Chapter 4
Reducing Human Hair Including Permanent Waving and Straightening

Abstract The physical chemistry of the primary reactions involved in permanent waving and reductive and alkaline straightening and depilation of human hair are described in detail focusing on the disulfide bond its reduction/degradation, neutralization and subsequent reactions. The influence of mercaptan structure, excess reactant, pH and cysteine in different parts of the fiber on the chemical equilibrium in this reaction is explained. Factors affecting the kinetics of this reaction such as mercaptan structure, temperature, different hair types, hair swelling and hair condition, counterion effects, other reducing agents such as sulfite or bisulfite and side reactions of the reduction process are also described. The chemistry of alkaline straightening is contrasted to permanent waving including the importance of supercontraction to its permanence. Discussion of water setting, set and supercontraction and the swelling of hair (primarily transverse changes in the fiber) at different stages of these processes are also considered. The current understanding of chemical changes to the different morphological regions of hair, the cuticle, the cell membrane complex and the cortex of hair produced by these reactions is also described.

4.1 Introduction

Significant additions to our understanding of chemical changes to the cuticle, the cell membranes, and the cortex produced by permanent waves have been added to this Chapter. In addition, thermal reconditioning or Japanese hair straightening which has been used in beauty salons has been added. Furthermore, the section on hair straightening has been expanded to include more on the mechanism of several different straightening methods and papers dealing with damage to hair by straighteners.

The primary reactions involved in permanent waving, reductive and alkaline straightening products and depilation of human hair begin with reduction or cleavage of the disulfide bond. In permanent waving and reductive hair straightening, reduced hair is stressed, i.e., curled or combed straight, while molecular

reorganization occurs somehow involving the intermediate filaments through a disulfide-mercaptan interchange process. Neutralization is then achieved either through mild oxidation or treatment with alkali (for some sulfite treatments).

Since reduction of the disulfide bond and its subsequent reactions are vital to several important cosmetic products, a large amount of research has been conducted that is relevant to those processes. This chapter is concerned with reducing the disulfide bond in hair by mercaptans, sulfites, alkalies and other reducing agents. Reactions of reduced hair are also considered, followed by a discussion of water setting, set and supercontraction, and swelling of hair, followed by an expanded section on hair straighteners, depilatories and concluding with a section on safety of these products.

In spite of the fact that research on permanent waving has decreased over the past several decades, significant findings have been made in this field within the past three decades. For example, Wortmann and Kure [1, 2] have developed a model and extended it to show that the bending stiffness of reduced and oxidized fibers controls the permanent waving behavior of human hair and that the cuticle plays a role in permanent waving. Further, these authors have shown that the cuticle functions not only as a barrier to reduction but its stiffness also contributes to fiber set. In addition, Wortmann and Souren [3] have suggested that reorganization in the intermediate filaments is important to a permanent wave set. Our understanding of hair straightening has been expanded showing that supercontraction is essential to permanent hair straightening.
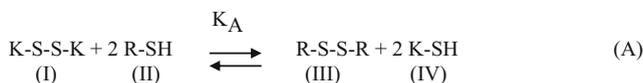
Work on fracturing reduced and oxidized-reduced keratin fibers at Textile Research Institute-Princeton provides some useful insights into damage by these reactions and a promising new test is offered to study damage to the cell membrane complex by reductive and oxidative systems. The permanent-waving process is considered in detail in this chapter including the model by Wortmann and Kure and a second useful model by Feughelman [4] followed by several cold wave compositions and procedures for making these same products in the laboratory. In addition several micrographs are included illustrating damage by reducing agents to the proteins of hair including the cell membrane complex and how these actions lead to the interesting phenomenon of scale lifting. The last section of this chapter as in previous editions describes literature relevant to the safety of reducing agents and permanent-wave products.
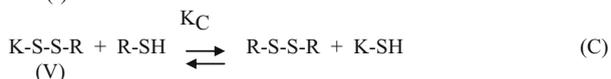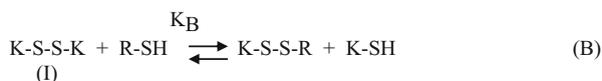
4.2 Reduction of the Disulfide Bond

4.2.1 Equilibrium Constants, Redox Potentials, and pH

Experiments relating to equilibrium reactions of disulfides with mercaptans commonly use reaction times of up to 24 h or longer. Although this may seem unrealistic to those in product development, extremely valuable information with practical implications has been gained from these studies.

The cleavage of the disulfide bond in keratin fibers (I) by mercaptans (II) is a reversible equilibrium reaction summarized by Equation A, where the K substituent represents hair keratin.

$$\text{K-S-S-K} + 2\ \text{R-SH} \xrightleftharpoons{K_A} \text{R-S-S-R} + 2\ \text{K-SH} \qquad (A)$$
$$\quad\ (I) \qquad\quad (II) \qquad\qquad\quad (III) \qquad\quad (IV)$$

This reaction actually proceeds through two steps, each a nucleophilic displacement reaction by mercaptide ion on the symmetrical disulfide of hair (I in Equations A and B), and then on the mixed disulfide of hair (V in Equation C).

$$\text{K-S-S-K} + \text{R-SH} \xrightleftharpoons{K_B} \text{K-S-S-R} + \text{K-SH} \qquad (B)$$
$$\quad\ (I)$$
$$\text{K-S-S-R} + \text{R-SH} \xrightleftharpoons{K_C} \text{R-S-S-R} + \text{K-SH} \qquad (C)$$
$$\quad\ (V)$$

In considering these disulfide scission reactions, the equilibrium constant of the reaction shown in Equation A tells to what extent the total process will go to completion.

$$\text{Equilibrium constant} = K_A = \frac{(\text{R-S-S-R})(\text{K-SH})^2}{(\text{K-S-S-K})(\text{R-SH})^2}$$

Among the ways to determine or approximate the equilibrium constant of this type of reaction are:

1. Analysis of ingredient concentrations at equilibrium, and
2. From redox potentials [5, 6].

In either case, one may use cystine as a model for hair, since the literature [5–7] shows that the redox potential of "cystine-type" disulfides is virtually independent of the charge group about the disulfide bond. However, reduction potentials of mercaptans do vary with pH [6]. Therefore, equilibrium constants for these reactions will also vary with pH. Patterson et al. [8] have shown that when wool fiber is reacted with 0.2 M thioglycolic acid solution for 20 h the extent of reduction increases with increasing pH above 6. Assuming equilibrium, this suggests that the difference in redox potential between thioglycolic acid and cysteine in keratin fibers increases with increasing pH above 6, and the equilibrium constant for this reaction increases similarly.
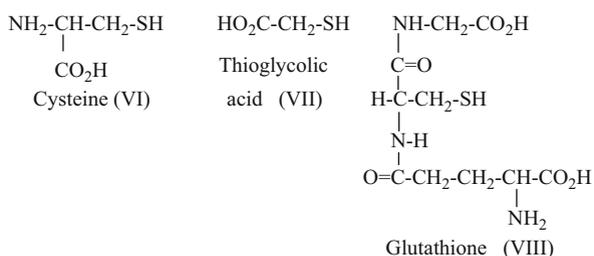
One may approximate the free energies and equilibrium constants of these reactions from these expressions:

$$\Delta F^\circ = -nfE^\circ \text{ and } \Delta F^\circ = -RT \ln K_{eq}$$

The number of electrons transferred during the reaction (2) is designated by n; f is Faraday's constant (23,061 calories per volt equivalent); E^o is the difference in standard redox potentials of the two mercaptans in volts; F^o is the standard free energy; R is the gas constant (1.987 calories per degree mole); and T the absolute temperature (°K). These calculations assume standard conditions; i.e., products and reactants are at unit activity.

4.2.2   Equilibrium Constants and Chemical Structure

Equilibrium constants at pH 7 or lower, for the reduction of cystine by simple mercaptans such as cysteine (VI), thioglycolic acid (VII), or even more complex mercaptans such as glutathione (VIII), are all approximately 1 [5, 6].

NH_2-CH-CH_2-SH HO_2C-CH_2-SH   NH-CH_2-CO_2H
| |
CO_2H Thioglycolic   C=O
Cysteine (VI)   acid   (VII)   H-C-CH_2-SH
                                                        |
                                                       N-H
                                                        |
                                      O=C-CH_2-CH_2-CH-CO_2H
                                                        |
                                                       NH_2
   Glutathione   (VIII)

Fruton and Clark [5] have shown that the redox potentials of other cysteine-type mercaptans are very similar at pH 7.15. However, Cleland [5] has shown that dithiothreitol (IX) and its isomer, dithioerythritol, have much lower redox potentials than cysteine at neutral pH.

S-H   H
| |
H-C-H   H-C————S
| |
CH-OH O_2 CH-OH
| ———————→ |
CH-OH   CH-OH
| |
H-C-H   H-C————S
| |
S-H   H
Dithiothreitol (IX)   (X)
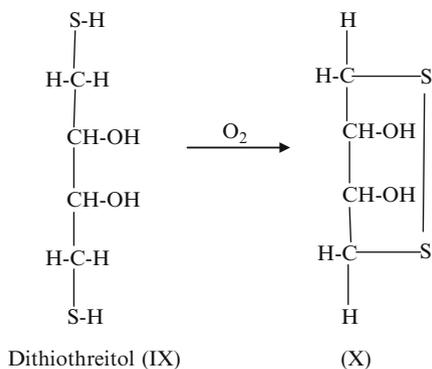
Weigmann and Rebenfeld [9] have reacted IX with wool fiber, showing that complete reduction of cystinyl residues can be approached at pH 6 to 6.5 using only a fourfold excess of IX to keratin disulfide. Cleland suggests that the equilibrium constant K_B in Equation B (of dithiothreitol and cystine) should be close to 1.

However, the cyclization of IX to a stable six membered ring disulfide (X), during the reaction described in Equation C, provides an equilibrium constant of the order of $10^4 = K_C$, and therefore $K_B \times K_C = K_A$ is of the order of 10^4.

Wickett and Barman [10–12] have expanded this area of research through a series of studies that involve reduction of hair fibers under stress using, dihydrolipoic acid (XI), and 1,3-dithiopropanol (XII) which are analogs of dithiothreitol. This study demonstrated that monothio analogs of dihydrolipoic acid reduce hair at a slower rate than the corresponding dithio compounds. This correlates with the higher equilibrium constant of reaction of dihydrolipoic acid vs. cysteine. The dithio compounds can cyclize to form stable five-membered ring disulfide structures during reduction (analogous to dithiothreitol), but the monothio compounds cannot. This confirms that cyclization to stable ring structures during the reduction step can be an important driving force in this reaction.

CH$_2$-SH   CH$_2$-SH
| |
CH$_2$ CH$_2$
| |
CH-SH   CH$_2$-SH
|
CH$_2$-CH$_2$-CH$_2$-CH$_2$-CO$_2$H
Dihydrolipoic acid (XI)   1,3 Dithiopropanol (XII)
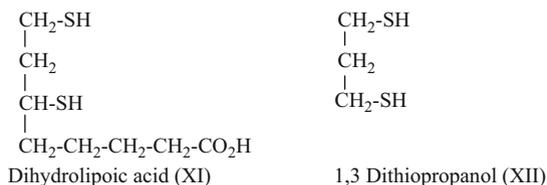
Wickett and Barman have further demonstrated that these five- and six-membered ring-forming reducing agents penetrate into hair via a moving boundary. This suggests nearly complete reduction as the thiol penetrates into the hair. Wickett and Barman have also demonstrated that thioglycolic acid below pH 9 does not exhibit moving boundary kinetics, but above pH 10 it does (see the section on kinetics in this Chapter). These scientists also studied structure-activity relationships of a variety of analogs of these three cyclizing dithiols illustrating the effects of hydroxyl groups and alkyl chain groupings on the rate of this reaction.

One purpose of these studies was to try to achieve essentially complete reduction of a smaller cross section of the fiber to determine if effective permanent-waving could still be achieved. A potential advantage to this type of process is to lessen cortical reduction and thereby to lessen cortical damage to the hair (the region primarily responsible for tensile properties) during the permanent-wave process.

Complete reduction in the annulus or outer regions of the hair does not occur with thioglycolic acid in current home permanent-wave products. To achieve a permanent wave, thioglycolic acid provides more diffuse reduction over a greater area of the fiber cross section [11]. This concept and its execution provide some interesting implications to the mechanism of permanent waving, suggesting that permanent set retention is not governed solely by the cortex and cannot be explained by considering only matrix reduction and consequent matrix-microfibril (matrix-intermediate filament) interactions. Moreover, strong cuticle interactions involving reduction and reshaping of the exocuticle and its A layer are probably relevant to permanent waving, and these cuticle changes should be considered in

any explanation of the permanent-wave process, as suggested and demonstrated by Wortmann and Kure [1, 2].

These ring-forming reducing agents have never been successfully introduced into the marketplace, primarily because they are sensitizing agents. Another possible concern must be greater cuticle damage by this type of action. It is conceivable that the effects of these extensive cuticle changes (essentially complete reduction of disulfide bonds in the exocuticle and A layer) on other hair properties and on long-term damaging effects from normal grooming operations could be prohibitive.

Further consideration of this two-step equilibrium process (Equations B and C) suggests the possibility for approaching complete fission of keratin cystinyl residues while producing only about 50% of the possible cysteinyl residues through formation of an extremely stable mixed disulfide (V). This type of reaction could be described as one with an extremely high K_B and a K_C of much less than 1. Haefele and Broge [13] have suggested that thioglycolamide (XIII) is such a mercaptan, on the basis of its ability to produce excellent waving characteristics in addition to excellent wet strength. No further supporting evidence has been offered to confirm this conclusion.

$$NH_2\text{-}CO\text{-}CH_2\text{-}SH$$

Thioglycolamide (XIII)

4.2.3   Equilibrium and Removal of One of the Reaction Products

O'Donnell [14] has shown that wool fiber, when reacted with thoglycolic acid at pH 5.6 approaches complete reduction of keratin disulfide by removing cysteinyl residues (IV) by means of alkylation followed by re-treatment with thioglycolic acid.

4.2.4   Equilibrium and Use of Excess Reactant

Leach and O'Donnell [15] have shown that the complete reduction of wool fiber with thioglycolic acid can be approached at pH 6.9 by employing extremely large concentrations of mercaptan (II) relative to keratin cystine (I). Similar results have been reported by Thompson and O'Donnell [16] for the reduction of wool fiber with mercaptoethanol.

4.2.5   *Cystinyl Residues of Different Reactivities in Keratin Fibers*

Since human hair is a complex substrate consisting of different morphological regions composed of different proteins (see Chap. 2), finding different reactivities for the same functional group is not surprising. Evidence for disulfide bonds of differing "reactivities" has been described by Middlebrook and Phillips [17] and by Carter et al. [18]. Different reactivities could be due to varying accessibilities or to differences in the electronic nature of certain disulfide bonds in the fibers resulting from differing adjacent amino acids [19]. This latter suggestion, based on work with pure disulfides and not with fibers, is contrary to the findings of Fruton and Clark [6] and to the opinion of this author. Differences are more likely to occur in reaction rate from differing accessibilities but not differences in the true equilibrium nature of the keratin disulfide reduction reaction from inductive effects.

The variation of equilibrium constant with structure, as a function of pH, has not been thoroughly explored. However, discussion of the behavior of keratin cystine in the presence of thioglycolic acid at different pH's is described in the first section of this Chapter.

Since this reduction process is a reversible equilibrium reaction, removal of one of the products of reaction (either III or IV), or use of higher concentrations of mercaptan (II) than disulfide (I), should drive the reaction to completion. Both of these principles have been confirmed.

4.3   Kinetics of the Reduction

All cleavages of simple disulfides by mercaptans that have been studied kinetically are bimolecular ionic reactions of the SN 2 type, involving direct displacement by mercaptide ion on disulfide as described by Foss [20] and most Organic Chemistry textbooks. Since the active species in this disulfide scission process is the mercaptide ion [21] rather than the unionized mercaptan, pH is a critical factor. As a consequence, pH can determine the rate-controlling step in the reductive cleavage of cystinyl residues in keratin fibers by mercaptans. For example, in the reaction of wool fiber with dithiothreitol, Weigmann [22] has shown that the rate-controlling step at pH 7.0 and above is diffusion of the reducing species into the fibers. However, at acidic pH (3.5), the chemical reaction itself appears to be rate-limiting. A similar change in mechanism with pH has been suggested by Kubu and Montgomery [23] for the reduction of wool fiber by cysteine and also for the reduction of human hair by several thiols, including thioglycolic acid [24].

Wickett [10] has shown that for the reaction of sodium thioglycolate with one lot of hair, at pH 9 or below, the rate of the reaction followed pseudo-first-order kinetics and therefore was reaction-controlled. However, at pH 10 and above,

moving boundary kinetics or diffusion of mercaptan into the hair controlled the reaction rate. Wickett further demonstrated under conditions closer to those of actual permanent waving (pH 9.5 and 0.6 M sodium thioglycolate) that for hair from one individual who exhibited high reactivity, the reaction rate followed pseudo first order kinetics. For hair from another individual, which was more difficult to wave, diffusion of the reducing agent into the hair was the rate-determining step. Thus for difficult-to-wave hair, the rate of the reaction of thioglycolate waves is governed by diffusion of the reducing agent into the hair.
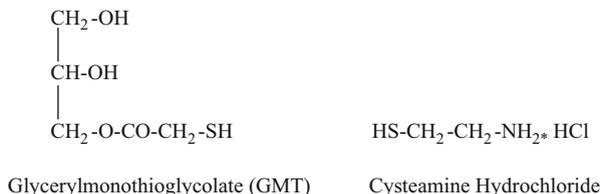
In other words, for difficult-to-wave hair or at high pH, the concentration of mercaptide ion is so high that cleavage of the disulfide bond can occur faster than mercaptide can diffuse into the fibers. As the pH is decreased to the acid side, or for easy-to-wave hair, the rate of chemical reaction decreases faster than diffusion to the point at which the chemical reaction itself becomes rate limiting. With many mercaptans [21], further lowering of the pH to about two freezes or stops the reduction reaction.

Evans et al. [25] have confirmed these conclusions of Wickett. In addition, the observation that Japanese hair is "easy to perm" and that fine Caucasian hair, less than 75 μm in diameter, is more "difficult to perm" was also confirmed. However, these scientists were unable to identify any common characteristics such as fiber diameter or cystine content that would account for this behavior. The fact that fine hair is more difficult to perm than thick hair may be due to the larger ratio of cuticle to cortex in fine hair and the fact that cortex plays a stronger role in waving than cuticle. This explanation is consistent with the experiments by Wortmann and Kure [2] demonstrating that the cuticle does inhibit the reduction reaction. In addition to pH, other important variables that influence the rate of reduction of keratin fibers by mercaptans are temperature, hair swelling, prior history of the hair, and structure of the mercaptan. These factors are described in the next section of this Chapter.

4.3.1   Factors Affecting the Rate of the Reduction Reaction

Since the rate-controlling step in this reaction can be diffusion of the reducing agent into the fibers or the chemical reaction itself, it is important to consider the rate in terms of these two potentially rate limiting factors.

The pH region most commonly employed for the reduction of hair fibers by mercaptans is above neutral (generally 9–9.5). In the professional field, glyceryl-monothioglycolate (GMT) was introduced in Europe in the 1960s and into the U.S. in the 1970s [24, 26]. This thiol is the active ingredient used in several commercial acid waves where the waving solution has a pH near 7. It would appear that the reaction of GMT with hair is a reaction-controlled rate process, since the pH of the system is near 7.

$$CH_2\text{-}OH$$
$$|$$
$$CH\text{-}OH$$
$$|$$
CH$_2$-O-CO-CH$_2$-SH   HS-CH$_2$-CH$_2$-NH$_{2*}$ HCl

Glycerylmonothioglycolate (GMT)   Cysteamine Hydrochloride

The processing time for a GMT permanent is about twice as long as for a conventional thioglycolate wave and it requires a covering cap and the heat of a dryer to enhance the rate of reduction. Wickett [10] has shown that for sodium thioglycolate under conditions where reaction rate control exists, the activation energy is lower than for diffusion rate control. Therefore, under these conditions an increase in temperature will have less of an effect on the reaction rate than if the reaction were a diffusion-controlled process. The acid wave supporters claim superiority due to reduced swelling and less damage; however, no data could be found to support these claims. To date, GMT acid waves have been used only by professionals and not in the retail field [26].

Cysteamine hydrochloride is another active thiol used in professional products at a lower pH about 8.3. Manuszak et al. [27] have compared the reduction of hair by cysteamine and thioglycolic acid. At a pH where similar concentrations of mercaptide ion were present, thioglycolic acid was more effective in reducing the fibers. One explanation is that cysteamine forms an internal five membered ring structure via internal hydrogen bonding from the protonated amine group to the mercaptide group, thereby reducing its availability for reaction.

### 4.3.2   Effect of Temperature on the Reaction Rate

The activation energy for the reduction of either human hair or wool fiber at alkaline pH is of the order of 12–28 kcal per degree mole [10, 22, 24]. Wickett [10] explains that when the mechanism is diffusion-rate-controlled, the activation energy is higher (28.0 kcal per degree mole) [10], because the boundary movement depends on both reaction and diffusion. However, when the rate depends only on the chemical reaction, the activation energy is lower (about 19.7 kcal per degree mole). Therefore, reaction rates for both of these systems are only moderately affected by increases in temperature. The activation energy for the chemical reaction at acid pH is slightly lower [22]. Therefore, the rate of reaction under acid conditions should be affected less by changes in temperature.

Japanese hair straightening a process that involves reducing the hair and then applying a hot straightening iron to it to achieve a permanent straightening hair treatment will be described later in this Chapter in Sect. 4.12.

### 4.3.3   Effect of Hair Swelling and Hair Condition on the Reaction Rate

Above the isoelectric point, the swelling of hair increases substantially with increasing pH [28, 29] (also see Chap. 9). Herrmann [24] has shown a corresponding increase in the rate of diffusion of mercaptans into hair fibers with increasing pH. Hydrogen bond breaking agents (hair swelling agents), namely urea and other amides, have been added to depilatory formulations for the purpose of enhancing the rate of reduction [24, 29]. Heilingotter [30] has shown that the addition of urea to thioglycolic acid solution increases the rate of swelling of the fibers. Depilatory systems are generally high-pH mercaptan systems (pH 11 to 12) where moving boundary kinetics exists under all conditions [10], and a common depilatory ingredient is calcium thioglycolate (see Fig. 4.1 and the section on depilatories in this Chapter). Note the axial folds created by the extreme swelling and then rapid dehydration on drying. These folds are created because of the differential shrinkage in the different cuticle layers due to extensive bond breaking and the leaching out of solubilized proteinaceous matter.

Undoubtedly, the condition of the hair also plays a role in the rate of reduction, especially under conditions where diffusion is rate-limiting. Permanent-waving [31] and bleaching [32] produce alterations to hair that result in increased swelling in solvents. Also, hair that has been previously bleached or permanent-waved displays more rapid rates of reduction than chemically unaltered fibers. As a consequence, weaker reducing systems are offered in the marketplace to permanent-wave
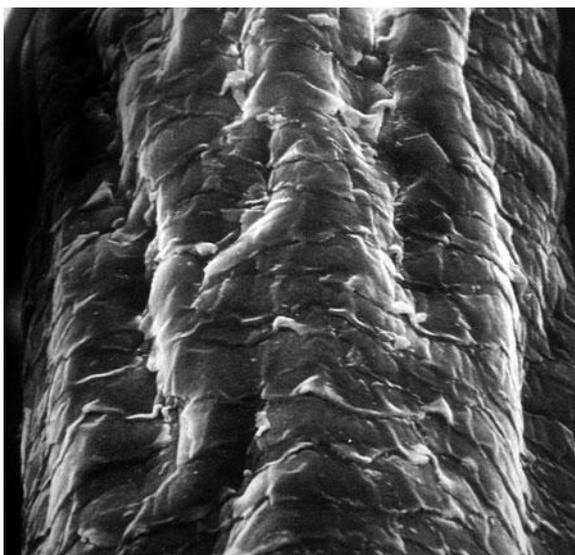
Fig. 4.1 Hair fiber after treatment with calcium thioglycolate (depilatory)

Fig. 4.2 Hair fiber oxidized with peroxide, reduced with thioglycolate and extended to fracture dry. *Bottom*: At low magnification, note the cracks perpendicular to the fiber axis. *Top*: Higher magnification shows cracks are through the entire cuticle (SEM kindly provided by Sigrid Ruetsch)
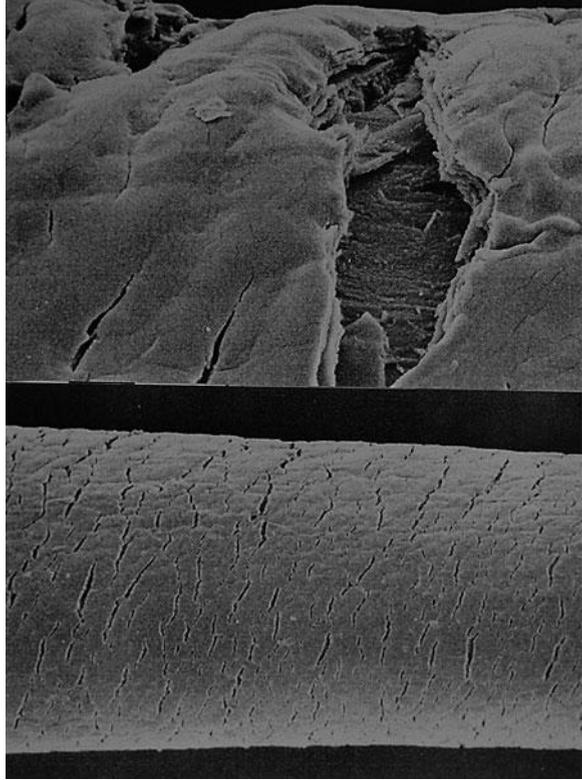
hair that has been previously damaged by bleaches and other damaging chemical treatments.

Figures 4.2 and 4.3 illustrate the large amount of damage inflicted on hair fibers by combined oxidation and reduction treatments. These fibers were oxidized with alkaline peroxide and then reduced and extended to fracture in the dry state. All of the fibers treated in this manner broke between only 10% and 20% extension as opposed to fibers that had been only reduced. The reduced fibers broke at a significantly higher extension. Figure 4.2 illustrates the large number of deep cracks in the cuticle perpendicular to the fiber axis that extend through all the cuticle layers. The SEM of Fig. 4.3 was taken at the fracture site itself and shows multiple step fractures and even torn cuticle and cortical cells resulting from extensive damage to the proteins of the cell membrane complex and to proteins in both cuticle and cortical cells. Although these treatments are stronger than generally used in practice, they illustrate the greater sensitivity of bleached hair to reductive treatments and also just how degrading combined bleaching and permanent waving can be.

An initiation time for the reduction reaction was found by Weigmann [22] in his kinetic study of the reduction of wool fiber. Weigmann attributed the initiation time
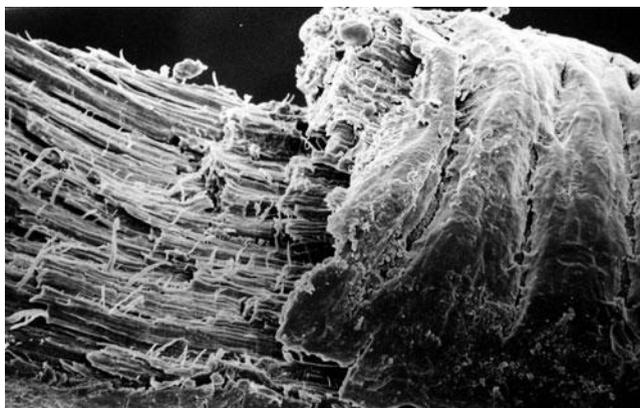
Fig. 4.3 Fiber was oxidized, reduced and extended to break dry. This SEM was taken at the fracture site. Note the multiple step fractures in the cell membrane complex (SEM kindly provided by Sigrid Ruetsch)

to the epicuticle the initial barrier to reduction that is eliminated after a short reduction time. It is likely that the initial reduction reaction cleaves some thioester linkages removing some 18-methyl eicosanoic acid from the surface but it would appear that the major breakdown in the cell membranes by permanent waves involves the cleavage of disulfide bonds by the thiol active in the permanent wave which weakens the membranes and leaves a high concentration of mercaptan groups to allow further membrane degradation under stress and in that manner the diffusion barrier of the hair surface is degraded. As a consequence, hair that has been permanent-waved or has undergone alterations to its outer layers should provide less or no initiation time in subsequent reductions or reactions.

Diffusion rates are significantly greater in wool fiber than in human hair [33]. This effect is due to the lower disulfide content of wool fiber relative to human hair. Therefore, one might anticipate a more rapid rate of reduction for wool fiber than for human hair, under conditions of diffusion-controlled reduction.

Scale lifting by alternating treatments of certain anionic and cationic surfactants can occur on hair previously permanent waved or extensively bleached, see Figs. 4.4 and 4.5. Furthermore, hair purchased from consumers who had been given a home or salon permanent wave on the head shows an even greater propensity for this type of scale damage than hair permed in the laboratory. We believe that this phenomenon involves scale lifting through a weakened cell membrane complex. Figure 4.6 depicts the damaging effects of reductive treatments on the cell membrane complex. This fiber was reduced and not re-oxidized chemically and then extended to break. Note the large gaps between cuticle cells and at the cuticle-cortex junction created by the weakened cell membrane complex. Such gaps do not occur in the cell membrane complex by extending chemically unaltered hair to break. This reaction likely involves cleavage of thioester in the surface and in each layer between cuticle cells by thiolate of the TGA because
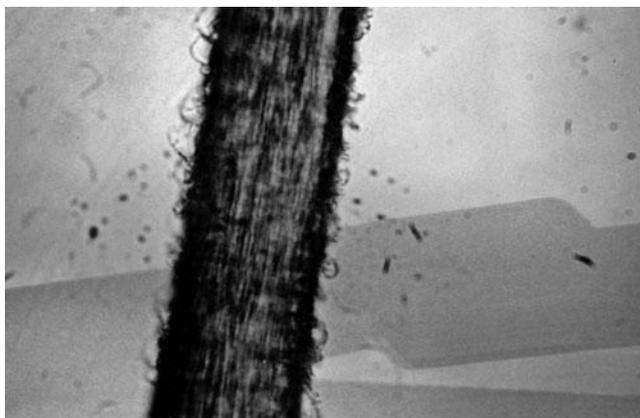
Fig. 4.4 Fiber was permanent waved on the head, after a few weeks cut, and treated with three alternating treatments of TEA lauryl sulfate and stearalkonium chloride and observed in the light microscope. Note the lifted cuticle scales
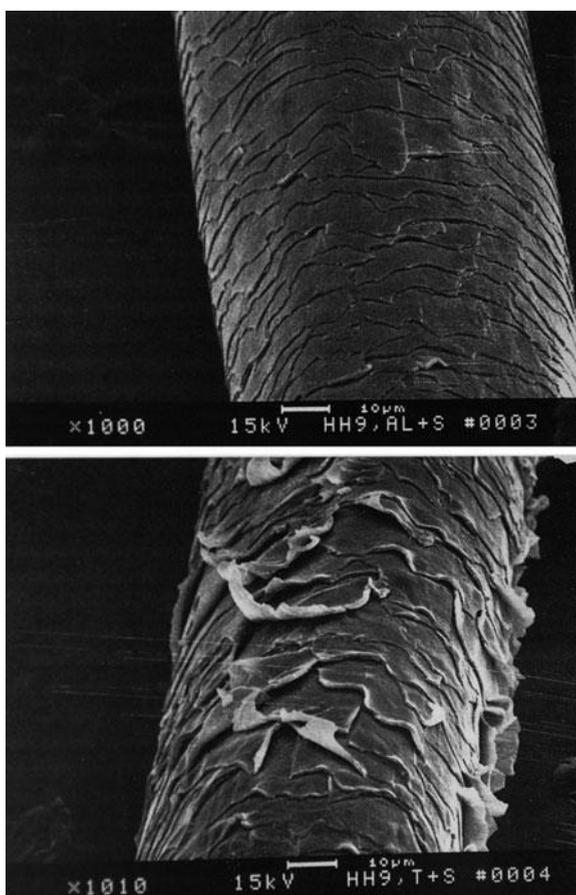
Fig. 4.5 Similar treatment as in Fig. 4.4, except this fiber was observed in the dry state by SEM. *Top*: Control treated with sodium deceth-3 sulfate and stearalkonium chloride. *Bottom*: Treated with TEA lauryl sulfate and stearalkonium chloride. Note the lifting of scales due to the weakened cell membrane complex
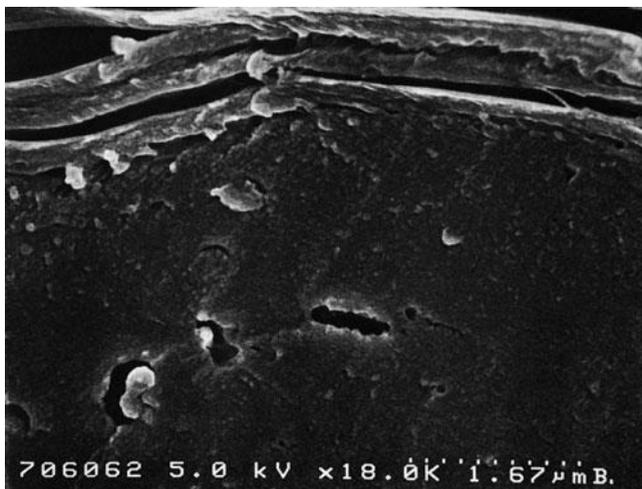
Fig. 4.6 Fiber reduced with TGA at pH 10 and extended to break dry. Note the cracks between the scales caused by a weakened CMC (SEM kindly provided by Sigrid Ruetsch)

thioester is sensitive to nucleophiles and the thiol grouping is one of the most powerful nucleophiles in organic chemistry.

The scale lifting phenomenon described above is due primarily to the penetration of cationic and anionic surfactant into the endocuticle and the cell membrane complex and the subsequent deposition and build-up of a hydrophobic anionic-cationic complex layer. When this layer is sufficiently large, a lifting action is created by the differential swelling action in the cuticle layers. This effect is analogous to the bending action of a laminar thermostat to heat changes. The fact that hair permed on heads is more reactive to this scale lifting phenomenon suggests greater cell membrane complex damage on live heads compared to laboratory waving. I believe this effect is due to weathering exposures on permanent waved hair such as "fatiguing like actions" during grooming that result primarily from combing and brushing actions or other damaging exposures such as UV radiation. This scale lifting phenomenon could provide a simple test to detect and define the extent of damage to the cell membrane complex. For a more complete description of this scale lifting phenomenon, see Chap. 6.

Figure 4.7 also represents hair fibers reduced and then extended to fracture and shows effects occurring deeper inside the fiber. The fracturing of this fiber clearly shows that reductive treatments do weaken the cell membrane complex extending across the entire fiber even into the medulla. This electron micrograph provides an interesting view of the structure of the medulla confirming that it consists of hollow spheres rather than simply a porous region of the fiber.
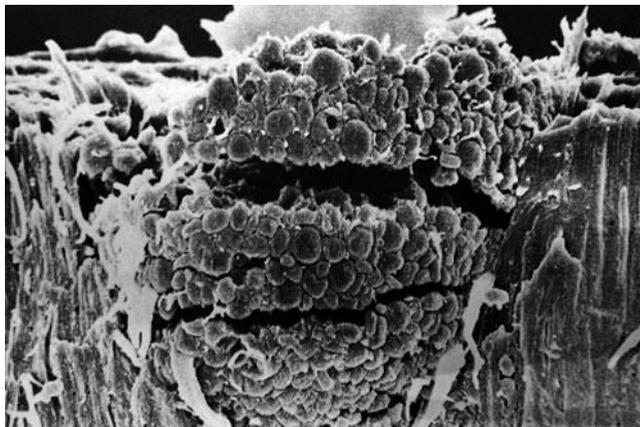
Fig. 4.7 Fiber reduced and extended to fracture dry. The medullary cracks show that reductive treatments weaken the intercellular structures of the entire fiber, even in the medulla (SEM kindly provided by Sigrid Ruetsch)

4.3.4   Effect of Mercaptan Structure on the Reaction Rate

4.3.4.1   Electrostatic Effects

Herrmann [24] described a minimum at acid pH for the diffusion of a cationic containing thiol (thioglycolhydrazide) into human hair. He also examined the influence of pH on the

$$HS\text{-}CH_2\text{-}CO\text{-}NH\text{-}NH_2$$

Thioglycolhydrazide

rate of diffusion of thio acids (thioglycolic and thiolactic acids) into human hair. For this latter type of mercaptan, the minimum in diffusion rate occurs near neutral pH. These thio acids are of anionic character in alkaline media, and they diffuse faster in alkaline than in acidic media. Therefore, hair swelling must play a more important role than electrostatics for the diffusion of these simple mercaptans into human hair.

4.3.4.2   Nucleophilicity of the Mercapto Group

The nucleophilicity of the mercaptan grouping depends on the nature of the groups directly attached or in close proximity to the mercaptan functional group. In general, nucleophilicity increases with increasing basicity of the mercaptan function [34]. Over the range of conditions where diffusion is rate-limiting, changes to the nucleophilicity of the mercapto group will have little effect on the rate of reduction. However, where the chemical reaction is rate-controlling, the

nucleophilicity of the mercapto group will be of greater importance. Theoretically, in a diffusion-controlled reduction, one could increase the rate of reduction by sacrificing nucleophilicity (decrease the basicity of the mercaptide ion) in order to increase diffusibility.

Haefele and Broge [35] have reported the mercapto acidities for a large number of mercaptans (pK RSH 4.3 to 10.2); thioglycolic acid is just above 10 (10.4). Hydrogen sulfide, the simplest mercaptan, has a pK RSH of 7.0 [35]. As one might predict, the substitution of electron-withdrawing groups (carbonyl, alkyl ester, alkyl amide) for a hydrogen atom increases the mercapto acidity. Electron- donating groups (carboxy, alkyl) decrease mercaptan acidity.

Under conditions of lower pH, where this reduction process is reaction-controlled rather than diffusion-controlled, Equation B or C can be rate-limiting. If Equation B is rate-limiting, the reaction is simply second order—first-order with respect to mercaptan and first-order with respect to keratin disulfide—and analysis is not as complicated as when Equation C is rate-limiting. In kinetic studies for a complex material like human hair or wool fiber, an excess of thiol is most commonly employed, and one generally assumes the reaction in Equation B to be rate-controlling. The reaction is then described by pseudo-first-order kinetics (first-order with respect to keratin disulfide).

4.3.4.3   Steric Effects

The rate of diffusion of mercaptans into human hair is undoubtedly influenced by steric considerations. For example, molecular size (effective minimum molecular diameter) of the mercaptan molecule should affect the rate of diffusion into hair. Therefore, the rate of reduction of human hair by ethyl mercaptan in neutral to alkaline media, where diffusion is rate-determining, should be faster than that of higher homologs. (The possible effects produced by varying the structure of cystinyl residues in hair on the rate of reduction were considered in the previous section on cystinyl residues of differing reactivities.)

4.3.4.4   Counterion Effects

Ammonia or alkanolamines such as monoethanol amine are the primary neutralizing bases for reducing solutions of thioglycolate permanent waves. Ammonia is said to facilitate diffusion of thioglycolate through hair as compared to sodium hydroxide [36].

Heilingotter [37, 38] has compared a large number of neutralizing bases including ammonia, monoethanol amine, sodium hydroxide, isopropanol amine, ethylene diamine, diethanol amine, and triethanol amine with regard to the ability of the corresponding salts of thioglycolic acid to decrease the 20% index (at a pH close to 9.2). This criterion was used to assess the ability of these different thioglycolates to function as permanent-wave reducing agents. He found that ammonia and

monoethanol amine provide the maximum effects. Furthermore, the reducing power of triethanolamine thioglycolate is so weak as to render it ineffective as a permanent-waving agent.

Heilingotter suggested that of the two most effective reducing systems, ammonium thioglycolate provides the more satisfactory waving characteristics. It would appear that this "catalytic activity" of nitrogen-containing bases is due to their ability to swell the hair, thus allowing faster diffusion of mercaptan into the interior of the fiber.

Other salts of thioglycolic acid have been described as potential permanent-waving agents, including potassium [39], magnesium [40] and of course esters such as glycerol monothioglycolate and other esters [41]. Magnesium thioglycolate has been described as an odorless permanent wave agent, although this system has never achieved commercial success.

4.3.4.5   Side Reactions During the Reduction of Keratin Fibers with Mercaptans

The reaction of mercaptans with keratin fibers is a relatively specific reaction in mild acid. However, in alkaline media, peptide bond hydrolysis and the formation of lanthionyl residues can also occur [42]. Zahn et al. [43] suggested that mercaptides such as thioglycolate or cysteinate can accelerate the rate of formation of lanthionyl residues in wool fiber. (A more detailed discussion of the formation of lanthionyl residues in keratin fibers is described later in this Chapter.)

$$
\begin{array}{ccc}
NH_2 & & NH_2 \\
| & & | \\
CH\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH \\
| & & | \\
CO_2H & & CO_2H
\end{array}
$$
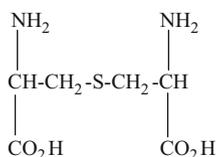
Lanthionine

Hydrolysis of peptide and amide linkages is also a possible complication in an alkaline medium. Hydrolysis of the amide groups of the residues of aspartic and glutamic acid amides will increase the ratio of acidic to basic groups in the fibers, conceivably altering the isoelectric and/or isoionic points of the hair.

$$
\begin{array}{ccccc}
\text{-CO-CH-NH-} & & & \text{-CO-CH-NH-} & \\
| & & & | & \\
CH_2 & & & CH_2 & \\
| & & & | & \\
C=O & + & OH^- \longrightarrow & C=O & + \quad NH_3 \\
| & & & | & \\
NH_2 & & & O\text{-} &
\end{array}
$$

Hydrolysis of amide of aspartic acid

Peptide bonds are the major repeating structural unit of polypeptides and proteins, and they form the structural backbone of human hair. Hydrolysis of peptide bonds can also occur at high pH, and both of these reactions (hydrolysis of amide and peptide bonds) are far more prevalent in the action of depilatories, formulated near pH 12, than in permanent waves. Permanent-waving lotions are usually formulated at a pH of approximately 9.2–9.6.

$$\begin{array}{c} \text{R} \quad\quad \text{O} \quad\quad\quad \text{R} \\ | \quad\quad\quad || \quad\quad\quad\quad | \\ \text{-C-CH-NH-C-CH-NH-C-CH-NH-} \\ || \quad\quad\quad | \quad\quad\quad || \\ \text{O} \quad\quad\quad \text{R} \quad\quad\quad \text{O} \end{array} \quad \text{OH}^- \quad \begin{array}{c} \text{O} \quad\quad\quad\quad \text{R} \\ || \quad\quad\quad\quad\quad | \\ {}^-\text{O-C-CH-NH-C-CH-NH-} \\ | \quad\quad\quad || \\ \text{R} \quad\quad\quad \text{O} \end{array}$$

$$\begin{array}{c} \text{R} \\ | \\ \text{-C-CH-NH}_2 \\ || \\ \text{O} \end{array}$$

Alkaline hydrolysis of the peptide bond

4.4   Reduction of Hair with Sulfite or Bisulfite

Sulfites or bisulfite (depending on pH) are another important reducing agent for the disulfide bonds in commercial permanent waves. The reaction of sulfite with hair involves nucleophilic attack of sulfite ion on disulfide. This reaction produces one equivalent of mercaptan and one equivalent of Bunte salt [44].

$$\text{K-S-S-K} + \text{M}_2\text{SO}_3 \rightleftharpoons \text{K-S-SO}_3{}^-\text{M}^+ + \text{K-S}^-\text{M}^+$$

Bunte salt

Reese and Eyring [45] demonstrated that the reaction of sulfite with hair is a pseudo-first-order reaction. In other words, the chemical reaction of sulfite with the disulfide bond of hair is slower than diffusion of sulfite into hair. Elsworth and Phillips [46, 47] and Volk [48] examined the sulfitolysis of keratin, demonstrating that the rate of cystine cleavage is optimal at acid pH. Wolfram and Underwood [49] found a broad optimum for cystine cleavage by sulfite at pH 4–6. The decrease in cystine cleavage at acidic pH (below pH 4) is due to a decrease in the concentration of the nucleophilic sulfite species. On the other hand, the decrease in cystine cleavage as pH is raised (alkaline pH) results from alkaline hydrolysis of the Bunte salt [50].

The patent literature teaches that rebuilding disulfide bonds in keratin after sulfitolysis may be accomplished through water rinsing. However, reversal of sulfitolysis by rinsing is normally slow and inefficient [26]. In addition, Bunte salt is resistant to oxidizing agents. Therefore, neutralizers such as bromate or hydrogen peroxide are not totally efficient in rebuilding disulfide bonds in sulfite waves.

Sneath [51] showed that the bisulfite waving treatment decreases the barrier function of the cell membrane complex as evidenced by cationic dye absorption,

however, part of this reaction is reversible, and therefore, probably involves the Bunte salt groupings. In addition, lipids (including 18-methyl eicosanoic acid) are removed from the cell membrane complex during bisulfite waving and this part of the reaction is not reversible and a higher concentration of mercaptan and oxidized sulfur are left in the hair to weaken it.

To summarize and to compare the two processes of thioglycolate and sulfite reduction of hair, we find that the thiol (or nucleophile) reacts with hair, producing cysteine residues in the following manner:

$$\text{K-S-S-K } + \text{ 2 R-SH } \rightleftarrows \text{ 2 K-SH } + \text{ R-S-S-R}$$

This reaction can be largely but not completely reversed by rinsing and oxidation in air. However, the most effective reversal is achieved through mild chemical oxidants.

On the other hand, sulfite reacts with the disulfide bonds in hair to produce mercaptan and Bunte salt:

$$\text{K-S-S-K } + \text{ SO}_3^- \rightleftarrows \text{ K-S}^- + \text{ K-S-SO}_3^-$$

$$\text{Bunte salt}$$
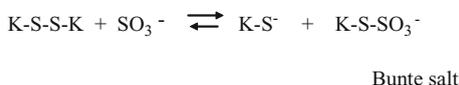
Rinsing of the sulfite-treated hair slowly reverses the reaction, rebuilding cystine bonds. The rate of cystine reformation increases with increasing pH, and good set stability is achieved at pH 8 or higher. Because of the efficiency of reversal of the sulfitolysis reaction with alkali, Albrecht and Wolfram [52] suggest that for low cleavage levels, sulfite is a more effective setting agent than thioglycolate. However, at higher cleavage levels, thioglycolate is the superior active ingredient.

In addition, thioglycolate at alkaline pH is more effective at higher cleavage levels, because thioglycolate is a stronger reducing agent than sulfite. Its greater effectiveness is borne out by the fact that under optimum conditions, for difficult-to-wave hair, the rate-controlling step for the thioglycolate reaction is diffusion of the reducing species into the fibers [10]. On the other hand, for sulfite at its optimum (acid pH), the rate-determining step is chemical reaction with the disulfide bond.

4.5   Summary of Chemical Changes to Hair by Permanent Waving

As hair is exposed to permanent waving, changes take place in the surface layers, the cell membrane complex, the A-Layer and exocuticle in addition to the cortex leading to the formation of increasing concentrations of these sulfur compounds, mercaptan, sulfinate and sulfonate groups and a decrease in the free lipid content in the surface layers. Zahn et al. [53] have shown an increase in the thiol content of

whole fiber from about 11 µmol/g in untreated hair to as high as 94 µmol/g for permanent waved hair and Robbins and Kelly [54] has shown similar amounts of cysteic acid in permanent waved hair actually waved on people's heads (49–94 µmol/g) vs. about 25 µmol/g for controls. Since a normal permanent wave usually reduces less than 50% of the whole fiber in cross-section these values are likely to be much higher in the outer layers of the fiber.

Kon et al. [55] examined Japanese hair permanent waved on live heads every 2–3 months comparing it to untreated controls. These scientists analyzed two types of permanent waved hair: Permed hair with many splits and permed hair with several broken hairs and a few split ends. This latter hair, by SEM analysis, showed considerably less cuticle most likely from abrasive actions such as combing and brushing. From analysis of 18-methyl eicosanoic acid and isopeptide (cuticle analyses) the following results were revealed, see Table 4.1.

The data of Table 4.1 were calculated from the results by Kon et al. [55] and show very little change in MEA from the control to the permed hair in the mid-sections compared with the tip ends. Because the thiol will not attack the isopeptide linkage and considering the fact that such large changes occur in the isopeptide content of the permed hair, these large changes suggest that greater effects are produced in this hair by abrasive actions which remove cuticle proteins and lipids than by direct chemical action of the thiol. Therefore the chemical and physical changes from permanent waving have a profound effect on reducing the abrasion resistance of hair.

With regard to effects on the cortex, Kon et al. [55] found that permanent waving produced a significant decrease in microfibril protein and an increase in high molecular weight protein which showed up most readily in the tip ends of the hair. This increase in high molecular weight protein probably results from a disulfide-mercaptan interchange reaction.

With regard to the changes most relevant to shampoos and hair conditioners, these reactions of permanent waving, convert the virgin hair surface from a hydrophobic, entity with little surface charge to a more hydrophilic, more polar and more negatively charged surface. More of the lower oxidation state sulfur compounds are formed in permanent waved hair and exist after waving as compared to chemically bleached hair or sunlight oxidized hair. These surface and

Table 4.1 18-MEA and isodipeptide in cuticle of permanent waved hair and control hair [55]

Hair/treatment	Mid-sections Δ at 10–20 cm[a]		Tip ends Δ at 30–40 cm[b]	
	IP[c]	MEA[d]	IP[c]	MEA[d]
Control	−9	−25	−18	−36
Perm (splits/more cuticle)	−27	−25	−64	−45
Perm (broken less cuticle via abrasion)	−36	−48	−82	−79

[a]Percentage change at 10–20 cm vs. control (560 µg/g at roots (0–10 cm))
[b]Percentage change at 30–40 cm vs. control (560 µg/g at roots (0–10 cm))
[c]Confidence levels from about ±25% to much higher
[d]Sensitivity = confidence levels ±10% to 15%

curvature changes produce higher rubbing forces resulting in more cuticle protein and lipid removal by hair grooming actions.

4.6   Reduction of Keratin Fibers with Other Reagents

In addition to mercaptans and sulfites, ingredients that have been used for nucleophilic cleavage of the disulfide bond in hair and/or wool fiber are sulfides, hydroxide, water (steam), a phosphine, borohydride, dithionite (hydrosulfite), and sulfoxylate. The interactions of some of these compounds with the disulfide bond in hair are described below.

4.6.1   Sulfides

Salts of hydrogen sulfide are extremely potent reducing agents for hair and have been used in depilatory compositions [56]. In a sense, salts of hydrogen sulfide are the simplest and among the most diffusible of all mercaptans. The initial reaction with the disulfide bond in keratin fibers is described by Equation D. Obviously, compound XIV can also ionize and react with cystinyl residues, forming organic polysulfides. Compound XIV can even react with hydrogen sulfide (anion) to form inorganic polysulfide.

$$K\text{-}S\text{-}S\text{-}K \ + \ M^+ \ {}^-S\text{-}H \ \rightleftharpoons \ K\text{-}S\text{-}SH \ + \ K\text{-}S^- \ {}^+M \qquad (D)$$
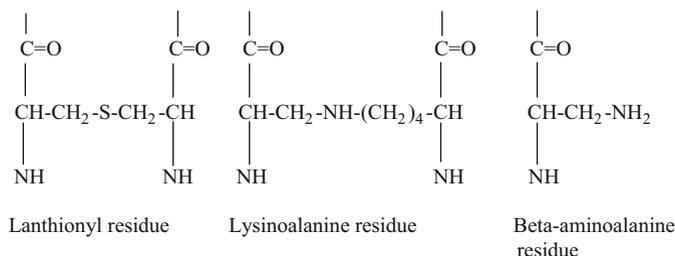$$(XIV)$$
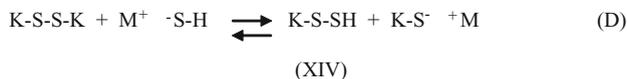
4.6.2   Steam and/or Alkali

Setting of wool and hair by either steam or hot alkaline solutions is a very old process [57]. Steam is also very effective for producing a permanent set. Alkali and steam are known to cleave the disulfide bond in keratins [58–60] and alkaline treatments are known to be the most effective hair straightening compositions because they provide the most permanent set (see the section on hair straightening in this Chapter). The reaction with hydroxide is summarized below by Equation E. Since sulfenic acids are generally unstable species [61], they have been suggested as intermediates that can react with the nucleophilic side chains in the keratin macromolecules [59].

$$K\text{-}S\text{-}S\text{-}K \ + \ M^+ \ {}^-O\text{-}H \ \rightleftharpoons \ K\text{-}S\text{-}OH \ + \ K\text{-}S^- \ M^+ \qquad (E)$$
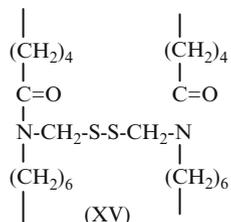$$\text{Sulfenic acid}$$

As mentioned before, hydrolytic cleavage of peptide bonds in keratins, as well as formation of lanthionyl residues can also occur in alkali. In addition to lanthionine, lysinoalanine [62] and Beta-aminoalanine [63] residues can be formed in some keratins under alkaline conditions.

$$
\begin{array}{ccccc}
| & | & | & | & | \\
C{=}O & C{=}O & C{=}O & C{=}O & C{=}O \\
| & | & | & | & | \\
CH{-}CH_2{-}S{-}CH_2{-}CH & & CH{-}CH_2{-}NH{-}(CH_2)_4{-}CH & & CH{-}CH_2{-}NH_2 \\
| & | & | & | & | \\
NH & NH & NH & NH & NH
\end{array}
$$

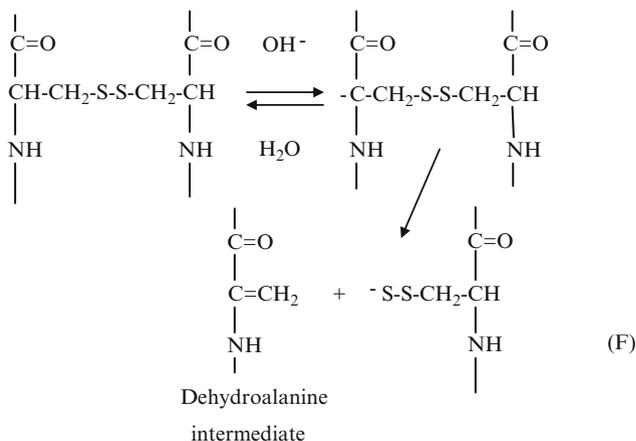Lanthionyl residue   Lysinoalanine residue   Beta-aminoalanine
residue

Formation of lanthionyl residues during alkaline treatment of keratin fibers was first suggested by Speakman [64] and later demonstrated by Horn et al. [65]. Lanthionyl residues may be formed from cystinyl residues in proteins under relatively mild alkaline conditions: 35°C and pH 9–14 [42]. However, under these same reaction conditions, lanthionine has not been identified from free cystine. For that matter, thioethers have not been formed from organic disulfides other than cystine-containing proteins, using similar reaction conditions [66]. At a higher reaction temperature (reflux), Swan [67] claims to have identified small quantities of lanthionine from reaction of alkali with free cystine.

Earland and Raven [68] have examined the reaction of N-(mercaptomethyl) polyhexamethyleneadipamide disulfide (XV) with alkali. Under alkaline conditions that produce lanthionyl residues in wool, no thioether is formed from this polymeric disulfide; however, cyanide readily produces thioether from both (XV) and wool fiber. Therefore, the mechanism for thioether formation must be different in these two reactions. Since this polymeric disulfide (XV) contains no betahydrogen atoms (beta to the disulfide group), a likely mechanism for formation of lanthionyl residues in keratins, under alkaline conditions, is the beta-elimination scheme [67] (the reaction depicted by Equation F). Other mechanisms that have been suggested for this reaction have been summarized by Danehy and Kreuz [69].

$$
\begin{array}{cc}
| & | \\
(CH_2)_4 & (CH_2)_4 \\
| & | \\
C{=}O & C{=}O \\
| & | \\
N{-}CH_2{-}S{-}S{-}CH_2{-}N \\
| & | \\
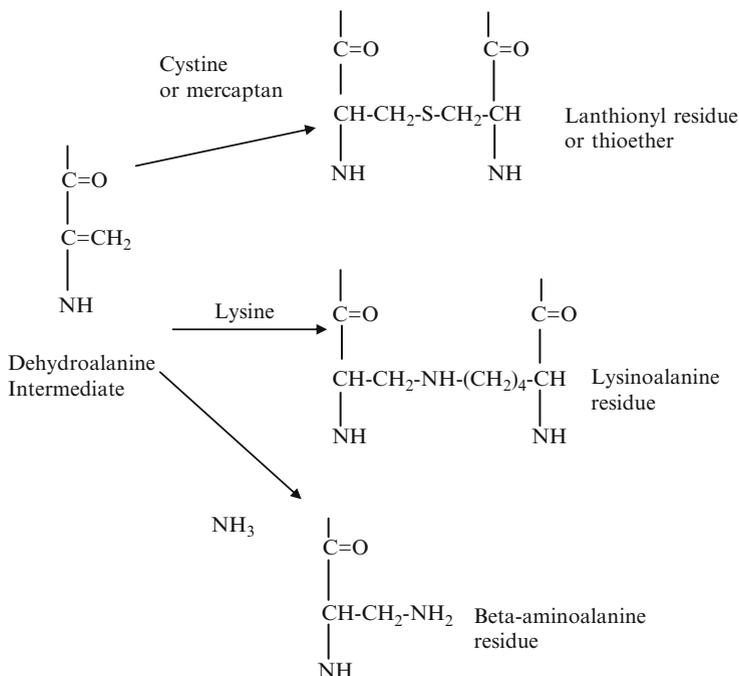(CH_2)_6 & (CH_2)_6 \\
| & | \\
 & (XV)
\end{array}
$$

The formation of lanthionine in keratin fibers is believed to involve two reaction sequences. The first sequence consists of beta-elimination to form dehydroalanine residues in hair:

$$
\begin{array}{ccccc}
| & & | & & | & & | \\
C=O & & C=O & OH^- & C=O & & C=O \\
| & & | & & | & & | \\
CH\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2\text{-}CH & \longrightarrow & \text{-}C\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2\text{-}CH \\
| & & | & H_2O & | & & | \\
NH & & NH & & NH & & NH \\
| & & | & & | & & | \\
\end{array}
$$

C=O   C=O
| |
C=CH$_2$ + $^-$S-S-CH$_2$-CH
| |
NH   NH   (F)
| |
Dehydroalanine
intermediate

Reaction sequence 1: beta-elimination to form dehydroalanine intermediate residue.

   The disulfide anion (of reaction sequence 1) may then eliminate sulfur to form mercaptide ion. In addition, the dehydroalanine intermediate is a very reactive species. It may react with any nucleophilic species present, such as mercaptan or amine, including mercaptan or amine residues on the hair or such groups in solution, to form lanthionine (other thioethers), or lysinoalanine [66, 70, 71], or beta-aminoalanine residues [63, 70–72] as shown below.

Cystine
or mercaptan

C=O   C=O
| |
CH-CH$_2$-S-CH$_2$-CH   Lanthionyl residue
| | or thioether
NH   NH

C=O
|
C=CH$_2$
|
NH

Dehydroalanine
Intermediate

Lysine

C=O   C=O
| |
CH-CH$_2$-NH-(CH$_2$)$_4$-CH   Lysinoalanine
| | residue
NH   NH

NH$_3$

C=O
|
CH-CH$_2$-NH$_2$ Beta-aminoalanine
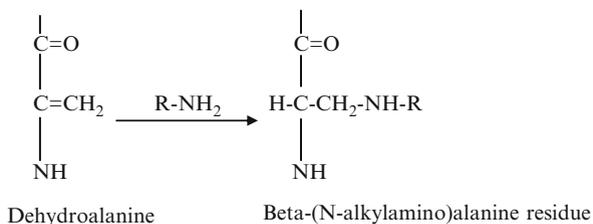| residue
NH

Second sequence of reactions: Nucleophilic addition to dehydroalanine

For wool fiber, all three residues-lanthionine, lysinoalanine, and beta-aminoalanine have been shown to form from reactions under alkaline conditions [70, 72, 73]. In the case of human hair, only lanthionine and lysinoalanine have been shown to form under alkaline conditions and lanthionine has been found at more than 100 micromoles per gram of hair in hair treated with 0.1 N sodium hydroxide under conditions similar to that of a hair straightener product [71], whereas no lanthionine was found in untreated control hair.

4.6.3   Amines

The discussion above on the reaction of alkalinity with wool and hair shows that a very reactive intermediate, dehydroalanine, is formed in hair and wool in the presence of alkalinity at elevated temperature (30–40°C or Chigher). Rivett [73] and Tolgyesi and Fang [71] have studied the reaction of wool and hair in the presence of alkaline amine solutions. Under these conditions, one might conclude that if amines are at a sufficient concentration they might add to the dehydroalanine intermediate to form beta-(N-alkylamino) alanine residues.

$$
\begin{array}{ccc}
| & & | \\
C=O & & C=O \\
| & & | \\
C=CH_2 & \xrightarrow{\ R\text{-}NH_2\ } & H\text{-}C\text{-}CH_2\text{-}NH\text{-}R \\
| & & | \\
NH & & NH
\end{array}
$$

Dehydroalanine   Beta-(N-alkylamino)alanine residue

Such is the case. However, the actual products formed depend on the substrate (hair vs. wool), the structure of the amine, its concentration, and the reaction temperature.

With short-chain amines like ethyl or n-butyl amine in the presence of wool fiber in alkali, the amounts of lanthionine and lysinoalanine are less (compared to alkali alone), but these two species are still produced in detectable quantities. However, longer-chain amines like pentyl amine react quantitatively with wool fiber and virtually no lanthionine or lysinoalanine is formed.

Tolgyesi and Fang [71] have found that alkaline amine solutions react differently with human hair. With human hair, all amines examined, including pentyl amine, compete less effectively with the amino and mercaptan residues of the hair for the dehydroalanine intermediate. As a result, more lanthionine and lysinoalanine cross links form than amine adduct, when human hair is the substrate. This is probably because diffusion rates are slower into human hair, decreasing the effective concentration of free amine in the fibers. Therefore, these species cannot compete as effectively for the dehydroalanine intermediate, and therefore lanthionine and lysinoalanine are formed.
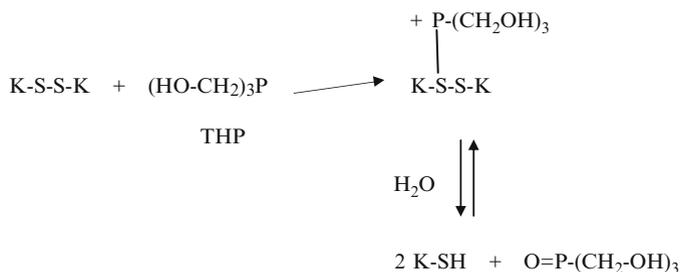
4.6.4 Cyanide

Salts of hydrogen cyanide have also been found to be capable of nucleophilic cleavage of the disulfide bond in keratin fibers [74]. In addition, nearly quantitative conversion of cystinyl residues to lanthionyl residues can be achieved in this reaction [75]. The most plausible mechanism is given in Equations G and H [65]. This mechanism consists of two nucleophilic displacement reactions: the first by cyanide on sulfur, and the second by mercaptide ion on carbon. The mechanism below is consistent with the observed formation of thioether from the reaction of N-(mercaptomethyl)polyhexamethyleneadipamide disulfide (XV) with cyanide, but not with alkali [68].

$$\text{K-S-S-K} \quad + \quad \text{M}^+ \ ^-\text{CN} \longrightarrow \text{K-S-CN} \quad + \quad \text{M}^+ \ ^-\text{S-K} \qquad \text{(G)}$$

$$\text{K-S-CN} \quad + \quad \text{M}^+ \ ^-\text{S-K} \longrightarrow \text{K-S-K} \quad + \quad \text{M}^+ \ ^-\text{S-CN} \qquad \text{(H)}$$

4.6.5 A Phosphine

Trihydroxymethyl phosphine (THP) or its precursor, tetrahydroxymethyl phosphonium chloride, has been used to reduce both human hair and wool fiber [75]. The mechanism of this reaction was studied by Jenkins and Wolfram [76], who discovered that this reaction proceeds by nucleophilic attack by the phosphine on sulfur, followed by hydrolysis of the intermediate addition compound to mercaptan and phosphine oxide.

$$
\begin{array}{ccc}
 & & + \ \text{P-(CH}_2\text{OH)}_3 \\
 & & | \\
\text{K-S-S-K} \quad + \quad \text{(HO-CH}_2)_3\text{P} \longrightarrow & & \text{K-S-S-K} \\
\text{THP} & & \\
 & & \text{H}_2\text{O} \ \updownarrow \\
 & & 2\ \text{K-SH} \quad + \quad \text{O=P-(CH}_2\text{-OH)}_3
\end{array}
$$

Above pH 7, the rate of reaction of THP appears to be controlled by diffusion of the reagent into the fibers [75] and, like the reaction of mercaptans with hair, increases rapidly with increasing pH in the vicinity of pH 9 to 12. Presumably, this increase in reaction rate results from increased swelling of the keratin substrate with increasing pH.

The equilibrium constant for the reaction of THP with cystyl residues in hair must be relatively large, since essentially complete reduction of human hair occurs with only a ten-fold excess of THP, at neutral pH [77].

4.6.6 Miscellaneous Reducing Agents

Borohydride (MBH_4) has also been used as a reducing agent for keratin fibers [78, 79], as well as dithionite ($M_2S_2O_4$)—sometimes called hydrosulfite [45]. Sulfoxylate (M_2SO_2) [80] or, more correctly, its ester salts—e.g., sodium formaldehyde sulfoxylate ($HO-CH_2-SO_2Na$) a weak reducing agent is used as a reductive bleach to lighten natural wool and is not an effective permanent waving agent.

4.7 Reactions of the Mercaptan Group

The previous section described various reagents that have been used for the reduction of the disulfide bond in keratin fibers. Most of these reactions produce cysteinyl residues, or mercaptan groups in the fibers.

The mercaptan group is one of the most reactive functional groups in all organic chemistry, and it readily undergoes oxidation, nucleophilic displacement, nucleophilic addition, and free-radical addition and displacement reactions. This section discusses some of the chemical literature pertaining to these types of reaction in reduced keratin fibers, and illustrates the potential reactivity of the mercaptan group in human hair.

4.7.1 Oxidation of Reduced Keratin Fibers

The oxidation of the mercaptan group can occur by two distinct pathways—the S-S fission route (pathway in the presence of most chemical oxidants), and the C-S fission route, the pathway for radiation-induced cleavage of the disulfide bond. Only the S-S fission route will be discussed in this section, because it is the most relevant pathway in relation to permanent waves and reducing agents. For a more complete discussion of both of these mechanistic schemes, see Chap. 5.

The oxidation of the mercaptan group can occur in several stages:

$$2\ K\text{-}SH \longrightarrow K\text{-}S\text{-}S\text{-}K \longrightarrow K\text{-}S\overset{\displaystyle O}{\text{-}}S\text{-}K \longrightarrow$$

Mercaptan   Disulfide   Disulfide monoxide

$$K\text{-}\overset{\displaystyle O}{\underset{\displaystyle O}{S}}\text{-}S\text{-}K \longrightarrow K\text{-}\overset{\displaystyle O}{\underset{\displaystyle O}{S}}\text{-}\overset{\displaystyle O}{S}\text{-}K \longrightarrow K\text{-}\overset{\displaystyle O\ O}{\underset{\displaystyle O\ O}{S}}\text{-}S\text{-}K \longrightarrow 2\ K\text{-}SO_3H$$

Disulfide   Disulfide   Disulfide   Sulfonic acid
dioxide   trioxide   tetroxide

Among this group of compounds, mercaptan, disulfide, and sulfonic acid have been isolated from the oxidation of reduced hair [53], the principle products being either disulfide or sulfonic acid depending on the strength of the oxidizing agent used. Since the primary intent in the oxidation of reduced hair in permanent-waving is to stop at the disulfide stage, milder oxidizing conditions are used than for bleaching hair. Some of the reagents that have been used for oxidation of reduced hair are bromates [81, 82, 83], iodate [85], perborate [84], acidic hydrogen peroxide [53], monopersulfate [85], and even air oxidation or metal-catalyzed air oxidation [79].

4.7.2   Nucleophilic Displacement

The mercaptan group is an extremely powerful nucleophile and it readily undergoes nucleophilic displacement reactions [86, 87]. This property is the basis of several quantitative tests for cysteine and/or cystine, including the Sullivan test, which involves nucleophilic displacement by mercaptide ion on iodoacetate [88].

$$K\text{-}SH \ + \ I\text{-}CH_2\text{-}CO_2H \longrightarrow K\text{-}S\text{-}CH_2\text{-}CO_2H \ + \ HI$$

Iodoacetic acid
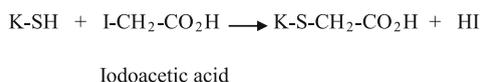
Methyl iodide has been used as a mercaptan blocking group in studies on keratin fibers [89]. Other monofunctional alkyl halides, including benzyl chloride, heptyl bromide, and dodecyl bromide, have also been reacted with reduced keratin fibers [8]. Hall and Wolfram [90] have used this reaction (alkyl iodides with reduced hair) as a means to introduce alkyl groups or non-polar residues into hair. These researchers found that methyl iodide was highly efficient in reacting with the mercaptan groups of reduced hair. Longer chain-length alkyl iodides, however, were not nearly as efficient for introducing alkyl groups into reduced hair.

$$K\text{-}SH \ + \ R\text{-}X \longrightarrow K\text{-}S\text{-}R \ + \ HX$$
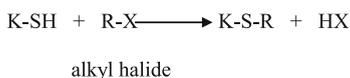
alkyl halide

The Bunte salt grouping has also been reacted with mercaptan in reduced keratin fibers [91] to form a mixed disulfide.

$$K\text{-}SH \ + \ R\text{-}S\text{-}SO_3Na \longrightarrow K\text{-}S\text{-}S\text{-}R \ + \ NaHSO_3$$

Bunte salt

Reaction of activated aryl halides, such as 2,4-dinitrofluorobenzene, with cysteine in unreduced and in reduced hair has been described by Zahn [53] as a quantitative assay for mercaptan and/or disulfide in keratin fibers.

Dinitrofluorobenzene
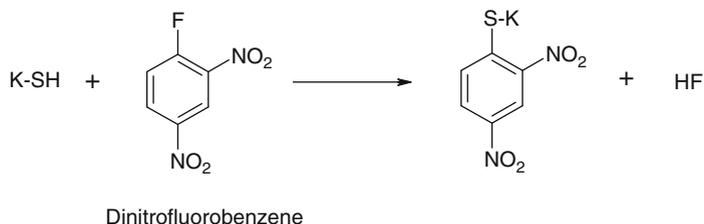
Halo mercury compounds such as methyl mercuric iodide also react readily with mercaptan in keratin fibers [92] and serve as the basis of Leach's method for cystine analysis.

$$K\text{-SH} + CH_3\text{-Hg-I} \longrightarrow K\text{-S-Hg-}CH_3 + HI$$

Methyl mercuric
Iodide
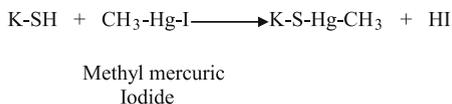
In fact, mercaptan in hair is capable of reacting with disulfide monoxide by nucleophilic displacement [93] or with most compounds that contain a group labile to nucleophilic displacement, if such labile groups are either formed in the hair or capable of diffusing into the hair.

Molecules containing two leaving groups similar to the previously described monofunctional compounds are capable of reacting with reduced keratin fibers and forming a new type of cross-link. Dihaloalkanes have been reacted with reduced wool fiber to provide a thioether cross-link [8]. This reaction is capable of promoting stability to moths in wool [94], thus confirming that the primary site that moths attack in wool fiber is the disulfide bond.

$$2\ K\text{-SH} + Br\text{-}(CH_2\text{-})_n Br \longrightarrow K\text{-S-}(CH_2)_n\text{-S-K} + 2\ HBr$$

Dihaloalkane

Di-Bunte salts have also been used to re-cross-link reduced keratin fibers through a bis-disulfide type of linkage [91, 93].

$$2\ K\text{-SH} + NaO_3\text{-S-S-}(CH_2)_n\text{-S-}SO_3Na \longrightarrow K\text{-S-S-}(CH_2)_n\text{-S-S-K} + 2\ NaHSO_3$$

Di-Bunte salt reaction

Other rather exotic bi-functional reagents have been reacted with both reduced and unaltered wool fiber and are described in Section C of the Proceedings of the International Wool Textile Research Conference (1955).

4.7.3 Treatment of Reduced Hair with Dithioglycolate Ester Derivatives of Polyoxyethylene

A novel treatment in permanent waving involves reacting reduced hair with polyoxyethylene esters of thioglycolic acid (mol. wt. 550–750) described by Salce et al. [95]. These esters are reported to bind to the fibers by displacement of reduced disulfide in hair on the ester linkage of the additive resulting in the formation of mixed disulfides, producing more hydrophobic hair fibers and improvement in the curl relaxation due to the increased hydrophobicity.

4.7.4 Nucleophilic Addition Reactions

Mercaptan groups in keratin fibers also undergo nucleophilic addition reactions with active olefins (olefins containing a strong electron-withdrawing group attached to the double bond). Schoberl [93] has shown that reduced wool fiber reacts with vinyl sulfones.

$$K\text{-}SH \ + \ CH_2\text{=}CH\text{-}SO_2\text{-}R \longrightarrow KS\text{-}CH_2\text{-}CH_2\text{-}SO_2\text{-}R$$

Vinyl sulfone
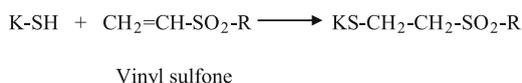
Maleimides are another example of activated olefins that react in this manner—e.g., N-ethyl maleimide (NEMI) [93, 96] reacts quantitatively with the mercaptan groups in reduced keratin fibers by a nucleophilic addition type reaction. Hall and Wolfram [90] have used this reaction to introduce N-substituted maleimide groups (N-ethyl, N-hexyl, and N-heptyl maleimides) into human hair to study the properties of hair modified by the introduction of non-polar residues. They report enhanced settability and high set retention, at all humidities, for hair modified in this manner with greater than 50% disulfide cleavage. However, hair having less than 50% disulfide scission does not show improved set characteristics.

N-substituted maleimide
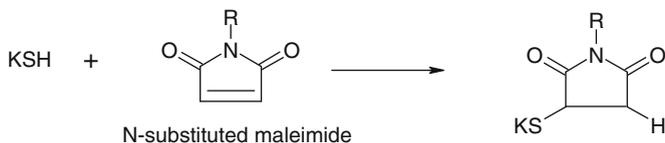
Acrylonitrile and phenyl acrylate have also been shown to react readily with the mercaptan groups of reduced hair [96].

$$K\text{-}SH \ + \ CH_2\text{=}CH\text{-}CN \longrightarrow K\text{-}S\text{-}CH_2\text{-}CH_2\text{-}CN$$

Acrylonitrile

$$K\text{-SH} \; + \; CH_2\text{=}CH\text{-CO-O-}\emptyset \longrightarrow K\text{-S-}CH_2\text{-}CH_2\text{-CO-O-}\emptyset$$
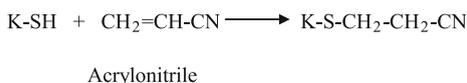
Phenylacrylate

Bi-functional reagents containing two active vinyl groups are capable of reacting with reduced keratin fibers and forming cross-links. Divinyl sulfone has been used for this purpose [93].

$$2 \; K\text{-SH} \; + \; CH_2\text{=}CH\text{-}SO_2\text{-}CH\text{=}CH_2 \longrightarrow K\text{-S-}CH_2\text{-}CH_2\text{-}SO_2\text{-}CH_2\text{-}CH_2\text{-S-K}$$

Divinyl sulfone reaction with keratin fibers

4.7.5   *Free-Radical Addition and Polymerization Reactions*

One form of polymerization that has been used in the chemistry of wool fiber involves reduction of the fibers followed by the addition of a vinyl monomer and an oxidizing agent [97, 98]. These reactions have been carried out in an inert atmosphere and provide rather large polymer add-ons. Related procedures have also been described for polymerizing into human hair in an air atmosphere and are described in detail in Chap. 8 [99–101].

In this type of reaction, the mercaptan group of the reduced keratin may serve as the reducing agent in a redox system for generating free radicals. The mercaptan group may also serve as a site for grafting, and it can serve as a chain transfer agent, limiting the degree of polymerization. Another advantage to this system is the increased swelling of the fibers accompanying reduction. This effect facilitates diffusion of all reagents necessary to polymerization into the fibers. (For additional details, see Chap. 8.)

Polymerization into wool fiber has also been accomplished using radiation grafting techniques [102, 103], although no such procedures could be found using human hair as substrate.

4.8   Water Setting Human Hair

If human hair is wet with water and held in a given configuration while drying, it will tend to remain in that configuration. This is the basis of what is called a water-set in human hair. It is well known; however, that exposure of water set hair to high humidity produces a loss of set. Recently, Diaz and co-workers [104] have demonstrated that exposure of water-set hair tresses to a lower humidity can also

Table 4.2 Low humidity effects on curl retention (all fibers set and dried at 60% RH)

Time exposed	Percent curl retention	
	60% RH	10% RH
2 h	73.5%	61.3%
24 h	59.6%	58.3%

produce a loss of set. In addition, Robbins and Reich [105] have demonstrated this same phenomenon with single hair fibers.

Table 4.2 summarizes one of the single-fiber experiments. Single hairs were water-set in a curled configuration on glass rods and dried at 60% RH. After removing the fibers from the rods, one group of hairs was exposed to a 60% RH atmosphere and another to 10% RH. Curl length was measured over time with a cathetometer.

The data in Table 4.2 were then analyzed by repeated measures ANOVA. Highly significant time effects, significant humidity effects, and significant interactions were found. Therefore, one may conclude that changing the environment of single hairs that have been water-set at a higher humidity (60% RH) to a lower humidity causes more rapid curl loss in short time intervals (2 h) than maintaining the hair at the higher humidity. This more rapid curl loss occurs in spite of the fact that hair equilibrated at a lower humidity will contain less water [106] and exhibit greater bending [107] and torsional stiffness [108] than hair equilibrated at a higher humidity.

The fibers when taken from 60% to 10% RH lose water until they re-equilibrate with the new environment (approximately 16% moisture at 60% RH to 5% moisture at 10% RH [106]). During this transition stage, as water migrates out of the fibers, hydrogen bonds are broken and reformed, and more rapid curl loss (set loss) occurs.

At the longer time interval (24 h), the hair fibers that were maintained at the higher humidity are equal (in curl retention) once again to the fibers transferred to the lower humidity. Apparently, after equilibration of moisture at the lower humidity, the rate of curl loss becomes less than for hair maintained at the higher humidity allowing the curl loss to equalize. Presumably at even longer times, the curl loss for the hair at the lower humidity would be less than for the hair at the higher humidity.

Diaz's experiments were with hair tresses and in a sense were more pragmatic than the single-fiber experiments; however, they include inter-fiber complications excluded from the single-fiber test. Fiber friction increases with RH for keratin fibers [108], and effects from frictional contributions tend to enhance the set stability of the hair at the higher humidity. Nevertheless, Diaz's results indicate the same general picture as with single hairs. Therefore, these two types of experiments complement each other with regard to providing a better understanding of the mechanism of water-setting human hair.

The following important insights are reflected in these results: Exposure of water-set hair to changes in humidity results in moisture either entering or leaving the fibers. The flow of or transfer of strongly bound water either into or out of hair produces cleavage of critical hydrogen bonds resulting in a decrease in water-set

stability. The behavior of hair equilibrated at different humidities may not reflect its behavior during the transition to different humidities, and changes in humidity are probably more likely to be encountered in the real world than constant humidity.

Water-setting hair provides a temporary reversible set to hair, because hydrogen bonds are involved. Therefore, a water set can be removed from hair by the transfer of moisture either into or out of hair. Permanent waves, in contrast, are more resistant to moisture transfer into and out of hair, because covalent bonding (the disulfide bond) and other molecular changes are involved and covalent bonds are relatively inert to moisture changes in hair.

4.9   Set and Supercontraction

Set has been defined by Brown et al. [109] as a treatment that enables a keratin fiber to maintain a length greater than its original length. As a contrast, supercontraction is the condition in which a keratin fiber is fixed at a length less than its original length [109]. Set is usually determined by a procedure similar to the one described by Speakman [58]. Fibers are stretched to 40%, treated, then rinsed and tested for their ability to retain the extended length when placed in water or buffer at elevated temperatures. The criterion for "permanent" set is the resistance to lengthwise shrinkage in boiling water. Supercontraction can also be followed by observing lengthwise changes in full-length fibers or by microscopic observation of fiber snippets [110].

The setting process is generally considered a three-stage process. Stage 1 is the stretching stage. Stage 2 is the period of structural rearrangement, consisting of the time period that the fibers are held in the stretched state. Stage 3 is the recovery period, the time after the external strain is removed.

Widely varying reaction conditions and gross alterations to the fibers have been made during the course of the study of the mechanism(s) of setting, although it appears that most of the literature on setting is concerned with establishing a single common mechanism for all treatments. Jenkins and Wolfram [111] suggested and provided evidence indicating that more than one mechanism may exist for setting keratin and highly altered keratin fibers. The discussion in this section is primarily concerned with the conditions of wool setting that are related to the permanent-waving process. Therefore, a single mechanism is considered.

When keratin fibers are stretched in an aqueous medium in the presence of a reducing agent, several bonds are broken owing to internal stresses resulting from the imposed strain. Hydrogen bonds are broken, their resistance to the imposed strain decrease with increasing temperature [101]. The importance of hydrogen bonds to stage 3 (recovery) and to structural rearrangement (stage 2) has been demonstrated. Farnworth [112] showed that urea plus, a reducing agent, is capable of producing permanent set in keratin fibers under conditions in which neither reagent alone will produce permanent set. Therefore, the breaking of additional

hydrogen bonds by urea permits structural rearrangements to occur in the presence of a reducing agent that reduction alone cannot achieve.

Weigmann et al. [113] and Milligan et al. [114] have clearly demonstrated the importance of the disulfide and mercaptan groups to all three stages of the setting process. Elimination of mercaptan before stretching prevents permanent set. On the other hand, permanent set is enhanced by elimination of mercaptan before releasing stretched fibers. Interestingly, mercaptan elimination in the latter circumstance may be accomplished either by re-oxidation to the disulfide or higher oxidation products, or even by blocking mercaptan with active reagents such as iodoacetate [114]. In fact, Menkart et al. [115] have suggested that a larger amount of set results from blocking mercaptan than from re-oxidation to disulfide. This suggestion is very reasonable because blocking mercaptan permanently blocks disulfide mercaptan interchange but re-oxidation to disulfide does not permanently prevent the interchange.

These experiments collectively demonstrate that structural reorganization during the setting of keratin fibers in aqueous reducing agents is facilitated not only through disulfide bond breakdown but also, to a large extent, through disulfide-mercaptan interchange reactions.

Since keratin fibers undergo crystallographic changes on stretching, X-ray diffraction can be used as a tool to study the setting mechanism. Setting of human hair by various means produces an alpha to beta transformation [84]. Therefore, setting hair is clearly different from water setting which involves small reversible deformations and only hydrogen bond breakage. Therefore, during setting some of the alpha helices of the filamentous regions of the cortical cells are stretched, and a beta configuration is formed. A number of forces including covalent bonds, hydrogen bonds, salt linkages, Van der Waals forces, and steric interferences oppose stretching and setting. The weak links in these "chains of forces" opposing strain probably exist primarily in the matrix of the cortex, the disulfide bonds in the intermediate filaments and in the A layer and exocuticle of the cuticle.

Certainly in aqueous reducing solutions, the weakest links in these "chains of forces" are the disulfide bonds and those associated hydrogen bonds that are broken and interchanged. These are the actions that permit the structural rearrangements in the microfibrils and other structural rearrangements that are critical to setting. However, as pointed out by Wortmann and Souren [1] a main effect of reduction or the breakage of disulfide bonds in setting must be on the crystalline filaments, that is on the interactions between the crystalline structures and the reorganization that occurs involving those structures rather than on the disulfide bonds themselves.

In addition to cortical changes, extensive changes occur in the cuticle during permanent waving. Wickett and Barman [11] have demonstrated that a satisfactory permanent wave can be achieved by greater cuticle/cortex reduction than with existing thioglycolate waves. The A layer and exocuticle contain high concentrations of cystine residues [116] and are therefore highly reactive to reducing agents. The endocuticle, on the other hand, contains relatively little cystine [116]. Therefore the primary reaction of the reducing agent in the cuticle will be with the stiff resistant

A layer and exocuticle regions. These stiff cuticle layers will be softened allowing for structural rearrangement. Upon re-oxidation, the macromolecules of the A layer and exocuticle layers will be re-hardened to a new configuration. Thus a combination of cortical and cuticle changes occurs in permanent-waving to provide a new "permanent" shape to the keratin fiber consistent with the observations of Wortmann and Kure [2, 3].

One might also anticipate greater cuticle contribution to a permanent wave in fine hair as compared to coarse hair, because of the greater ratio of cuticle to cortex in fine hair; see Wolfram and Lindemann [117]. This is because thin and coarse hair contains the same number of cuticle layers, with essentially the same thickness. Therefore, fine hair contains a greater proportion of cuticle to cortex than coarse hair. Assuming a 4-micron-thick cuticle, for coarse, 100-micron-diameter hair fibers the cuticle would comprise only 15% of the fiber cross section. However, for thin, 40-micron hair fibers, the cuticle would comprise 36% of the total fiber cross-section.

Fine hair is known to be resistant to waving. This effect is likely due to its high cuticle content. Wortmann and Kure [2] have demonstrated that the cuticle decreases the rate of reduction of hair fibers and it most likely plays a role in the permanent set of human hair due to its stiffness. The cuticle may play a lesser role than the cortex in permanent waving, nevertheless, it is difficult to conceive of the cuticle not playing an important role in waving reactions that involve reduction, shaping, and re-hardening of the high-sulfur A layers and exocuticle layers.

Hair swelling agents, such as concentrated solutions of alkali metal halides [118] or aqueous solutions of reducing agents [119], are capable of promoting supercontraction as well as setting; see the section on hair straightening in this Chapter. The types of reagents that promote supercontraction suggest that hydrogen bond breakage is important to supercontraction. Burley [120] has shown that disulfide-mercaptan interchange can also be involved in supercontraction. In addition, keratin fibers, while undergoing supercontraction, suffer a loss in birefringence, and the alpha-X-ray diagram disappears [121, 122]. This suggests molecular reorientation in the filamentous regions of the cortex. The alpha keratin is thus rearranged to a less organized structure. Therefore, supercontraction, with the exception of the driving force, and the final molecular orientation is very much related mechanistically to the process of setting.

In the first edition of this book, I proposed that one might consider the curling (waving) of a human hair fiber as a combination of setting and supercontraction. A bent hair fiber that is treated with an aqueous solution of a reducing agent is undergoing concomitant extension (setting) and compression (which should be more analogous to supercontraction than to setting). If one perceives the waving or straightening of human hair in this manner, one may then apply the testing procedures and mechanisms for these two phenomena to arrive at a picture of the waving process. In the future, perms and straighteners that are more resistant to washout are possible by developing compositions that provide for more extensive molecular conformational changes (loss of alpha keratin structure) as described by Wong et al. [123] for alkaline hair straighteners.

Wortmann and Kure [1] have been able to provide a model that explains the set behavior obtained in the permanent waving of human hair in terms of the bending stiffness of single hairs during the reduction and the oxidation reactions. Wortmann and Kure propose a distribution of Young's moduli from the hair surface to the center of the fiber and a diffusion controlled breakdown during reduction. This model is simple, yet elegant, and it is highly satisfactory in spite of the fact that it does not consider the two-phase composite nature of the cortex of human hair. Feughelman [4] extended this model, by proposing a model for setting a bent fiber and taking into account the two-phase composite nature of the cortex of keratin fibers.

Even though the criterion for permanent set in the wool industry is markedly different from that in the hair-waving industry (boiling water vs. neutral pH shampoos near room temperature), much can be gained in the understanding of hair waving and straightening by using the test procedures employed for wool and by drawing analogies to the mechanisms of setting and supercontraction.

4.10   Swelling: During and After Treatment

The microscopic method (change in volume) [124] and the centrifugation method (change in weight) have been used for studying the swelling of human hair by aqueous solutions of mercaptans. Both the rate and the extent of the swelling of human hair by mercaptan solutions are pH-dependent and increase dramatically with increasing pH above neutrality [29, 125]. At high pH, using a high solution-to-hair ratio, swelling in excess of 300% is possible with thioglycolic acid even at relatively short reaction times [125]. The swelling of human hair in aqueous mercaptan solutions is a direct reflection of the chemical reactions occurring inside the fibers and can therefore be described in terms of the reactivity considerations outlined in the section on the kinetics of this reaction.

Shansky [126] studied the swelling action of hair fibers during reduction, rinsing, and chemical neutralization—i.e., a simulated cold wave process. During the reaction with mercaptan, the swelling action is extensive. Upon rinsing, swelling continues, but at a reduced rate. This decreased swelling rate is attributed to osmotic forces arising from the rapid decrease in salt concentration outside the hair compared to inside the fiber. During neutralization, de-swelling occurs.

Hair fibers reduced and re-oxidized approach the original fiber diameter. Eckstrom [124] suggested that the milder the conditions of reduction, the closer the fiber will return to its original dry-state diameter on neutralization.

Fiber diameter determined in the wet or swollen state is sensitive to changes produced by damaging treatments like permanent waves or bleaches. The swelling action of permanent-waved hair [29] and bleached fibers [31] is greater than in unaltered hair and has been used to estimate the extent of alteration produced by reduction and re-oxidation [30]. For additional discussion on hair swelling, see Chaps. 1 and 9.

4.11   Permanent Waving of Human Hair

Charles Nessler is a key figure in the invention of the permanent wave in London in 1905 [127]. The first permanent waves were concentrated solutions of alkali (5–15%) or alkaline sulfites [127, 128] that reacted with hair at elevated temperatures. In these treatments, high temperatures were achieved by using curling irons, chemical heating pads, or electric heaters [129].

Current permanent waves are vastly superior to the early hot waves and do not require elevated temperature; thus the designation "cold waves." Cold waves became successful during World War II and have not changed substantially for nearly 70 years. These products are based on mercaptans or sulfites, the most common of these being thioglycolic acid, which is generally employed at a concentration of approximately 0.6 N and a pH of 9 to 9.5.

Sulfite waves employ a pH near 6 and a hydrogen peroxide neutralizer. This type of product generally claims to provide a wave that does not "frizzle" the hair, i.e., is gentle to your hair, and can be used on any type of hair (damaged or undamaged) [130]. This image is consistent with the fact that sulfite is a weaker reducing agent than thioglycolate (see the discussion on the reduction of hair by sulfite earlier in this Chapter).

Thioglycolate and sulfite waves are the primary reducing agents used in home permanent waves today. Although as indicated, glycerylmonothioglycolate (GMT) and cysteamine hydrochloride are being used in the professional field in commercial acid waves or waves that are formulated closer to neutral pH. GMT requires a covering cap and the heat of a dryer to accomplish sufficient reduction to provide a satisfactory permanent wave [26].

4.11.1   Cold Wave Formulations and Making Cold Wave Products

A typical thiol permanent wave consists of two compositions. The first, a reducing solution often called a waving lotion, is a composition similar to that in Table 4.3. To make this permanent wave formulation, first melt the emulsifier/wetting agents (steareth-20) and add them to oxygen free water, under an inert atmosphere, at

Table 4.3 A thiol permanent wave waving lotion

Ingredient	Percent
Thioglycolic acid	6.0
Steareth-20	2.5
Fragrance	0.5
Ethylene diamine tetraacetic acid	0.2
Colors	As required
Water	q.s.[a]
Ammonium hydroxide	To pH 9.3

[a]q.s., add water to 100%

Table 4.4 Neutralizer for a permanent wave product[a]

Ingredient	Percent
Hydrogen peroxide (30%)	7.0
Polysorbate-40	2.5
Phenacetin	0.5
Water	q.s.[b]
Phosphoric acid (85%)	To pH 4

[a]For making the neutralizer (Table 4.4), heat the water to 75° and melt the polysorbate-40 and slowly add it to the water with stirring. Cool to room temperature and then add the peroxide, the phosphoric acid and the preservative
[b]q.s., add water to 100%

Table 4.5 Waving lotion for softwave formulation

Ingredient	Percent
Ammonium bisulfite	4
Ammonium sulfite	3
Laureth-23	2.5
Fragrance	~0.5
Water	q.s.[a]
Ammonium hydroxide	To pH 8

[a]q.s., add water to 100%

about 50° while stirring. Cool to room temperature. Add about 3% concentrated ammonium hydroxide, then add thioglycolic acid with stirring. Add other ingredients and adjust the pH with ammonium hydroxide or the preferred form of alkalinity.

Consider the following precautions for making thiol perms. One should use a lined vessel [glass, plastic (polyethylene or teflon or other inert plastic) or stainless steel]. One should avoid contact with all metals, because thiols react with many metals to form colored salts. Note, salts of thioglycolic acid may be handled in stainless steel, but thioglycolic acid may not. Also minimize heat whenever thioglycolic acid is present. Exposure to air and oxygen should be avoided, for example use oxygen free water and package with a minimum of headspace, because thiols are sensitive to air oxidation (Table 4.4).

A milder waving lotion sometimes called a softwave (Table 4.5) can be made in the following manner. Add the laureth-23 to water at 70° with stirring. Cool to room temperature and dissolve the bisulfite and the sulfite. Then add the fragrance and adjust the pH to 8 with ammonium hydroxide. Oxygen free water should be used and the mixing in an inert atmosphere. For the softwave product, the neutralizer described above in Table 4.4 for the ammonium thioglycolate wave can also be used.

4.11.2 Acid Waves

Acid waves are generally based on glycerolmonothioglycolate (GMT) although some bisulfite systems are also sold as acid waves. For a GMT wave, the waving

Table 4.6 Waving lotion for an acid wave based on GMT[a]

Ingredient	Percent
Part I	
Glycerol thioglycolate (GMT) (75%)	77.3
Glycerine (oxygen free dry glycerine)	22.7
Part II	
Urea	4.1
Neodol 91–8	1.0
Dodecyl benzene sulfonate	0.5
Triethanolamine	0.8
Potassium sorbate	0.35
Ammonium carbonate	0.2
Disodium EDTA	0.2
Water (oxygen free)	q.s.[b]

[a]The neutralizer described in Table 4.4 can also be used with this product
[b]q.s., add water to 100%

lotion itself consists of two parts because GMT is not stable for long periods of time in water.

To make the acid wave, for Part I of the waving lotion described in Table 4.6, add glycerol thioglycolate to glycerine (oxygen free) in an inert atmosphere taking the same precautions as described for the thiol wave. For Part II of the waving lotion, dissolve the sulfonate and the neodol in water; then add the remaining ingredients in the order listed in the formula. Immediately before application to the hair, mix parts I and part II of the waving lotions.

Other cold-wave formulations and related products are described by Gershon et al. [130], and by Flick [131, 132]. Product ingredient labels provide the most up-to-date qualitative information on these types of products.

4.11.3 Properties of Cold-Waved Hair

The chemical changes produced in hair by permanent waving, as indicated by amino acid analysis, are quantitatively small and do not reflect the vast structural changes that have taken place in the fibers during a permanent wave. Small decreases in cystine [53, 54, 133] and corresponding increases in cysteic acid [53, 54, 133] and in cysteine [53, 54] have been reported. Small quantities of mixed disulfide [133], sorbed thioglycolic [53], and dithiodiglycolic acids [133] have also been detected in hair that has undergone cold-waving treatments. Zahn et al. [134] also demonstrated small quantities of intermediate oxidation products of cystine in permanent-waved hair. For additional details of the chemical changes occurring in hair that has undergone permanent waving, see Chap. 2.

The wet tensile properties of hair are decreased by permanent waving. However, the dry tensile properties remain virtually unchanged; see Chap. 9 for

additional details. The torsional behavior of hair that has been permanent-waved is also changed. Bogaty [135] demonstrated that waved hair is more rigid in the dry state yet less rigid in the wet state than unwaved hair. Schwartz and Knowles [136] determined that the frictional resistance of human hair is increased by permanent waving providing evidence of changes (damage) in the cuticle of hair. Increased fiber friction results in more difficult combing of hair that has undergone permanent-wave treatment. For additional details on the changes in these properties, see Chap. 9.

The swelling capacity of permanent-waved hair increases in proportion to the damage rendered by the waving process [124]. Increased swelling is evidence of cuticle and cortical damage to hair. Greater swelling produces a substantial increase in the chemical reactivity of hair toward those reactions in which diffusion is rate-limiting. And since most of the whole-fiber chemical reactions that human hair undergoes are diffusion-controlled, permanent waving can markedly alter the chemical character of human scalp hair.

4.11.4   The Nature of the Cold-Wave Process

4.11.4.1   The Reduction Step

A very important factor in cold-waving hair on heads is the solution-to-hair ratio, which is limited by the capillary spaces between the fibers, and the amount of solution absorbed into the hair excluding solution runoff. Assuming a solution to hair ratio of 2:1 for a two-fold addition of reducing solution to hair, a 0.6 M mercaptan solution, and a favorable equilibrium constant (for thioglycolate at alkaline pH), there is insufficient mercaptan for total reduction of the disulfide bonds in hair. Randebrook and Eckert [137] and Reed et al. [138] suggested that only about 20% of the cystine in hair is reduced during an average thioglycolate permanent-wave treatment. Less reduction occurs for an average sulfite wave.

During the reduction step, a highly reduced zone proceeds into the cuticle and eventually into the outer regions of the cortex. This leaves an inner zone of unreduced hair. The relative quantities of reduced vs. unreduced fiber depend on the reducing agent (thioglycolate vs. sulfite), its concentration, the solution-to-hair ratio, pH of the reaction medium, time of reaction, fiber diameter, and the condition of the hair; variables which, for the most part, have already been considered in this Chapter. For another useful discussion of the waving process, see the article by Gershon et al. [130].

The relatively high cleavage of cystine residues and the resultant high concentration of cysteinyl residues produced from the reaction of thioglycolic acid or sulfite with hair and the physical stress from curling the fiber produce molecular reorientation that is facilitated by disulfide-mercaptan interchange. Reduction occurs in the high-sulfur regions of the fibers, i.e., the A layer and exocuticle of the cuticle and the matrix and intermediate filaments of the cortex, permitting

molecular reorientation and structural changes to occur in both the cuticle and cortex, as described in the section on setting and supercontraction. Molecular changes including reorientation in the intermediate filaments are believed to be very important to the cold wave process as suggested by Wortmann and Souren [3]. However, changes in the high disulfide regions of the cuticle are also involved as demonstrated by the relationship of fiber stiffness and the gradient of stiffness changes involved in the permanent wave process as shown by Wortmann and Kure [1, 2].

4.11.4.2   Rinsing

Cessation of the reduction reaction and removal of most of the reducing agent to minimize hair damage is the primary function of rinsing. The continued increase in swelling during the rinse by osmotic forces has already been described.

4.11.4.3   Creep Period

After rinsing, the hair is often wrapped in a towel and maintained in the desired configuration for a given period of time (up to 30 min). This step has been called the "creep period" and was introduced into the waving process in the early 1950s [139]. Continued molecular reorientation through disulfide-mercaptan interchange and secondary bond formation (other than covalent bond formation) occurs during this step. Since secondary bonds contribute to wave stability [140], this step is important to the total permanent-wave process.

4.11.4.4   Neutralization

Neutralization or re-oxidation is accomplished primarily through chemical means such as by mild oxidation for thioglycolate waves or mild oxidation or mild alkali for sulfite waves. Neutralization rapidly decreases the mercaptan content in the fibers, decreasing the probability of disulfide-mercaptan interchange, and thereby stabilizes the permanent wave.

4.12   Hair Straightening and Hair Straightener Products

4.12.1   Hair Straightener Compositions

During the past century, several different types of products have been used to straighten curly to kinky hair. In this discussion, we will consider five different types of products/processes used for this purpose.

Gums, resins or waxes are used to temporarily straighten the hair by plastering it down. These are generally very simple mixtures such as petrolatum and waxes or paraffins or even more complex waxes, gums or resinous ingredients with fragrances. Obviously, these products do not alter the hair chemically, and thus, are not permanent straighteners.

Hot combs and straightening irons have been widely used for straightening hair. In fact, some people actually iron their hair straight with a clothes iron. Straightening irons sometimes called crimping irons or curling irons generally are electrically heated crimping devices that open and are then clamped on the hair to remove or add curl. Oftentimes, petrolatum based oils called pressing oils are used in conjunction with the iron or the hot comb to lubricate the hair so the device can slide more easily through the hair and thus facilitate this process. These oils usually contain waxes and hair conditioners in a petrolatum base that is perfumed. This type of process produces only temporary straightening, functioning partly through cohesive and adhesive forces in a highly viscous system to help keep the fibers parallel.

Alkaline based straighteners, sometimes called chemical relaxers, are used primarily by men or by women with short hair and are the main permanent straightening products used today. Alkaline straighteners usually contain 1–10% sodium hydroxide, lithium hydroxide, calcium hydroxide or a combination of these alkaline ingredients or their salts. Alkaline straighteners are often sold as cremes containing conditioning ingredients such as stearic acid, cetyl and/or stearyl alcohol, mineral oil, etc. that thicken the product, see Table 4.7.

These alkaline hair relaxers are highly viscous creams. The high viscosity functions to help control run-off, because care must be taken to avoid contact with the eyes and minimize contact with the scalp to prevent alkaline burns. The hair should be washed prior to application. Product use instructions frequently recommend placing petrolatum along the hair-line and on the ears before application of the straightener. The product is then combed through the hair starting near the root ends, while combing away from the scalp. After processing, the hair is rinsed carefully under a running tap.

Table 4.7 An alkaline hair straightener[a]

Ingredient	Percent
Stearic acid	17
Oleic acid	3
Stearyl alcohol	2
Glycerine	5
Sodium hydroxide	9.5
Fragrance	0.5
Water	q.s.[b]

[a]Dissolve the alkali and glycerine in the water and then heat to 90°. Melt the stearyl alcohol and add it to the heated alkaline solution while stirring. Heat the acids to 95 and add to the aqueous emulsion while stirring. Cool and add the fragrance
[b]q.s., add water to 100%

4.12.2   Reactions of Hair Straighteners

The section of this Chapter entitled, *Side reactions during the reduction of keratin fibers with mercaptans*, summarizes the chemistry of the reactions of alkaline reagents with hair proteins. As indicated, alkalies react with cystine groups producing lanthionyl residues, a stable thioether crosslink. They also react with peptide bonds, hydrolytically cleaving this linkage, producing acid and amine groups. The reaction of alkaline species with amide groups of proteins produces acidic residues of aspartic and glutamic acids. Chemical hair straighteners and relaxers are among the top consumer complaint products including complaints dealing with hair breakage, hair damage and scalp burns. While many of these complaints are due to product misuse by either the consumer or a hair stylist, the incidence of complaints is still very high relative to other products.

Wong et al. [123] determined that alkaline hair straighteners provide the most permanent hair straightening. These authors examined ten different reagents for hair swelling, supercontraction and permanent hair straightening. They found that "permanent" straightening can be achieved only when the hair fiber has supercontracted more than 5%, see the data of Table 4.8. Furthermore, these scientists demonstrated that supercontracting agents like lithium chloride, which cause supercontraction with virtually no cystine reduction, can also produce permanent hair straightening. Therefore, they concluded that the molecular conformational changes that accompany supercontraction, e.g., part of which is the rearrangement of alpha-keratin to a less organized structure (see the Sect. 4.9) are more important to permanent hair straightening than the reduction reaction. Furthermore, this result also suggests that these molecular conformational changes are more important to this process than lanthionine formation.

The pH of alkaline straighteners varies from about 12 to above 13 and damage to the hair from these products is largely related to pH. Guanidine carbonate and calcium hydroxide are often used in combination in some products. A lithium hydroxide product with a pH as low as 12.8 can be made that is quite effective.

Table 4.8 Permanent straightening by several reagents and supercontraction

Composition	Straightening	Swelling	% Supercontraction
NaOH (1 N) pH 14	Permanent	>40%	5.7
NaOH (0.1 N) pH 13	Temporary	40%	0
THP (1 M) pH 8.5	Permanent	>50%	6
TGA (1.2 M) pH 9.6	Temporary	80%	2
LiCl (40%)	Permanent	60%	11.5
Boiling water	Permanent	>15%	6
DTT (0.8 M) pH 3.5	Temporary	>50%	0
Resorcinol (40%)	Permanent	>50%	10
Hot Press[a]	Temporary	–	0
Reduction/Hot Press[a]	Permanent	–	5–10

[a]Most of the above data is from Wong et al. [123] except for these two facts from the paper by Ogawa et al. [141]

Of course other additives are used to control the viscosity to make a safer and a more aesthetic product.

Wong et al. [123] demonstrated that for hair straightening, unlike permanent waving, the application of an external force is not necessary because the transitions that occur while the fiber is supercontracting provide sufficient stress to straighten the fiber. Furthermore, reducing solutions such as thioglycolic acid (TGA 1.2 M at pH 9.6) or dithiothreitol (DTT 0.8 M at pH 3.5) even though they cause extreme swelling (greater than 50% increase in diametric swelling) do not provide permanent hair straightening because they do not provide supercontraction beyond 2% (with the accompanying molecular rearrangements), see Table 4.8. Sodium hydroxide (1 N) can straighten hair in about 20 min but it takes more than 1 h to straighten hair with either LiCl or cuprammonium hydroxides, suggesting one reason for the superiority of sodium hydroxide to these other treatments.

Ogawa et al. [141], only a few years ago, provided additional insights into the mechanism of permanent hair straightening. These scientists demonstrated both by X-ray diffraction and high pressure differential scanning calorimetry that supercontraction of around 12.5% is accompanied by and is likely caused by the transformation of alpha-helical proteins to amorphous proteins (as explained by Wong et al., see Table 4.9). This irreversible molecular transformation stabilizes the straightened hair fiber providing permanence to hair straightening.

Ogawa et al. [141] confirmed the long known facts that reductive methods or hot irons when used separately provide only temporary hair straightening in which the hair will revert to its original curvature, or close to it, either by washing or on exposure to high humidity. However, these scientists demonstrated that by combining reducing solutions such as TGA or TGA/DTDG (dithiodiglycolic acid (DTDG)) followed by a hot press application immediately after the reduction that permanent straightening can be achieved. This is the basis for the process called Japanese hair straightening or Thermal Reconditioning. These scientists further demonstrated that this type of permanent straightening is also accompanied by the transformation of alpha-helical (crystalline) proteins to amorphous proteins. Thus, Thermal Reconditioning involves supercontraction of hair fibers (see Table 4.9).

Similar to Wong et al. [123], Ogawa and associates found 5–8% supercontraction as optimal for permanent straightening. With their reductive-hot press straightening systems, Ogawa et al. found that approximately 90% of the initial cystine content was retained in the straightened hair with about 10% additional cystine as cysteic acid, suggesting no lanthionine formation during this process. Lanthionine is formed from beta-elimination of cystine residues. Since cystine is

Table 4.9 Supercontraction and crystallinity of hair from Ogawa et al. [141]		Degree of crystallinity	Percent supercontraction
	Untreated hair	29%	0
	Treatment 1	16%	8.4
	Treatment 2	12.2	9.9
	Treatment 3	5.8	12.5

fully accounted for, lanthionine could not be formed during this process. Also, since the lysine content was essentially unchanged by this reaction, no lysino-alanine cross-links are formed during this process either.

As mentioned earlier, another type of hair straightener is based on a reducing agent without the use of hot irons. This type of straightener is related compositionally to permanent waves. These are thioglycolate and sulfite based hair straighteners. The chemistry for these products is essentially the same as for the permanent wave based thioglycolate and sulfite based products. However, compositionally these products do differ subtly from permanent waves. The reducing solution of a hair straightener is often called a relaxer solution rather than a waving lotion. In general, relaxer solutions of hair straighteners are more viscous compositions than permanent waving lotions and thus often contain thickening agents. These are usually creams that are thickened with polymers such as carbopol, e.g., carbopol 941, or glyceryl monostearate, stearic acid or long chain alcohols, see the formula in Table 4.10. The relaxer solution of thioglycolate straighteners is also slightly lower in pH usually 8.8–9.1 as compared to 9.2–9.6 for permanent waving lotions. For straightening with this type of composition it is necessary to comb the hair straight while the hair is in the reduced state.

An even lower pH product is based on sodium sulfite or even ammonium bisulfite. The pH of this latter product can be as low as 7.6. As one might expect, this type of product is not as effective at straightening very curly hair as the alkaline straighteners and it must be left on the hair for a longer period of time (as long as 50 min) to be effective.

The neutralizers of thiol reducing hair straighteners (Table 4.10) are similar to those of permanent wave products and are usually based on hydrogen peroxide or

Table 4.10 Thiol based hair relaxer solution for a hair straightener product[a]

Ingredient	Percent
Glyceryl monostearate	15.0
Stearic acid	3.0
Paraffin	1.0
Sodium lauryl sulfate	1.0
Thioglycolic acid	6.6
Ammonium hydroxide	20.0
Fragrance	1.0
Water	q.s.

[a]Solution 1: Stir the glyceryl monostearate, stearic acid, paraffin, and sodium lauryl sulfate with 35 parts water and heat to 95 , until the mixture is homogeneous and then quickly cool to 50°. Solution 2: Add the thioglycolic acid to the remaining water under an inert atmosphere and then add ammonium hydroxide while cooling making certain the temperature does not go above 50°. Slowly add the thioglycolate solution at 50° to solution 1. Make final pH adjustments with ammonium hydroxide to pH 9.0. Quickly cool to 40° and add the fragrance and then add water to 100%

sodium bromate. The sulfite based systems use either a similar oxidizing neutralizer or an alkaline system described earlier. The higher viscosity for hair straighteners is to facilitate holding the hair reasonably straight. However, to effectively straighten the hair with these products one must periodically comb and stretch the hair straight.

As indicated by the data of Table 4.8, the reductive type of hair straightener that does not employ hot irons does not provide supercontraction nor a loss of crystallinity. Therefore, it does not provide permanent hair straightening. In addition, this same redox chemistry when applied to a permanent wave provides more permanence for a wave than for hair straightening. The molecular rearrangements that produce permanent straightening and permanent waving (bending) involve some form of compressive forces on the fibers (supercontraction in bending) that either accompanies or facilitates the molecular rearrangements necessary for some permanent. Note that in reductive type straighteners extension or combing the hair is used and not bending as in a curl for waving and straightening is less permanent than waving.

4.12.3   Damage by Hair Straightening Products

The wax, resinous petrolatum type of hair straighteners do not alter the hair chemically and do not damage it. When used with lubricating oils, these products can help prevent damage to the hair. On the other hand, hot combs and straightening irons or curling irons are also temporary hair straightening or curling treatments, but these products can damage the hair [142]. Of course the reductive hair relaxer products also damage the hair and despite their advertising Japanese hair straightening also damages hair. However, the alkaline hair straightening products are the most damaging of all hair straightening products.

4.12.3.1   Damage by Heat Straightening

Thermal treatments have been shown to produce decomposition of tryptophan residues to kyneurenine type oxidation products, both thermally and via oxidation. In addition, thermally induced changes produce yellowing of white hair and bleached hair shows a slight darkening from thermally induced changes [142]. These color changes most likely arise from further oxidation of the above kyneurenine products. Furthermore, treatment of hair tresses either by a single or multiple treatments reveals a gradual increase in combing forces as a function of thermal exposure time.
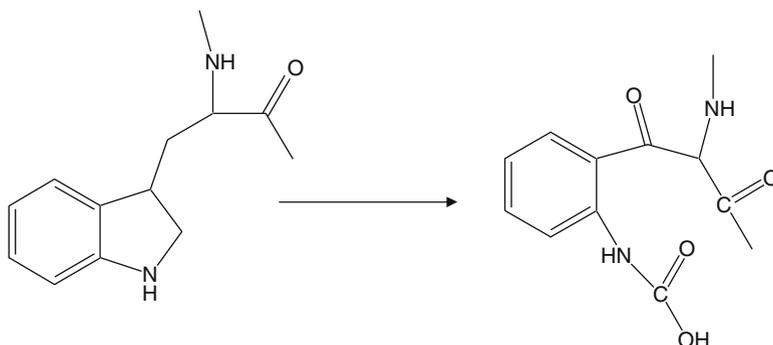
A tryptophan residue in hair   Opening of the tryptophan ring to a Kyneurenine product

Even though most of the thermal studies of hair have involved Caucasian hair or wool fiber [142–149] the chemical changes that occur on straight to wavy Caucasian hair or to curly to highly coiled African hair should be relatively similar. However, less degradation of tryptophan occurs with heavily pigmented hair vs. lightly pigmented hair of the same type [142]. This effect suggests a retardation of the thermal degradation of these chromophoric reaction products and a similarity to photochemical degradation of these same amino acid residues in hair. Furthermore, it suggests that thermal degradation of tryptophan likely involves free radical attack.

After thermal treatments, hair switches generally show a small decrease in combing forces [142]. However, after shampooing the combing forces are distinctly higher than for control hair. These effects were explained by thermal treatments that drive lipid material to the hair surface that is removed by shampooing, thus drying out the hair and unmasking surface damage to the fibers [142].

4.12.3.2 Damage by Reductive Hair Straighteners

Damage by reduction-oxidation type hair straighteners should produce damage similar to that of reduction-oxidation permanent wave products providing a decrease of about 5–20% in the wet tensile properties [150]. The chemistry of the reactions of permanent waves with hair involves reduction of disulfide bonds, followed by molecular shifting produced by stressing the hair on rollers followed by re-oxidation. The chemistry of reduction-oxidation hair straighteners is similar involving reduction of disulfide bonds and molecular shifting produced by stressing the hair by combing it straight followed by re-oxidation. One unanswered question is how much damage is done to the hair by combing it straight in the reduced state. The question involving a lack of permanence in straightening African American hair by a reduction-oxidation system was addressed in a previous part of this Chapter.

For the reduction step by this type of hair straightener, most of the commonly used reducing agents for hair have been used, the primary ones being TGA and sulfite. Albrecht and Wolfram [52] suggested that for low cleavage levels, sulfite is a more effective setting agent than thioglycolate, but at higher cleavage levels, thioglycolate is the most effective reducing g agent.

The pH of relaxer solutions of TGA hair straighteners is generally slightly lower (pH 8.8–9.1) than in permanent waving lotions (pH 9.2–9.6). Lower pH produces less disulfide cleavage and at low cleavage levels less hair damage results. So to minimize damage for this type of product sulfite is the preferred reducing agent. In addition, stressing the hair by combing it straight is a less controlled action than curling the hair on rollers. Therefore, considering only hair damage sulfite would be the preferred reducing agent.

The re-oxidation step with thiols usually involves mild oxidizing agents (sodium bromate or hydrogen peroxide) or when sulfite is the reducing agent, effective reformation of cystine can be achieved with alkaline solutions generally above pH 8, which reverses the sulfitolysis reaction below reforming cystine disulfide:

$$\text{K-S-S-K} + \text{M}_2\text{SO}_3 \rightleftharpoons \text{K-S-SO}_3 \text{ M} + \text{K-S}^{\cdot} \text{ M}^+$$

From the perspective of tensile damage, I would expect similar tensile damage from hair straightening and a permanent wave [150]. However, I would add the caution that more damage could be produced from "misuse" of the products and a lack of care during combing hair in the reduced state. I could not find any scientific literature that directly examines the tensile properties of African American hair treated with reduction-oxidation type hair straighteners. However, a reference by Kamath et al. [151] compared a reduction straightener without oxidation with an alkaline straightener and determined the fatiguing properties of the fibers showing greater damage to the African type hair from the alkaline straightener, see Table 4.11.

The hair used in this study was from a Black male age 31 and had never been treated with chemical or heat relaxers. After shampooing rinsing and drying, half of the fibers were treated with a commercial alkaline creme relaxer, stroking the product through the hair with the fingers for 20 min and then rinsing and shampooing. The other half of the fibers were treated with TGA using 5% thioglycolic acid at pH 9.3 for 20 min and then the hair was rinsed and shampooed.

Table 4.11 Damage to African American hair by an alkaline relaxer and a reduction relaxer [151]

% Failures during 0–500 cycles of fatiguing		
Treatment	10 g load	30 g load
Untreated	18	50
Alkali relaxed	58	60
TGA (air oxidized)	46	56

4.12.3.3 Damage Comparison Between a Reductive and Alkaline Hair Straightener

The hair used in this study was from a Black male age 31. It had never been treated with chemical or heat treatments. Both of these types of relaxers weaken the hair. During treatment with the alkaline straightener 8% of the fibers broke (during treatment), but for the TGA treatment zero fibers broke suggesting more damage by the alkaline straightener in spite of the fact that a chemical neutralizer was not used after the TGA treatment.

The fatiguing process involves attaching weights to the fibers and then dropping the weights repeatedly to stress the hair analogous to the way it might be stressed by continuous combing. The data shows the greatest distinction between untreated and treated fibers using the lower weights. Therefore this condition is probably the most meaningful indicator of damage to the hair. These data clearly show damage by both straightener treatments; however, greater damage is produced by the alkaline straightener providing 8% vs. 0% failures in the hair treated by the alkaline straightener vs. the reduction straightener simply by stroking the product through the hair and 58% failures vs. 46% failures by fatiguing the hair at the 10 g load see Table 4.11.

Other than the example described in Table 4.11, damage by alkaline straighteners is described only generally in the literature. Nevertheless, alkaline relaxers are among the top consumer complaint products because of hair breakage and alkaline burns. These products are combed through the hair starting near the root ends and combing away from the scalp. However, Wong et al. [123] demonstrated, permanent hair straightening is generally achieved without the application of an external force. So combing an alkaline straightener into the hair is mainly for even distribution of product throughout the hair and not for straightening of the hair per se. After processing, the hair is rinsed carefully with running tap water.

From a chemical perspective of hair damage, we understand what happens during alkaline hair straightening more than we understand the physical implications, however, we do know from the fatiguing experiment by Kamath et al. [151] (Table 4.11) that alkaline straightened African American hair is more brittle and it breaks more readily than un-straightened hair from that same source. We also know that supercontraction of 5–9% [123] occurs during alkaline hair straightening and that straightened hair fibers absorb dye more readily than controls [141], indicative of a more porous fiber and hair damage.

From a chemical perspective, we know that chemical changes occur in the protein regions of all hair structures as well as in the fatty acid regions of the cell membrane complex. Ionization of carboxylic acid and phenolic groups of the amino acid side chains also occurs producing a very negatively charged fiber surface. Alkaline hydrolysis of amide and peptide bonds and beta elimination of cystine are among the many chemical reactions that occur with alkaline hair straighteners. These collective actions allow the unfolding of alpha-helical chains (crystalline

proteins) and reorganization in the filamentous regions to less structured proteins. It would also appear that greater changes occur in the concave part of a curl than in the convex part to allow for permanent straightening to occur. The concave part of a curl being analogous to paracortical cells in wool fiber is higher in cystine rich proteins [152, 153] and contains more cross-links [152, 153] and a higher ratio of matrix to intermediate filaments [154–156]

Hydrolysis of ester and thioester groups of the cell membrane complex occurs at the high pH conditions of alkaline hair straighteners which provides for removal of 18-MEA from the hair surface [157] and weakening of CMC bonding between cuticle and cortical cells. Beyond the delipidation of the fiber surface, the creation of lanthionine residues and loss of crystallinity, few specific reactions have been reported for African type hair after treatment with alkaline straighteners. The lack of more information is most likely from a lack of study. For more on hair damage see the section in Chap. 10 on hair breakage.

4.12.4   Why Alkaline Hair Straighteners Are Permanent and Reductive Are Not But Reductives Provide Some Permanence for Curling

Thibaut et al. [158] studying hair from six persons of Caucasian, North African and African descent found that the hair described as straight had three types of cells arranged in a symmetrical annular arrangement. A core of paracortical type cells were generally surrounded by mesocortical with orthocortical type cells in the outer part of the cortex. However, for high curvature hair the cells were distributed asymmetrically with the orthocortical type cells predominately on the convex side of the curl and the paracortical type cells on the concave side, see Fig. 1.42. Bryson et al. [159] examined curved hair and straight hair from Japanese subjects and found four types of cells rather than three, but found similar distributions to those found by Thibaut et al.

As explained in the previous section, when alkaline straighteners act on curved hair fibers, they cleave disulfide and peptide bonds producing supercontraction of 8–10% and a decrease in crystallinity as shown by X-ray diffraction [141]. To straighten a curl, more contraction must be produced on the convex side of a curl than on the concave side. Therefore more contraction is produced in the paracortical type cells or those containing a higher concentration of cystine [152, 153] and a higher proportion of matrix to intermediate filaments [154–156]. The alkaline straightener also converts some cystine to lanthionine which creates an irreversible situation in that intermediate vicinity.

With a reductive type straightener, no contraction occurs but elongation is produced by combing the hair in the reduced state. However, with no contractive changes in the region of the intermediate filaments and no irreversible bonds being formed such as lanthionine, more mercaptan remains to provide reversible changes

through disulfide-mercaptan interchange. Therefore, permanent straightening is not achieved.

Now when we use the same reductive system to produce a curl there are a few important differences. First and foremost, the hair is relatively straight to begin with. Therefore the arrangement of cortical cell types are in an annular symmetrical fashion as in Fig. 1.42. Secondly, the action of the reducing agent is primarily on the orthocortical type cells which are in the outer regions of the cortex. The third important difference is that when a hair fiber is put into a curled configuration it is stretched on the convex side and compressed or contracted on the concave side of the curl. Apparently these differences, include simultaneous compression and extension as opposed to stretching alone. I conclude that compression allows for more extensive molecular rearrangements analogous to supercontraction to occur primarily in the orthocortical type cells which allows for some degree of permanence to the curvature change compared to similar but not identical changes in the straightening process.

4.13   Depilatories

Most depilatories are of the same basic chemistry as thiol permanent waves and hair straighteners, but are more reactive compositions. These products generally contain thioglycolic acid formulated at a higher pH from 11 to 12.5, and therefore produce a more rapid and more complete reduction of the hair with greater alkaline degradation. See the section described earlier in this Chapter entitled, *Side reactions during the reduction of hair with mercaptans* that describes the reaction of hair with alkaline reagents. More complete reduction with alkaline degradation helps to fulfill the purpose of a depilatory, i.e., to degrade the hair to the point that it can be removed or broken off easily by simply rubbing the area with a washcloth or other device.

Figure 4.1 illustrates the swelling effects of a calcium thioglycolate depilatory on hair. Figures 4.5, 4.6 and 4.7 depict damage induced to the cell membrane complex of different parts of the fiber by reductive treatments. Thus, strong alkaline-reductive treatments degrade the hair proteins to the point where many of these are solubilized in aqueous media.

A very large order swelling occurs with depilatories because of the almost complete reduction of disulfide bonds in the A-layer and the exocuticle of the cuticle and the matrix and intermediate filaments of the cortex and because of the alkaline degradation. The reaction of a depilatory with human hair can be followed nicely with optical microscopy by observing the large order swelling and the loss of birefringence that occurs through the moving boundary kinetics by observing the boundary as it moves rapidly from the periphery of the fiber to the core.

The composition described in Table 4.12 is a thiol type depilatory. This product can be made into either a cream or lotion by controlling the ratio of Part I to Part II. For higher viscosities, a higher ratio of Part I to Part II is used. To make this depilatory described in Table 4.12, disperse the ceteareth-20 into water (part II) by

Table 4.12 Depilatory cream/lotion

Ingredient	Percent
Part I	
Mineral oil	4.5
Ceteareth-20	2.5
Cetearyl alcohol	3.0
Part II	
Water (oxygen free)	q.s.[a]
Part III	
Sodium thioglycolate	3.5
Calcium thioglycolate	3.0
Calcium hydroxide	~1.5 (to pH 11.5)
Fragrance	<1.0

[a]q.s., add water to 100%

heating to 75 . Then add the cetearyl alcohol and mineral oil and continue heating and stirring for about 10 min Cool to 40° while stirring, then add the individual ingredients of Part III and homogenize. Similar precautions as described for the thiol wave such as the exclusion of oxygen and metals from the system must also be exercised for making a thiol depilatory.

Another popular depilatory is the wax type product. This depilatory is applied as a viscous liquid over the hair area to be removed. It is often warmed under the tap prior to application and applied in the direction of hair growth. The wax is sometimes covered with a paper-cloth oftentimes supplied with the product. The cloth adheres to the sticky wax composition on the skin and is pulled in the direction against the hair growth removing much of the sticky wax with the hair. This procedure is repeated until the desired area is depilated. The residual wax is then washed and peeled from the skin.

4.14   Safety Considerations for Permanent Waves

As for other reactive hair products, the primary safety concerns for permanent waves generally arise from misuse or failure to comply with the product's usage instructions. Skin irritation, hair breakage, oral toxicity, sensitization, and scarring alopecia either have been reported in the literature or are referred to in the warning instructions for home permanent-wave products.

A safety assessment of thioglycolic acid by the CTFA [160] summarizes safety data for thioglycolic acid, its salts and esters. Thioglycolates are moderately toxic yet comparable to bisulfite. Sodium thioglycolate has a LD_{50} of 148 mg/kg (i.p. in rats) [161] vs. 115 mg/kg (i.v. in rats) for sodium bisulfite [162].

Thioglycolate waving lotions can irritate skin [163]; however, irritation in home use is rare and may in part be related to the alkalinity of the system [164]. Among the different thioglycolate salts, monoethanolamine thioglycolate is reported to be less irritating to skin than ammonium thioglycolate [165].

Although ammonium thioglycolate has been reported as having a low sensitization potential [166], a few incidents of sensitization have been reported among hairdressers where contact is frequent [166].

Hair breakage and some permanent hair loss have been reported by Bergfeld [167] from misuse of these products, attributed to scarring alopecia. Bergfeld did not specify the extent of hair loss observed; however, he concludes that side effects from home permanent-waving products are minimal if consumers are aware of their hair damage and any inherent skin diseases and if they comply with the product usage instructions [167]. A more recent update on the safety assessment of thioglycolic acid its salts and esters has been published by Burnett et al. [168]. This report included assessment of ammonium thioglycolate, butyl thioglycolate, calcium thioglycolate, ethanolamine thioglycolate, ethyl thioglycolate, glyceryl thioglycolate, isooctyl thioglycolate, isopropyl thioglycolate, magnesium thioglycolate methyl thioglycolate, potassium thioglycolate, sodium thioglycolate and thioglycolic acid. The conclusions of this report are that thioglycolates can be skin irritants in animal and in vitro tests and can also be sensitizing. However, "clinically significant adverse reactions to these ingredients used in depilatories are not commonly seen". Thioglycolates are minimal to severe ocular irritants. They are not mutagenic and show no evidence of carcinogenicity. Similar safety concerns exist for the thiol based hair straighteners.

For alkaline hair relaxers, care must be taken to avoid contact with the scalp to prevent alkaline burns and hair breakage can result from misuse of these products also. Chemical hair straighteners and relaxers are among the top consumer complaint products including complaints of hair breakage, hair damage and scalp burns. While many of these complaints are due to product misuse by either the consumer or a hair stylist, the incidence of complaints are still very high relative to other products.

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