1966 Literature Award Acceptance Address

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The news that I was to be the recipient of the 1966 Literature Award of the SOCIETY OF COSMETIC CHEMISTS came as a great and very pleasant surprise, and I am deeply conscious of the honor which the Society has conferred upon me. Great as is my own delight, it would have given even greater pleasure to two old friends of mine, Mr. William and Hugh MacDonald, now deceased, who may be known to some of you as the founders of MacDonald steam waving. It was through them that I came to take an interest in permanent waving processes. Hugh MacDonald was a practicing hairdresser in Inverness, who enlisted the help of his brother, William, a graduate in mathematics of the University of Aberdeen, in the development of a steam-waving process shortly after the end of World War I. In this they were so successful that the manufacture of the machines was soon transferred to London, and showrooms were opened in Regent Street in the West End. By this time Mr. William had abandoned mathematics for a business career, but he satisfied his scientific interests by following the progress of research on human hair and related fibers, such as wool. Unknown to me, he was taking a special interest in our work on one of the finishing processes of the wool textile industry, because of its close similarity to his method of permanent waving.

The process is that of "blowing" or "decatizing," in which the scoured wool cloth is stretched to the desired width, dried, and then wound with a cotton wrapper onto a perforated roller through which steam is blown for a few minutes. Unlike stretched and dried cloth, which would return to its original width on being released in cold water, the stretched, dried, and *steamed* cloth does not, and the similarity to permanent waving is obvious. The chemical mechanism of the setting (fixation) process was investigated, and by 1933 it had been shown that the permanent set which strained wool fibers acquire in steam or boiling water is due to two consecutive intramolecular reactions: disulfide bond breakdown, which dissipates stress, followed by linkage rebuilding, which fixes the relaxed structure in the strained configuration. In the

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light of this knowledge, low-temperature setting was an obvious possibility, especially as the first of the reactions, disulfide bond breakdown, can be carried out so easily by a multitude of reagents at ordinary temperatures.

It was at this stage of the work that I first met the MacDonald brothers. They arrived at the University without warning, explained that, as makers of permanent waving machines, they had been interested in our work on high-temperature setting, and foresaw that we might develop low-temperature methods of setting. The advent of such methods would destroy their business as machine makers and they must, therefore, be the first to develop them. This was the beginning of a long period of collaboration, in which we were joined by Dr. N. H. Chamberlain, and by the end of 1934 the first patent applications for low-temperature permanent waving had been lodged in England. One of these was based on the use of reducing agents to promote disulfide bond breakdown, followed by treatment with oxidizing agents to reform disulfide bonds and thus fix the relaxed structure in its new configuration. This early emergence of processes for permanently waving hair in the cold is due principally to the remarkable foresight of William MacDonald, and it affords an excellent illustration of the advantages which accrue from having at least one person within an industry who is able and willing to take an interest in developments outside his own specialized field.

But this is not the only, or even the main, reason for the respect in which I hold the MacDonald brothers. What this is will be clear from the following experience. During the early part of their career as makers of permanent waving machines, they had made many friendships among professional hairdressers, who were intended to have the exclusive use of the new methods of cold permanent waving. The production of "home-perm" outfits was never contemplated, and it was only when what is now one of the largest producers of such outfits sought a license to use the processes, that the MacDonalds realized the full extent of the danger to which they had exposed the professional hairdresser. After some days' consideration, they informed the firm that they could not grant a license, although they realized that this could not prevent the marketing of home-perm outfits, since only the individual user could be charged with infringement, but it was impossible for them (the MacDonalds) to profit from what they then believed would be the distresses of their friends, the professional hairdressers. The matchless

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integrity which compelled so quixotic a rejection of riches will, I hope, excuse my devoting so much of this address to those friends of earlier days.

When the first of the cold permanent waving processes was invented, knowledge of the constitution and reactivity of keratin was still very primitive. It could be summarized in the statement that fibers like wool and hair consist of long, folded polypeptide chains with salt and cystine linkages between them. During the past 35 years, however, there have been great advances in understanding, based on the use of new techniques such as electron microscopy and chromatographic methods of amino-acid analysis, but without any fundamental changes in the methods of permanent waving. These are still based on reduction, followed by oxidation, and it is important to inquire why the new knowledge has found so little industrial application. For this purpose, different developments will be considered in turn.

AMINO-ACID ANALYSIS

The first complete amino-acid analyses of keratin became available in 1955 (1), but the knowledge was not as useful as was once expected, because earlier evidence that keratin is not homogeneous was reinforced by the results of electron microscope studies. The latter revealed the existence of ordered (crystalline) microfibrils embedded in a disordered (amorphous) matrix, and during the past decade much effort has been given to the fractionation of keratin, identification of the histological origin of the fractions, and to their amino-acid analysis. The most usual method of experiment has been to oxidize cystine cross linkages into cysteic acid side chains, to extract the oxidized keratin with dilute ammonia, and then fractionally precipitate the extracted proteins with acid. There is evidence to link the two main fractions with microfibrils and matrix, and some of the differences in composition are given in Table I (2).

The fact that the two fractions differ so greatly in content of cystine, lysine, and serine, all of which are now known to be involved in high-temperature setting reactions, is one of the reasons why early X-ray studies of fibers set at high temperatures showed such a difference in rate of response of the ordered and disordered regions. Because of this difference in rate of response, and also of rate of loss of set during relaxation in steam or boiling water, it became clear also that no exact understanding of the chemical mechanism of setting with different reagents could be obtained from dimensional changes alone. It was

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Table I

Fraction	Percentage of Total Nitrogen			
	Cysteic Acid	Lysine	Arginine	Serine
α-keratose (microfibrils)	3.72	4.60	20.8	6.70
β-keratose (matrix)	14.5	1.03	19.0	9.70

Astbury who stressed the need to supplement the measurement of dimensional changes by X-ray examination, his most striking evidence being that a supercontracted fiber might give a disordered β-photograph, the supercontraction in such a case being due to disorientation of β-crystallites and not to loss of set by transformation of β-keratin (set keratin) into α-keratin. So far as I am aware, corresponding X-ray and dimensional studies of fibers (a) set at low temperatures and (b) afterward relaxed in boiling water have not been made. This is unfortunate, because a clear understanding of the fate of both the crystalline and amorphous regions in low-temperature setting is essential as a basis for the development of improved processes.

AMINO-ACID SEQUENCE IN KERATIN FRACTIONS

The slow growth of fundamental knowledge, as well as delay in using what is available, is a more serious barrier to technical advance. All possible support should be given to determinations of the amino-acid sequence in the various fractions of keratin, because until this information is available there can be no constructive study of improved methods of cross-linking keratin, which must be the basis of improved methods of cold permanent waving. To see how imperfect is our present knowledge we need only ask why it has so far been impossible to set strained fibers with alkalies at low temperatures, using conditions which promote the formation of lanthionine cross linkages, when such setting is possible with potassium cyanide according to the following reaction scheme:

$$\mathrm{R{-}S{-}S{-}R + KCN \rightarrow R{-}SK + R{-}SCN \rightarrow R{-}S{-}R + KCNS}$$

It seems unlikely that the answer is connected with the fact, which has emerged from recent work on the amino-acid sequence in wool keratin (3), that certain of the peptide bonds are highly sensitive to attack by alkalis. This knowledge does, however, suggest that some advantage may be found in using neutral or mildly acidic linkage-rebuilding agents with reduced keratin in the conventional low-temperature permanent

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Table II

Reagent	Percentage Reduction in Resistance to 25% Extension in Water: Reduced Fibers	Reduced and Oxidized Fibers
Mesoxaldehyde	33.3	14.8
Dehydroascorbic acid	33.1	13.0
Pentan-2:3:4-trione	31.1	12.9
Cyclopentan-1:2:3-trione	31.1	−0.6

waving process. How effective these agents are will be seen from the results of Table II (4). The fibers were first reduced with thioglycollic acid (*M*) at pH 4.55 and 25 °C for twenty-four hours, washed overnight in running water, and then treated with a 2.5% solution of a vicinal tricarbonyl compound at 25 °C.

INTERNAL POLYMERIZATION

As a direct consequence of the lack of knowledge of the amino-acid sequence in the keratin proteins, and the difficulty of making a constructive attack on cross-linking problems, much attention has been given to the synthesis of polymers inside animal fibers as a means of modifying their properties. Many methods have been evolved, usually for use with vinyl compounds, but in the case of permanent waving they are commonly associated with two disadvantages, swelling of the fibers and a reduction in the affinity for water; both of which harm the feel. Hydrophilic polymers are clearly desirable, and it is interesting that an aqueous solution of reductone (10%), which is slightly acidic, polymerizes inside wool fibers at 25 °C without any assistant (4). Although the polymer is hydrophilic, the resistance of the fibers to 25% extension in water can be increased by as much as 54%. Compounds of this general type are likely to find important uses in modifying the properties of keratin, at least until the results of more systematic studies of cross linking become available.

SURFACE DEPOSITS OF POLYMER

More important than the formation of polymers inside keratin fibers at the present time, is the application of preformed polymers from solution to the surface of the fibers for the purpose of improving appearance and feel. Rapid systematic progress in this field is possible with the Stereoscan—the Cambridge scanning electron microscope. It cer-

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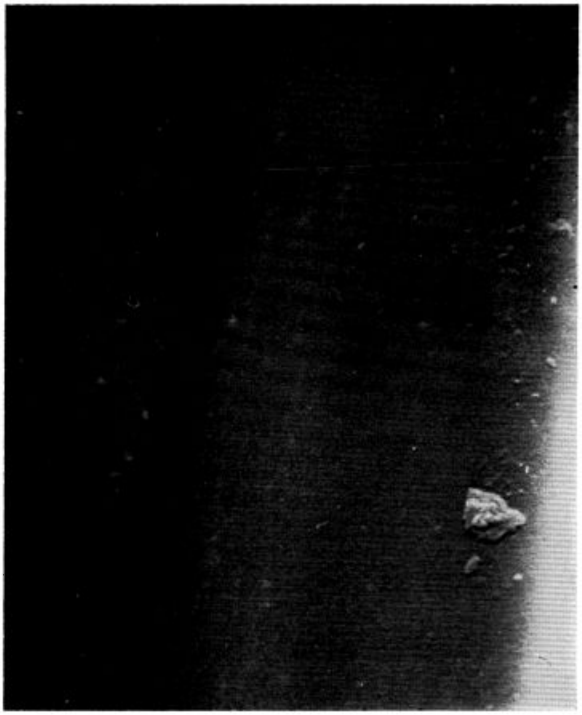

Figure 1. Electron micrograph of untreated cellulose acetate staple fiber.

tainly reveals some surprising facts, as the accompanying electron micrographs of cellulose acetate staple fiber show (5). The untreated fibers (Fig. 1) are smooth, but their feel is most unpleasant, whereas the treated fibers (Fig. 2) have a soft, vicuna-like feel in spite (perhaps, because) of the fact that the surface deposit of silicone is irregular. By means of the Stereoscan the extent to which feel is influenced by the nature and distribution of the deposit can be readily elucidated and the art transformed into an applied science.

HYDROPHOBIC SIDE-CHAINS

Proteins like zein, which are rich in hydrophobic side chains, are remarkable in being soluble in aqueous propanol. Although the complete amino-acid analyses of wool, which were obtained in 1955 (1), revealed the presence of a high proportion of acids with hydrophobic side chains, as shown in Table III, little use has been made of the information.

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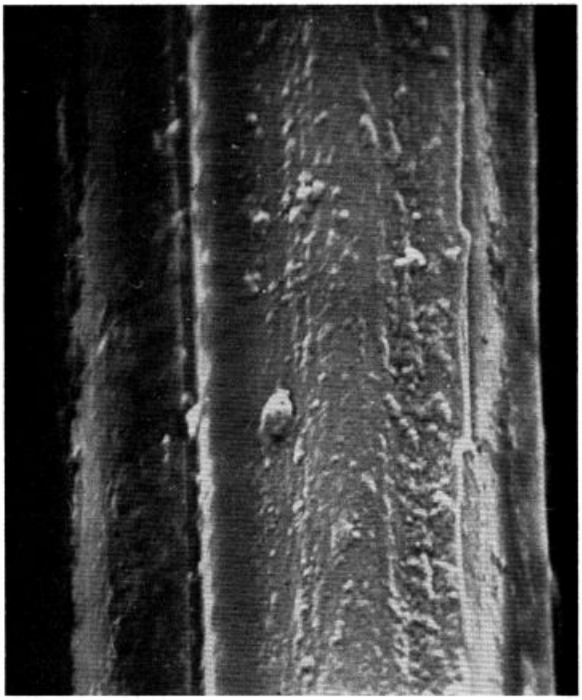

Figure 2. Electron micrograph of cellulose acetate staple fiber treated with a surface deposit of silicone

It was only in 1959 (6) that wool fibers were found to be *more* resistant to extension in water than in *n*-butanol saturated with water, and further study of the action of aqueous alcohols on wool and hair has since shown that the maximum weakening is given by an aqueous solution of *n*-propanol (45% w/w) (7). The weakening, which is associated with enhanced swelling, is clearly analogous to the dissolution of zein by aqueous propanol, and is presumably due to the action of the alcohol molecules in associating with the hydrophobic side chains of the fiber and reducing the cohesion between them. This unexpected behavior of aqueous alcohols has some bearing on solvent-assisted methods of dyeing keratin at low temperatures, and further work has revealed other new media for increasing the swelling and accessibility of wool and hair to different reagents (7). The available media cover a wide range of conditions: aqueous propanol (45% w/w) and aqueous formamide (89% w/w) are neutral, aqueous pyridine (54% w/w) is weakly alkaline (pH 8.3), and aqueous trichloroacetic acid, or, better, a solution of the acid in aqueous propanol (50% w/w) is acidic.

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Table III

Amino-Acid	64s Merino Wool (Nitrogen Content as a Percentage of Total Nitrogen in Wool)
Alanine	4.12
Valine	4.16
Leucine	5.85
iso-Leucine	2.44
Phenylalanine	2.12

With these additions to the list of available swelling agents for keratin, it should be possible to ensure access of almost any type of reagent to the fine structure under conditions that ensure optimum reactivity. Similarly, means are now available for introducing fatty and waxy substances into parts of the structure of animal fibers that have not hitherto been accessible, and thus ensuring their retention under the different conditions which prevail in, for example, subsequent washing. New methods of softening, tinting, and perfuming both intact and damaged fibers must now be expected to emerge from the systematic use of mixed solvents as media for the introduction of both inert and reactive compounds.

REFERENCES

(1) Simmonds, D. H., Variations in the amino acid composition of merino wool, *Proc. Int Wool Text. Res. Conference*, C 65-74 (1955); Corfield, M. C., and Robson, A., The amino acid composition of wool, *Biochem. J.*, **59**, 62–68 (1955).

(2) Corfield, M. C., Robson, A., and Skinner, B., The amino acid compositions of three fractions from oxidised wool, *Biochem. J.*, **68**, 348–52 (1958).

(3) Cassie, A. B. D., Wool Industries Research Association, Leeds University, private communication.

(4) Holker, J. R., The action of reductone on wool, Ph.D. Thesis, Leeds University (1956).

(5) Kindly supplied by Dr. J. Sikorski, Textile Physics Laboratory, Leeds University.

(6) Atkinson, J. C., Filson, A., and Speakman, J. B., Action of mixed solvents on wool, *Nature*, **184**, 444 (1959).

(7) Atkinson, J. C., and Speakman, J. B., The action of mixed solvents on wool, *J. Textile Inst.*, **55**, T433–47 (1964).

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