ponding *n*-butyl derivative (pale liquid; Hg: found, 44.9 per cent; calc. $(C_{13}H_{18}O.SHg)$, 45.7 per cent) were obtained in practically quantitative yields from ethylmercuribromide, sodium hydroxide and the thiosalicylic esters. Both compounds are insoluble in water but readily soluble in lipid solvents, an obvious advantage when applying the materials to paints and lacquers; moreover, the methyl ester can be obtained in a pure condition much more conveniently than the sodium salt.

The action mechanism of the sodium salt as a fungistatic and fungicidal agent is uncertain. It has been proved to act at a distance, but it is improbable that a sodium salt of this configuration would possess a significant vapour pressure. Kharasch has pointed out that aqueous solutions of the sodium salt tend to break down to ethylmercurihydroxide (III) and sodium thiosalicylate, the latter, in the presence of oxygen, passing irreversibly to the dithiosalicylate (IV). Thus the access of water vapour, providing conditions for fungal growth, might also favour a similar breakdown of the lacquer-incorporated mercurial, or even further to more volatile substances.

¹ Scientific Liaison Bureau, Australia. "Report on the condition of Service Material under tropical conditions in New Guinea."—Restricted—October 21, 1943.

² Scientific Instrument and Optical Panel, Ministry of Munitions, Australia. "The Tropic Proofing of Optical Instruments, Part I", July 1944.

³ O.S.R.D. Reports, U.S.A., No. 1833, July 1943, No. 4188, September 1944.

⁴ Reports of Optical Instruments Panel of Conference on Tropic Proofing, Controller of Chemical Research and Development, Ministry of Supply, Great Britain, papers issued under MG/OPT.

⁵ Hutchinson, W. G., in O.S.R.D. Report, No. 1833, July 1943.

⁶ Campbell, Major I. G., "Fungi in Optical Instruments under Tropical Conditions, and Possible Control", D.M.E. War Office, Great Britain, December 1944.

Simmons, R. T., and Woods, E. F., *Austr. J. Sci.*, **8**, 108 (1946).

⁸ Kharasch, M. S., U.S.P., **1**, 672, 615 (1928).

⁹ Waldo, J. *Amer. Chem. Soc.*, **53**, 993 (1931).

Comments by Dr. J. W. J. Fay, Ministry of Supply

I AM glad to have seen these two interesting papers, and take the opportunity of offering the following comments on British experience.

Two factors have militated against the use in Britain of M.T.S. on other than an experimental scale.

First, in the design of new instruments, or the modification of old types, the tendency has throughout been towards the improvement of sealing and of packaging. This, coupled with the use, if necessary, of a desiccating agent, is considered the ideal at which to aim, since the need of a fungicide is eliminated.

Secondly, in connexion with the protection of old instruments, including ex-civilian surrendered types of unknown history, the incorporation of volatile fungicides was not without its dangers. Thus, various substances tried gave rise to such troubles as softening of cements, corrosion and filming. Nevertheless, the need for a suitable fungicide was recognized and many were tested.

Among these, M.T.S., of which the vapour pressure is extremely low, was found to depend for its action upon a decomposition in the presence of moisture, giving rise to a volatile mercury compound which is presumably the active agent. The decomposition was found to be accompanied by a corrosion danger, and in the lacquers we have used this danger has not yet been overcome. We are, however, now awaiting samples of Australian lacquer for test.

In general, therefore, even in the case of old-type instruments, our attitude has been to improve sealing and methods of servicing, packing and storing, and the tendency is in any case to regard the incorporation of a desiccant as preferable to the use of fungicides.

With reference to the New Guinea experiments, we have had the opportunity of examining a few of the instruments tested, and our view is that while the results afford evidence of the superiority of the new complete Australian 'tropical treated' method over the old one, it is not entirely clear, in the absence of true controls, how much of the improvement is to be ascribed to the use of M.T.S. For this reason, we shall look forward with great interest to the results of the long-term New Britain experiments in which rigid controls are apparently included.

FIBROUS PROTEINS

BOTH the man of science and the technologist are greatly indebted to the Society of Dyers and Colourists for its enterprise in organising a symposium on fibrous proteins so soon after the end of the War. The meetings were held at the University of Leeds during May 23–25, and among the three hundred in attendance were visitors from Australia, Belgium, France, Holland, Norway, Sweden and the United States. Full details of the proceedings will appear in a volume which is to be issued shortly by the Society. Some thirty papers were read and discussed: they covered subjects ranging from the structure of protein molecules to the production of synthetic protein fibres; from the thermodynamics of water adsorption by proteins to the production of an unshrinkable finish on wool. No distinction could be drawn between science and technology, for new methods of examining the structure of wool and silk were shown to give results with a profound bearing on recent hypotheses concerning the structure of protein molecules in general, and technological advances were found to be the direct outcome of a clearer understanding of the nature of the proteins.

Our present conception of the structure of protein molecules is based to a large extent on the results of X-ray analysis in the hands of Prof. W. T. Astbury and his collaborators. In their view, proteins of the keratin-myosin-epidermis-fibrinogen group are characterized by long-range elasticity and the reversible α – β intramolecular transformation. When wool fibres are steamed for two minutes at 50 per cent extension, they contract to a length 30 per cent less than the original length on release in steam. Supercontraction of this type has been referred by Astbury to more severe folding of the polypeptide chains than in the case of α -keratin. Dr. K. M. Rudall pointed out at the time when this hypothesis was advanced that folding of this type should be revealed by a cross- β pattern on examination by X-ray methods. A cross- β pattern had been obtained by Astbury in work on the denaturation of egg-white in boiling water, and has since been observed in a number of other cases.

In his paper on the structure of epidermal protein, Rudall showed that a cross- β pattern could be obtained with strips of cow's lip epidermis which had been supercontracted in water at 100° C. Similar behaviour was observed with films of the protein extracted from the epidermis with 50 per

cent urea. The most striking of Rudall's observations was, however, the demonstration that the cross- β pattern of supercontracted epidermis and epidermin disappeared and was replaced by a normal α -pattern when the protein was treated with 50 per cent urea. This at once prompted Rudall to examine the effect of 50 per cent urea on steam-set β -keratin. Cotswold wool stretched 70 per cent and set in boiling water for five minutes showed a complete return of the α -photograph after forty-eight hours in saturated urea. The return was less complete with fibres which had been steamed for thirty minutes at 60 per cent extension; but Rudall was led to inquire whether the setting of β -proteins is not mainly a process whereby the chains are locked by close fitting in the backbone direction. Both Prof. J. B. Speakman and Mr. H. J. Woods pointed out, however, that the set released by saturated urea was probably simply temporary set, that is, the set which disappears when the fibres are released in steam. According to Speakman, true permanent set is due to disulphide bond hydrolysis, which permits relaxation, followed by linkage rebuilding, through the combination of basic side chains with the products of hydrolysis of the disulphide linkages, which gives, stability to the relaxed structure. Further support to the structure is, of course, afforded by hydrogen bonding between the main peptide chains, but true permanent set was believed to be impossible without the formation of new cross-linkages between the peptide chains.

Curiously enough, Dr. H. Phillips, in his paper on the division of the combined cystine in wool into four sub-fractions of differing chemical reactivity, was led, on different grounds, to make the same suggestion that permanent set is due to hydrogen bonding between the main chains of the relaxed fibre. Phillips's reason for making this suggestion was a doubt whether disulphide bond hydrolysis could take place in the very short time of steaming necessary to relax the extended fibre. It seemed to him much more likely that the weaker hydrogen bonds of the extended fibre are broken by the initial steaming and re-form slowly in the relaxed fibre. Against this view it was pointed out that stretched fibres could not be set by immersion in concentrated solutions of weak acids which eliminate hydrogen bonding between the main peptide chains, followed by washing and drying to permit re-formation of hydrogen bonds.

The special problems involved in the structure analysis of high polymers by X-ray methods were discussed by Dr. I. MacArthur in a paper which included an exhaustive summary of recent developments in experimental technique. Data of great value in supplementing the results of X-ray analysis are likely to be obtained by Dr. A. J. P. Martin's methods of examining partial hydrolysates of proteins. He outlined the results so far obtained in an examination of a partial hydrolysate of wool, with an average chain length of a little more than two units, by ionophoresis and partition chromatography. Up to the present, only that fraction of the hydrolysate which moves towards the anode in ionophoresis has been examined; but the results are of far-reaching importance. Seventeen dipeptides involving aspartic and glutamic acids were isolated and identified, and Martin argued that the existence of so many dipeptides is sufficient to disprove Bergmann and Niemann's view that "the radicals of each sort of amino-acid occur at regular intervals in the peptide chain . . . the intervals being of the form 2^*3^* places". Further, as regards Astbury's view that the amino-acids in the

polypeptide chains of keratin are alternately polar and non-polar, he concluded that the hypothesis cannot be correct because he succeeded in isolating from the partial hydrolysate a number of polar-polar dipeptides, including aspartyl glutamic, glutamyl glutamic, seryl aspartic, seryl glutamic and tyrosyl glutamic acids.

During the course of the subsequent discussion, Prof. Astbury replied that his proposal was that polar and non-polar residues *for the most part* follow one another alternately; wool is not necessarily a single protein, and room for the occurrence of polar-polar dipeptides is thus provided. Martin was, however, unable to accept even the suggestion that polar and non-polar residues follow one another alternately *for the most part* because, although he had no quantitative data, the individual dipeptide of the polar-polar type was not notably weaker than that of the polar non-polar or non-polar polar types. In fact, glutamyl glutamic acid "was one of the strongest present". Before any final conclusions can be drawn, however, data for the neutral and positive fractions of the partial hydrolysate must be obtained.

The Bergmann-Niemann hypothesis was also discussed by Dr. D. Coleman and Dr. F. O. Howitt in a paper on the structure of silk fibroin. They have found that silk can be brought into solution by means of cupri-ethylene diamine, each combined copper atom being co-ordinated with the nitrogen atoms of two adjacent amino-acid residues. When the solution is neutralized with acetic acid and dialysed until free from copper, a clear solution of fibroin is obtained. The mean molecular weight of the dissolved protein was about 30,000, but, on digestion with trypsin, a substance having a mean molecular weight of 8,000-10,000 separated out. This substance was free from proline and contained less than 1 per cent tyrosine. The Bergmann-Niemann hypothesis, however, requires that, of the 420-430 amino-acid residues in the silk molecule, the four proline and the twenty or so tyrosine residues are regularly spaced along the chain. Since the product of tryptic digestion is composed of molecules which are about one third the length of the parent molecule and contain no proline and very little tyrosine, it is obvious that the Bergmann-Niemann hypothesis is invalid for silk fibroin. All or most of the tyrosine residues and all the proline residues appear to be situated at points roughly one third and two thirds along the length of the molecule from one end.

Closely related to the work of Coleman and Howitt is that of Dr. C. S. Whewell and Mr. H. J. Woods, who found that roughly one atom of copper is associated with every two amino-acid residues when wool is treated with a solution of cuprammonium hydroxide. The wool does not, however, pass into solution, presumably because the main peptide chains are cross-linked by cystine. Instead, the fibres contract 26 per cent with progressive weakening of the α -photograph, which returns when the fibres resume their original length on removal of copper with sulphuric acid. Supercontraction appears to be due to additional folding of the main peptide chains, brought about by co-ordination of copper with neighbouring nitrogen atoms in the chains.

In the case of fibroin, solubilization by means of cupri-ethylene diamine is due to separation of chains in the β -configuration through hydrogen bond breakdown, when the nitrogen atoms of neighbouring amino-acid residues are co-ordinated with copper

atoms, followed by folding of the molecules at the points rich in proline and tyrosine. In agreement with this view, films prepared from the dissolved protein were found to be capable of extension to three or four times their original length. Further, whereas the original film was water-soluble, the stretched film was insoluble in water. These observations lend considerable support to Astbury's conception of a common structural pattern for all proteins, for fibroin appears to be an ideal example of denaturation, and Coleman and Howitt have succeeded in converting it into the globular form, and from the globular form into the fibrous form. Hitherto, in fibre technology, it has merely been possible to convert globular proteins, such as casein, arachin and egg albumin, into the fibrous form.

Various aspects of the production of fibres from globular proteins were discussed by a number of speakers. The optimum conditions for extracting protein from groundnuts and soya beans were defined in a paper by Mr. R. H. K. Thomson, but fibres spun from solutions obtained under such conditions are weak and highly extensible in water, even after hardening with formaldehyde. As indicated by Dr. M. Harris and Dr. E. Brown in their comparison of natural and synthetic protein fibres, more effective cross-linking of the main peptide chains in the latter is a pressing need. The problem was discussed by Dr. F. Happey and Dr. R. L. Wormell, who showed that the strength of casein fibre could be increased by after-treatment with basic zinc chloride and formaldehyde, owing to the formation of metal-containing cross-linkages. Even then, however, the rate of dyeing of casein fibre with acid dyes is much greater than that of wool, as indicated by Mr. C. P. Tattersfield. In practice, accurate control over the degree of cross-linking of the casein is essential, and Dr. L. Maaskant, in an interesting paper, showed how the surface film technique could be used for this purpose. The orientation of macromolecules by interfaces was also discussed by Dr. D. J. Crisp.

One of the most interesting features of the symposium was the discussion on the mechanism of water adsorption by proteins. Dr. G. A. Gilbert criticized the three theories at present in use for describing the adsorption of water by textile fibres, namely, those of Peirce, Cassie, and Brunauer, Emmett and Teller. Cassie's theory is a modification of that of Brunauer, Emmett and Teller, and its nature and consequences were summarized by the author. After discussing the effect of swelling on the sorption isotherm he proceeded to derive a stress-free isotherm. From an analysis of the latter he concluded that the water-attracting groups in keratin are —CO— groups. Objection to the view that the multilayer of water is under very great pressure was taken by Gilbert, and Dr. P. H. Hermans believed that "the entire theoretical reasoning in Dr. Cassie's paper supports the solution theory". Dr. R. M. Barrer thought it doubtful whether the model on which the Brunauer, Emmett and Teller isotherm is based can be applied to compact, non-porous sorbing media such as wool, and he outlined an alternative theory based on (a) an initial, rather energetic, sorption of water molecules upon a finite number of localized sites obeying the Langmuir type of sorption, and (b) a simultaneous and independent process of sorption by mixing of water and polymer chains. Opinion seemed strongly in favour of this conception, the elaboration of which will be awaited with interest. It has an important bearing on the attempts which have been made to determine

the 'free' and 'bound' water in proteins, a problem which was discussed by Dr. H. Eilers and Dr. J. W. A. Labout in connexion with hides and the processes of leather manufacture.

Turning now to technological processes, a number of papers were concerned with the dyeing of textile fibres. Dr. B. Nilssen discussed the formation of strongly coloured complexes when tyrosine-containing fibres are treated with nitrites and metallic salts. As regards the usual methods of dyeing, Dr. R. M. Barrer believed that the art has outstripped its scientific foundation, and he laid the foundation for a fundamental study of the kinetics of dyeing by deriving four differential equations to describe the non-steady state of flow. Methods of obtaining the diffusion coefficient from each of these equations were indicated, and procedures for determining the activity of the sorbed molecules were described. The application of these methods to the study of dyeing processes is likely to bring about a marked improvement in our understanding of their nature.

The combination of wool with acids and acid dyes was also discussed by Prof. J. B. Speakman and Dr. G. H. Elliott, chief attention being given to the apparent conflict between the chemical and X-ray evidence concerning the mode of combination of colour acids with wool. The nature of the conflict is best illustrated by taking the case of Coomassie Milling Scarlet G. The combining capacity of wool for the colour acid is the same as for hydrochloric acid, suggesting that all the free amino groups of wool are accessible to the colour acid. X-ray examination of the dyed fibres by Dr. I. MacArthur, however, revealed no distortion of the normal α -photograph, suggesting that the dye anions had not penetrated the crystalline phase, though penetration of hydrogen ions was indicated by its impaired setting properties. The authors suggested that the two sets of observations could be reconciled if hydrogen ions were to penetrate the micelles and leave an equivalent number of dye anions on their surfaces. A safeguard against the development of an excessive potential is provided by micellar subdivision and by the electron mobility of the protein molecule itself.

The properties of damaged wools were discussed by Dr. D. R. Lemin and Dr. T. Vickerstaff, normal wool being compared with chlorinated, peroxide-treated, alkali-treated and carbonized wools. After establishing the isoionic points of the wools, they determined their titration curves with hydrochloric acid and their affinities for Naphthalene Orange G, but the differences in affinity for the dye were small. Analysis of the hydrochloric acid titration curve led the authors to suggest the presence of two types of carboxyl group in the fibre, but objection to the mathematical treatment was made by Mr. L. Peters. As regards the combination of wool with acid and determinations of the isoelectric point, he emphasized that much confusion would be avoided if attention were given to the internal pH of the fibre and not, as is usual, to the pH of the solution with which it is in equilibrium. Using the Donnan theory of membrane equilibrium, he was able to show that a single curve will describe the titration of wool with solutions of hydrochloric acid containing sodium chloride in all concentrations up to 1.0M. Similarly, Dr. T. H. Morton, in a paper on the equilibrium between silk and aqueous solutions, stressed the importance of the internal pH value of silk whenever its chemical reactivity is being studied.

Considerable attention was also given to processes for making wool textile materials unshrinkable, that is, for preventing the kind of shrinkage which wool fabrics, as distinct from those composed of cotton or rayon, undergo when they are rubbed in aqueous media. Shrinkage of this kind is due primarily to the surface scale structure of wool fibres. The scales function as a ratchet and cause the fibres to migrate under pressure in the direction of their root ends, thus consolidating the structure. Shrinkage can be prevented by treating the wool with gaseous chlorine or chlorine water, which leads to the formation of a gelatinous degradation product of keratin on or under the scales of the fibres. According to Speakman, the essential reaction in the chlorination process is disulphide bond breakdown in the surface layers of the fibre, and it is interesting that most present-day processes, which were exhaustively reviewed by Mr. M. Freney, are based on the use of reagents such as chlorine, sulphuryl chloride and sodium hydroxide, which are known to be capable of causing disulphide bond breakdown. Further support for this view was provided by Dr. R. F. Hudson and Dr. P. Alexander, who showed that when wool is made unshrinkable with fluorine, sulphur is removed as the volatile hexafluoride. Dr. Alexander also found that wool could be made unshrinkable by treatment for only fifteen seconds in a 0.5 per cent solution of potassium

permanganate in 0.5N sulphuric acid. Curiously enough, the treated material shrinks on being worked in acid solution, although it is unshrinkable in soap solution, possibly because of the greater swelling of the degraded protein in alkali.

In recent years, several new methods of making wool fabrics unshrinkable have been proposed. Instead of attacking the surface scale structure of the fibres, their elastic properties are modified. One such method, which was described by Dr. J. R. Dudley and Dr. J. E. Lynn, consists in impregnating the fabric with a solution of methylated methylol melamines and an acid catalyst, drying, and baking at 285° F. A high degree of unshrinkability is obtained with 10 per cent of polymer within the fibres. Alternatively, the elastic properties of the fibres can be altered by increasing the number of cross-linkages between the peptide chains, and the advantage of these new processes is that the weight and wear-resistance of the fabrics are increased. Even better results, as regards wear-resistance, are obtained when anchored films of polymer are formed on the surface of the fibres, unshrinkability being obtained in this case by masking of the scales. In the light of these and other developments there can be little doubt that polymerization reactions will continue to find extensive applications in the textile industries.

J. B. SPEAKMAN

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NEWS and VIEWS

Imperial College of Tropical Agriculture :

Mr. O. T. Faulkner, C.M.G.

MR. O. T. FAULKNER has just retired from Trinidad, where he occupied the post of principal of the Imperial College of Tropical Agriculture since September 1938. He had only been in charge for a year when war broke out. It fell to his lot, therefore, to administer the College during a period of exceeding difficulty, and all schemes for development and progress had perforce to be kept in abeyance. That he has been able to keep the Institution alive as a going concern and in a fit state to tackle future developments is all the more to his credit. For it must be remembered that the College is perhaps unique in that its governing body, from which its policy emanates, is four thousand miles away. In peace-time, this alone presents certain problems; but during a war, when all communications are liable to be upset and personal visits are prohibited owing to transport dislocations, the difficulties are greatly increased. On the academic side, one of the main problems was to arrange for the lecture courses, as students were liable to arrive at all sorts of times owing to shipping difficulties. Further problems arose when, after the Cambridge School of Agriculture closed early on in the War, it was decided to send the Colonial Office agricultural scholars to Trinidad for two years instead of the customary one. With no additional personnel and a depleted staff long overdue for leave in a temperate climate, it can readily be imagined that the problem was not an easy one. In spite of this, and of the difficult economic and social problems in Trinidad caused by war conditions, the new duties were cheerfully accepted.

On the research side an immense amount has been done by Faulkner and his staff in planning for the future and in continuing existing lines of work.

Although the report of the 1939 Royal Commission on the West Indies was not published in full until after the War ended, its recommendations to make the College the centre of research for all the Caribbean Colonies were examined in detail in conjunction with the Comptroller of Development and Welfare and his staff. Now after long discussion, a definite plan for the development of the College with greatly increased duties on the research side and wider contacts with other scientific and academic institutions has finally been achieved, and Mr. Faulkner will be able to retire with the full knowledge and satisfaction that all his labour and careful thought during the war years will not have been in vain.

Physics in the University of Dublin : Dr. E. T. S. Walton

THE appointment of Dr. E. T. S. Walton to the Erasmus Smith professorship of natural and experimental philosophy in the University of Dublin, in succession to Prof. R. W. Ditchburn, will be welcomed by all those who know Dr. Walton's work. Dr. Walton joined the Cavendish Laboratory as a research student in 1927, after a good experimental record in classical physics at Trinity College. Rutherford suggested that he should investigate the possibility of a new method of accelerating electrons, by spinning them in the circular electric field surrounding a changing magnetic field—the method which was later to be developed into the betatron. Walton first investigated theoretically the conditions for stable orbits in the system and obtained two of the well-known betatron stability equations—the flux condition and the radial field variation condition. He built an apparatus in which the induction field was obtained by discharging a condenser through a coil wrapped round an evacuated glass tube of about