally occurring minerals. When this is exposed to fluoride it forms an even harder mineral: fluoroapatite. Unfortunately both this and hydroxyapatite are slightly porous and this is why teeth become stained by chemicals such as polyphenols and other dark coloured substances that are present in coffee, tea, red wine, bilberries, blueberries, and cigarette smoke. (Staining can also be caused by tetracycline antibiotics, especially when taken by children whose teeth are developing. This type of discoloration is permanent, which is why such antibiotics are now only prescribed for adults.)

The answer to discolouration is to bleach the stains using tooth whiteners. An earlier method of doing this was to use nitric acid which is an oxidising agent and capable of removing stains, but it also removed a layer of the enamel as well. Tooth whiteners now rely on  $\rightarrow$ hydrogen peroxide as the bleaching agent and sales are in excess of \$1.5 billion a year in the US alone, and the rest of world is catching up on

the fashion for sparkling white teeth, as popularised by young television and movie stars. A dentist can bleach teeth very quickly by using a paste containing 35% hydrogen peroxide, sometimes in combination with a laser beam – supposedly to speed up the process, although the need for this is questionable – and stains will be gone within the hour. The paste is applied and rinsed off several times during the treatment, and it has to be carried out by a dentist because hydrogen peroxide of this strength can damage the lining of the mouth if not carefully applied. Dentists can also provide a treatment to be used at home. They make a mould of the teeth into which a strip of peroxide gel can be inserted and then pressed against the teeth. This ‘nightguard’ can even be worn while sleeping, thereby speeding up the whitening process.

For those who prefer a less expensive way of bleaching their teeth, there are products which contain a chemical that reacts with water to release hydrogen peroxide. This chemical is carbamide peroxide, also known as →urea peroxide,<sup>10</sup> and this is the ingredient in several over-the-counter whitening agents. Carbamide peroxide is made from urea and hydrogen peroxide. The former chemical is perfectly safe because it is a normal end-product of our body’s metabolism and is one of the ways we dispose of unwanted nitrogenous material via our urine. In earlier times it was even prescribed by doctors because of its diuretic action, in other words it encouraged the body to remove excess water by stimulating the kidneys. When carbamide peroxide is in contact with water it releases its hydrogen peroxide which then gets to work, although a lot of this is lost to enzyme breakdown before it can do its job. This is why over-the-counter tooth whitening products need to be applied many times to achieve maximum effect. The most convenient way of whitening teeth is to stick a polyethylene strip bearing a peroxide gel to the teeth and leave it there for 30 minutes. If this procedure is repeated every day then after a couple of weeks the teeth will be noticeably whiter.

Those who engage in tooth whitening should be aware that it has a weakening effect on the enamel. This was reported at a meeting of the US Materials Research Society in Boston in November 2005 by Michelle Dickinson who works for Hysitron, an instrument maker based in Minneapolis. This company has developed a piece of equipment capable of measuring the hardness profile of teeth across the enamel and dentine

10) It also has trade names such as Exterol, Hyperol, Perhydrit, etc.

See also **urea** in Glossary.

boundary. Dickinson examined the effect on extracted human teeth of the carbamide peroxide solution of over-the-counter whiteners, and of the much stronger paste used by dentists. She subjected teeth to seven one-hour treatments of each kind of whitener and found that the former decreased tooth hardness by 22% and the latter by a worrying 82%. The result would be an increased sensitivity of the teeth to hot and cold. These findings have yet to be confirmed, but they are a warning that tooth whitening should not be undertaken too often.

There are ways of obtaining an instant gleaming smile, such as having your teeth covered with resin or porcelain veneers. The cost of these can be prohibitive, with the porcelain ones being twice as expensive as the plastic ones. Over time, these too can become stained.

So what might we expect in the future? Ideally we should try and make tooth enamel impervious to stains. One product that might soon become available is a chewing gum which contains both calcium and phosphate to help teeth to repair cavities by boosting the natural level of these components in our saliva, part of whose job is to repair teeth – see box. However, the best agent for strengthening teeth is still fluoride.

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### The Chemistry of Saliva

The average mouth excretes half a litre (500 ml) of saliva a day. This does not just lubricate the mouth and aid digestion, it contains substances that benefit the teeth, among which are calcium ions (120 mg per litre of saliva) and phosphate (14,000 mg per litre of saliva). The pH of saliva is effectively neutral, being 6.8, and this is ideal for the tooth enamel to reabsorb calcium and phosphate to repair itself. If the pH falls below 5.5, then the reverse happens and there is some loss of these components from the teeth.

What saliva also supports are the millions of bacteria living in our mouth, of which more than 300 different types have been identified. While this sounds alarming, it is not too worrying because most of them are harmless and some even appear to protect the mouth. Anthony van

Leeuwenhoek first demonstrated the presence of bacteria on teeth as long ago as 1683, using the microscope that he had invented, and he described what he had found as follows:

*“...in the said matter [plaque] there were many very little living animalcules. There are more animals living in the scum on the teeth in a man’s mouth than there are men in the whole kingdom – especially in those who never clean their teeth, whereby such a stench comes from the mouth of many of them that you can scarce bear to talk to them...”*

That was more than 300 years ago and yet oral hygiene is still a problem. The answer is to clean the teeth and gums by brushing and rinsing, and to stimulate saliva by chewing gum.

It has been known for more than 200 years that teeth naturally contain some fluoride, and we now know that this element strengthens tooth enamel by forming fluoroapatite, which resists the effect of the acids formed by oral bacteria. The fluoride also inhibits bacteria from multiplying. For this reason fluoride is added to toothpastes and public water supplies. The average diet provides up to 3 mg of fluoride a day, depending on how much fluoride-containing food a person eats, such as chicken, sardines, mackerel, salmon, eggs, and potatoes, and on how much tea they drink, with a cup of this beverage providing 0.4 mg. Using sea salt to flavour their food will add more fluoride because the sea contains 1 mg per litre. Procter & Gamble introduced the first fluoride toothpaste, Crest, in 1955 and it contained tin fluoride ( $\text{SnF}_2$ ) as the protective agent, this having been discovered to be the form which worked best, thanks to research by Joseph Muhler at the University of Indiana in the 1940s. This fluoride was eventually replaced by sodium monofluorophosphate ( $\text{Na}_2\text{PO}_3\text{F}$ ) which works even better.

Another protective element is strontium. The regular version of Sensodyne toothpaste contains 10% strontium chloride, which has the advantage of helping to build up the enamel, especially round the gum line. As gums begin to shrink with age they can expose the dentine layer making a tooth very sensitive to the brushing action of the toothbrush, as well as to heat, cold, and acids. There are lots of tiny tubes (tubules) in the dentine and these contain fluid which reacts to changes in temperature or pressure and transmits a signal to the tooth nerve which then registers intense pain. Strontium helps to block them.

Soon there may be another ingredient in toothpaste: hydroxyapatite nanoparticles<sup>11)</sup>. Not only is this the same chemical as the tooth enamel but the particles are small enough to get into the pores and seal them, and it is pleasingly white. Ralf Nörenberg of the chemical giant BASF reported the new form of calcium phosphate in 2003. More recently another group of researchers, led by Kazue Yamagishi, and based at the FAP Dental Institute in Tokyo, have developed a synthetic enamel based on the same nanoparticles. They observed that when this was applied to a tooth, along with hydrogen peroxide, then new crystals grew inside the tooth's tubules and within 15 minutes these

11) A million nanoparticles measure around 1 millimetre.

crystals had bonded to the natural tooth enamel. It is more than likely that one day there will be toothpaste based on hydroxyapatite nanoparticles.

## **Nailed**

When people meet for the first time they surreptitiously examine each other: clothes, face, hair, and teeth come under scrutiny and we have already discussed how to improve some of these. They may also glance at each other's hands and then they may judge a person by the condition of their fingernails. Clean, well-cut nails suggest self-confidence and careful attention to detail. Other conditions of the nails may send out less-flattering messages. A man with long fingernails may be thought slightly odd and probably without a partner, while someone with bitten fingernails may be seen as nervous and stressed, and dirty fingernails will speak of slovenliness and lack of personal hygienic. Men take little interest in their fingernails apart from cutting them regularly and keeping them clean. Women on the other hand have turned fingernails into a minor art form.

Many women simply want carefully shaped, well-manicured nails, and many of those who paint their nails use unobtrusive shades. On the other hand there are those who enjoy showing off their nails with brightly coloured varnishes, and may even enhance them with artificial extensions on which are painted intricate designs. Media celebrities and the wives of high profile sportsmen seem particularly attracted to wearing them as glamour accessories. All over the UK and the USA there are nail salons and nail booths, manned by manicurists who now prefer to be called nail technicians. Even the ancient market town where I live has two nail salons. Its clients may not appreciate the role of the chemist in meeting their needs, but a lot of research has gone into nail varnish and nail extensions.

Nail varnish should offer a wide range of colours and textures, adhere fast to the nail, and not chip. It should also be water-resistant, but easy to remove with a non-hazardous solvent that does not damage the nail, the skin, or the environment. All these conditions have been met with a blend of colours, polymers, plasticizers, and solvents. Nail varnish contains a pigment or dye, plus nitrocellulose to provide a gloss, and butyl stearate plasticizer to keep the varnish flexible when it has

dried and to ensure that it doesn't chip. Toluene sulfonamide formaldehyde (TSF) may be added to increase the strength of the final film because this is strong and durable. There are some nail varnishes that do not include nitrocellulose – manufacturers would like to remove this because it is highly flammable and explosive in bulk – and they use methacrylate polymers instead. The various ingredients of a nail varnish are suspended in a mixture of solvents such as acetone, toluene, isopropanol, and pentyl acetate, designed to give a varnish that runs easily when applied, but dries quickly. Isopropanol is used specifically to hold particles such as glitter in suspension. Before applying varnish to a nail it might be necessary to remove a cuticle and there are solutions for doing this, and these consist of potassium hydroxide (KOH) in a solvent mixture consisting of 12% glycerol and 88% water. Eventually the wearer will want to remove old nail varnish and then it is necessary to wipe it off with a solvent like acetone or ethyl acetate, and this will contain small amounts of things like glycerol and lanolin, which are there to rehydrate and replenish the natural oil of the nail and the surrounding skin.

Polymers for artificial nails first appeared in the 1970s. Before then there were porcelain ones but these were brittle. The new polymer nails were much better and they could be trimmed with scissors and smoothly shaped with a nail file. Nail extensions are the more technical side of nail culture and they have been made from various plastics but are usually either polyacrylate or the copolymer ABS, short for poly(acrylonitrile-butadiene-styrene), which has the stiffness and flexibility very similar to those of natural fingernails.

Ideally an artificial nail should cover about half the real nail whose surface has to be roughened slightly before an adhesive is applied and the artificial nail stuck on. How far the extension protrudes beyond the end of the finger is up to the client but this will increase as the natural nail grows, which is why trim-ability and file-ability are essential. Artificial nail tips can be glued to the existing nail with an adhesive like rosin, which is the sticky residue left when tree oils have been distilled to remove their volatile oils. Alternatively, the artificial nail may be bonded to the real nail with methyl cyanoacrylate (popularly called superglue). This is a chemical that remains stable until it absorbs a little water from the air, whereupon it immediately starts to polymerise to form a tough resin that will stick two surfaces together permanently. The glue can work within 10 seconds. Equally good are ethyl cyano-

acrylate and butyl cyanoacrylate. The vapour from superglue is unpleasant to breathe and if there is more than 2 ppm in the air it is intensely irritating, which is why the less volatile ethyl form is sometimes used. However, though ethyl cyanoacrylate is a more preferable adhesive, it can cause an adverse reaction in some people with the result that the natural nail withers and the ends of the fingers develop eczema. Three such cases came to light in the Department of Medical Sciences at the University of Arkansas in 1998. The US National Institute for Occupational Safety and Health (NIOSH) has issued guidelines for nail technicians, the main suggestion being that they should sit at specially ventilated tables that extract any vapours given off by the chemicals being used.

Having secured the nail extension, and smoothed over the joint it makes with the real nail, the next job is to cover the whole with a film that inconspicuously unites the two parts. This is done by applying a paste made from powdered methacrylate polymer which is smoothed on to the nail where it will harden by absorbing oxygen from the air. Sometimes a little benzoyl peroxide can be added to speed up the process, sometimes it is hardened by exposure to UV light, and there are even some films that harden under ordinary light. Several layers of gel are applied until the desired smoothness from the base of the nail to the tip has been achieved. Finally the nail can be painted and decorated, sometimes to stunning effect with tiny diamonds.

Of course nothing can stop such nails from moving up the finger and eventually they have to be removed. The solvent for doing this is acetonitrile<sup>12)</sup> which must be used carefully because it can be absorbed through the skin, which is why it is only available at nail salons.

Of course there are dangers in having synthetic nails. One worry that preoccupied American chemists a few years ago, and led to papers in the *Journal of Chemical Education*, was the possibility that they might be dangerously flammable. If young chemists had to use a naked flame, such as that of a Bunsen burner whose temperature is around 500 °C, then serious burns might be caused if they wore plastic nail extensions. The paper reported that an artificial nail would ignite in less than a second. Even when they come into contact with the flame of a candle on a birthday cake, which has a much lower temperature, they can still ignite in just over a second. Once ignited, they

12) Chemical formula  $\text{CH}_3\text{CN}$ .

start to curl and drop molten balls of plastic. If the burning finger is shaken, which is the natural reaction to what is happening, it only makes things worse. The upshot was a reminder that students in chemistry labs should not wear such fingernail extensions. No doubt there are other situations involving a naked flame when these nails should not be worn, such as when cooking over a gas-fired stove or while using matches, and nail technicians can no doubt recount stories of clients who have suffered such accidents.

Bacteria pose a bigger threat than fire. Natural fingernails, or rather the dirt beneath them, account for 80% of the microbes on the hands. Some of the bacteria, yeasts, and fungi that live there can be dangerous. Artificial fingernails and nail extensions are even more dangerous, especially if they are worn by health care workers and nurses. Not only do they harbour more bacteria, they may also puncture latex gloves. For this reason it has been made illegal in the US for those in the caring professions to wear artificial nails, and this means nurses, doctors, and therapists. According to guidelines issued by the US Centers for Disease Control in 2000, these groups of workers should always have nails shorter than the tips of their fingers and should be well scrubbed.

Outbreaks of disease have been caused by those with artificial fingernails. In 2004 there was an outbreak of *Klebsiella pneumoniae* among premature babies in a US intensive care unit, caused by bacteria from a nurse's artificial nails. A few years previously it was *Pseudomonas aeruginosa* that threatened several newborn babies in a New York hospital and this was traced to the same cause. In Canada three patients who had had surgery on their spinal cord developed *Candida* infections of the spinal disks and this was traced to an operating theatre technician who had artificial nails. An intensive care unit in Oklahoma City saw 16 patients die as a result of contracting *Pseudomonas aeruginosa* from two nurses who had artificial nails. Thankfully such outbreaks are now extremely rare.

For many women, painted nails and artificial nails are harmless affectations that give pleasure and there is no need to worry about them. While their wearers may not acknowledge their debt to chemistry, they nevertheless are gentle reminders of the way chemistry can help us feel better about ourselves. Sadly many still see 'chemicals' as an ever-present danger and worry unnecessarily. The following item may serve to assure them that the risks to health are negligible.

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## Issue: Are Natural Ingredients for Cosmetics Better than Those Made by the Chemical Industry?

It sometimes says on the packaging of cosmetics that the contents are 'organic', 'pure', and 'natural', suggesting by these and similar terms that the products are better than those made from synthetic ingredients. Nothing could be further from the truth, if only for the simple reason that natural materials are not quality controlled and are often impure while those from the chemical industry are quality controlled and pure.

Some natural impurities can cause an allergic reaction and this is true of traces of enzymes, which are large molecules that living things produce in order to carry out essential chemical reactions inside living cells. A person's immune system may perceive unfamiliar enzymes as a threat and will attack them, the result being the uncomfortable symptoms of an itchy rash, hives, inflammation, runny nose, headache – or worse. It is possible to become allergic to a synthetic chemical, as we saw with the PPD used in hair dyes, but such allergies are exceedingly rare.

Another threat which comes with natural products is microbes. The ingredients in cosmetics, such as water, oils, carbohydrates, minerals, and proteins, make them an ideal medium in which bacteria can multiply, as some purchasers of purely natural beauty products have discovered to their cost, not least of which is the disagreeable odour they emit which indicates they are going off. Even such natural products must now contain anti-bacterial agents and these must be proven to work, which is why they are generally synthetic chemicals. The ones most used and most effective at

killing bacterial are the parabens. These are simple molecules that are modified versions of a naturally occurring fruit acid,<sup>13)</sup> yet rather perversely there are those who campaign against them on the grounds that they are 'chemicals', meaning they are products of the chemical industry, and that of course is where they are made.

In fact Nature is much more prolific than chemists at making chemicals, and among them are some that really do have healing benefits, not that Nature designed them with this in mind. Traditional cures may be based on a plant or marine extract and it then becomes a challenge for chemists in the pharmaceutical industries to make exactly the same molecule in the laboratory. If it is truly beneficial, and without harmful side effects, then a way may be found to manufacture the material on a larger scale. Even if tests show the natural chemical has harmful side effects, it may be possible to change the molecule in a way that keeps the active centre but eliminates the dangerous part or replaces it with something that is much safer.

Examine the list of contents of most cosmetics and you will see a bewildering array of chemical names, but you can be sure that these have all been manufactured to agreed standards of purity and have been tested to ensure they are safe to use. By all means buy the cosmetics that appear to be 'nature resourced' but don't imagine that this somehow confers an added benefit – it doesn't. And don't fool yourself into thinking that because it is 'free of chemicals' that you are somehow protecting yourself – you aren't.

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13) This is para-benzoic acid, more correctly called 4-hydroxybenzoic acid, found in strawberries and grapes.

