https://theses.gla.ac.uk/

Theses Digitisation:

https://www.gla.ac.uk/myglasgow/research/enlighten/theses/digitisation/

This is a digitised version of the original print thesis.

Copyright and moral rights for this work are retained by the author

A copy can be downloaded for personal non-commercial research or study, without prior permission or charge

This work cannot be reproduced or quoted extensively from without first obtaining permission in writing from the author

The content must not be changed in any way or sold commercially in any format or medium without the formal permission of the author

When referring to this work, full bibliographic details including the author, title, awarding institution and date of the thesis must be given

Enlighten: Theses
https://theses.gla.ac.uk/
research-enlighten@glasgow.ac.uk

MODIFICATION OF SOME PHYSICAL PROPERTIES OF WOOL BY FINISHING PROCESSES INVOLVING REDUCTION.

T H E S I S

presented to

the UNIVERSITY OF GLASGOW

for the degree of

DOCTOR OF PHILOSOPHY

by

Pravin J. Shah

Fibre Science Research Laboratory,
The University of Strathclyde,
(formerly the Royal College of Science and Technology),
GLASGOW.

December, 1964.

ProQuest Number: 10645988

All rights reserved

INFORMATION TO ALL USERS
The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript
and there are missing pages, these will be noted. Also, if material had to be removed,
a note will indicate the deletion.

ProQuest 10645988

Published by ProQuest LLC (2017). Copyright of the Dissertation is held by the Author.

All rights reserved.
This work is protected against unauthorized copying under Title 17, United States Code
Microform Edition © ProQuest LLC.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

S U M M A R Y

The effects on dyed woollen material of permanent pleating processes such as the sodium bisulphite (Immacula), the ammonium thioglycollate (Siroset) and the urea-bisulphite have been investigated. By exposing the material to various conditions e.g. during a sea voyage, has been assessed and some dyes have been found to be sensitive to the presence of reducing agents. In light-fastness tests an ever wider range of dyes has been found to be sensitive.

A comparative study of some mechanical properties of the woollen materials treated with reducing agents and steamed for various intervals of time, ranging from 20 to 120 seconds, has been made and a relationship has been found between the percentage swelling and the tensile strength of the treated material. A considerable loss in the tensile strength has been found in the case of yarn given the urea-bisulphite treatment. The crease-retention of the material stored under various humidity conditions has been studied and found to vary very little.

Optical and electron microscope investigations have been made on the wool which has been given the above treatments and the investigations have been further

extended to the fibres treated with urea-reducer solutions under various conditions of concentration, pH, time and temperature. Different staining methods have been employed to differentiate between the ortho- and the para-cortex of the fibres. The results are discussed in relation to the histological location in the fibre of the action of these reagents. There is an evidence that in merino wool fibres having a bilateral cortical structure, under the condition of neutral pH, the urea-reducer solution attacks the cuticle around the ortho-cortex, first dissolving ~~beginning at~~ the outer layer of the exocuticle and, within the fibre, dissolves material only from the ortho- cortex.

C O N T E N T S

Page

CHAPTER III

CHAPTER IV.

A C K N O W L E D G E M E N T S

I am indebted to Professor R. Meredith for providing the opportunity and facilities for this work, to Dr. N. Peacock for his keen interest and guidance throughout this work. To all my colleagues, past and present, in the Textile Technology Department, my thanks are due for friendly co-operation at all times.

I should also like to thank Dr. C.H. Giles of Chemical Technology Department for the use of the centrifuge and the mercury vapour lamp, to Miss H. Laird of Food Science Department for her co-operation in using the ultra-microtome and to Dr. C. Weaver and Mr. J. MacKay of Natural Philosophy Department for making the electron microscopical examinations.

I wish to express my gratitude to I.C.I. Ltd. for supplying N-butylmethacrylate and the dyestuffs used in this work.

A B S T R A C T.

The effects on dyed woollen material of permanent pleating processes such as the sodium bisulphite (Immacula), the ammonium thioglycollate (Siroset) and the urea-bisulphite have been investigated. By exposing the material to various conditions of humidity and temperature, the effect of storage conditions e.g. during a sea voyage, has been assessed and some dyes have been found to be sensitive to the presence of reducing agents. In light-fastness tests an even wider range of dyes has been found to be sensitive.

A comparative study of some mechanical properties of the woollen materials treated with reducing agents and steamed for various intervals of time, ranging from 20 to 120 seconds, has been made and a relationship has been found between the percentage swelling and the tensile strength of the treated material. A considerable loss in the tensile strength has been found in the case of yarn given the urea-bisulphite treatment. The crease-retention of the material stored under various humidity conditions has been studied and found to vary very little.

Optical and electron microscope investigations have been made on the wool which has been given the above treatments and the investigations have been further extended to the fibres treated with urea-reducer solutions under

various conditions of concentration, pH, time and temperature. Different staining methods have been employed to differentiate between the ortho- and the para-cortex of the fibres. The results are discussed in relation to the histological location in the fibre of the action of these reagents. There is an evidence that in merino wool fibres having a bilateral cortical structure, under the condition of neutral pH, the urea-reducer solution attacks the cuticle around the ortho-cortex, first dissolving the outer layer of the exocuticle and, within the fibre, dissolves material mainly from the ortho-cortex.

CHAPTER I

I N T R O D U C T I O N

The introduction of synthetic fibres such as "Terylene", "Acrilan", "Tricel", Courtelle", during the past decade has created ~~a great~~ rivals to the wool textile industry and recent surveys conducted in U.S.A. show a decline in the amount of wool used for clothing, presumably due to the impact of the acrylic fibres.

Before the advent of the synthetic fibres the user's choice was restricted to fabrics that were made from the cellulosic and natural protein fibres. Wool was considered to have valuable pleating properties. The pleats obtained in wool fabrics by steaming and drying are of temporary nature as they are destroyed if the fabric is moistened.

The modern synthetic fibres possess exceptionally good pleating properties due to their thermo-plasticity and are amenable to permanent distortion if treated under suitable conditions of temperature and pressure. Fabrics made from yarns prepared by blending Terylene staple fibre and wool (approx. 50-50) can very easily be given permanent creases and pleats by exposing to super-heated steam for a short period and these have a high resistance to washing and laundering.

The remarkable commercial success of durably pleated or creased garments made from synthetic fibres has had a serious impact on wool commerce. It was because of this success that

research into the finishing of wool fabrics was started and in recent years this ~~research~~ work has met with some success. There are now available two permanent pleating or creasing processes for wool fabrics: an Australian process known as Si-Ro-Set[1] which is based on use of ammonium thioglycollate and a British process called Immacula[2] which makes use of sodium bisulphite. Very recently these permanent pleating processes have been successfully combined with the shrink-proofing treatment to impart to woollen materials a non-iron property[3], e.g. the "Sironized" finish for "Easy-care" properties developed by the C.S.I.R.O. of Australia[4]. Recently the reactions in permanent pleating processes have been developed to give a high permanent lustre to all-wool fabrics. A new organic chemical called Measac, manufactured and sold by the Associated Chemical Companies, has been especially developed in co-operation with the International Wool Secretariat to provide a simple, effective and very economic method of processing woollen and worsted fabrics to obtain a flat finish, durable creasing and crease-shedding properties. Investigations have further shown that with a Measac treatment a lustrous finish stated to be permanent to Hoffman pressing, can be obtained on pile and worsted fabrics.

It is logical to think that, the more processing wool~~len~~ material receives, the further will its properties such as strength, quality, handle, depart from those of the

original and that in the case of dyed goods, finishing processes may alter such things as shade, lightfastness, washfastness. The following introduction serves as general survey of the mechanism and application of durable pleating processes and their effects on protein fibres.

THE MORPHOLOGY AND HISTOLOGY OF WOOL FIBRES

As revealed by optical microscopy, the finer wool fibres are cellular structures consisting of two distinct regions: the cuticle or scales and the cortex, each made of different kinds of cell. Many fibres, in particular the coarser ones, have a medulla also.

Cuticle

The cuticle cells have two main components, the exocuticle and the endocuticle (fig. 1) and on the outside of the exocuticle there is a chemically resistant ~~uniform~~ outer membrane, about 100 A thick, called the epicuticle.[5,6,7] The exocuticle is enzyme-resistant but easily attacked by keratinolytic agents, while the endocuticle is susceptible to enzyme attack but resistant to keratinolytic reagents. Recently a differentiation of the outer layer of the exocuticle has been indicated.[8,9,10,11,12,13] The presence of two sheath like layers enveloping the cortex or in other words a second layer underneath the cuticle proper, called the "subcutis" was suggested by Reumuth[28] and other workers[25,26,27,37] but various other workers have rejected this idea.[9,29]

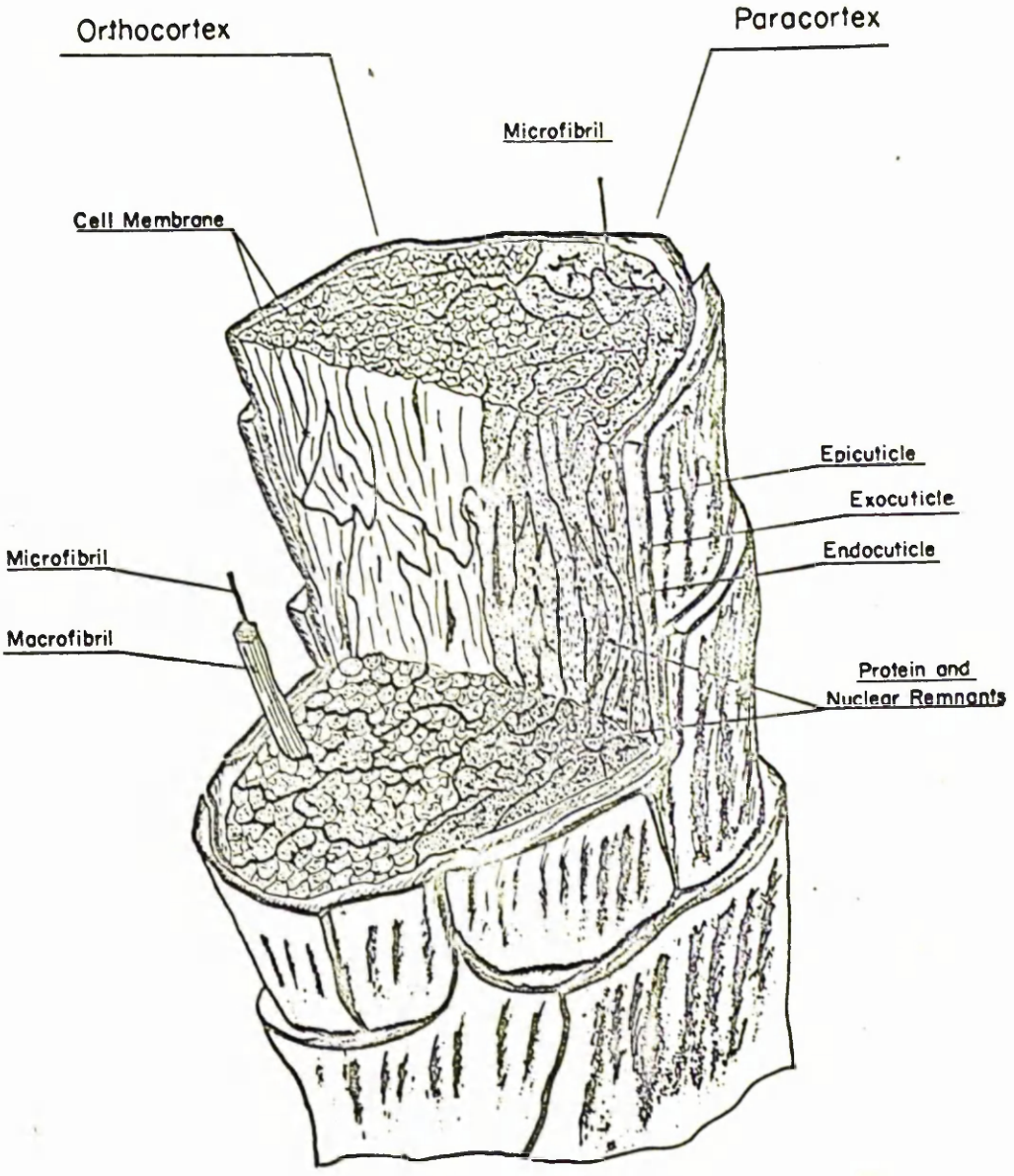

Orthocortex
Paracortex
Microfibril
Cell Membrane
Epicuticle
Exocuticle
Endocuticle
Microfibril
Macrofibril
Protein and
Nuclear Remnants

FIG.1

Cortex

The cortical cells comprise more than 90 per cent of the total fibre mass of most wool fibres. In 1953, Horio and Kondo,[14] by their differential dyeing technique, demonstrated the existence of a bilateral cortical structure in fine merino wool and since then the presence of two different kinds of cell in the cortex of fine wool has been confirmed by many research workers employing various techniques.[15,16,17,18,19] The two regions of the cortex are generally referred to as ortho- and para- cortex and the occurrence of mixed types of cell called heterotypes, which lie in between the ortho- and para- types of cell, has been indicated.[20] In the coarser types of wool such as Lincoln, a radially symmetrical distribution of cortical segments has been shown: the orthocortex surrounds the paracortex.[21]

A great deal of controversy exists regarding the packing of microfibrils of the two segments of the bilateral cortex. It has been suggested that the microfibrils are arranged in whorls in the orthocortex; whereas there is nearly perfect hexagonal packing in the paracortex.[22] These lateral aggregates of microfibrils may form macrofibrils which, in a fine wool having a bilateral cortex, are clearly defined in the orthocortex but are indistinct in the para-cortex. Is it suggested that the microfibrils, about 60-70 A in diameter are made up of subunits called "protofibrils" and

each "protofibril" is made up of three protein chains in the form of modified helices.[23,24]

CHEMICAL STRUCTURE AND PROPERTIES OF PROTEIN FIBRES

All proteins are polymers formed by the linear condensation of α - amino acids through the peptide linkage as shown in fig. 2. The structural formula of an α - amino acid is

$$NH \text{ -- } \underset{\underset{R}{|}}{CH} \text{ -- } COOH$$

R varies in the different amino acids from the simplest case, where R = hydrogen in glycine, to the most complicated, where R = methylene indole in tryptophane. It will be seen that these R groups form side chains such as ~~non-~~ neutral, basic, acidic and cross-linking.

Wool, hair, and fur fibres are composed of a specific group of proteins called the keratins. The keratins differ somewhat among themselves in chemical compositions but they are all characterized by a high content of cystine residues, which render them insoluble in many reagents. The neutral side groups have little effect on the dyeing and finishing of wool but the acidic and basic groups influence many of the chemical and physical properties.

Cross linkages

The side chains, neutral, acid, basic and sulphur containing, may be linked in various possible ways between

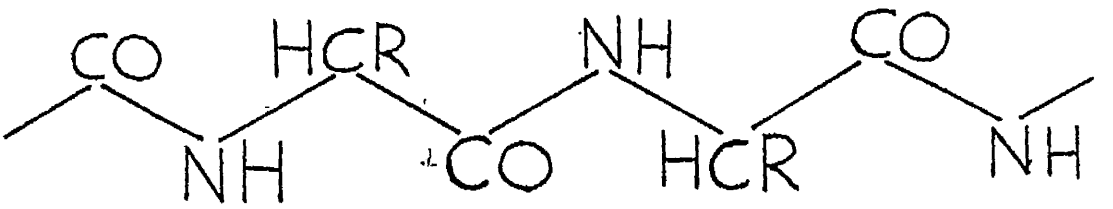


FIG. 2

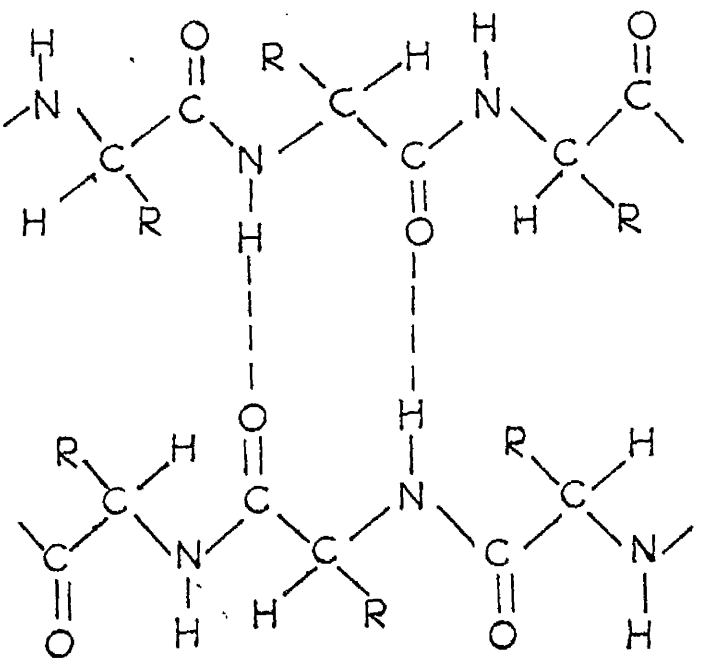


FIG. 3

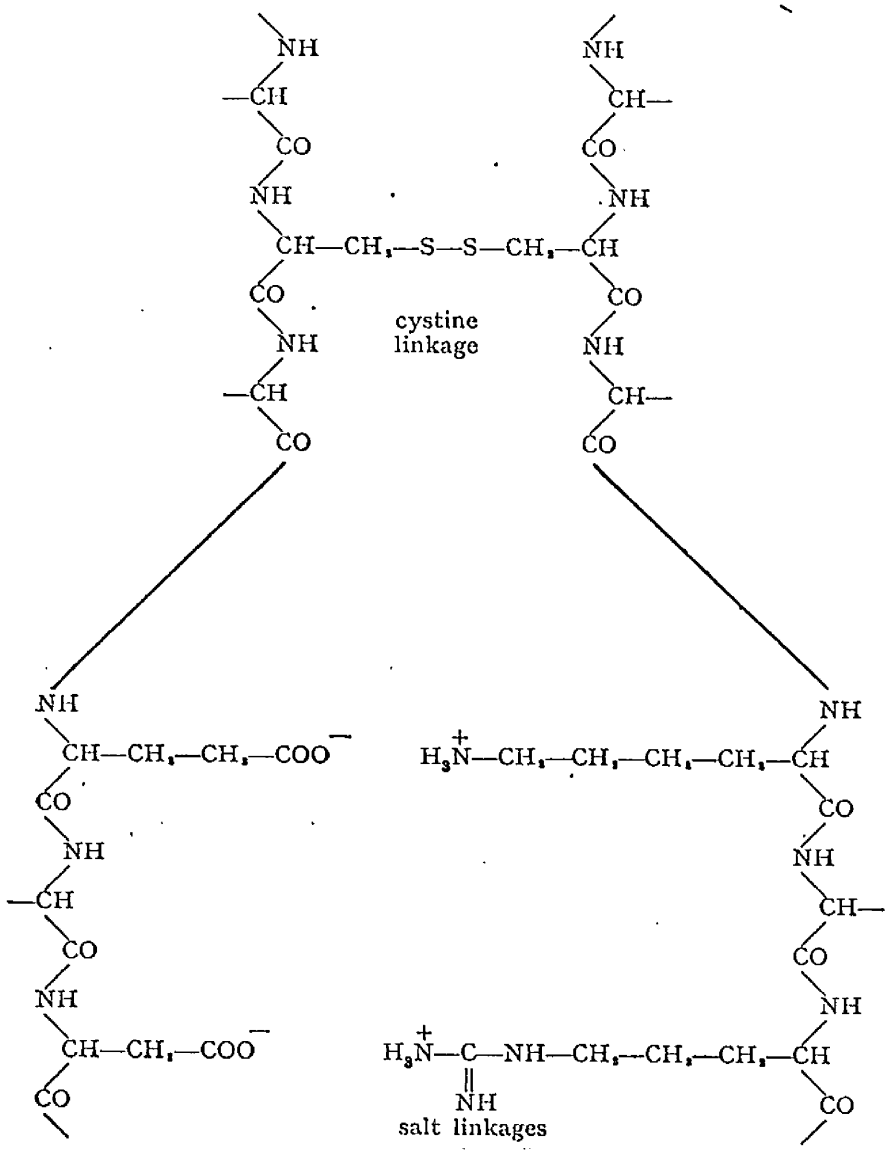


FIG. 4

different parts of the main chains and between separate chains. The following four important types of linkages are known:

(1) van der Waals forces: generalised inter-chain forces,

(2) hydrogen bonding, in which a proton forms the link between two electro-negative atoms (an example of this type is hydrogen bonding between CO and NH groups in parallel folds or helices in the same chain (fig. 3). These bonds are believed to hold adjacent chains together in the crystallites.

(3) salt linkages formed by a basic radical (e.g. lysine, arginine) associating with an acidic radical (e.g. glutamic acid, aspartic acid), see fig. 4.

(4) disulphide linkages, in which a cystine residue links two adjacent, more or less parallel chains or two parts of one chain. The disulphide bond is a relatively short one but is more stable than the salt linkages which are generally more reactive (fig. 4). One school believes that some of the disulphide bonds in the keratin are intra-chain as in insulin[30] but so far the precise nature and distribution of the covalent disulphide linkages are not known and in particular there is some dispute as to whether they occur in the crystalline regions. Undoubtedly however the disulphide bonds are responsible to a

considerable extent for the great chemical and physical stability of keratin fibres.

The polypeptide chains are believed to exist in different conformations in different proteins. Examples are:

(a) in fibroin,[31] the silk protein, chains are in the fully extended form and are arranged fairly parallel to the fibre axis,

(b) in keratin and collagen,[31,32] chains are in the form of twists or folds,

(c) in globular proteins,[33,34] the polypeptide chains are super-folded as well as folded.

The chain molecules in wool normally exist in the folded form (α-keratin) and stretching of the fibre in water results in an unfolding of the molecules (β-keratin) as in fibroin. Unless the chains are set in their extended configuration by formation of new bonds they return to their original form upon release in water.

Various chemical and physical investigations have been made regarding the molecular chain conformation in the unstretched protein fibre. The early suggestions were of flat folds[38] but recent work strongly favours the theory put forward by Pauling and Corey[35,36] that there is a helical arrangement of the individual chains in α-keratin. It is suggested that the helical chain itself may be coiled around a ~~single simple~~

~~helix with~~ linear axis and thus forming a 'coiled coil' structure.

The polymer chain molecule in protein fibres appear to lie with their length roughly along the fibre axis and to be arranged in an oriented manner in certain parts and in a more random manner in others to form the so-called crystalline and amorphous portions of the fibre. It has been suggested by Hailwood and Horrobin,[39] from an analysis of the water adsorption isotherm, that the fraction of wool accessible to water, i.e. the "amorphous" phase, is a little more than half (56%) of the whole but X-ray results[40] indicate higher value of 70-80 %.

Action of reducing agents on disulphide bonds

The disulphide bonds are best broken by application of an acid or alkali, or a reducing or oxidizing agent, while the salt linkages are best broken by fairly strong acid treatment or by steaming. If either type of bond is broken under reasonably mild conditions so that substantial further chemical decomposition of the wool is avoided then, on removal of the bond breaking conditions, there is opportunity for the bonds to be re-formed or new types of bonds to be formed in their place. Although acids and alkalis are known to break the disulphide bonds, they are not suitable for finishing processes as they remain within the fibre during linkage rebuilding and are

capable of breaking the polypeptide chains. Therefore it is necessary to use a volatile or thermally unstable agent. In the light of this consideration, ammonium thioglycollate and sodium bisulphite are used in permanent pleating processes.

The reaction with thioglycollic acid was originally studied by Goddard and Michaelis[41] who showed that the disulphide bond is rapidly converted to thiol groups in alkaline solution. Harris[42] and his collaborators showed that the reaction with thiols in neutral solution is confined to the reduction of the disulphide bond. The thiol groups produced by reduction are very labile and can be re-oxidized, either by prolonged exposure to the atmosphere or by treatment with mild oxidizing agents e.g. hydrogen peroxide or potassium bromate and this reversible process forms the basis of all the 'home permanent waves'.

The reaction of wool with bisulphite is of considerable industrial interest as bisulphite is used for bleaching wool, as "anti-chlor" in some antishrink processes and for permanent pleating of wool fibres. The disulphide bond is not significantly attacked by cold dilute solutions of bisulphite[43] but under more severe conditions, Elsworth and Phillips[44] showed that 50 per cent of the total cystine can be reduced by this reagent according as the equation

$$\begin{array}{l} CH\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2\text{-}CH \quad + \quad NaHSO_3 \\ \qquad\qquad\qquad\qquad \downarrow \\ CH\text{-}CH_2SH \quad + \quad NaOSO_2\text{-}S\text{-}CH_2\text{-}CH \end{array}$$

It can be observed that half the sulphur forms sodium cysteine sulphonate and only one half is converted to thiol groups. It seems that of the cysteine groups produced in the wool this way, half are more labile than the remainder and revert to cystine on rinsing with cold water. Wool fibres boiled in 5 per cent sodium bisulphite supercontract and this is taken as evidence of the reduction of cystine crosslinks.[45] If wool is kept stretched while boiled in dilute bisulphite and subsequently washed in water, it remains permanently elongated, the disulphide links having been reformed in new positions.

Ammonium thioglycollate has a similar action on wool to bisulphite solution.[137]

$$\begin{array}{ccc} CH\text{-}CH_2\text{-}S\text{-}S\text{-}CH & + & HS\text{-}CH_2\text{-}COONH_4 \\ \updownarrow & & \\ CH\text{-}CH_2\text{-}SH & + & CH\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2COONH_4 \end{array}$$

DEVELOPMENT OF DURABLE PLEATING PROCESSES.[138]

DEVELOPMENT OF DURABLE PLEATING PROCESSES

The creasing of textile material is a complex effect involving tensile, flexing, compressive and torsional stresses. The bending elasticity seems to be of the greatest importance; creases appear when the material is distorted in such a manner that part of it is stretched beyond its small limit of elastic recovery. The bending of the fibres which takes place during creasing leads to an extension of the upper surface and a

compression of the under surface[46] and any durable pleating process must "set" this deformation.

The ability of wool fibres to take a permanent set was investigated by many early workers.[38,134-136] Though it was shown, some twenty years ago that the setting of strained fibres in steam or aqueous media is assisted by alkalis, sulphites, bisulphites,[45,47,48] no systematic attempt was made to find out which of the many possible reagents would be the most suitable for obtaining permanent pleats in all wool fabrics, nor to determine the conditions of its use to give maximum set with minimum damage to the woollen fabric.

In order to understand the new pleating processes it is important that the chemical mechanism of the process i.e. the manner in which the molecular bonds are broken and re-formed should be known. However, it is unfortunate that the chemical aspect of the process is not very clear.

Steam setting

The study made by Speakman regarding the mechanism of permanent set was the basis for defining optimum conditions for setting wool fabrics with water and buffer solutions [49] i.e. the normal steam-pressing process. This work also led to the procedures for permanent pleating and setting of crepes.[50]

The degree of permanence of the set depends on the pH of the fabric, temperature, time and the presence of an adequate

amount of moisture. The success of the setting process depends mainly on the reaction of the solution: little or no set can be obtained in acid media, while a high degree of set is achieved in alkaline solutions. However, because of the possibility of damage at high pH values, the process is carried out at pH less than 9.

Some years ago Speakman[47] and his co-workers very carefully investigated the manner in which a wool fibre could be stretched in steam to bring about its permanent elongation and advanced a theory of the chemical mechanism of permanent set.

According to this theory set is due to two consecutive inter-molecular reactions, viz. rupture of the disulphide bonds and reformation of new bonds by reaction of the terminal sulphenic acid groups with free amino groups made available for this purpose by a simultaneous rupturing of some of the salt linkages:

$$W\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2\text{-}W \xrightarrow{H_2O} W\text{-}CH_2\text{-}SH + SOH\text{-}CH_2\text{-}W$$

sulphenic acid

$$W\text{-}CH_2\text{-}SOH + NH_2\text{-}W' \longrightarrow W\text{-}CH_2\text{-}S\text{-}NH\text{-}W'$$

It is also suggested by Speakman that in the presence of alkali the sulphenic acid group might react as:

$$W\text{-}CH_2\text{-}SOH \longrightarrow W\text{-}CHO + H_2S$$

$$W\text{-}CHO + H_2N\text{-}W' \longrightarrow W\text{-}CH{=}N\text{-}W'$$

The new bonds arise from reaction between ruptured disulphide bonds and salt linkages.

However, more recently the permanent setting of wool fibres has been very carefully studied by many workers[51,52,53] and they consider that the setting depends on a breakdown of both hydrogen and covalent bonds by the ~~hot moisture~~ steam and a subsequent reformation of hydrogen bonds between adjacent molecular chains in their enforced configuration. New ~~salt~~ linkages may be formed but no stronger bonds resulting from reformed disulphide or modified disulphide bonds. The existence of two different mechanisms of setting namely co-operative chain unfolding and molecular slip has been suggested.[54]

Setting with reducing agents

In order to obtain a durable pleat in a wool fabric, the fibre must first be converted into a plastic state; the plastic fibre is then given the desired conformation. Reducing agents such as ammonium thioglycollate, sodium bisulphite, ethanolamine sulphite,[55] which are capable of breaking disulphide bonds, are used in order to bring about plasticization. These reducing agents are cheap, readily available and cause little damage to wool. The steaming which usually forms part of the process also ruptures the so-called salt-linkages. In the following account the various possible commercial processes are described

separately, although the findings on one process are often relevant to the others.

Si-ro-set process

The Si-Ro-Set[1,50,55,56,57] process for permanent pleating of wool fabric was developed by the Commonwealth Scientific and Industrial Research Organisation in Australia.

It has been shown by Farnworth[58] that a very rapid and high degree of permanent set can be imparted to the wool fibres in boiling solutions of reducing agents. The SiRoSet process which is based on the use of a dilute solution of ammonium thioglycollate at pH 7 and steam pressing treatment, followed directly from this work. The nature of the reaction has been discussed on p. 10 .

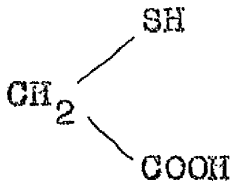
In actually carrying out the SiRoSet process, the wool fabric is treated with a dilute solution of ammonium thioglycollate at pH 7 and a durable crease or pleat is then formed by steaming for a short time under suitable conditions of temperature and pressure. Usually the steaming is carried out in the Hoffman Press, first for 20 seconds at a steam pressure of 57 psi, then for 20 seconds without steam and, finally, for 20 seconds under vacuum.[59] Pleats may also be set in the autoclave, in which case they require 3-5 minutes at 20-24 psi or 20 minutes at atmospheric pressure.

For garments, such as men's trousers and ladies' dresses and skirts, the ammonium thioglycollate is applied by a spray gun, especially made from aluminium, glass or plastic. The solution should be sprayed in such an amount that the area of the wool sprayed gains about 40% in weight (this amount is calculated on the area of wool sprayed). It has been suggested that the spraying should not be confined too closely to the desired crease since cockling may develop due to a difference of texture being established between sprayed and unsprayed part of the fabric.[60] As the proportion of water present in the wool during steaming plays an important part, the treated material should not be allowed to dry out and also to prevent any decomposition of ammonium thioglycollate, which may occur during storage, the interval of 15 to 30 minutes between treatment and steam pressing is generally recommended.

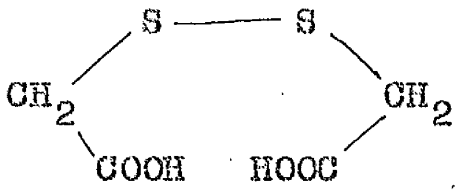
The ammonium thioglycollate solution used in the SiRoSet process is not ultimately washed out. Hence it is interesting to know what happens to the residual chemical in the finished wool material. Springell [61] carried out some investigations by using radioactive form of thioglycollate in which the sulphur atoms were an isotopic form of sulphur S35.

It was shown that the steam-ironing is not associated with loss of S35 labelled thioglycollate, whereas washing with water results in rapid loss of radioactivity, followed by a

much slower decrease. Almost complete loss of radioactivity can be brought about by treatment with sulphide, sulphite, or alkaline cyanide whereas lithium bromide or urea has little effect. It was concluded that of the 4 to 9 mg. of thioglycollate initially applied per gram of wool, 3 to 5 mg. are in a labile but nonvolatile state, whereas the remaining 1 to 4 mg. are probably with the cystine residue, in wool, in a mixed disulphide form. According to Springell[61] the labile part consists of unchanged thioglycollate or possibly some dithioglycollate,



thioglycollic acid



dithioglycollic acid

while the less easily removable part may consist of mixed disulphide[62] of formula

$$W\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2\text{-}COOH$$

cystine residue (from wool molecule)	thioglycollic acid residue (from ammonium thioglycollate)

The formation of such a mixed disulphide can be explained by the following reactions:

$$W\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2 \longrightarrow W\text{-}CH_2\text{-}SH + HOS\text{-}CH_2\text{-}W$$

$$W\text{-}CH_2\text{-}SOH + HS\text{-}CH_2\text{-}COOH \rightarrow W\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2\text{-}COOH$$

wool sulphenic acid | thioglycollic acid | a mixed disulphide

Springell[61] considered that less than 8% of the disulphide bonds present in the wool molecule enter into such a reaction. Further, he thought that the presence of residual thioglycollate in the wool fabric plays no part in the retention of crease. He supported the theory explaining the mechanism of permanent set put forward by Farnworth.[38]

Gerthsen and Zahn[63,64] investigated the problem of finding reliable methods for detection of mixed disulphide bonds as assumed by Springell[61] which in fact can serve as methods for detection of SiRoSet treatment in wool fabric. They concluded that it is possible to detect the mixed disulphide as well as the thioglycollic acid in treated fabric by using the conventional methods of chemical analysis of wool. Kondo and his co-workers investigated the influence of free thioglycollic acid adsorbed in wool on setting ability.[66]

Immacula process

This new durable crease finish for wool was introduced by Proban Ltd.[2] The manufacturer treats the fabric with a 2% solution of sodium bisulphite for 15 minutes at room

temperature. At the end of this time, excess bisulphite is removed by rinsing and the fabric is then dried at a low temperature. To obtain permanent creases with the treated fabric the tailor has merely to steam in the Hoffman Press with the fabric between damp cloths.

According to Speakman[50] when wool is treated with sodium bisulphite solution, the following reaction takes place:

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

When the material is rinsed, there is some reversal of the reaction but much of the bisulphite remains in combination with broken disulphide bonds. During steaming of the fabric, disulphide bonds are re-formed, and the liberated sulphur dioxide is free to break other disulphide bonds elsewhere in the structure. The presence of water promotes migration of sodium bisulphite and sulphur dioxide through the structure.

Davidson and Howitt[65] attempted to study the mechanism of setting reactions by the determination of the chemical changes that occur in wool keratin during the actual setting process. They first investigated the action of bisulphite on the model substance cystine, and then applied the same procedure to bisulphite-treated wool fabrics. They were not successful in obtaining satisfactory results.

Urea-reducer treatment

Farnworth[58] investigated the use of urea, which is very effective in breaking hydrogen bonds and salt-linkages, together with reducing agents such as ammonium thioglycollate and sodium bisulphite. He found, for instance, that a good permanent setting of a crease can be obtained by treatment with a liquor containing 1.6% of sodium metabisulphite and 40 to 50% of urea, at 30°C.

STRUCTURAL EFFECTS OF REDUCING AGENTS

Various reducing agents, alone or along with substances such as urea, under different pH conditions, have been employed by several workers[41,67-77] in attempts to render wool soluble. Following the observation that urea-reducer solutions could dissolve only part of wool[75] some histochemical investigations were carried out. Mercer,[74] whose work followed the discovery of bilateral structure in merino wool fibre,[14] found that the fraction extracted with urea-reducer solution from wool fibre had a definite histological location viz. it came from orthocortex. Histochemical study of wool treated with thioglycollic acid has recently been reported.[78]

The treatment of wool fibres with reducing agents such as thioglycollic acid under certain pH value, prior to

staining with heavy metals[13,22,24,79,80] such as lead, osmium, silver, has been widely employed in order to achieve improved contrast under the electron microscope. The account of the X-ray study of the structural changes in the wool fibres by above treatment has been given by Sikorski and Woods.[79] It has been suggested that in fully keratinized wool fibre, which has very few sulfhydryl groups, the chemical treatment greatly increases the number of these groups by reduction of the disulphide bonds in sulphur-rich cementing material in the cortex, known as "matrix", resulting in dense staining of this region with heavy metals.

MECHANICAL EFFECTS OF REDUCING AGENTS

Very little work seems to have been done regarding the measurement of mechanical properties, under the normal conditions of humidity and temperature, of the wool fibres treated with reducing agents. Very recently studies of the mechanical properties of cystine-reduced wool fibres at various relative humidities have been reported by Feughelman.[81] He observed that the reduction of disulphide content of a wool fibre produces progressive modification of mechanical properties of the fibre at all humidities.

Most of the work [42, 125, 139-142] on the mechanical properties of wool fibres treated with reducing agents, such as sodium bisulphite and ammonium thioglycollate, appears to have consisted of measurements on single fibres immeresed in either water or the solutions of reagents. The purpose of these investigations has been to discover the effects of disulphide linkages on the mechanical properties and to interpret them in terms of the chemical structure of the fibres. As a result they are not particularly relevant to the present work which concerns yarns and fabrics used under normal "dry" conditions.

CHAPTER II

EFFECTS OF REDUCING AGENTS ON DYESTUFFS AND THEIR LIGHTFASTNESS

INTRODUCTION

As the setting processes must be carried out near the end of the finishing routine one must take into consideration their effect on dyestuffs. It is clear from the literature that the use of ammonium thioglycollate and sodium bisulphite as reducing agents in pleating processes causes a marked change in the shade of some of the dyes used for woollen materials.[3,65,85,86,127] With many acid dyes there is a possibility of bleeding under the influence of the Siroset process and also the ammonium thioglycollate is capable of reacting with the metals such as iron to form coloured complexes and this may create alteration in shade.

Several dye manufacturers have published reports[59,82,83,84] showing the fastness of their entire range of wool dyes to the Siroset and the Immacula processes. They have taken into account various factors such as (1) neutralization of the dyed material before subjecting to the Siroset process (2) effects of reducing agents (3) effects of steam pressing.

It appears that the suitability of a given dyestuff for subsequent Siroset or Immacula processing is dependent on the particular finishing process and the trade for which the particular article is intended. Also the degree of susceptibility of each dye depends on the depth of the shade employed. It is thus difficult to arrive at any general

conclusion from the results given. The effect on the dyes seems to be specific for individual dyes and not characteristic of a class or range. Few of the chrome range which comprises metal-containing dyes are completely unaffected, many are satisfactory, only a few are very poor. Also groups of dyes e.g. oranges and, particularly, yellows are more affected than others by the above pleating processes. The changes in shade brought by permanent pleating processes in wool dyes are irreversible except in the case of Ultralan types where the original colour can be restored by a mild oxidation treatment of 2-vol. hydrogen peroxide.[85]

In the recent ICI[4] publication, account has been given of the work done on the fastness of wool dyestuffs to the latest finish for wool called the "Sironized" - "Easy care" finish. In the presentation of results, the effect of a combined shrink-process and setting treatment, which corresponds to the full Sironized process after dyeing, and also the effect of setting on pre-shrinkproofed dyed wool, which corresponds to the processing sequence shrinkproofing-dyeing-setting, are discussed.

It is known from the literature survey that so far no attempt has been made to investigate the effects of these processes on the light fastness and washing fastness of the

material, Only some suggestions have been made that treatment of dyed fabric with thioglycollate may affect the photo-sensitivity of the dyes.[3,65,86,126,127,132] Moreover, it is understood that if the dyed and permanently pleated material is exported to overseas countries, a change in shade is observed. The material, as usually sent by ship, may take between two and eight weeks before it reaches the destination and during this period it is possible that the material is stored under the condition of high humidity and sometimes high temperature.

In the present work attempts have been made to study the effects of storage conditions by exposing the samples, dyed with different dyes and treated variously, to different relative humidity and temperature for a period of two weeks. Also, attempts have been made to compare the lightfastness of the dyed, treated and untreated material.

Methods for assessing the changes in colour

The methods for the evaluation of the changes in colour of the dyed and treated samples can be divided into the following two classes.

(1) Visual methods

(2) Instrumental methods

Visual methods

They are based on the use of the Society of Dyers and

Colourists' 1-5 grey scale. The samples are graded from 5 to 1; 5 indicates no change in shade. The use of the designations such as B bluer, Br brighter, D duller, G greener, R redder, W weaker, Y yellower, is also made along with the grading number. Several dye manufacturers have assessed the changes in the colour due to permanent pleating processes by employing this method.

Instrumental methods

The quantitative assessment of any change in shade of a coloured fabric sample involves all the three characteristics of colour viz. purity, brightness and the hue or dominant wave-length and for this purpose a reflectance photometer may be employed. In some instruments a coloured pattern is illuminated by monochromatic light from a spectrometer or filter and the intensity of the reflected light at a series of wave-length is compared with that reflected by a white surface. In other instruments filters simulating red, green, and blue or X,Y and Z (C.I.E.) standards are used. Thus either indirectly or directly the characteristics of the pattern may be found and the hue plotted on the CIE chromaticity chart.128

EXPERIMENTAL PROCEDURE

Materials

Wool

All treatments described in this and the following chapters were made on all-wool flannel of plain weave which had been previously scoured, carbonized, neutralized, soap milled and washed off with Calgon to remove residual lime and soaps.

Chemicals

2 per cent ammonium thioglycollate solution was prepared by adding (by volume)

Thioglycollic acid (98%)	20 parts/1000
Ammonia (sp.gr. 0.880) ... ... approx.	20 parts/1000
Lissapol N	2 parts/1000

to iron-free water and the pH value of the solution was adjusted to 6.75. Fresh solutions were used since decomposition of the solution may occur on storage.

2 per cent sodium meta-bisulphite solution was prepared by dissolving 20 gms. of sodium meta-bisulphite in 1000 cc. of distilled water. Fresh solutions were used since decomposition, with the evolution of sulphur dioxide, takes place in old solutions.

Urea-bisulphite solution was prepared by dissolving 1 gm. of sodium meta-bisulphite and 30 gms. of urea (laboratory reagent) in 100 cc. of distilled water. The pH of the solution was 6.

Dyes

The following dyes used in these experiments were commercial samples obtained from the ICI.

Levelling dyes

(1)	Naphthalene Green GS	or	CI ACID GREEN 3
(2)	Solway Blue RNS	or	CI ACID BLUE 47
(3)	Lissamine Red 7BPS	or	CI ACID VIOLET 5
(4)	Naphthalene Black 12 B	or	CI ACID BLACK 12 B

After chrome dye

Solochromate Fast Red 3 GS	or	CI MORDANT RED 19

Acid milling dye

Solway Green G (150)	or	CI ACID GREEN 25

EXPERIMENTAL METHODS

Preparation of dyed samples

The depth of shade of each dye used for dyeing woollen material is shown in TABLE I.

TABLE I

Dye	Depth of Shade %
Naphthalene Green GS	2.50
Solway Blue RNS	0.75
Lissamine Red 7BPS	0.70
Naphthalene Black 12 B	10.00
Solochromate Fast Red 3GS	1.30
Propolan Yellow 3GX	1.50
Solway Green G	1.70

Dyeing Methods

Dyeing was carried out by standard procedures, described briefly below, on the woollen fabric samples weighing approximately 30 gms. The material to liquor ratio was kept as 1:50 . In the following recipes percentages are calculated on the weight of the material being dyed.

Levelling acid dyes

The sample was dyed in a dye solution containing 10% of Glauber's salt and 3% of sulphuric acid (Conc.). It was immersed in the warm dyebath (60°C), which was raised to the boil in 20 minutes and continued boiling for 1 hour and was

then rinsed and dried.

Chrome dyes

The sample was immersed in a cold solution containing 10% of Glauber's salt, 1% of acetic acid and 1% of formic acid (85%) which was then raised to boil in 20 minutes and boiled for 45 minutes. After-chroming was done by lifting the sample from the bath and adding 50 cc. of cold water and 1% potassium dichromate then replacing the sample and boiling for 30 minutes. The sample was rinsed and dried.

Acid milling dyes

The sample was immersed into a cold dye solution containing 10% Glauber's salt and 1% acetic acid which was raised to boil in 20 minutes and boiled for 1 hour; after boiling for 45 minutes 1% acetic acid, previously diluted with water, was added.

Methods and conditions of treatment

The dyed samples were cut into 3" x 4" pieces (approx.) and equal numbers of these pieces (usually four) were given each of the following treatments.

(a) Siroset treatment

The dyed samples were thoroughly wetted with 2% ammonium thioglycollate solution at room temperature and were squeezed in a padding mangle so as to obtain 50% moisture content (determined by weighing).

(b) Immacula treatment

The dyed samples were treated with 2% solution of sodium bisulphite for 15 minutes at room temperature and were then rinsed with water, squeezed and air dried.

(c) Urea-bisulphite treatment

The dyed samples were treated with urea-bisulphite solution for 15 minutes at room temperature and then squeezed as in (a).

(d) Water treatment

The dyed samples were treated with distilled water and squeezed to 50% (approx.) moisture content.

Steaming in Hoffman Press

The samples a, c, d, were sandwiched between "dry" wool or cotton and the samples b between cotton containing 50% moisture and then were steamed in the Hoffman Press at 65 lbs./sq. inch gauge pressure for 20 seconds. The typical sequence of operation of steaming being as follows:

(1) steaming for 20 seconds,

(2) further steaming for 20 seconds with the supply of steam cut off,

(3) vacuum treatment for 20 seconds.

"Immacula-I" means that the sample was first treated with bisulphite solution and then steam pressed.

"Immacula-II" means the sample was treated with sodium bisulphite solution and dried without steaming.

All the above samples were allowed to condition for at least 24 hours and then were subjected to colour assessment as described later in this chapter.

Conditions of the exposure

A closed plastic cabinet, in which the atmosphere was maintained at constant temperature ($\pm$ 1°C) and humidity ($\pm$ 2%) using different saturated salt solutions (TABLE II), was used for exposing samples in series of experiments. In each series, a set of treated samples along with a control sample was exposed to a particular humidity and temperature for two weeks.

TABLE II

Temperature °C	salt	%RH
20	sodium chlorate	75
	ammonium dihydrogen phosphate	93
25	magnesium chloride	32
	sodium chloride	75
	ammonium dihydrogen phosphate	93
30	sodium chloride	75
	potasium nitrate	93

A difficulty was observed during the high humidity and temperature exposure ($30^{o}C$ & 93% RH) as there was condensation of water inside the cabinet. This was avoided by lagging the outside of the cabinet with thick layer of wool and cotton fabrics.

At the end of exposure time, the samples were removed from the cabinet and were allowed to condition for at least 48 hours at $20^{o}C$ and 65% RH prior to any colour assessment.

Measurement of colour

All the colour measurements were performed on the 'ESL' reflectance spectro-photometer using a three filter "wheel", which gives the X,Y,Z tristimulus values directly. A brief description of the instrument and its working is as follows.

The light source is a tungsten lamp operating at a colour temperature $2848^{o}K$ (Source A - C.I.E. artificial light standard) and has coefficients of X = 0.448, Y = 0.407, Z = 0.145. The incident light from the source falls on the sample at 45^{o}, is reflected on to the photocell placed normally with respect to the sample and the current generated is passed to the galvanometer unit.

The instrument sensitivity on the standard white (magnesium carbonate block) is adjusted in such a way that the galvanometer reads

100 for X filter

90.8 for Y filter

32.4 for Z filter

Readings on the samples are taken directly by using filters X, Y and Z, from which the coefficients are calculated as follows:

$$x = \frac{X}{X+Y+Z} \quad , \quad y = \frac{Y}{X+Y+Z} \quad , \quad z = \frac{Z}{X+Y+Z}$$

In this work 5 readings were taken on each side of each of the 4 samples from any one treatment; each of the 5 readings being taken in 5 different regions of each sample.

Hue

The x and y coefficients of a sample were plotted on the chromaticity chart. The line drawn through the resulting point from the reference point of the light source was continued to cut the colour locus and the resulting point of intersection was taken as the 'dominant wavelength' of the sample. It was found that the 'EEL' reflectance spectrophotometer was not capable of indicating the proper Hue (dominant wavelength) of a sample: readings tended to red-blue end of the chromaticity diagram. However, in the present work, the instrument was used for relative measurements.

Brightness

The brightness of the sample was obtained by multiplying the Y reflectance reading of the sample by $\frac{100}{90.8}$.

Mercury vapour light

An Osira lamp of 400 w. power, which ran directly from the main supply, was used. A cylinder of sheet aluminium 17 inches in diameter and 15 inches high, centred on the lamp with an internal circular shelf for the samples was used. The lamp had a weak continuous spectrum as background with a number of superimposed strong monochromatic bands at 3700 A, 4000 A, 5600 A, and 5800 A.[87]

The nature of the light emitted from the mercury lamp used in this experiment is quite different from daylight, but, since the aim of the present work was a comparative study of the effects of reducing agents on light fastness of different dyes and not the absolute determination, it was thought reasonable to use the mercury vapour lamp as source of light in place of sunlight. As regards the reliability of the test, it is observed that the difference between the fastness ratings of the samples, at standard depth, exposed to the light from mercury lamp

and sunlight (ratings obtained from the Colour Index) for equivalent dyes is ± 1 grading, see TABLE III .

TABLE III

Dye	Grading number	
	After exposure to mercury vapour lamp	After exposure to sunlight *
Naphthalene Green GS	3	2
Solway Green G	7	6
Solway Blue RNS	5-6	5
Solochromate Fast Res 3GS	7	6
Lissamine Red 7BPS	5	4-5
Propolan Yellow 3GX	6	-

* Gradings obtained from the Colour Index.

Methods and conditions of exposure to light

A strip of 1 cm x 6 cm was cut from each sample, treated, untreated, and standard. The strips were mounted

on cardboard and one quarter of the total length of each sample was covered with cardboard[88] and they were then exposed to the direct light of a mercury vapour lamp.

The effect of light was followed by lifting the cardboard cover periodically and inspecting the standards.

When a change in standard 3 was just perceived, the specimens were inspected and their light fastness were rated by comparing the changes that had occurred with the changes in standards 1,2, and 3.

The cover was replaced in the same position and the exposure was continued until a change in standard 4 was just perceived; at this point an additional card which covered half the total length of the samples, overlapping the first cover, was fixed. The exposure was continued until a change in standard 6 was just perceived, then the final card covering three quarter of the total length of the samples was fixed, keeping the other two cards in the same position. The exposure was further continued until a contrast was produced on standard 7 equal to the contrast illustrated by grade 4 of the Society of Dyers and Colourist grey scale.

All the three covers were removed and the changes in the specimens were compared with those in the standards.

The light-fastness grading of the specimen was the number of the standard which showed a similar change in colour (visual contrast between exposed and unexposed parts of the specimen). Hence 1 means very poor and 7 means very good light-fastness.

EXPERIMENTAL RESULTS

Hue

The general range of results is shown on the full chromaticity chart in fig. 5 and the detailed results are shown on the enlarged portions of the chart. Only Naphthalene Green showed a significant difference and for this the detailed results are shown on enlarged portions of the chromaticity chart in figs. 6,7,8.

Brightness

Table IV shows the difference between the percentage brightness of the treated and the control samples exposed to similar conditions of temperature and relative humidity, for the dye Naphthalene Green.

TABLE IV

Temperature in °C	20		25			30	
% R.H.	75	93	32	75	93	75	93
Siroset	7.1	5.4	9.1	6.0	1.1	5.6	2.1
Immacula-I	12.0	6.6	7.2	17.4	1.0	1.3	1.5
Immacula-II	9.3	6.0	12.8	13.1	2.3	-	-
Water	0.3	0.3	0.7	0.1	0	0	0.3

Naphthalene Green GS, difference between % brightness of treated and control samples.

Immacula-I- treated samples with steam pressing.

Immacula-II- treated samples without steam pressing.

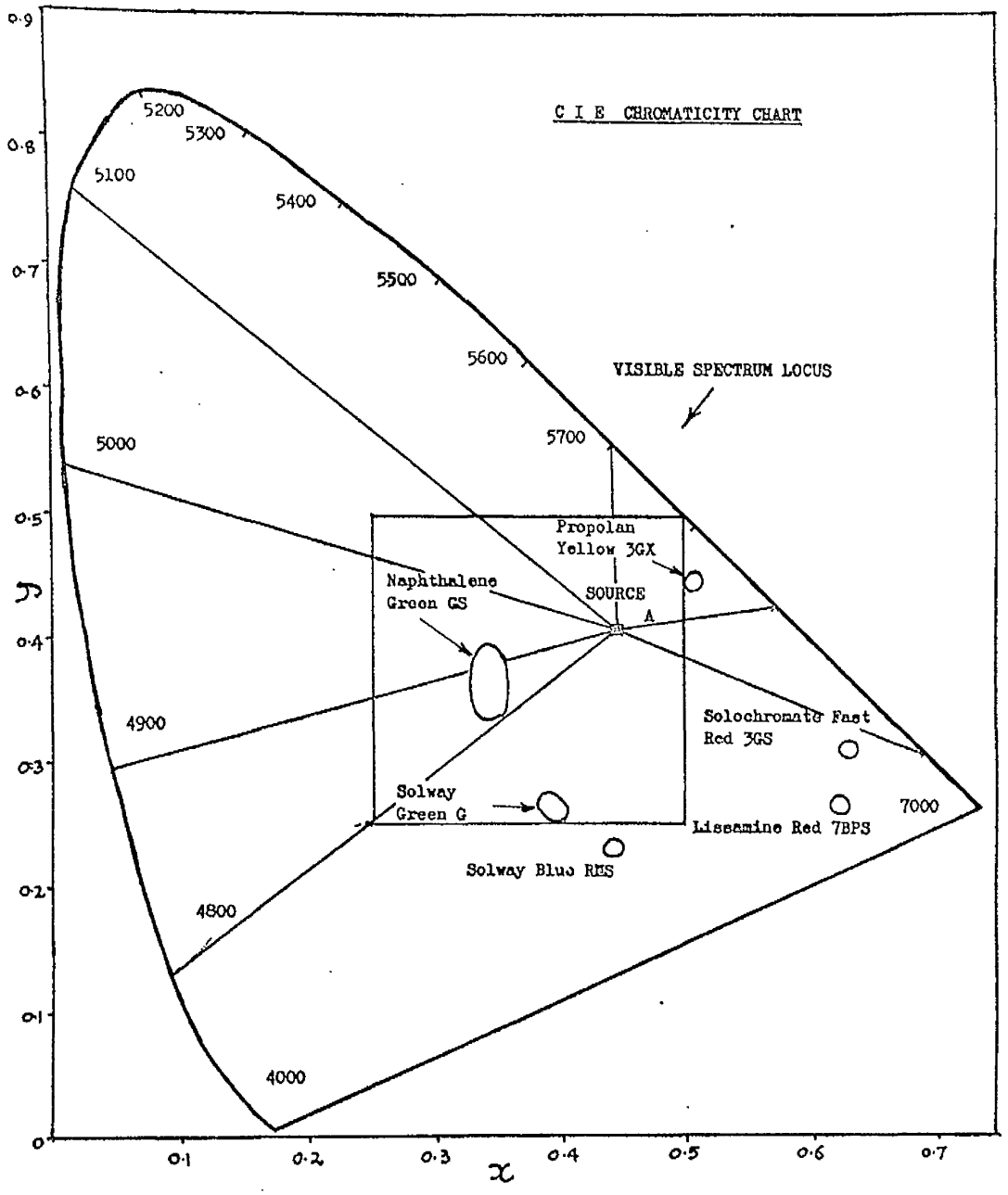

C I E CHROMATICITY CHART
VISIBLE SPECTRUM LOCUS
5200
5300
5100
5400
5500
5600
5700
5000
4900
4800
4000
Propolan
Yellow 3GX
SOURCE
A
Naphthalene
Green GS
Solochromate Fast
Red 3GS
Solway
Green G
Lissamine Red 7BPS
7000
Solway Blue RES
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
y
0·1
0·2
0·3
0·4
0·5
0·6
0·7
x

FIG. 5

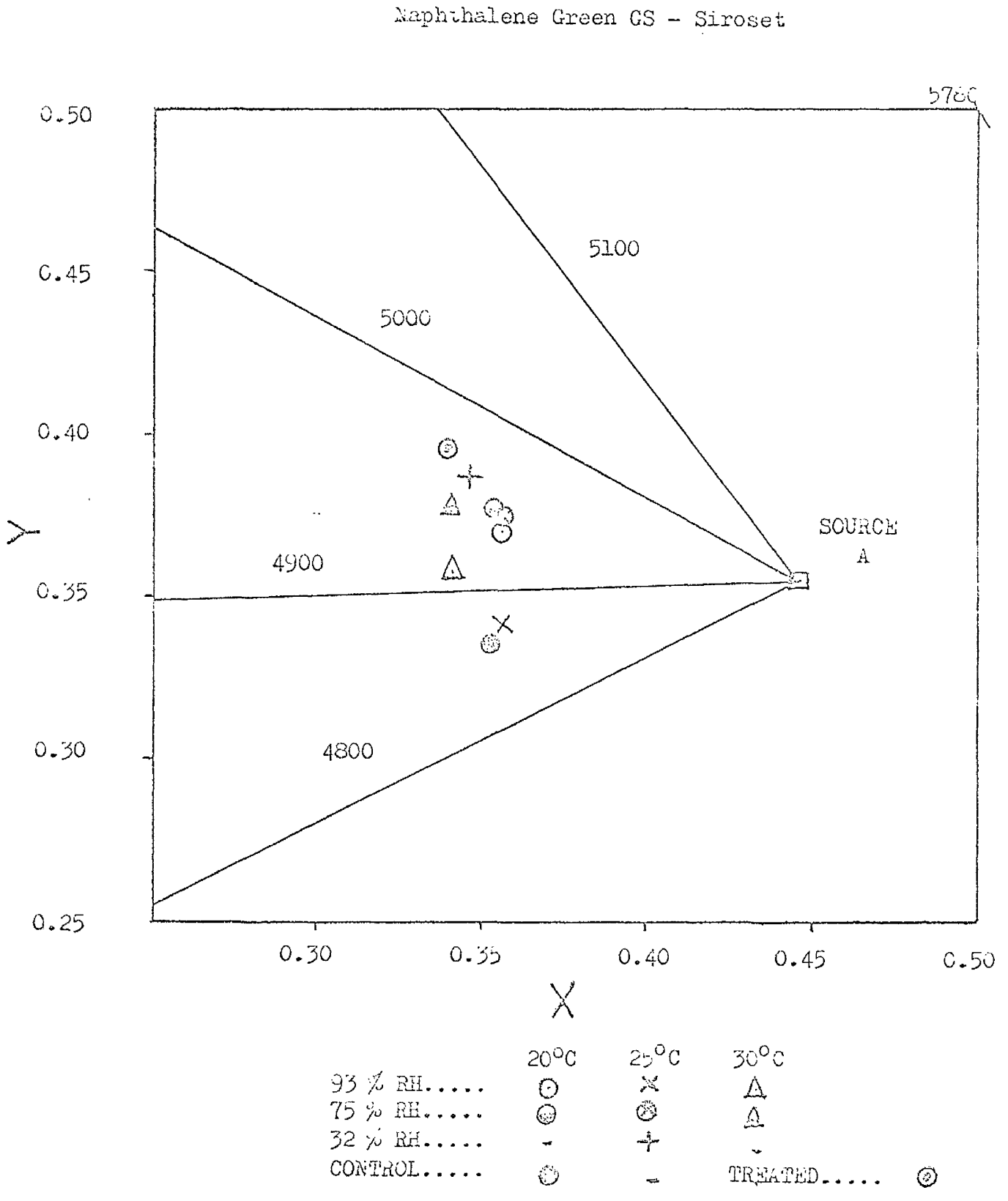

Naphthalene Green GS - Siroset
5700
0.50
0.45
0.40
0.35
0.30
0.25
Y
5100
5000
4900
4800
SOURCE
A
0.30
0.35
0.40
0.45
0.50
X
20°C
25°C
30°C
93 % RH.....
75 % RH.....
32 % RH.....
CONTROL.....
TREATED.....

FIG. 6

Naphthalene Green GS – Immacula-I

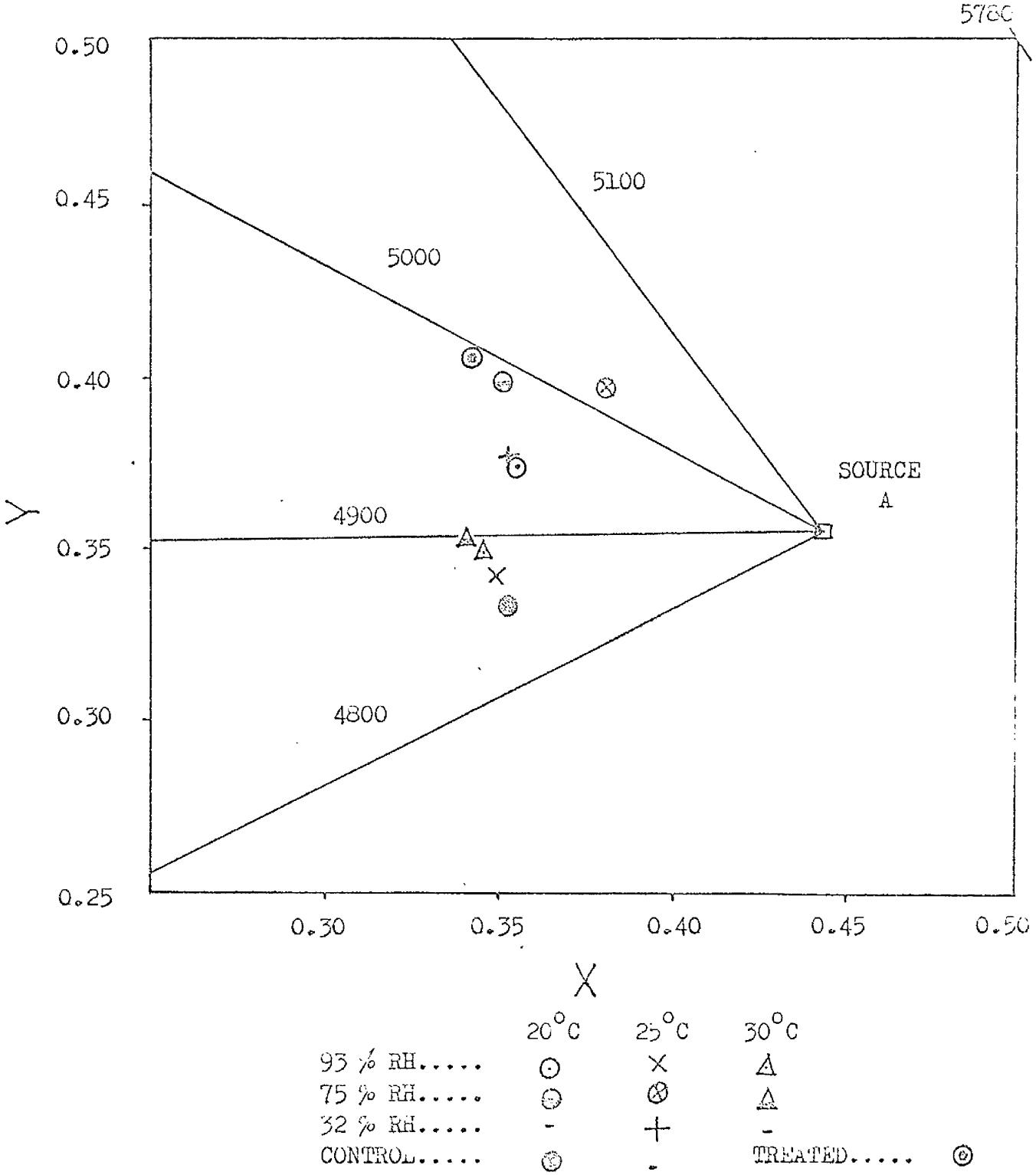
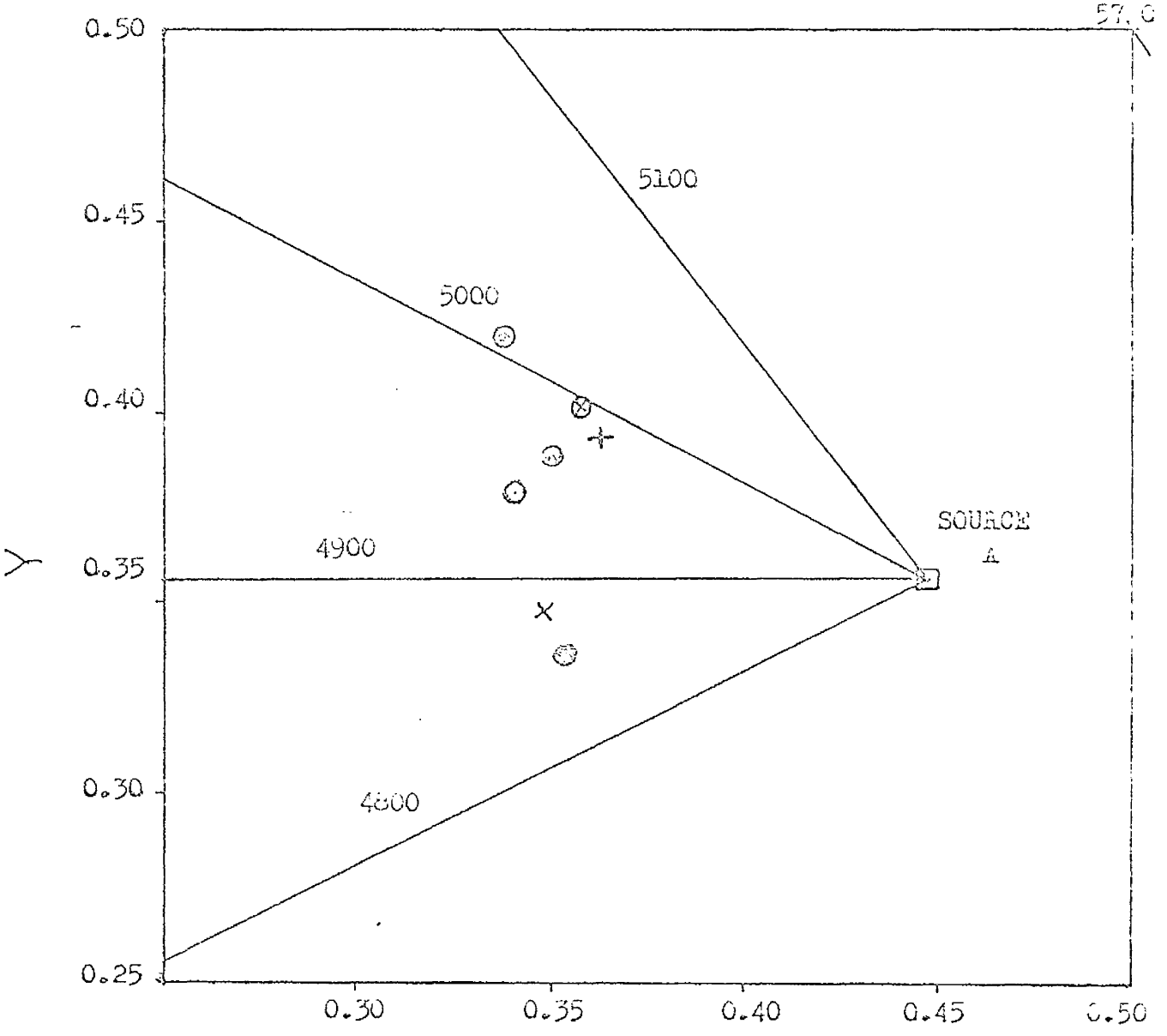


FIG. 7

Naphthalene Green GS - Immacula-II



	20°C	25°C
93 % RH.....	⊙	×
75 % RH.....	⊚	⊗
32 % RH.....	-	+
CONTROL.....	◎	TREATED..... ⊛

FIG. 8

TABLE V

Lightfastness gradings of the dyed and treated samples after exposure to the mercury vapour lamp.

Dye	Treatment				
	Siroset (2% ammonium thio-glycollate)	Immacula-I (2% sodium bi-sulphite)	Urea-bi-sulphite	Water	Control
Naphthalene Green GS	1	2	2	3	3
Solway Green G	6	7	7	7	7
Solway Blue RNS	4-5	5	5	5-6	5-6
Solochromate Fast Red 3GS	6	7	7	7	7
Idsoamine Red 7BPS	3	5	5	5	5
Propolan Yellow 3GX	5	6	6	6	6

DISCUSSION OF RESULTS

It is observed that the samples dyed with dyes such as Solway Blue RNS, Solway Green G, Lissamine Red 7BPS, Solochromate Fast Red 3GS, and Propolan Yellow 3GX, show very little change in dominant wavelength or brightness (± 1%) when they are exposed to various relative humidities and temperature after being given Siroset or Immacula treatment, fig. 5. This is expected because the dyed samples when subjected to either of the treatments show very little change in hue or brightness. However, Naphthalene Green GS shows considerable changes in dominant wavelength, fig. 6,7,8, and brightness (up to 17%) after being treated and exposed.

It appears that in the case of Naphthalene Green GS, the dominant wavelength of the Siroset treated samples tends to revert to that of the control (untreated) when they are exposed to high humidity and temperature. The difference between the dominant wavelength of the control and treated sample which is exposed to 32% RH at 25°C is greater than the difference for a sample exposed to 93% RH at the same temperature, fig. 6. The difference between the percentage brightness of the treated and control samples decreases with the increase in % RH at constant

temperature and with increase in temperature at the corresponding humidity, Table IV.

In the case of the other two treatments, Immacula-I and Immacula-II, the samples dyed with the Naphthalene Green GS show a similar reversal in hue and brightness as observed in the Siroset treatment, after exposure to similar conditions, fig. 7,8.

In order to explain the considerable change in hue and brightness, in the case of the samples dyed with Naphthalene Green GS, it is first necessary to understand why the treatments cause the changes in the samples. Unfortunately, a great deal of controversy exists regarding the mechanism of the changes in hue and brightness brought about by these treatments. However, it may be suggested that the change in shade of a dyed sample when given the Siroset treatment is either because of the sensitivity of the Siroset solution to the metals which may be present in the dye or the reduction of the dye itself.

The first suggestion cannot be supported by the present results firstly, as it was observed that the chrome dyed sample did not show any change in shade. Secondly, the reversal of hue and brightness of the dyed and treated sample on exposure to high humidity and temperature cannot

be possible if the change in shade is due to the formation of colour complexes by the Siroset solution. Thirdly, the sodium bisulphite solution which is used in Immacula process, in spite of being insensitive to metals, produced similar changes in the shade of dyed material to those caused by Siroset solution.

The second suggestion that the dye may undergo reduction on the treatment means that there may be some changes in the chemical constitution of the dye, for example reduction of certain groups in the dye molecule. Unfortunately it is not yet clear which groups may be responsible for this. However, if such reduction is possible, then the reversal of hue and brightness may be because of the slow oxidation of the reduced dye under the conditions of high humidity and temperature.

It is apparent from above that it is very difficult to derive any conclusion regarding the reversal of hue and brightness after the exposure, unless a definite reason as to why the dye undergoes change on treatment with either of the processes is sought. However, present results definitely indicate that those dyes which are sensitive to permanent pleating processes, show reversal in hue and brightness when the dyed samples after being treated, are exposed to the high humidity and temperature. This is

sufficient to justify our assumption that the change in shade of the material, dyed with such dyes and given permanent pleating treatment before exportation may be because of the storage conditions on the journey.

The dyed, Siroset treated samples appear to have lower light fastness compared to control (untreated) samples. The decrease in fastness may be due to the effect of either steaming or ammonium thioglycollate solution. The possibility of the former effect can be excluded as it appears that mere steam pressing does not alter the light fastness and hence it is suggested that the decrease is because of the action of ammonium thioglycollate solution.

Schiecke [86] suggested that if the dye is fast to the Siroset (ammonium thioglycollate) treatment, then its light fastness would alter negligibly on the Siroset treatment of a sample with the same dye. But it appears that all the dyes investigated in the present work, which have fairly good fastness to the Siroset treatment, show a decrease in the lightfastness when exposed to the light from the mercury lamp; the decrease is most pronounced in the case of Lissamine Red 7BPS. Naphthalene Green GS which has very low fastness to Siroset treatment, suffers nearly a complete loss in light fastness.

From above it can be suggested that the use of dyes such as Naphthalene Green GS, which have very low fastness to the Siroset treatment should be rejected if the dyed sample is to receive this treatment. Secondly, even though some dyes are fast to the Siroset treatment, it is advisable to test them for their fastness to light after Siroset treatment.

It is observed that the sodium bisulphite and urea-bisulphite treatments have no effect on the lightfastness of the dyes which are fast to the Immacula (sodium bisulphite) treatment. However, both the treatments cause a decrease in the lightfastness of Naphthalene Green GS, though not as much as that caused by the Siroset treatment.

It can be concluded that among all the three treatments investigated viz. Siroset, Immacula, and urea-bisulphite, only the Siroset has some effect on the light-fastness of dyes, irrespective of their fastness to the treatment. If good lightfastness is one of the require-ments of a dyed material receiving permanent pleating treatment, then the Siroset treatment should be avoided unless it is known directly that the lightfastness of the dye is not affected by the treatment.

CHAPTER III

THE SWELLING, CREASE-RETENTION AND TENSILE STRENGTH OF THE WOOL TREATED WITH REDUCING AGENTS

INTRODUCTION

Swelling properties

The swelling properties of wool fibres depend primarily on the cystine linkages although the electrovalent salt linkages may also be responsible to a smaller extent. Any rupture of the cystine (disulphide) linkages will immediately affect the swelling of the fibre. Swelling measurements, therefore, make it possible to estimate any damage that may be caused by reagents which are known to attack cystine bonds in wool fibres.

Many microscopical techniques have been employed to study the swelling of a wool fibre but because of their inaccuracy they cannot be relied upon. Centrifuge methods of swelling measurement have been used by various workers: Brown [89] in particular used the method to study the damage suffered by wool on treatment with various alkaline and acidic reagents used in wool processing. According to Brown the swelling can be measured accurately by weighing the centrifuged fibres, which have previously been wetted with a certain buffer solution, then drying and weighing again. It appears from the literature that no attempt has been made to extend such tests to measure the damage caused by reducing agents, used in permanent

pleating processes, to wool.

Mechanical properties

In order to determine whether the fabrics were damaged by the pleating processes, Wolfram and Speakman[91] carried out tensile strength measurements on the samples of fabric, which were untreated, treated with different concentrations of sodium bisulphite (with and without rinsing treatment) and treated with ammonium thioglycollate solutions. They found that fabrics treated with the 2% solution of bisulphite, rinsed, dried and pressed were stronger than corresponding fabrics pressed after impregnation with a solution of sodium bisulphite or ammonium thioglycollate. Davidson and Howitt [65] measured the breaking load of various samples of fabric and yarns extracted from the fabric that had been given urea-bisulphite and resin treatments. They found that the loss in tensile strength suffered by the treated fabrics was small or, especially with the resin treated fabrics, negligible. Satlow and Gerthsen [93] measured the tensile strength of yarns from the wool fabrics given Siroset treatment under various conditions of concentration of reagent, steaming time and pressure. They concluded that the wool was not damaged by processing.

The resistance to wear of variously treated samples was examined by Wolfram and Speakman [91]. They found that the fabrics pretreated with the 2% solution of bisulphite had a greater resistance to abrasion than those pressed after impregnation with the reducing agent, though all methods of pressing caused a fall in wear resistance. Davidson and Howitt's [65] results showed that the loss in resistance to abrasion was in some instances small, but, with certain treatments appeared to assume serious proportions. They concluded that, generally, the resistance to abrasion tended to follow the changes in breaking load. Recently the mechanical properties of disulphide-reduced wool fibres, measured over a range of humidities has been reported.[81] It was observed that the reduction of disulphide content of a wool fibre produced progressive modification of mechanical properties of the fibre at all humidities.

Crease-retention

The wash-and-wear concept introduced a new requisite for garments e.g. retention of acceptable crease or pleats after washing and drying. The term "Crease" is defined as the deliberate fold in a fabric introduced by the application of heat, pressure and moisture. The properties

such as crease-resistance, crease-recovery and crease-retention can be classified under the single heading of resilience. All protein fibres are highly resilient and this is probably because of the great flexibility of the protein molecules and the existence of bulky side chains. Whilst the qualitative concept of crease-retention is clear, its quantitative definition is difficult: it has been defined as the relation of the crease angle in a subsequent state to the crease angle in the initial state. The crease angle of a sample is the angle between the two arms of the sample.

For the fabrics other than of wool, it is possible to study the crease-retention of a creased material by measuring the angle of crease by any of the apparatus used for crease-recovery angle measurement. In the case of wool fabrics, because of their thickness, ~~limpness,~~ and tendency to curl, there is no satisfactory method for measuring a crease angle of a creased fabric. However, in the past few years some workers have tried to measure the crease-retention of creased wool~~len~~ fabrics by different methods.

Wolfram and Speakman [91] investigated the problem of the optimum conditions of treatments for imparting permanent creases or pleats to all-wool fabrics and also

compared the merits of the bisulphite and the thioglycollate processes. They concluded that if the fabric treated with a 2% solution of sodium bisulphite for 15 minutes at room temperature and pressed for 15 seconds between damp cloth in the Hoffman Press, the angle of crease retained after 3 hour immersion in a solution of Teepol (0.3%) at room temperature ranges from 80° for a light weight tropical suitings to 99° for a grey flannel. Further they thought that better results were obtained if, instead of pretreating the fabrics with sodium bisulphite solution, they were merely impregnated with a dilute solution of sodium bisulphite immediately before pressing for 15 seconds in the Hoffman Press. The sodium bisulphite gave much sharper creases than ammonium thioglycollate in corresponding concentration. Davidson and Howitt [65] studied the crease retention of the samples of fabric treated with different reagents such as urea-bisulphite, detergent-bisulphite, reducing agents other than bisulphite and thioglycollate, organic bases impregnated with sulphur dioxide, resins, and some other reagents. They found that if the materials were stored for 6 months after treatment with urea-bisulphite and then pressed, the efficiency of crease-retention was practically unchanged.

It is known that the absorption of water by wool fibres has a profound effect on their mechanical properties. It is also known that in the case of synthetic-fibre fabrics a crease impressed by commercial pressing techniques is well retained under high humidity or even after wetting, whereas it disappears in wool fabrics under such conditions [92]. It appears from the literature that so far no attempt has been made to investigate the effect of high humidity and temperature, which prevail in tropical countries, on the crease retention of woollen fabric given either Immacula or Siroset treatment. Moreover, it would be interesting to examine some dyed and treated sample as most of the woollen materials which are subjected to permanent pleating processes, such as men's suits, ladies' skirts, are usually dyed.

In the present work attempts have been to study:

(a) the swelling of wool from fabric treated with reducing agents (used in permanent pleating processes), and steamed for various times;

(b) the tensile strength of the dyed and undyed yarns treated with reducing agents and steamed for various durations;

(c) the different methods of permanent pleating of dyed and undyed woollen fabrics and the optimum conditions of steaming for each;

(d) the effects of storage at various humidities and temperatures on the crease-retention of the treated sample.

EXPERIMENTAL PROCEDURE

Materials

Wool

The woollen fabric used in these experiments was that described in Chapter II. In addition, for tensile measurements, worsted yarns 48/2 Tex (12/2 worsted) were soxhlet extracted with methylene chloride and washed with distilled water and dried at room temperature and humidity.

Chemicals

In addition to the solutions described in Chapter II, a buffer solution was prepared by dissolving 6.26 gms. of sodium dihydrogen phosphate, 0.95 gm. of disodium hydrogen phosphate and 2 ml of Lissapol N in distilled water and the volume was made up to 100 ml. The pH of the solution was adjusted to 5.95 at 20°C.

Experimental methods

The woollen fabric and the yarn were dyed with Naphthalene Green GS as described in Chapter II.

Dyed and undyed wool fabrics were cut in to 3" x 6" pieces and each piece was given one of the four different treatments namely (a) Siroset (b) Immacula-I (c) urea-bisulphite (d) water, under the same conditions as described in Chapter II. The dyed and undyed yarns were treated similarly except that in the case of urea-bisulphite treatment (c), the yarns were divided into two batches; one batch was rinsed in water after the treatment while the other was not rinsed but squeezed out and air dried.

The creases were then inserted in the treated material by steaming them in the Hoffman press for different intervals of time from 20 up to 120 seconds; the typical sequence of operation for 20 seconds of steaming is described in Chapter II.

Swelling measurements

The undyed samples were cut into $\frac{1}{4}$" x $\frac{1}{4}$" square pieces. About 1 gm. of each sample was then placed in a beaker which was filled with a buffer solution. The samples were allowed to remain in this solution for 1 hour,

at the end of which they were taken out and blotted twice between filter paper to remove excess liquid and then were introduced into 15 ml centrifuge tubes prepared as follows. The bottom 2 inches of the tube was filled with absorbent cotton-wool rammed down tight with a glass rod, a small circle of filter paper (prepared from a wad of filter paper using a cork borer) was then introduced and the wool sample was placed on top of this.

The tubes were centrifuged at 1,200g for exactly 15 minutes. The speed employed was 3,700 rpm and was calculated from the formula

$$N = 298\sqrt{F/r}$$

where F is the gravitational factor required, r cm, the distance of the sample from the axis and N, the number of revolutions per minute. A tachometer was used to adjust the correct speed.

After centrifuging, the tubes were withdrawn one by one from the instrument and the wool samples were transferred without delay into weighing bottles fitted with ground glass stoppers. The weighing bottles were next weighed, giving the amount of fibre and absorbed water, and bottle and fibre were dried for 4 hours at 110°C and weighed again, giving the dry weight of the fibre.

Calculation of swelling percentage
Calculation of swelling percentage

Weighing bottle + centrifuged wool	(a)
Weighing bottle + dried wool	(b)
Weighing bottle	(c)
Absorbed water	(a-b)

$$\text{Swelling} = \frac{a-b}{b-c} \times 100\ \%$$

For each sample three readings of percentage swelling were averaged.

Tensile strength

Storage condition

The yarns treated with urea-bisulphite (without rinsing treatment) were exposed to 90% RH at 25°C for four weeks.

Tensile strength measurements

In all cases the yarns were allowed to condition in a room controlled at 20°C and 65% RH for 72 hours prior to submission to tensile tests. The measurements were done on a pendulum type single-thread testing machine. The lower grip attached to the machine drive traversed at a constant rate of 12 inches per minute. The grips were adjusted to accommodate 18 inches of yarn sample. Breaking load and extension at break were recorded. 40 readings for each sample were taken. All the tests were

carried out in a conditioned room at 20°C and 65% RH.

Crease-retention

Storage conditions

(1) Dyed samples treated by the method (a), the Siroset process, were allowed to lie flat on the glass plates for 6 months in conditioned room which was maintained at 20°C and 65% RH.

(2) Undyed samples which were given treatments (b), the Immacula, and (c), the urea-bisulphite process, were kept flat on glass plates arranged in a closed chamber controlled at 30°C and 93% RH for 6 weeks.

Measurement of crease angle

A small piece of fabric, 2 cm x 1 cm creased centrally across the length was cut from the above samples and was mounted on a razor blade. An image was projected by means of a slide projector onto a screen made up of drawing paper and the angle of crease was measured directly. In all cases the samples were conditioned at 20°C and 65% RH prior to testing and all the measurements of crease angle were carried out in a conditioned room maintained at 20°C and 65% RH. For each sample ten values of the crease angle were averaged.

EXPERIMENTAL RESULTS

TABLE VI

The percentage swelling of samples treated with sodium bisulphite (1%) and steam pressed for different intervals of time.

Swelling of untreated sample = 38.6%

Steaming time in seconds	Percentage swelling			
	Individual values			Mean
10	40.1	40.9	40.4	40.5
20	41.2	41.4	41.5	41.4
30	41.6	41.2	41.7	41.5
40	41.5	42.0	42.4	42.0
50	43.1	42.4	43.1	42.9
60	42.6	43.3	42.6	42.8
70	42.7	43.2	42.9	42.9
80	40.4	42.9	42.7	42.0
90	37.9	36.5	41.4	38.6
100	39.1	-	42.1	-
110	37.5	35.6	39.5	37.5
120	38.9	36.9	38.7	38.2

The reproducibility of the results appears to be satisfactory up to the steaming of 80 seconds, beyond which varied results are obtained. Up to 80 seconds steaming time values appear to be reliable to ± 0.6%

TABLE VII

The percentage swelling of samples treated with ammonium thioglycollate, sodium bisulphite, urea-bisulphite or water and steamed for different intervals of time.

Swelling of untreated sample = 38.6%.

Steaming time in seconds	Percentage swelling				
	Ammonium thioglycollate 2% (Siroset)	Sodium bisulphite 1% (Immaculate I)	Sodium bisulphite 2% (Immaculate I)	Urea-bisulphite	Water
20	40.7	41.4	-	39.5	39.9
40	46.1	42.0	40.6	41.3	41.3
60	42.4	42.8	42.7	41.9	41.3
80	39.6	42.0	38.8	41.6	41.5

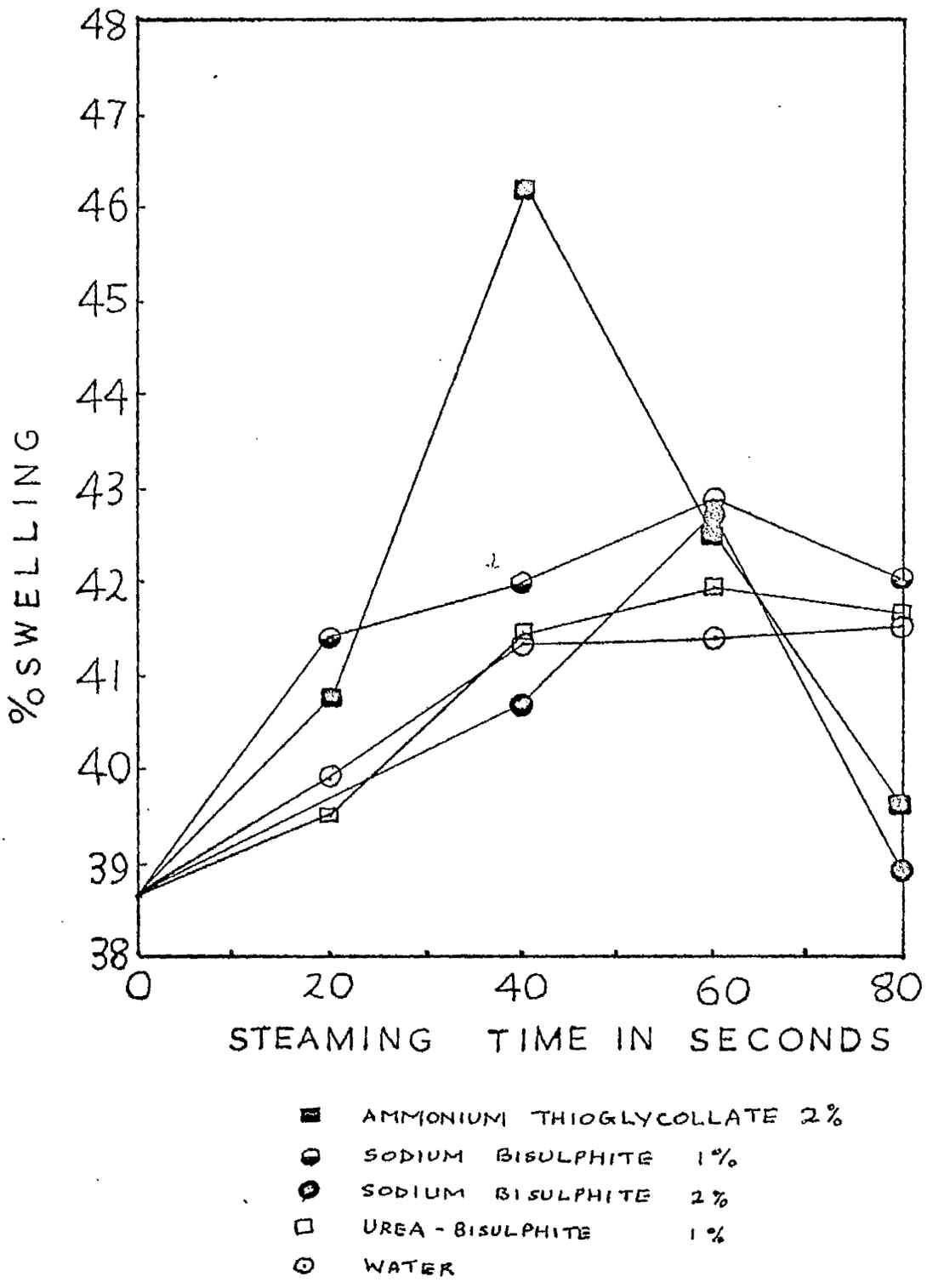

48
47
46
45
44
43
42
41
40
39
38
% SWELLING
0
20
40
60
80
STEAMING TIME IN SECONDS
AMMONIUM THIOGLYCOLLATE 2%
SODIUM BISULPHITE 1%
SODIUM BISULPHITE 2%
UREA - BISULPHITE 1%
WATER

FIG. 9

TABLE VIII

The breaking load and percentage extension at break of the dyed and undyed yarns treated differently and steamed for 20 seconds

Treatment	Undyed				Dyed			
	Breaking load in gms	S.E. gms.	% Extn. at break.	S.E. %	Breaking load in gms	S.E. gms	% Extn at break	S.E. %
Ammonium thio-glycoll-ate 2% (Siroset)	329	4	17	0.5	317	4	20	0.6
Ammonium thio-glycoll-ate 1% (Siroset)	342	4	19	0.5	-	-	-	-
Sodium bi-sulphite 1% (Immacula-I)	314	5	17	0.5	307	3	19	0.5
Water	346	5	20	0.6	291	7	19	0.5
Un-treated	350	4	21	0.5	313	4	20	0.6

TABLE IX

Undyed yarns treated with 2% ammonium thioglycollate solution

Steaming time in seconds	Breaking load in gms.	S.E. gms.	% Extension at break	S.E. %
Untreated	350	4	21	0.5
20	329	4	17	0.5
40	300	2	15	0.3
60	300	4	16	0.5
80	290	5	15	0.5

TABLE X

Undyed yarn treated with 1% sodium bisulphite solution.

Steaming time in seconds	Breaking load in gms.	S.E. gms.	% Extension at break	S.E. %
Untreated	350	4	21	0.5
20	314	5	17	0.5
40	303	4	17	0.5
60	291	4	16	0.3
80	292	4	15	0.3

TABLE XI

Undyed yarns treated with urea-bisulphite solution and rinsed in water.

Steaming time in seconds	Breaking load in gms.	S.E. gms.	% Extension at break	S.E. %
Untreated	350	4	21	0.5
20	310	5	21	0.3
40	298	5	21	0.6
60	297	6	19	0.4
80	301	5	16	0.2

TABLE XII

Undyed yarns treated with urea-bisulphite solution but not rinsed.

Steaming time in seconds	Breaking load in gms.	S.E. gms.	% Extension at break	S.E. %
Untreated	350	4	21	0.5
20	278	4	24	0.6
40	265	3	22	0.6
60	273	2	22	0.5
80	260	4	23	0.6

TABLE XIII

Undyed yarns treated with urea-bisulphite solution, without rinse, and exposed to 90% R.H. at 25°C for 4 weeks.

Steaming time in seconds	Breaking load in gms.	S.E. gms.	% Extension at break	S.E. %
20	245	4	37	0.8
40	242	3	37	0.6
60	222	4	36	0.6
80	191	5	32	1.0

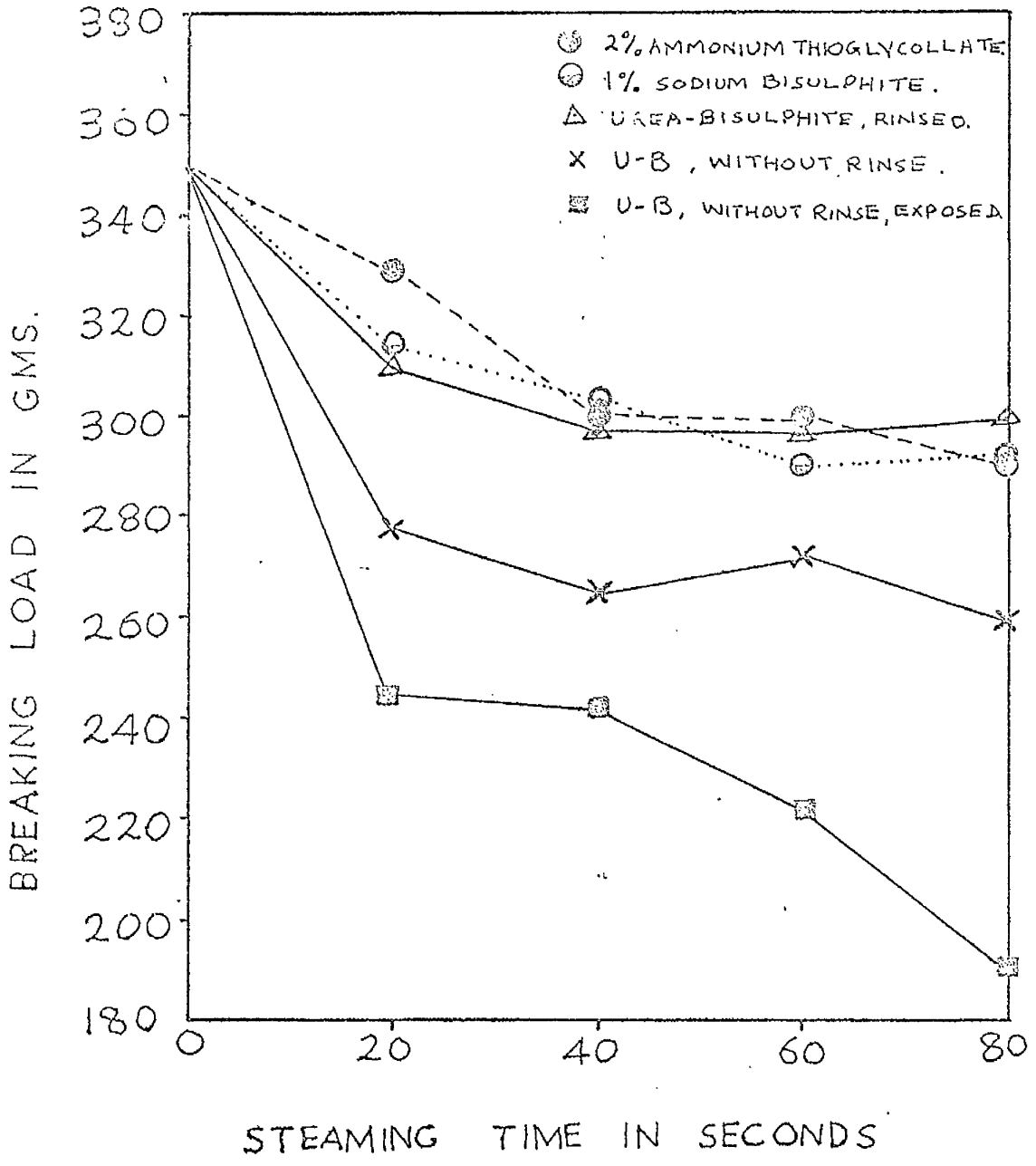

2% AMMONIUM THIOGLYCOLLATE.
1% SODIUM BISULPHITE.
UREA-BISULPHITE, RINSED.
U-B, WITHOUT RINSE.
U-B, WITHOUT RINSE, EXPOSED.
BREAKING LOAD IN GMS.
330
300
340
320
300
280
260
240
220
200
180
0
20
40
60
80
STEAMING TIME IN SECONDS

FIG. 10

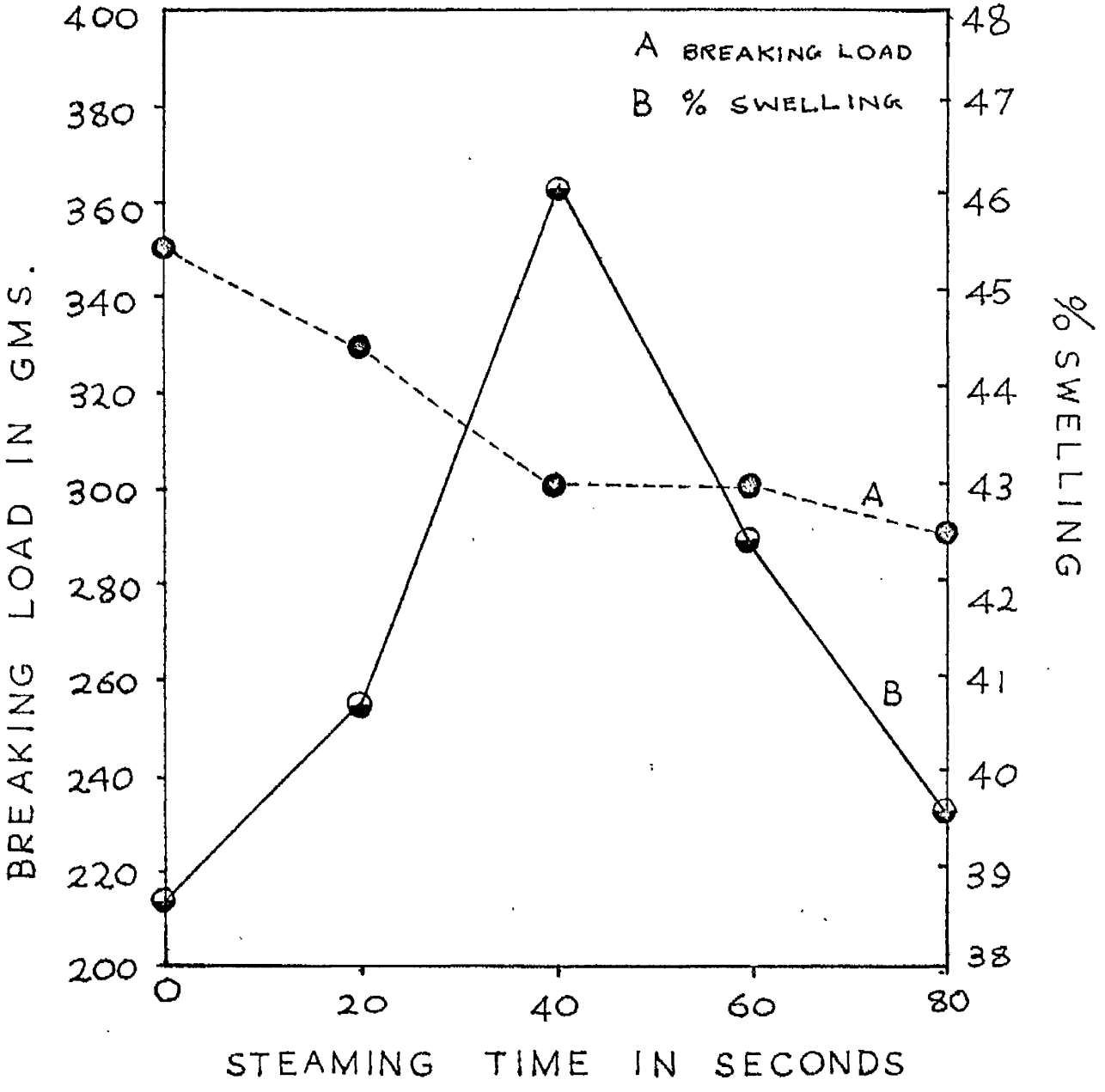

A BREAKING LOAD
B % SWELLING
400
380
360
340
320
300
280
260
240
220
200
48
47
46
45
44
43
42
41
40
39
38
A
B
0
20
40
60
80
BREAKING LOAD IN GMS.
% SWELLING
STEAMING TIME IN SECONDS

FIG. II

Immacula-I (1% sodium bisulphite) treatment.

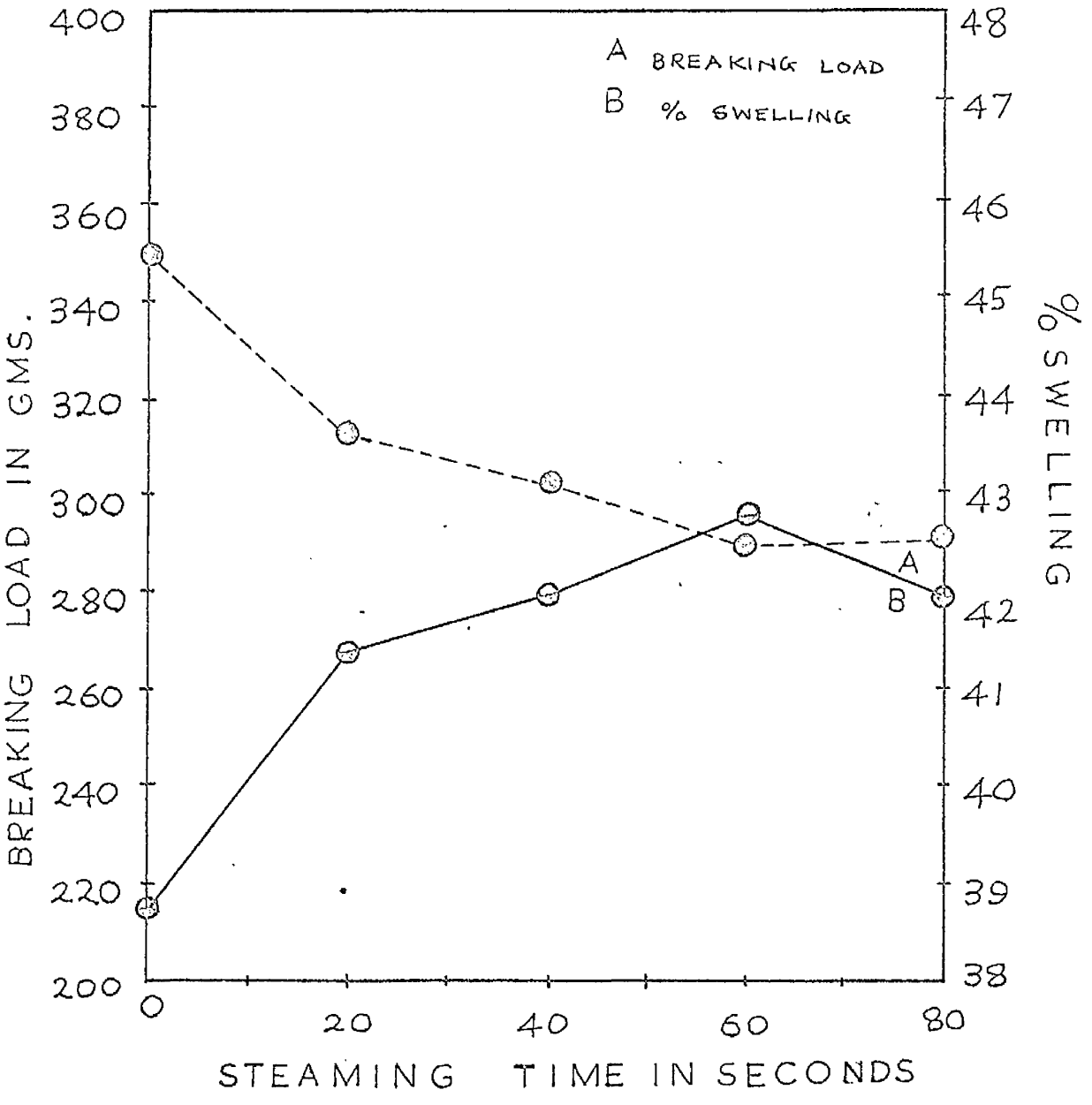


FIG.12

Urea-bisulphite treatment (without rinse).

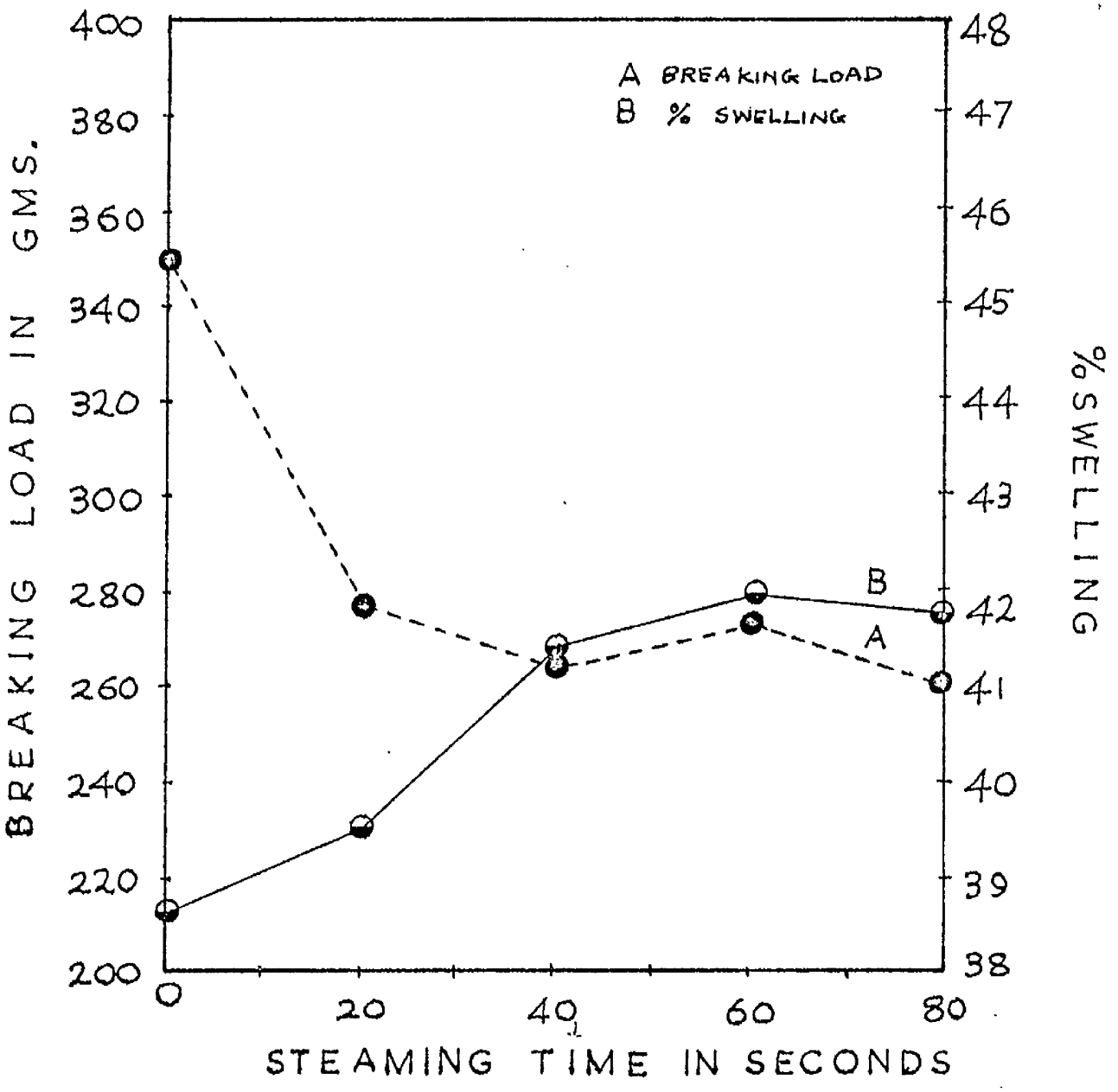


FIG.13

The term 'crease angle', used in the following results means the angle formed by the two sides of the crease of a sample; an ideal crease is with the adjacent sides parallel i.e., angle = 0. 'Dyed' means the samples dyed with Naphthalene Green GS.

TABLE XIV

The dyed samples treated with 2% ammonium thioglycollate solution (Siroset) and steam pressed for different intervals of time.

No.	Crease angle (°)			
	Steaming time in seconds			
	20	40	60	80
1	23	25	21	22
2	24	25	21	23
3	19	24	20	25
4	24	27	21	24
5	23	20	23	24
6	23	24	21	26
7	22	27	27	23
8	26	24	24	22
9	26	24	24	26
10	24	24	25	28
Mean	23	24	23	24
SE	0.6	0.6	0.7	0.6

TABLE XV

Crease angles for dyed and undyed samples treated with 2% ammonium thioglycollate (Siroset), 2% sodium bisulphite (Immaoula-I) and urea-bisulphite and steam pressed for different intervals of time

Steam pressing time in sec.	Crease angle (°)					
	Siroset		Immaoula-I		Urea-bisulphite	
	Undyed	dyed	Undyed	Dyed	Undyed	Dyed
20	24	23	29	22	23	-
40	25	24	27	22	22	-
60	24	23	26	22	23	-
80	25	24	23	24	24	-

TABLE XVI

Crease angles for undyed samples treated with 2% sodium bisulphite (Immaoula-I) and urea-bisulphite and steam pressed for different intervals of time and then exposed to 30°C and 93% RH for 6 weeks

Steaming time in seconds	Crease angle (°)			
	Immaoula-I		Urea-bisulphite	
	Unexposed	Exposed	Unexposed	Exposed
20	29	24	23	22
40	27	24	22	22
60	26	23	23	22
80	23	23	24	22

TABLE XVII

Crease angles for dyed samples treated with 2% ammonium thioglycollate (Siroset) and steam pressed for different intervals of time and then stored for 6 months at 20°C and 65% RH.

Steaming time in seconds	Crease angle (°)	
	Unexposed	Exposed
20	23	22
40	24	22
60	23	21
80	24	23

DISCUSSION OF RESULTS

Wool keratin possess the characteristic of extreme insolubility, which, it is believed, is because of the numerous stable covalent cross-linkages arising from the high proportion of cystine in the molecule. The swelling properties of wool also depend chiefly on the cystine linkages, [42] though salt linkages may have some influence. It is obvious that any rupture of the disulphide bonds, which may occur by treatment of wool with strong reducing agents such as ammonium thioglycollate, sodium bisulphite, used in permanent pleating processes, will immediately affect the swelling properties of the fibre.

Ammonium thioglycollate treated samples show a rapid increase in swelling up to the steaming time of 40 seconds. As the steaming time is further increased to 60 or 80 seconds there is a decrease in the swelling (fig. 9). This would indicate that ammonium thioglycollate ruptures the disulphide bonds rapidly when the sample is steam-pressed and the maximum rupture occurs at the time of 40 seconds. If the time of steaming is increased further than that there may occur a reformation of the same or new types of links which in turn may restrict swelling as observed above. The reformation of the ruptured bonds does not appear to be complete at the

steaming time of 80 seconds as the value of swelling does not fall to that of the untreated sample.

The swelling of the samples treated with 1% solution of sodium bisulphite rapidly increases during first 20 seconds and then less rapidly, to reach a maximum in the region 50 to 70 seconds, after which it decreases slowly at first and then more rapidly, reaching the value for untreated fibres at a steaming time longer than 90 seconds (fig. 9). The initial rapid swelling of the samples suggests the rapid rupture of the disulphide bonds as for the ammonium thioglycollate treatment. The maximum rupture of the bonds occurs at a steaming time of about 60 seconds, thereafter the reformation of bonds is slow but is complete after 120 seconds. In the case of the treatment with 2% solution, the maximum amount of ruptured bonds is more or less the same, but most of the ruptured bonds seem to get reformed after 80 seconds of steaming, since the swelling at this time is nearly equal to that of the untreated sample.

Urea-bisulphite treated samples show an increase in swelling up to the steaming time of 40 seconds, after which the swelling is nearly constant. This suggests that (1) the rupture of disulphide bonds occurs up to 40 seconds and (2) the reformation of the bonds does not

occur at the steaming time of 80 seconds.

The water-treated samples show a similar trend of swelling, and hence rupture of disulphide bonds, to the urea-bisulphite treated samples, as described above. This suggests that steam is as effective as reducing agents in breaking disulphide bonds. However, the reformation of bonds may require a very long time of steaming since it is apparent from the treatments described above that the greater the amount of reducing agent in the solution, the less the time of steaming required to reform the bonds and secondly, the percentage swelling curve for water-treated and steamed samples appear to be in general agreement with Astbury and Woods' supercontraction curve [38] for wool fibres stretched and relaxed in steam, which shows a maximum supercontraction for 120 seconds relaxation.

The comparison of the various treatments described above reveals that, in all the cases, except the ammonium thioglycollate treatment, the general trend of rupture of disulphide bonds is similar. In all cases, the extent of reformation of the bonds, either the same or new type, varies with concentration of the reducing agent in the solution employed. The above observations support the view of Speakman [47] that steaming of fibres, untreated

or treated with reducing agents such as ammonium thioglycollate or sodium bisulphite, causes a rupture of the disulphide bonds which are then reformed under suitable conditions.

The comparison of the tensile properties of the yarn given the three different treatments mentioned above (fig.10) reveals that in all the cases, the breaking load decreases rapidly with the steaming time up to 40 or 60 seconds and thereafter it becomes steady at a limiting value of 80% which is about the same for all three treatments. The initial rapid decrease in tensile strength may be explained as the result of the rupture of the disulphide bonds since it is known that in wool keratin, the disulphide bonds, which hold each chain molecule to its neighbour, make a major contribution towards the tensile strength. It is concluded that all the treatments mentioned above can cause damage to wool.

Yarn treated with urea-bisulphite but not rinsed before steaming, shows a more rapid decrease in breaking load and reaches a lower limiting strength (74%) than yarn given the above mentioned three treatments. In addition to this, if the unrinsed yarn is exposed to high humidity for four weeks before tensile measurements, the breaking

load decreases drastically for the steaming time of 20 seconds (fig. 10) and continues to decrease without apparently reaching any limiting value, so that its strength is almost halved after 80 seconds of steaming.

For all the three treatments namely, ammonium thioglycollate, sodium bisulphite and urea-bisulphite (rinsed), the extension at break shows a decrease. The limiting value of the extension 15 - 17% is almost the same at the steaming time of 80 seconds (Tables IX, X and XI). If the yarns given urea-bisulphite treatment are not rinsed, the extension remains nearly constant (Table XII), but if the same yarns are exposed to high humidity, they show a considerable increase (to almost twice the value of the untreated) in the extension (Table XIII). It is unwise to attempt to interpret this considerable increase in the extension on the basis of observations limited to yarns and no tests on the single fibres were carried out. Nevertheless, the observations are most striking and demand further investigation.

Since swelling and tensile strength of wool are primarily dependent on the disulphide links, an increase in swelling and a decrease in tensile strength may be anticipated. The results obtained by the swelling

measurements, in the case of treated fabric, are in fair agreement with the results of the tensile strength measurements of the treated yarn. It should be noted that though the swelling and the tensile strength measurement are done respectively on the fabric and the yarn, the type of the wool in both the cases is the same, namely merino.

In the case of 2% ammonium thioglycollate treated yarn, the swelling increases with the steaming time up to 40 seconds (fig. 11) and correspondingly, the tensile strength decreases. 1% sodium bisulphite and also urea-bisulphite (unrinsed) samples appear to follow a similar course of increase in swelling and decrease in tensile strength (figs. 12 & 13).

It has been suggested earlier that the decrease in swelling at longer times of steaming may be because of the reformation of the same or new type of links. The possibility of the reformation of the same type of linkages (disulphide bonds) can be excluded as it appears that neither the tensile strength nor the extensibility increases with the decrease in swelling and it is concluded that new types of links, which are capable of restricting swelling, alone are formed.

Phillips and co-workers [125] suggested the existence of two main fractions, namely (A+B) and (C+D), of the cystine-S of wool. According to them (C+D) does not react with cold bisulphite but does react with hot bisulphite. They further suggested that of the two fractions, fraction (A+B) influences the physical properties of keratin fibres more profoundly than fraction (C+D). If these views are extended to the present observations it is suggested that both the fractions, (A+B) and (C+D), may be involved since the material is steamed after it is treated with reducing agents and the reduction in tensile strength may be because of the rupture of bonds in fraction (A+B). However, in the case of urea-bisulphite treated samples where the urea is not rinsed before steaming, the loss in tensile strength may be due to the rupture of both the cystine bonds of the (A+B) fraction and the hydrogen bonds. If the material is rinsed before steaming most of the urea may be rinsed away, allowing the reformation of hydrogen bonds and this is what is indicated in the observations that the loss in the tensile strength of urea-bisulphite treated and rinsed yarn is nearly equal to that of the yarn treated with reducing agents alone.

The breaking load of the yarn dyed with Naphthalene Green GS is smaller than that of the undyed yarn

(Table VIII). The change in breaking load is almost nil for the dyed yarn, either treated with 2% ammonium thioglycollate or 1% sodium bisulphite, when compared with dyed and untreated yarn, but there is a change in the breaking load if the dyed yarn is treated with water. On the other hand, the breaking load of the undyed yarn, given either of the treatments with reducing agent mentioned earlier, changes when compared with that of the untreated, but there is almost no change in the breaking load of the yarn treated with water.

It is apparent from the above that mere dyeing with particular dyes can cause a loss in the tensile strength of the material. The fact that, with undyed yarn, the reducing agents cause a marked loss in the tensile strength while it does not cause considerable loss in the dyed yarn, can be explained as follows. The dye Naphthalene Green GS is very sensitive to reducing agents and when yarn dyed with this dye is treated with reducing agent and steam pressed, the activity of the agent may be mainly diverted towards attacking the dye and bringing about the change in shade and hence causing a small loss in tensile strength. Secondly, it is possible that most of the bonds susceptible to the reducing agents may have been attacked during dyeing, as the loss in the

tensile strength is observed, leaving behind a few bonds to be attacked by the reducing agents. The steaming alone does not affect the dye, but it causes a loss in tensile strength of the yarn.

It is suggested that treatment with the reducing agents, employed in the present case, of the woollen material dyed with the dyes such as Naphthalene Green GS, sensitive to the agents, does not alter the tensile strength i.e. the reduction affects the dye in preference to the fibre. Though tensile tests were not made on the yarn dyed with an insensitive dye and then treated with reducing agents, it is suggested that the reducing agent may cause a loss in the tensile strength of the yarn dyed with such dyes.

(Table xVI)

The crease angle measurements show that the exposure to high relative humidity and temperature (93% RH and 30°C) for six weeks has no negative effect on the crease-retention of the undyed samples given either Immacula or urea-bisulphite (unrinsed) treatment. This suggests that the absorption of moisture, which can cause the disappearance of a steam-set crease does not affect the crease produced by permanent pleating processes.

It appears from the crease angle measurements of dyed, ammonium thioglycollate treated and stored samples

that the exposure for six months to normal conditions of relative humidity and temperature (65% RH and 20°C) does not impair the sharpness of the crease (Table XVII). This observation along with the findings of Davidson and Howitt [65], that storage for six months had no effect on the efficiency of the crease-retention of the undyed and sodium bisulphite treated samples, suggest that the storage for prolonged time under normal conditions has no effect on crease-retention of the dyed or undyed sample creased by either of the two permanent pleating processes.

It seems that of the various treatments given to undyed material, the thioglycollate one gives a sharper crease than the sodium bisulphite one, and urea-bisulphite one gives the sharpest of all, under corresponding steam pressing times. An increase in the time of steam pressing, which has practically little effect on the sharpness of the crease of the ammonium thioglycollate and urea-bisulphite treated samples, causes a very slight improvement in sodium bisulphite treated samples, as observed by Speakman and Wolfram [91]. Sharper creases are obtained on the material dyed with Naphthalene Green GS than the undyed, when treated with sodium bisulphite and steam pressed for corresponding intervals of time (Table XV). This suggests that the presence of this dye in wool assists the reaction

of reducing agents with disulphide linkages and favours the suggestion made earlier that, in wool, most of the linkages susceptible to the reducing agents are attacked during dyeing with this particular dye.

The conclusion drawn from the results is that, for all the treatments investigated, a steaming time of 20 seconds is found to be the ideal one since at this time:

(1) the net number of broken disulphide linkages is less than for longer times, as found from the swelling measurements,

(2) the loss in tensile strength is also least,

(3) the crease that is obtained is nearly as sharp as that obtained at a steaming time of 80 seconds.

The above observations that the samples treated with ammonium thioglycollate gives sharper creases than those treated with sodium bisulphite and rinsed before steaming, along with the observation of Speakman and Wolfram [91], that the fabrics impregnated with solutions of sodium bisulphite before pressing, without rinsing, gave much sharper creases than ammonium thioglycollate, suggest that the 'rinsing' treatment reduces the effectiveness of the reducing agent in producing sharp creases and this can be explained as follows. When the treated

sample is rinsed, there may be some reversal of the reaction

$$R.S.S.R + NaHSO_3 \rightleftharpoons RSH + R.S.SO_3Na$$

and this may reduce the amount of sodium bisulphite combined with the fibre.

A possible explanation for the very sharp crease in the case of urea-bisulphite treatment is that the woollen material become less limp as the urea in the material is not rinsed away and the two sides forming the crease angle in a sample are almost straight compared to those of the samples given either the Immacula or the Siroset treatment. However, even though the urea-bisulphite (unrinsed) treatment can produce the sharpest crease in the woollen material, the evidence that it causes a considerable reduction in tensile strength suggests that the treatment has a very little practical value. On the other hand if the material is rinsed before steaming, the loss in tensile strength is less, but at the same time a less sharp crease can be expected because of the loss in the effectiveness of the reducing agent due to rinsing and also loss of stiffness of the material because urea is washed out. It is concluded that the use of urea-bisulphite in permanent pleating processes of wool material as suggested by Farnworth[58] is not very satisfactory.

CHAPTER IV

OPTICAL AND ELECTRON MICROSCOPY OF THE FIBRES TREATED WITH REDUCING AGENTS AND UREA-REDUCER SOLUTIONS

INTRODUCTION

It is a known fact that the disulphide bonds are responsible to a considerable extent for the chemical and the physical stability of wool fibres and it is also known that the bonds are susceptible to attack if wool is treated with reducing agents under certain conditions. Various properties of wool such as setting, supercontraction and tensile strength have been associated with the disulphide linkages.[129] Following the discovery of the bilateral cortical structure in wool,[14] various workers have reported an uneven distribution of sulphur in different segments of the cortex: it has been suggested that the para-cortex is richer in sulphur than the ortho-cortex.[101-105] Many data have been accumulated about the relative response of the two segments [74,77,96-100] (the ortho- and the para-) to chemicals: it has been suggested that the difference in sulphur may be responsible for the difference in the reactivity between the two parts of the bilateral cortex.[100] However, very little appears to have been said whether the properties of wool such as setting, supercontraction and tensile strength depend more on the disulphide linkages in one segment than the other, and this makes it more difficult to associate any change in the properties of wool on treatment with chemicals, with the disulphide linkages in a particular segment of the cortex,

e.g. the change in tensile strength of wool, as observed in the last chapter, given the urea-bisulphite treatment.

The high resolving power of the electron microscope along with the improved contrast given by phase-contrast in the optical microscope has made it possible to study the changes in the morphological structure of wool fibres as a result of various chemical treatments. It is advantageous to employ such methods in order to define the portion of the cortex, histologically, which may undergo modification as a result of the treatment of wool with chemicals such as reducing agents. It is possible that the treatment of wool with reducing agents, under the conditions such as are employed in permanent pleating processes, may not be severe enough to produce any change in the structure of wool detectable under the optical or even the electron microscope and hence it is necessary to treat the wool with very active reagents such as saturated urea solution containing reducing agents.

In an effort to elucidate the very complex structure and composition of wool fibres, various treatments involving the use of keratinolytic agents such as sulphides and urea-bisulphite have been employed by many workers.[74,94,95,115] During early investigations it was observed by Mercer[74] that when wool fibres were treated with urea solution

containing reducing agents, only part of the fibres was dissolved and the extractable fraction came from ortho-cortex, the insoluble residue consisted of (a) the para-cortex (b) the cortical cell membranes of the ortho-cortex, and (c) the resistant cuticular sheath. He concluded that (i) wool keratin formed two histologically definable regions differing in stability and (ii) that difference in solubility of the keratin fractions corresponded to degrees in keratinization i.e. the difference in degree of cystine cross-linking. He suggested that the insolubility of the para-cortex in saturated urea solution at pH 8 was because of the location of (C + D) fraction of Phillips[125] cystine cross-linkages in this region.

In the present work attempts have been made, with the help of the phase-contrast and electron microscopes, to study the effects of reducing agents, both those involved in permanent pleating processes (described in earlier chapters) and the strong urea-reducer solutions. In particular efforts have been made to determine the identity of the portion of the wool fibre involved in any particular situation.

Techniques for the preparation of the samples for examination under the optical and the electron microscope

Fibre embedding and section cutting

Optical examination of fibre sections does not present great difficulty and sections a few microns thick can easily be cut by embedding fibres in paraffin wax and using an ordinary microtome.

Direct electron microscope examination of a fibre requires ultra-thin sections, about 500 A, and hence the embedding medium deserves special attention. In 1949, Newman[108] and his colleagues suggested their polymethacrylate embedding technique for ultra-thin section but it suffers from certain disadvantages such as shrinkage. In 1956, Glauert[109] proposed the epoxide resin "Araldite" as embedding media. "Araldite" contracts far less than methacrylates and is more resistant to electron bombardment. Recently a survey[110,111] of embedding media for electron microscopy has been published in which the properties of the methacrylates, the epoxy resins and the polyester resins are compared and the basic similarities between the different mixtures containing epoxy resins are emphasized.

The actual cutting of very thin sections is difficult. However, if the general rules about such things as

preparation of the glass knives and the degree of hardness of the embedding medium are observed, excellent results can be obtained. Several books (see bibliography) on electron microscope techniques deal with the experimental details. The improved techniques of ultra-thin sectioning and mounting of sections of fibres have been published by various authors. Thin sections have been cut, with glass knives and also diamond knives, on a variety of microtomes.

Staining techniques

In optical microscopy, the use of dyes as specific staining agents for differentiation of structural elements is not uncommon. In addition to the dyes the use of various metals and metal salts as staining agents for wool fibres has been reported.[100,107,112,113]

In electron microscopy the heavy metals and metal salts such as osmium tetroxide, silver nitrate, uranyl acetate, lanthanum acetate, lead acetate and hydroxide, mercury salts, phosphotungstic acid have been employed as specific staining reagents;[12,79,114,116-121] it is a common practice to reduce the fibres before staining. These staining reagents contain atoms which have atomic numbers higher than those of the atoms from which the fibrous substances are built up and the resulting production of contrast is specific to the extent that the

metal is preferentially fixed in certain molecular groups of the fibres. In certain cases, such as staining of reduced merino wool fibres with lead and mercury salts, the migration of salt molecules was observed.[119] In short, a great deal of controversy exists regarding the distribution of the 'active' groups and the reaction between metal atoms and the groups[12,118-120] and doubts have been expressed as to the correct interpretation of staining with metals.

EXPERIMENTAL PROCEDURE

Materials

Wool

Lincoln wool fibres were soxhlet-extracted with methylene chloride, thoroughly washed in distilled water and dried at room temperature and humidity. Fibres, obtained from yarns employed in previous experiments, were also used in the present work. The microscopical examination showed them to be of merino type and hence throughout the present work they are labelled as 'Y merino'.

Chemicals

Saturated urea solution was prepared by dissolving 120 gms. of urea (laboratory reagent) in 100 cc of distilled water at 25°C.

Urea-bisulphite solution was prepared by dissolving 5 gms. of sodium metabisulphite in 100 cc of saturated urea solution and the pH of the solution was adjusted to 7 by adding sodium bicarbonate.

Urea-thioglycollate solution was prepared by adding 5 cc of thioglycollic acid to 100 cc of saturated urea solution. The pH of the solution was 2.5.

Urea-bisulphite solutions containing 80 gms. of urea and 5 gms. of sodium metabisulphite per 100 cc of water were prepared. The pH values of the solutions were adjusted to 3 and 11 by adding hydrochloric acid and sodium hydroxide respectively. The addition of these reagents were carried out prior to making up to volume. These more dilute solutions were prepared because it was difficult to adjust the pH of the saturated urea solution.

Another urea-bisulphite solution was prepared by dissolving 50 gms. of urea and 3 gms. of sodium meta-bisulphite in distilled water and making the volume to 100 cc. at 25°C. The pH of the solution was adjusted to 7 by adding sodium bicarbonate. This is the solution used in urea-bisulphite solubility test.

Partially hydrolysed starch was prepared by mixing 3 gms. of starch with 30 cc. of cold water and making a smooth paste. To the paste were added 60 cc. of boiling water and 0.5 cc. of hydrochloric acid (10%).

The mixture was boiled for 5 minutes and after it had cooled 0.1 gm. of thymol was added.

Embedding media

"Araldite" resin was prepared by mixing the following chemicals in proportions as recommended by Glauert,[122]

Araldite CY	——212	10 cc.
Araldite hardener HY	——964	10 cc.
Araldite plasticiser DY	——042	1 cc.
Araldite accelerator DY	——064	0.5 cc.

Fresh mixtures were prepared each time before embedding fibres.

N-butyl methacrylate (supplied by ICI) was used along with benzoyl peroxide (1 gm/100 cc. of monomer) as catalyst. Fresh solutions were prepared by adding the catalyst to the monomer each time just before embedding wool fibres.

Staining reagents

Methylene Blue solution (0.05%) was buffered to pH 6.8 with 0.05 M phosphate.

Osmic acid (2%) was unbuffered and was employed directly from the ampoule. A silver-ammonium-nitrate complex was prepared[123] by the addition of ammonia, drop by drop, to 0.1 M $AgNO_3$ solution till a brown precipitate was obtained. The precipitate was dissolved by further,

dropwise, addition of ammonia and the pH of the solution was measured to be 7.05 at 20°C.

Mounting media

The abbreviations OCP and PO refer respectively to orthochlorophenol (refractive index 1.550) and paraffin oil (refractive index 1.470) which were used in the optical examination.

Experimental methods

About one hundred fibres of each type of wool were treated with 30 cc solutions contained in 50 cc stoppered flasks (Quickfit). The flasks were placed in a water bath which was maintained at appropriate temperatures. The conditions of treatments were as shown in the Table XVIII.

TABLE XVIII

Treatment number	Urea solution Urea: water	Reducer %	pH of the solution	Time of treatment in hours	Temperature °C
I A	120:100	Bisulphite 5	7	3	40
I B	120:100	Bisulphite 5	7	20	40
II	120:100	Thioglycollic acid 5	2.5	6	45
III	80:100	Bisulphite 5	3	6	40
IV	80:100	Bisulphite 5	11	6	40
V A	50:100	Bisulphite 3	7	1	65
V B	50:100	Bisulphite 3	7	3	65

At the end of the appropriate time of reaction, the fibres were removed from the solutions and were thoroughly washed with distilled water for several hours and then they were dried at room temperature and humidity for one week.

In addition to fibres, given the treatments as mentioned above, those from the yarns given (1) Siroset (2) Immacula-I (3) urea-bisulphite (rinsed) treatments were also examined.

Staining methods

(1) The fibres were immersed in unbuffered osmic acid for 24 hours at room temperature and then were rinsed with water and dried in a conditioned room before embedding.

(2) The fibres were immersed in silver-ammonium-nitrate solution for 40 hours at room temperature and were rinsed and dried as in (1) before embedding.

Preparation of specimen blocks for section cutting

Embedding

The fibres, either previously stained or unstained, were embedded in (a) Araldite or (b) butyl methacrylate as follows.

(a) The fibres were soaked in the "Araldite" resin mixture (without accelerator) for about 24 hours and after that a few impregnated fibres were placed in two

diametrically opposite notches across an open end of a gelatin capsule (No. 00), containing resin mixture with accelerator. The fibres were kept taut by catching their free ends between the two sliding portions of the capsule and the cover of the capsule was placed in position. The whole assembly was inverted so that the fibres became completely embedded in resin. The capsule was then heated in an oven at a temperature of 50°C: care was taken to heat the capsule evenly over its entire surface by suspending it with strips of cellophane tape in the oven. It was observed that, in order to produce a proper hardness for section cutting, a longer time (up to 60 hours) than the 48 hours of heating suggested by Glauert[122] was necessary.

(b) The procedure of embedding was similar to that described in (a) except that n-butylmethacrylate was used in place of the Araldite resin mixture.

Trimming of the blocks

The gelatin capsule was stripped with a sharp razor blade and the block thus obtained was trimmed to a small cylinder having a diameter of approximately 0.5 cm. It was ensured that the fibres were embedded nearly parallel to the axis of the cylinder. The cylinder was then firmly fixed in the specimen holder from the microtome by a collet and one end of the cylinder was trimmed in to

a pyramid; the height of the pyramid was about 1 mm. and the tip was about 0.2 mm. square. The sample was then ready for section cutting.

Section cutting

The sections were cut on a ultra-microtome (A.F. Huxley Pattern), operating on a mechanical advance mechanism, with glass knives. For optical work the sections about 2 μ thick were cut, whereas for electron microscopical examination, the thickness of the sections was between 400 A to 600 A according to the colour scale given by Peachey.[133]

Optical microscopy

(1) The cross-sections of the samples, previously stained with silver-ammonium-nitrate, were directly examined, using PO as mounting medium, under the phase-contrast microscope (Watson Service I microscope with phase-contrast equipment).

(2) The cross-section of the samples which had not been stained previously, were dyed with methylene blue in the following way. The cross-sections were flattened in alcohol and attached to glass slides by means of partially hydrolysed starch. The slide was heated to 50°C in an oven for 30 minutes to harden the starch and the methacrylate was then removed by Soxhlet extraction with methylene chloride. The fibre sections thus glued to the slide were dyed in the

buffered methylene blue solution at 60°C for 5 minutes. They were then mounted in PO and examined under an ordinary microscope.

(3) In certain cases the cross-sections anchored to glass slides, as described above, were exposed to mercury and water vapour for 36 hours at 78°C.

(4) The cross-sections anchored to the glass slide were stained by putting a drop of osmic acid on the sections and allowing it to react for 1 hour and then rinsing with distilled water.

(5) Some unstained fibre cross-sections were mounted in OCP and were left for 2 to 4 hours before examination under phase-contrast microscope.

Results which were thought useful, were recorded photographically using a Watson 2.5" x 3.5" eyepiece camera; Ilford R 5.50, panchro-line cut films were used: they were developed in ID2 developer for 4 minutes at 20°C. It should be pointed out that the figures show parts of original photographs and so far as possible 3 or more cross-sections are shown in each illustration but where sections were far apart it was impossible to do this.

Electron microscopy

A water bath was prepared by putting a drop of wax with a fine brush near the cutting edge of a glass knife;

the water in the bath contained about 20% acetone. The ultra-thin sections (approx. 400 A to 600 A) were directly mounted from the water bath on the glass knife on the copper grids (3 mm diameter, Philips grids). A few of the grids used in the experiments were coated with a thin carbon film whereas the rest were without any kind of coating. The specimen mounted grids were examined under the Elmiskop I electron microscope operating at 80 kv.

EXPERIMENTAL RESULTS

Optical microscopy

Untreated fibres

(A) 'Y merino' fibres:- The fibre cross-sections mounted in PO or OCP do not show any structural features. The cross-sections dyed before section cutting, indicate the presence of bilateral cortical structure; the heavily dyed portion is known as ortho-cortex while the other is called para-cortex (plate 1).

The serial sections of the untreated fibres (i) dyed on a slide and examined under the ordinary microscope, (ii) exposed to mercury vapour and examined under the phase-contrast, are respectively shown in Plates 3A and 3B. The presence of the bilateral cortical structure, though not very distinct, can be observed (Plate 3A). The poor

contrast between the two segments of the dyed sections may be because the sections were not rinsed with dilute acid solution after dyeing as suggested by Horio and Kondo.[14] No clear bilateral differentiation is observed on exposing the sections to mercury vapour (Plate 3B) as found by Menkart and Coe.[100] According to them, examination of serial sections of the fibre having bilateral structure, shows that the portion which is not heavily dyed by methylene blue (i.e. para-cortex) has a dark brown colouration due to the formation of mercury sulphide.

The cross-sections of the fibres stained with the silver-ammonium-nitrate complex, when examined under the phase-contrast, distinctly show the bilateral structure (Plate 2). The heavily stained area is the para-cortex, the ortho-cortex is comparatively very faintly stained. It is interesting to note that the differentiation of the cortical structure can be observed under the ordinary microscope but the sharpness of the image increases if phase-contrast is employed.

(B) Lincoln wool fibres:- These fibres were found extremely difficult to handle during the experiments. It was observed that during the section cutting and transferring to a glass slide the fibre cross-sections came out of the embedding medium. Moreover, if they were successfully transferred

to a slide, they were washed away during dyeing. The big diameter or the stiffness of the fibres may be responsible for this.

However, it was possible to dye a few cross-sections of the fibres (Plate 4). The narrow outer ring (undyed portion) is the para-cortex whereas the heavily dyed inner portion is ortho-cortex by analogy with the effects in merino fibres.

The cross-sections of the fibres stained with silver-ammonium-nitrate complex (Plate 5) show that the outer annular portion is mainly heavily stained compared to the inner portion.

Treated fibres

(A) 'Y merino' fibres.

Immacula-I treatment (2% sodium bisulphite)

When the fibre sections mounted in OCP are left for a certain time, the following things are observed: (a) the cross-sections swell, (b) the cortical cells in particular region of the sections become visible (Plate 6) and (c) after some time these cells disappear and the sections appear to be almost homogeneous.

The examination of the cross-sections, exposed to mercury vapour and mounted in PO, under either the ordinary

or the phase-contrast microscope show that a few of the sections are mottled in the cortical regions (Plates 7A & B). The dyed as well as silver-ammonium-nitrate stained cross-sections are differentially stained (Plates 8 & 9).

Siroset treatment (2% ammonium thioglycollate)

The observations for the cross-sections (a) mounted in OCP (Plate 10), (b) exposed to mercury vapour, (c) dyed, (d) stained with silver-ammonium-nitrate, are similar to those for the Immacula-treated fibre sections.

Urea-bisulphite treatment (followed by rinsing with water)

The observations for the cross-sections of the fibres when mounted in OCP (Plate 11) are similar to those mentioned in the above two treatments with the only difference that in the present case the cell boundaries between the individual cells are very distinct. The examination of the cross-sections either dyed or stained with silver-ammonium-nitrate show the bilateral cortical differentiation.

Urea-reducer treatment (I A)

The photomicrograph (Plate 12) shows the profile of the cross-sections of the fibres mounted in PO and examined under the phase-contrast microscope. It indicates the presence of lobes on the periphery (cuticle region) of the sections.

In the case of the cross-sections mounted in OCP, the lobes are sharply defined on the boundary of half the area of each section, whereas the periphery of the other half is even. The cortical region near the smooth boundary appears slightly darker than the region near the uneven or lobed boundary in each section (Plate 13).

The examination of serial cross-sections, either exposed to mercury vapour or stained with osmic acid, under phase-contrast does not reveal any structural details (Plates 14 & 15). The light and dark areas observed in some sections may be due to artefacts. Under the ordinary microscope the sections exposed to mercury vapour do not show any detail except that a few sections appear mottled (Plate 16).

The dyed cross-sections show that in each section that area, about half the total, which has lobes on its periphery, is heavily dyed compared to the other half which has a smooth boundary (Plates 18 & 19).

When the cross-sections of the fibres, stained with silver-ammonium-nitrate, are examined under the phase-contrast, it is observed that, in each section, the cortical region which has an even boundary, is heavily stained, whereas the other having a lobed boundary is comparatively poorly stained (Plate 17).

It should be noted as a matter of interest that the observations for the sections mounted in OCP (Plate 13) and stained with silver-ammonium-nitrate (Plate 17) agree with each other that is to say that in both the cases the regions having smooth boundaries are darker than those having lobed boundaries. In the case of the dyed sections, the situation of the dark regions is quite opposite to that mentioned in the above two observations.

Urea-reducer treatment (I B)

The observations for the cross-sections (1) mounted in OCP (Plate 20) and (2) dyed (Plate 21), are similar to those for the treatment (I A). These cross-sections are poorer because of the more drastic treatment they have received.

Urea-reducer treatment (II)

The examination of the cross-sections mounted in PO shows the presence of lobes, rather smaller in size compared to those observed in urea-bisulphite treatment (I A), over the entire periphery of each section. The photomicrograph (Plate 22) is a profile of the sections as observed under the ordinary microscope and it does not reveal any detailed structure. The image of the lobed boundaries appear sharp when the sections are examined under the phase-contrast (Plate 24).

The dyed cross-sections show differential staining. A close examination indicates that, unlike in the case of urea-bisulphite treatment (I A), in each section the lobes are present on the entire boundary, which covers both the more and less heavily stained areas of the section (Plate 23).

Urea-reducer treatment (III)

The photomicrograph (Plate 25) of the cross-sections, mounted in PO, does not indicate the presence of any unevenness in the boundaries of the section, but it appears that the peripheral region of the sections is loose.

The dyed cross-sections, in addition to differential bilateral staining, show that the peripheral region is comparatively heavily stained (Plate 26). The sections of the fibres stained with silver-ammonium-nitrate indicate the differential bilateral staining (Plate 27).

Urea-reducer treatment (IV)

The cross-sections mounted in PO and examined under the ordinary microscope (Plate 28) show the presence of uneven (not lobed but jagged) boundaries all the way round.

The bilateral differentiation in the dyed sections appears to be almost lost (Plate 29) and nearly all sections are heavily dyed. The examination of the cross-sections of the fibres stained with silver-ammonium-nitrate indicates differential staining and also an uneven boundary (Plate 30).

Urea-reducer treatment (V A)

The cross-sections (a) mounted in PO (b) dyed (c) stained with silver-ammonium-nitrate, do not show any modifications of the sections such as have been observed in some of the treatments mentioned earlier (Plates 31, 32 and 33).

Urea-reducer treatment (V B)

The observations in the present case are similar to those made in the treatment (I A), namely (1) the sections mounted in PO when examined under microscope show the presence of lobes in the particular area of each section (Plate 34), (2) in the dyed cross-sections, these lobes appear on boundary of the heavily stained area of a section (Plate 35), (3) the cross-sections of the fibres stained with silver-ammonium-nitrate show that the lobes are present on the periphery of the lightly stained area (Plate 36) of each section.

(B) Lincoln wool fibres

Urea-reducer treatment (I A)

The examination of the cross-sections mounted in OOP indicate the uneven periphery in each section (Plate 37). The dyed sections show cortical assymetry but this is not bilateral (Plate 38). The sections (i) exposed to mercury vapour (Plate 39) and (ii) stained with osmic acid (Plate 40),

when examined under phase-contrast do not show any details except the presence of lobes as mentioned above.

Urea-reducer treatment (II)

The cross-sections mounted in PO and examined under the ordinary microscope (Plate 41) show a slightly irregular periphery. The dyed sections do not exhibit differential dyeing and appear ortho-like (heavily dyed) with irregular boundaries (Plate 42).

Urea-reducer treatment (IV)

Under the ordinary microscope the cross-sections show a drastic and irregular change in the shape of the sections (Plate 43). The dyed cross-sections appear heavily stained without any indication of asymmetrical cortex (Plate 44).

Electron microscopy

'X merino' fibres

Untreated

Since the aim of the present work was to study the effect of various reducing agents on wool fibres, it was thought necessary to use a stain which did not involve pretreatment of wool fibres with reducing agents, in order to produce contrast under the electron microscope but keep the fibres untreated in the true sense. The cross-sections

of the untreated fibres stained with osmic acid (without prior reduction with thioglycollic acid) did not produce any contrast when examined under the electron microscope. The cross-sections of the fibres stained with silver-ammonium-nitrate without pre-reduction, produced a very good contrast hence this stain was used throughout the present investigations.

The low power electron micrographs (Plates 45 & 46) show the presence of two different types of cells; the bigger, clearly definable and heavily stained cells are of the para-type, whereas the smaller and poorly stained cells are of the ortho- type. The dark lines appearing across the section are due to creasing.

The high power electron micrograph (Plate 47) of a portion of the section in the Plate 45, shows the different layers of cuticle. The small dark spots appearing in the photomicrograph may be due to the ~~pigment granules or the~~ metal salts. Two composite sheath-like layers envelop the cortex: in the outer one, the heavily stained part, the comparatively less stained part and the unstained part can be respectively identified with the "a" layer, exo-cuticle (x) and endo-cuticle (n). ~~In~~ The inner sheath-like layer, may be similar to the outer one, having a heavily stained exo-cuticle (r), lightly stained endo-cuticle (n') or alternatively the inner and outer layers may form a single cell with nuclear residue (r) surrounded by endo-cuticle (n & n'), with an inner cell

membrane (m). The epicuticle (p), an outer layer, which surrounds all the layers mentioned above is not visible.

Immacula-I treatment (2% sodium bisulphite)

The cross-section under the electron microscope indicates the bilateral distribution of the cortical cells. The big cells (para-cortex) are not as sharply defined as in the case of the untreated fibres. The dark spots may be salt particles and the large dark patches may be dirt on the carbon film (Plates 48, 49A, 49B).

Urea-reducer treatment (IA)

Plates 50A and 50B are, respectively, the low and the high magnification electron micrographs. The broad line running across the section (Plates 50A) is a knife mark, whereas the parallel fringes in the section, perpendicular to the knife mark are probably due to the folding or creasing of the section. It is observed that the cortical differentiation is obscured by transverse "fringes" and hence it is not as distinct as in the untreated fibres. The cuticle layer is almost continuous and intact on the side of the bigger cells (para-cortex) and the different layers in the cuticle are visible. However, the cuticle does not appear on the side of the ortho-cortex region and instead a thin continuous, stained film appears to surround the unevenly shaped ortho-cortex region.

Urea-reducer treatment (V A)

It can be observed from the electron micrograph (Plate 51A) that half the portion of the cuticle has a smooth surface whereas the surface of the other on the left side is slightly corrugated. The cortex underlying the smooth surface appears to be of para- type. Plate 51B is a high magnification micrograph of the right hand portion of the cuticle (i.e. the portion with smooth surface in the Plate 51A). The big cortical cells (para- type) are faintly visible and a further examination indicates the presence of very fine granules in this region.

Urea-reducer treatment (V B)

Plate 52 shows the electron micrograph of the fibre cross-section mounted on a carbon coated grid. The thin line running across the section is probably a knife mark. The big and heavily stained cells (para-), though not very distinct, are visible. Similar observations to those for the saturated urea-bisulphite treatment above, namely the presence of an even and continuous cuticle on the para-cortex region and the absence of a cuticle on the ortho-cortex, are made.

DISCUSSION OF RESULTS

It would be appropriate to begin with the staining techniques since most of the results in the work are based on these techniques.

It has been suggested that the para-cortex being richer in sulphur than the ortho-cortex forms dark coloured metal sulphides, when the fibres are treated with metal salts and also that the ortho-cortex, being more reactive, takes more dye than the para-cortex.[100] As in the present work it was intended to study the exact histological location of the reaction of the reducing agents in wool, it was thought reasonable to take the advantage of these staining methods.

It has been observed that whilst the dyeing technique gave satisfactory results, exposure to mercury vapour, as suggested by Menkart and Coe[100], failed to produce differential staining. The cross-sections of the fibres stained with osmic acid also did not show any differential staining under the phase-contrast microscope. The explanation for the failure of both the stains has not been found. The silver-ammonium-nitrate has been found to be an excellent stain as regards the bilateral differentiation of the cortex. A part of the fibre cross-section appears to be heavily stained with an indication of the presence of big cells (para-cortex). This establishes the two different stains for identifying

two histologically different components of the wool fibre.

It was observed by Appleyard and Dymoke[124] that if the Lincoln wool fibres were mounted in OCP it was possible to see clearly a complete network of cell boundaries across the fibre sections and also that the cell boundaries began to disappear as the swelling of the cross-section started. They suggested that OCP dissolved a fraction of the fibre since the cortical cell boundaries were made visible. The disappearance of the cell boundaries, as the fibre swells, might be due to the closing of the spaces that arise by dissolution of protein matter from the cortical cells. No such network of cell boundaries in untreated fibres either Lincoln or merino was observed in the present work though the fibre sections swelled when mounted in OCP. However, if the cross-sections of the 'Y merino' fibres, given (1) the Siroset (2) the Immacula and (3) urea-bisulphite (rinsed) treatments, are mounted in OCP, it has been found that, in all the cases, a few cortical cells are visible but only in a certain area of each cross-section. These cell boundaries disappear after a time as observed by Appleyard.[124]

A possible explanation of the obscurity of the network of cortical cells in the untreated fibres is that, since the cross-sections appear swollen under the microscope, there may be a rapid appearance and disappearance of the cell boundaries

during the time for which the sections were left in OCP before examination. The area, in the cross-section of a fibre given the reducing agent treatment, in which the cortical cells are visible (Plates 6, 10 and 11) can be identified as the most reactive part of the fibre namely the ortho-cortex.

The fibres, given the above mentioned treatments with reducing agents, do not show any modification, histologically speaking, in the cross-sections and show the normal bilateral staining phenomena with both the dye and the silver-ammonium-nitrate solution.

The cross-sections of the fibres treated with the saturated urea solution containing bisulphite at neutral pH, show neither a network of cell boundaries nor swelling when mounted in OCP and examined under the microscope (Plate 13) and this is not surprising as a fraction of the fibre material dissolves in the urea-reducer solution and there is a likelihood that protein matter, on which the visibility of cell network and swelling depends according to Appleyard[124] may also have been extracted.

A fraction of the fibre material which dissolves in the urea-reducer solution has a definite histological location. It has been observed (Plates 18 & 19) that the lobes, in the treated and dyed sections of the fibres having a bilateral

cortex ('Y merino'), are present in the heavily stained area of the sections (i.e. ortho-cortex) and also that in the case of cross-sections stained with silver-ammonium-nitrate, the lobes are present in poorly stained areas (i.e. ortho-cortex), Plate 17. This suggests that the action of urea-reducer solution at neutral pH, is mainly confined to the ortho-cortex region in a fibre having bilateral cortex and this confirms Mercer's findings.[74]

The differential staining in the cortex of the fibres exists even after 20 hours' treatment with the solution and the presence of the whole of the para-cortex and about half of the ortho-cortex is observed (Plate 20). This also confirms Mercer's findings[74] that, under somewhat similar conditions of treatment, nearly 20 to 25 percent of merino wool dissolves in the solution.

The treatment of wool fibres with saturated urea-solution containing thioglycollic acid at pH 2.5 seems to extract the material from both, the ortho- and the para-, regions of the fibres. This is in contrast with the preferential action of the urea-bisulphite solution at neutral pH.

If unsaturated urea solution containing bisulphite at pH 3 is employed there is no indication of dissolution of material, histologically, but the cuticle region of a fibre

appears greatly modified as indicated by heavy uptake of dye by this region (Plate 26). However, when the pH of the solution is kept at 11, both the regions (the ortho- and the para-) seem to be attacked and the amount of material extracted appears to be considerable (Plate 28) compared to that in the urea-thioglycollate treatment described above. The material which dissolves at high pH such as 11 may be identified as the major protein component of wool, namely "kerateine II".[130]

The examination of wool fibres treated with urea-bisulphite solution, under the conditions such as employed in the "urea-bisulphite solubility test"[131] does not indicate any dissolution of material (Plate 31). However, increase in the time of treatment in the above case, shows some dissolution of material from the ortho-cortex region of wool. (Plate 34). The present results create some doubts about the usefulness of the "solubility test" which has been widely accepted as the standard test in the wool textile industry. For instance, in the case of merino wool, where only the ortho-cortex dissolves at neutral pH condition, for two batches of wool the solubility may differ according to the proportions of the ortho-cortex to the para-cortex in the wool, but it is possible that this difference in solubility may be misinterpreted.

When Lincoln wool fibres, having a radial cortical asymmetry (where the ortho-cortex is surrounded by the outer para-cortex), are treated with saturated urea solution containing bisulphite at neutral pH, the entire periphery of the fibre section is affected, which suggests that the extracted material is removed chiefly from the para-cortex (Plate 37). Lincoln fibres treated with (1) saturated urea solution containing thioglycollic acid, at pH 2.5 (Plate 41) and (2) urea solution (unsaturated) containing sodium bisulphite at pH 11 (Plate 43) are also attacked around the whole periphery but, as for 'Y merino' fibres, the amount of material dissolved in (2) is considerable whilst that dissolved in (1) is very little. Low solubility at pH less than 6 has already been noted by Peacock[115] and high solubility at alkaline pH is well known.[130]

From the results discussed above, for both types of wool, it is apparent that, though it is possible to locate the segments of the fibres reacting with the urea-reducer solution by examining the stained cross-sections, the detailed study of the different components of the segment is not possible because of the limited resolving power of the optical microscope. For instance, it is known that, when the fibre is treated with urea-bisulphite solution at neutral pH, the material is extracted from the ortho- region but it is not

clear whether the material dissolves from the cortex or cuticle or both.

The electron microscope examination of the cross-section of the fibre given 2% sodium bisulphite (Immacula) treatment shows the normal bilateral differentiation of the cortical cells (Plates 48 & 49) and the different layers of cuticle surrounding both the regions of cortex, the ortho- and the para-, are intact. However, the examination of the cross-section of the fibre treated with urea-bisulphite solution at neutral pH for 1 hour (treatment V A) reveals that some of the material is dissolved from the heavily stained layer "a" of the ortho-region (Plate 51A) and if the time of the treatment is increased to 3 hours, the whole of the cuticle on the ortho-cortex region disappears leaving behind (a) a resistant thin layer, (b) ortho-cortex, (c) para-cortex with intact cuticle (Plate 52).

If, instead of the comparatively mild solution of urea-bisulphite as mentioned above, saturated urea solution containing sodium bisulphite at the same pH is employed, it is found that after 3 hours treatment, in addition to the removal of the cuticle in the ortho-region, some material from the ortho-cortex is also extracted. This is evident from the uneven shape, the ortho-cortex assumes after the treatment (Plate 50).

Various possibilities exist to account for the absence of cuticle on the ortho-cortex region in the cross-section of the fibre treated with urea-bisulphite solution for 3 hours described above. Firstly, it is possible that the cuticle might have been detached during the rinsing of fibres with water which follows the treatment with the solution. Secondly, it is possible that the cuticle round the ortho-cortex might have been pulled away by the embedding medium as suggested by Sikorski and his colleagues.[8] Lastly, it is possible that the cuticle layer might have been dissolved in the solution. The former two possibilities can be rejected since it is evident from 1 hour treatment that some material dissolves from the layer "a" (Plate 51) and hence it is logical to think that if the time of treatment is increased to 3 hours, the reaction would progress further dissolving the whole cuticle in the ortho-region. Secondly, in Plate 52, where the section is mounted on a coated grid, though the embedding material appears to be separated from the cross-section on both the sides, namely the ortho- and the para-, there is no sign that the cuticle might have been detached because of this. Plate 50, where the embedding medium is not separated at all from the section, conclusively rejects the idea of embedding medium playing any part, in the present work, towards the disappearance of the cuticle on

the ortho- side of the fibres treated with urea-reducer solution.

At the end of the 3 hours' treatment with urea-bisulphite solution at neutral pH, there appears to be a continuous, thin resistant layer, which surrounds the ortho-cortex and runs round the para-cortex (beneath the intact cuticle on this side); here overlapping of the layer appears to occur (Plate 50). The resistance of this layer to the urea-bisulphite solution leads to suggest that immediately underneath this layer there may exist a resistant and invisible membrane of the type found by various workers[26-28,37] and known as sub-cuticle membrane. A great deal of controversy exists regarding the existence of such membrane, but the present results support the observations of Alexander and Earland,[37] who, after treating the wool with peracetic acid-ammonia, obtained a continuous membrane. It is possible that, if the subcuticle membrane exists beneath the thin layer as suggested earlier, on complete dissolution of material from wool, the overlapping membranes in the sub-cuticle may fuse together and as a result one may obtain a continuous membrane.

It is apparent, from the stepwise reactions and observations, how the reaction in the fibre progresses from the layer "a" in the cuticle on the ortho-cortex side

to the cortex. Though the fibres sections after 20 hours' treatment have not been examined under the electron microscope, it is suggested from the above observations, along with the optical microscope observations, that the residue left after the treatment of merino fibre with urea-reducer solution at pH 7, consists of (1) the part of the ortho-cortex (2) the resistant membrane surrounding the ortho-cortex (3) the whole of the para-cortex with intact cuticle.

The irregular shape of the ortho-cortex (Plates 50A and B) can be explained as follows. The extraction of the material from the ortho-cortex creates some room and as a result, the surrounding resistant thin layer collapses and folds to give the irregular periphery. It is suggested, from this and the absence of the occurrence of the fragmentation in ortho-cortex, that the material does not dissolve in bits and pieces but uniformly from this region. Though it is clear that the material dissolves from both the ortho-cortex and the cuticle surrounding it, it is difficult to say which one dissolves first. Also, because of the lack of the detailed study of cortical structure of the treated fibres under the electron microscope, it is not possible to suggest the mechanism of extraction of material from the wool.

The 'Y merino' fibres given the treatments at pH other

than neutral and also the Lincoln wool fibres have not been examined under the electron microscope. However, it would be interesting to see what happens to, (1) the para-cortex and the cuticle on this side in merino fibres treated with solution at high pH, since under the optical microscope, considerable material appears to have been dissolved from both parts of the cortex; (2) the para-cortex and the cuticle surrounding it in the Lincoln wool fibres treated with solutions at various pH, since under the optical microscope the material dissolved from these fibres appear to vary according to the pH of the solution employed.

A possible explanation for the difference in reactivity of the fibres having cortical asymmetry, toward the urea-reducer solutions at different pH is not known. It was found by Mercer[107] and his colleagues that among the various fractions of Phillips[45] cystine cross-linkages (A,B,C,D), the most reactive fraction namely the (A + B) is located in the ortho-cortex whereas the resistant (C + D) fraction is situated in the para-cortex. Also it was suggested by Mercer[74] that the insolubility of the para-cortex in saturated urea solution at pH 8 is because of the location of (C + D) fraction in this region. The observation that in merino fibres the material dissolves from both regions of the cortex suggests, according to Mercer's idea, that both

the (A + B) and the (C + D) fractions of cross-linkages are involved. But this cannot be true since, according to Phillips,[125] the urea-thioglycollate is likely to cause reduction of the (A + B) fraction chiefly. Secondly, if the above ideas of Mercer are extended to the Lincoln fibres, the dissolution of the para-cortex, on the treatment of the fibres with urea-bisulphite solution at neutral pH, which occurs in the present work, would not be possible. From this, it is suggested that the allocation of cystine cross-linkages of (A + B) type to the ortho-, and (C + D) type to the para-cortex is not possible and hence Mercer's views that the difference in reactivity is due to the presence of certain fractions of Phillips cystine cross-linkages cannot be favoured.

The insolubility of the 'Y merino' fibres in the urea-bisulphite solution at pH 3 may be explained as due either to the decomposition of sodium bisulphite by hydrochloric acid which is added to the solution to adjust the pH or to the denaturation of protein. At low pH such as 2.5 (urea-thioglycollate treatment) the material dissolved is less, in both types of fibres, compared to that at pH 11 (urea-bisulphite) and this may be because at low pH, the number of disulphide bonds broken may be smaller compared to that at high pH; at high complete reduction of cystine occurs.[67]

It is thus apparent that neither optical nor electron microscope examination of wool given finishing treatments such as the Immacula, the Siroset or the suggested mild urea-bisulphite one, gives any indication of modification of structure, histologically speaking, and hence does not provide any information regarding the specificity of the reaction of reducing agents in the cortex. However, results in the case of wool treated more drastically with urea-bisulphite at neutral pH, suggests that the attack of reducing agent at this pH is chiefly confined to the ortho-cortex and hence to the cystine linkages in this portion. From this it is suggested that the setting and the modification of tensile strength of wool, as observed in the last chapter, given the treatments such as the Siroset and the urea-bisulphite, where the solutions of reducing agent are at near-neutral pH, are due to the cystine linkages mainly in the ortho-cortex and that the para-cortex plays very little part.

REFERENCES

1. C.S.I.R.O., Report No. G6 and Trade Circular No. 4.
2. Man-made Textiles, 36, 64, 1959.
3. FARNWORTH, A.J., LIPSON, M., McPHEE, J.R., Text. Res. J. 30, 22, 1960.
4. ICI Technical Information, Dye House No. 575.
5. LINDBERG, J., PHILIP, B., GRALEN, N., Nature, 162, 458, 1949.
6. LINDBERG, J., Text. Res. J., 19, 43, 1949.
7. LAGERMALM, G., Text. Res. J., 24, 17, 1954.
8. DOBB, M.G., JOHNSTON, F.R., NOTT, J.A., OSTER, L., SIKORSKI, J., SIMPSON, W.S., J. Text. Inst., 52,T153,1961.
9. LINDBERG, J., MERCER, E.H., PHILIP, B., GRALEN, N., Text. Res. J., 19, 673, 1949.
10. FRASER, R.D.B., ROGERS, G.E., Aust. J. Biol. Sci., 8, 129, 1955.
11. FRASER, R.D.B., ROGERS, G.E., Biochim., et Biophys.Acta, 16, 307, 1955.
12. BIRBECK, M.S.C., MERCER, E.H., J. Biophys. Biochem. Cytol., 3, 215, 1957.
13. KASSENBECK, P., Bull. Inst. Text. France, p.51, July,1961.
14. HORIO, M., KONDO, T., Text. Res. J., 23, 373, 1953.
15. MERCER, E.H., Text. Res. J., 23, 387, 1953.
16. KASSENBECK, P., Bull. Inst. Text. France, p.75, July, 1961.
17. DUSENBURY, J.H., COE, A.B., Text. Res. J., 25, 354, 1955.
18. SNYMANN, J.G., Text. Res. J., 33, 217, 1963.
19. KASSENBECK, P., Bull. Inst. Text. France, No.83, 25, 1959.

20. BROWN, T.D., ONIONS, W.J., Nature, 186, 93, 1960.

21. FRASER, R.D.B., MacRAE, T.P., Text. Res. J., 26, 618,1956.

22. ROGERS, G.E., J. Ultrastructure Res., 2, 309, 1959.

23. FRASER, R.D.B., MacRAE, T.P., ROGERS, G.E., Nature, 193, 1052, 1962.

24. FRASER, R.D.B., MacRAE, T.P., ROGERS, G.E., J. Text. Inst., 51, T497, 1960.

25. ELÖD.E.ZAHN, H., Naturwiss, 33, 158, 1946.

26. LEHMAN, E., Melliand Textilber, 25, 1, 1944.

27. LEHMAN, E., Kolloid-Z, 108, 6, 1944.

28. REUMUTH, H., Melliand Textilber, 23, 1, 53, 1942.

29. MERCER, E.H., LINDBERG, J., PHILIP, B., Text. Res. J., 19, 678, 1949.

30. CREWTHER, W.G., DOWLING, L.M., J. Text. Inst., 51, T775, 1960.

31. FOX, S.W., FOSTER, J.F., Protein Chemistry, 287;290.

32. ANSON, M.L., BAILEY, K., EDSALL, J.T., Advances in Protein Chemistry, 7, 153, 1952.

33. HAUROWITZ, F., The Chemistry and Functions of Proteins,222.

34. PAULING, L., COREY, R.B., Proc. Nat. Acad. Sci., 37, 261, 1951.

35. PAULING, L., COREY, R.B., BRANSON, R.B., Proc. Nat. Acad. Sci., 37, 205, 1951.

36. PAULING, L., COREY, R.B., Nature, 59, 171, 1953.

37. ALEXANDER, P., EARLAND, C., Text. Res. J., 20, 300, 1950.

38. ASTBURY, W.T., WOODS, H.J., Phil. Trans. Royal Soc., A232, 333, 1933.

39. HAILWOOD, A.J., HORROBIN, S., Trans. Faraday Soc., 42B, 84, 1946.

40. TURNER, J.D., WOODS, H.J., 'Structure de la laine', Inst. Text. France, p.20, July, 1961.

41. GODDARD, D.R., MICHAELIS, L., J. Biol. Chem., 106, 605, 1934; 112, 361, 1935.

42. HARRIS, M., MIZELL, L.R., FOURT, L., Ind. Eng. Chem., 34, 833, 1942.

43. ALEXANDER, P., CARTER, D., HUDSON, R.F., J. Soc. Dyers and Col., 65, 152, 1949.

44. ELSWORTH, F.F., PHILLIPS, H., Biochem. J., 32, 837, 1938; 35, 137, 1941.

45. SPEAKMAN, J.B., J. Soc. Dyers and Col., 52, 335, 1936.

46. BOOTH, J.E., Principles of Textile Testing, 261.

47. SPEAKMAN, J.B., J. Soc. Dyers and Col., 52, 423, 1936.

48. SPEAKMAN, J.B., WHEWELL, C.S., J. Soc. Dyers and Col., 52, 380, 1936.

49. HIND, J.R., SPEAKMAN, J.B., J. Text. Inst., 36, T19, 1945.

50. SPEAKMAN, J.B., British Patent, 775, 486, 1957.

51. MITCHELL, T.W., FEUGHELMAN, M., Text. Res. J., 28, 453, 1958.

52. FEUGHELMAN, M., HALY, A.R., MITCHELL, T.W., Text. Res. J., 28, 655, 1958.

53. SPEAKMAN, P.T., Nature, 184, 339, 1959.

54. JENKINS, A.D., WOLFRAM, L.J., J. Soc. Dyers and Col., 80, 65, 1964.

55. Technicus, The Text. Manfr., 88, 212, 1962.

56. SPEAKMAN, J.B., The Text. Manfr., 85, 427, 1959.

57. The Dyer, 120, 173, 1958.

58. FARNWORTH, A.J., Text. Res. J., 27, 632, 1957.

59. Geigy Technical Bulletin, W7, October, 1959.

60. DORSET, B.C.M., The Text. Manfr., 85, 85, 1959.

61. SPRINGELL, P.H., Text. Res. J., 28, 874, 1958.

62. HUMAN, J.P.E., SPRINGELL, P.H., Aust. J. Chem., 12, 508, 1959.

63. GERTHSEN, T., ZAHN, H., J. Soc. Dyers and Col., 75, 604, 1959.

64. GERTHSEN, T., ZAHN, H., Melliand Textilbeichte, 41, 757, 1960.

65. DAVIDSON, A.N., HOWITT, F.O., J. Text. Inst., 53, 64, 1962.

66. NAKAMURA, Y., NEMOTO, Y., KONDO, T., J. Soc. Text. Cellulose Indstr., Japan, 19, 11, 881, 1963.

67. GEIGER, W.B., KOBOYASHI, F.F.' HARRIS, M., Ind. Eng. Chem., 34, 1942.

68. JONES, C.B., MECHAM, D.K., Arch. Biochem., 2, 209, 1943.

69. GILLESPIE, J.M., LENNOX, F.G., Biochim. Biophys. Acta, 12, 491, 1953.

70. MERCER, E.H., OLOFSSON, B., J. Polymer Sci., 6, 671, 1951.

71. WARD, W.H., Text. Res. J., 22, 405, 1952.

72. WOODS, E.F., Aust. J. Sci. Res., A5, 555, 1952.

73. FRIEND, J.A., O'DONNELL, I.J., Aust. J. Biol. Sci., 6, 630, 1953.

74. MERCER, E.H., Text. Res. J., 24, 835, 1954.

75. JONES, C.B., MECHAM, D.K., Arch. Biochem., 3, 193, 1943.

76. MERCER, E.H., REES, A.L.G., Aust. J. Expt. Biol.,

77. KASSENBECK, P., Inst. Text. France, No.100, 431, May-June, 1962.

78. NAKAMURA, Y., KONDO, T., J.Soc. Cellulose Indstr., Japan, 19, 11, 893, 1963.

79. SIKORSKI, J., WOODS, H.J., J. Text. Inst., 51, T506, 1960.

80. FILSHIE, B.K., ROGERS, G.E., J. Mol. Biol., 3, 784, 1961.

81. FEUGHELMAN, M., Text. Res. J., 33, 1013, 1963.

82. CIBA Clayton Ltd., Technical Bulletin, Dec., 1958.

83. ICI Technical Information, Dyehouse No. 459.

84. ICI Technical Information, Dyehouse No. 531.

85. SWINTON, G.M., J. Soc. Dyers and Col., 75, 153, 1959.

86. SCHIECKE, H.E., Textil Praxis, I, 25, International Edtn., 1962.

87. CHIPALKATTI, H.R., DESAI, N.F., GILES, C.H., MACAULAY, N., J. Soc. Dyers and Col., 70, 498, 1954.

88. Standard methods for the determination of Fastness, Soc. Dyers and Co., Second Edit.,1960.

89. BROWN, J.C., J. Soc. Dyers and Col., 75, 11, 1959.

90. WILKINSON, P.R., IRELAND, D.W., Text. Res. J., 28, 675, 1958.

91. WOLFRAM, M.A., SPEAKMAN, J.B., J. Soc. Dyers and Col., 76, 169, 1960.

92. QUIG, J.B., DENNISON, R.W., Ind. Eng. Chem., 44, 2176, 1952.

93. SATLOW, G., GERTHSEN, T., Deut. Forschung gemeinschaft., 30, 45, 1960.

94. O'DONNELL, I.J., WOODS, E.F., Proc. Int. Wool Text. Res. Conf. Aust., B-48, 1955.

95. HAPPEY, F., WORMELL, R.L., J. Text. Inst., 40, T855, 1949.

96. LEVEAU, M., CEBE, N., PARISOT, A., Bull. Inst. Text. France, 42, 6, 1953.

97. DUSENBURY, J.H., MERCER, E.H., WAKELIN, J.H., Text. Res. J., 24, 890, 1954.

98. ELLIOT, R.L., ROBERTS, J.B., J. Soc. Dyers and Col., 72, 370, 1956.

99. FRASER, R.D.B., ROGERS, G.E., Proc. Int. Wool Text. Res. Conf. Aust., F-151, 1955.

100. MENKART, J., COE, A.B., Text. Res. J., 28, 220, 1958.

101. FRASER, R.D.B., LINDLEY, H., ROGERS, G.E., Biochem. et Biophys., Acta B, 295, 1954.

102. GOLDEN R.L., WHITWELL, J.C., MERCER, E.H., Text. Res. J., 25, 334, 1955.

103. WARD, W.H., BARTULOWICH, J.J., Text. Res. J., 25, 888, 1955.

104. SNYMANN, J.G., Text. Res. J., 33, 803, 1963.

105. LEVEAU, M., Bull. Inst., Text., France, No. 74, 75, 1958.

106. MERCER, E.H., Proc. Int. Wool Text. Res. Conf. Aust., B-275, 1955.

107. MERCER, E.H., GOLDEN, R.L., JEFFRIES, E.B., Text. Res. J., 24, 615, 1954.

108. NEWMAN, S., BORYSKO, E., SWERDLOW, M., J. Res. National Bur. Stand., 43, 183, 1949.

109. GLAUERT, A.M., ROGERS, G.E., GLAUERT, R.H., Nature, 178, 803, 1956.

110. GLAUERT, A.M., J. Roy. Microscopical Soc., 80, 269, 1962.

111. LASSE, R., Textil-Rdsch., 18, No.11, 589, 1963.

112. SMITH, A.L., HARRIS, M., J. Res. Nat. Bur. Stand., 16, 309, 1936.

113. RUDALL, K.M., Proc. Leeds Phil. Soc. (Sci.Sec.), 4, 178, 1944.

114. KASSENBECK, P., Bull. Inst. Text. France, p.88, July, 1961.

115. PEACOCK, N., M.Sc. Thesis, 1952; Ph.D. Thesis, 1958, Leeds University.

116. SIKORSKI, J., SIMPSON, W.S., J. Roy. Microscopical Soc., 78, 35, 1958.

117. SIMPSON, W.S., WOODS, H.J., Nature, 185, 157, 1960.

118. ROGERS, G.E., Summarised Proc. Conf. Electron Microscopy of Fibres, British J. Appl. Phys., 8, 1, 1957.

119. SIKORSKI, J., SIMPSON, W.S., WOODS, H.J., Fourth International Conf. Electron Microscopy, Berlin, 707, 1958.

120. FRASER, R.D.B., MacRAE, T.P., Biochim. biophys. Acta, 29, 229, 1958.

121. DOBB, M.G., SIKORSKI, J., 'Structure de la laine', Inst. Text. France, p.37, July, 1961.

122. GLAUERT, A.M., GLAUERT, R.H., J. Biophys. Biochem. Cytol., 4, 191, 1958.

123. KASSENBECK, P., Personal communication.

124. APPLEYARD, H.M., DYMOKE, C.M., J. Text. Inst., 45, T480, 1954.

125. CARTER, E.G.H., MIDDLEBROOK, W.R., PHILLIPS, H., J. Soc. Dyers and Col., 62, 203, 1946.

126. DAVIDSON, A.N., A lecture on 'permanent pleating processes for wool' arranged by the Society of Dyers and Colourist at Paisley.

127. BLUM, O., Textil-Praxis, I, 24, International Ed., 1962.

128. WRIGHT, W.D., The measurement of colour, 1958 (second edtn.)

129. SPEAKMAN, J.B., J. Text. Inst., 28, T102, 1947.

130. LENNOX, F.G., Proc. Int. Wool Text. Res. Conf. Aust., B-22, 1955.

131. 'Tentative Textile Standard No. 69', J. Text. Inst., 52, P681, 1961.

132. W.I.R.A. Bulletin, 23, 34, 1961; 24, 6, 1962.

33. PEACHEY, L.D., Fourth International Conf. Electron Microscopy, Berlin, 72, 1958.

34. HARRISON, W., Proc. Roy. Soc., 94A , 460, 1918.

35. SHORTER, S.A., J. Soc. Dyers and Col., 41 , 141, 1925.

36. SPEAKMAN, J.B., Trans. Faraday Soc., 25 , 169, 1929.

37. LIPSON, M., Research, 12 , 122, 1959.

38. CEDNAS, M., American Dyestuff Reptr., 51 , 543, 1962.

39. WHITELEY, K.J., Text. Res. J., 32 , 123, 1962.

40. HIROSHI SOBUE, Proc. Int. Wool Text. Res. Conf. Aust., D-83, 1955.

41. REESE, C.E., EYRING, H., Text. Res. J., 20 , 743, 1950.

42. KUBU, E.T., MONTGOMERY, D.J., Text. Res. J., 22 , 778, 1952.

BIBLIOGRAPHY

COSLETT, V.E., Practical Electron Microscopy, Academic Press, New York, 1951.

KAY, D., Techniques for Electron Microscopy, Blackwell Scientific Publication, Oxford, 1961.

HAINE, M.E., COSLETT, V.E., The Electron Microscope, E. & F.N. Spon Ltd., London, 1961.

BORASKY, R., Ultrastructure of Protein Fibres, Academic Press, New York and London, 1963.

ALEXANDER, P., HUDSON, R.F., Wool; Its Chemistry and Physics, Chapman and Hall Ltd., London, 1954.

INDEX TO PLATES

Plates 1 - 44 are optical micrographs of wool fibre cross-sections mounted, unless otherwise stated, in PO under the ordinary microscope. The terms PO, OCP, T.M. and O.M., in the following description, are respectively the abbreviations for paraffin oil, orthochlorophenol, total magnification and original magnification.

1. Untreated 'Y merino' wool dyed with Naphthalene Green GS before section cutting.

   T.M. x 800 (O.M. x 800).

2. Untreated 'Y merino' wool stained with silver-ammonium-nitrate and examined under the phase-contrast.

   T.M. x 1400 (O.M. x 500).

3. A and B are serial sections of the same untreated 'Y merino' wool: A - section dyed with methylene blue,

   B - sections exposed to mercury vapour,

   T.M. x 800 (O.M. x 200)

4. Sections of untreated Lincoln wool, dyed with methylene blue.

   T.M. x 225 (O.M. x 50).

5. Untreated Lincoln wool stained with silver-ammonium-nitrate.

   T.M. x 1000 (O.M. x 500).

INDEX TO PLATES (Continued)

6. 'Y merino' wool treated with 2% sodium bisulphite solution and steam pressed for 20 seconds (Immacula-I): the sections mounted in OCP and under phase-contrast.

T.M. x 1100 (O.M. x 700).

7. 'Y merino' wool treated as for Plate 6, then sections exposed to mercury vapour:

A - under the ordinary microscope,

B - under phase-contrast,

T.M. x 500 (O.M. x 200).

8. 'Y merino' wool treated as for Plate 6, and then sections dyed with methylene blue:

T.M. x 1500 (O.M. x 500).

9. 'Y merino' wool treated as for Plate 6 and then stained with silver-ammonium-nitrate solution: under phase contrast.

T.M. x 2000 (O.M. x 500).

10. 'Y merino' wool treated with 2% ammonium thioglycollate and steamed for 20 seconds (Siroset): mounted in OCP and under phase-contrast.

T.M. x 1100 (O.M. x 700).

11. 'Y merino' wool given urea-bisulphite (rinsed) treatment: mounted in OCP and under phase-contrast.

T.M. x 850 (O.M. x 700).

12. 'Y merino' wool treated with saturated urea solution containing 5 gms. of sodium bisulphite per 100 cc of solution at pH 7 at 40°C for 3 hours (treatment IA): under phase-contrast.

T.M. x 400 (O.M. x 200).

13. 'Y merino' wool treated as for Plate 12: mounted in OCP and under phase-contrast.

T.M. x 1250 (O.M. x 500).

14. 'Y merino' wool treated as for Plate 12, then sections exposed to mercury vapour: under phase-contrast.

T.M. x 500 (O.M. x 200).

15. 'Y merino' wool treated as for Plate 12, then sections treated with osmic acid: under phase-contrast.

T.M. x 500 (O.M. x 200).

16. 'Y merino' wool treated as for Plate 12, then sections exposed to mercury vapour: under the ordinary microscope.

T.M. x 560 (O.M. x 200).

17. 'Y merino' wool treated as for Plate 12, then stained with silver-ammonium-nitrate solution: under phase-contrast.

T.M. x 1350 (O.M. x 500).

18 and 19. 'Y merino' wool treated as for Plate 12, then sections dyed with methylene blue.

T.M. x 1000 (O.M. x 500).

20. 'Y merino' wool treated with saturated urea solution containing 5 gms. of sodium bisulphite per 100 cc of solution at pH 7 at 40°C for 20 hours (treatment IB): mounted in CCP and under phase-contrast.

T.M. x 580 (O.M. x 200).

21. 'Y merino' wool treated as for Plate 20, then sections dyed with methylene blue.

T.M. x 300 (O.M. x 50).

22. 'Y merino' wool treated with saturated urea solution containing 5 cc of thioglycollic acid per 100 cc of solution at pH 2.5 at 45°C for 6 hours (treatment II).

T.M. x 1500 (O.M. x 500).

23. 'Y merino' wool treated as for Plate 22, then sections dyed with methylene blue.

T.M. x 1500 (O.M. x 500).

24. 'Y merino' wool treated as for Plate 22: under phase-contrast.

T.M. x 700 (O.M. x 200).

25. 'Y merino' wool treated with urea-bisulphite solution (80 gms. of urea and 5 gms. of sodium bisulphite per 100 cc of water) at pH 3 at 40°C for 6 hours (treatment III).

T.M. x 1500 (O.M. x 500).

26. 'Y merino' wool treated as for Plate 25, then sections dyed with methylene blue.

T.M. x 1500 (O.M. x 500).

27. 'Y merino' wool treated as for Plate 25, then stained with silver-ammonium-nitrate solution: under phase-contrast.

T.M. x 1300 (O.M. x 500).

28. 'Y merino' wool treated with urea-bisulphite solution (80 gms. of urea and 5 gms. of sodium bisulphite per 100 cc of water) at pH 11 at 40°C for 6 hours (treatment IV).

T.M. x 1500 (O.M. x 500).

29. 'Y merino' wool treated as for Plate 28, then sections dyed with methylene blue.

T.M. x 1200 (O.M. x 500).

30. 'Y merino' wool treated as for Plate 30, then stained with silver-ammonium-nitrate solution: under phase-contrast.

T.M. x 1400 (O.M. x 500).

31. 'Y merino' wool treated with urea-reducer solution (50 gms. of urea and 3 gms. of sodium bisulphite per 100 cc of solution) at pH 7 at 65°C for 1 hour (treatment V A).

T.M. x 1500 (O.M. x 500).

32. 'Y merino' wool treated as for Plate 31, then sections dyed with methylene blue.

T.M. x 1500 (O.M. x 500).

33. 'Y merino' wool treated as for Plate 31, then stained with silver-ammonium-nitrate solution: under phase-contrast.

T.M. x 1500 (O.M. x 500).

34. 'Y merino' wool treated with urea-bisulphite solution (50 gms. of urea and 3 gms. of sodium bisulphite per 100 cc of solution) at pH 7 at 65°C for 3 hours (treatment V B).

T.M. x 1500 (O.M. x 500).

35. 'Y merino' wool as treated for Plate 34, then sections dyed with methylene blue.

T.M. x 1500 (O.M. x 500).

36. 'Y merino' wool as treated for Plate 34, then stained with silver-ammonium-nitrate solution: under phase-contrast.

T.M. x 1500 (O.M. x 500).

37. Lincoln wool treated with saturated urea solution containing 5 gms. of sodium bisulphite per 100 cc of solution at pH 7 at 40°C for 3 hours (treatment I A): mounted in OCP and under phase-contrast.

T.M. x 1200 (O.M. x 500).

38. Lincoln wool as treated for Plate 37, then sections dyed with methylene blue.

T.M. x 1750 (O.M. x 500).

39. Lincoln wool as treated for Plate 37, then sections exposed to mercury vapour: under phase-contrast.

T.M. x 800 (O.M. x 200).

40. Lincoln wool as treated for Plate 37, then sections treated with osmic acid: under phase-contrast.

T.M. x 800 (O.M. x 200).

41. Lincoln wool treated with saturated urea solution containing 5 cc of thioglycollic acid per 100 cc. of solution at pH 2.5 at 45°C for 6 hours (treatment II).

T.M. x 1500 (O.M. x 500).

42. Lincoln wool treated as for Plate 41, then sections dyed with methylene blue.

T.M. x 1350 (O.M. x 500).

43. Lincoln wool treated with urea-bisulphite solution (80 gms. of urea and 5 gms. of sodium bisulphite per 100 cc of water) at pH 11 at 40°C for 6 hours (treatment IV).

T.M. x 1000 (O.M. x 500).

INDEX TO PLATES (Continued)

44. Lincoln wool treated as for Plate 43, then sections dyed with methylene blue.

T.M. x 1000 (O.M. x 500).

Plates 45 - 52 are electron micrographs, obtained on the Elmiskop I instrument at 80 kV.

45 and 46. Untreated 'Y merino' wool, stained with silver-ammonium-nitrate solution.

T.M. x 5600 (O.M. x 4000).

47. Part of the untreated 'Y merino' wool (Plate 45), at higher magnification.

T.M. x 68000 (O.M. x 40000).

48 and 49. 'Y merino' wool treated with 2% sodium bisulphite solution and steam pressed for 20 seconds (Immacula-I) then stained with silver-ammonium-nitrate solution.

T.M. x 7000 (O.M. x 5000).

50. 'Y merino' wool treated with saturated urea solution containing 5 gms. of sodium bisulphite per 100 cc of solution at pH 7 at 40°C for 3 hours (treatment I A), then stained with silver-ammonium-nitrate solution.

A low magnification micrograph,
T.M. x 6500 (O.M. x 5000).

B high magnification micrograph,
T.M. x 26000 (O.M. x 20000).

51. 'Y merino' wool treated with urea-reducer solution (50 gms. of urea and 3 gms. of sodium bisulphite per 100 cc of solution) at pH 7 at 65°C for 1 hour (treatment V A), then stained with silver-ammonium-nitrate solution.

A low magnification micrograph,
T.M. x 37500 (O.M. x 10000).

B high magnification micrograph,
T.M. x 68000 (O.M. x 20000).

52. 'Y merino' wool treated with urea-reducer solution (50 gms. of urea and 3 gms. of sodium bisulphite per 100 cc of solution) at pH 7 at 65°C for 3 hours (treatment V B), then stained with silver-ammonium-nitrate solution.

T.M. x 8500 (O.M. x 5000).

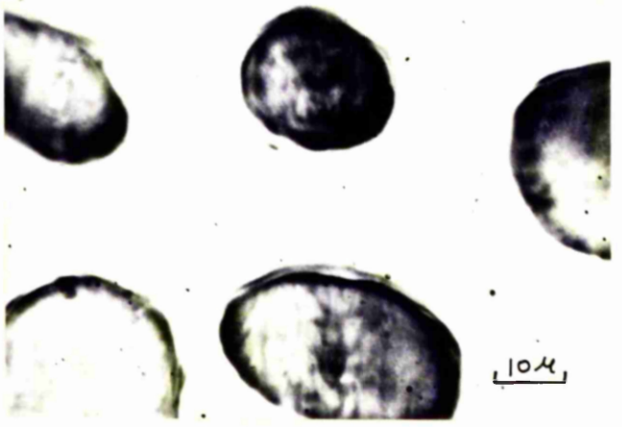


PLATE 1

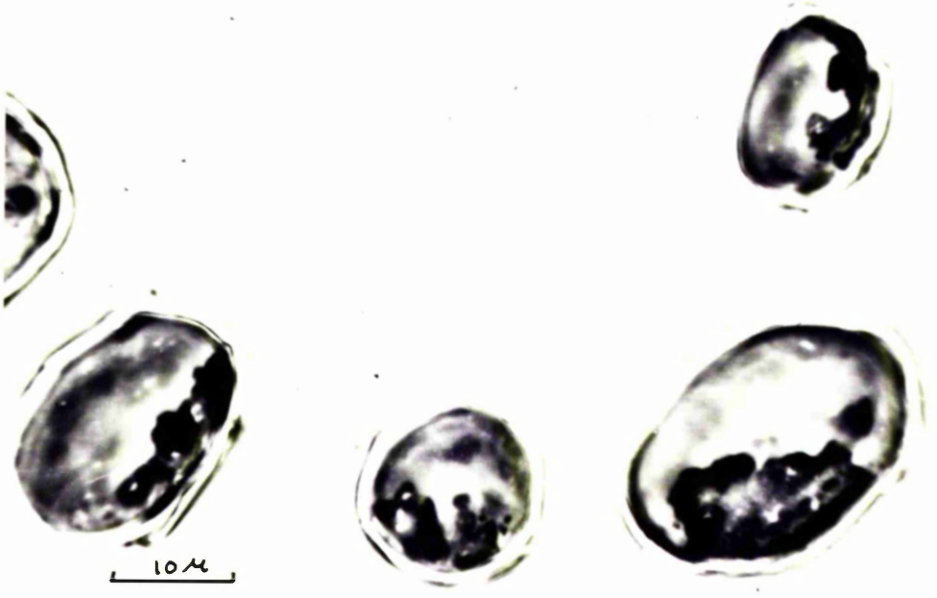


PLATE 2

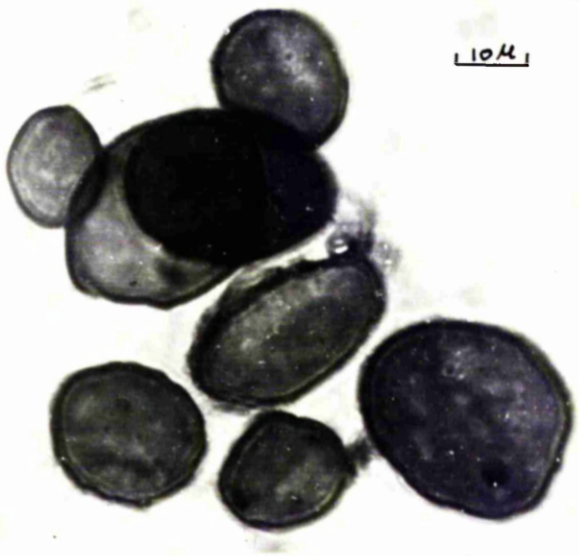


PLATE 3A

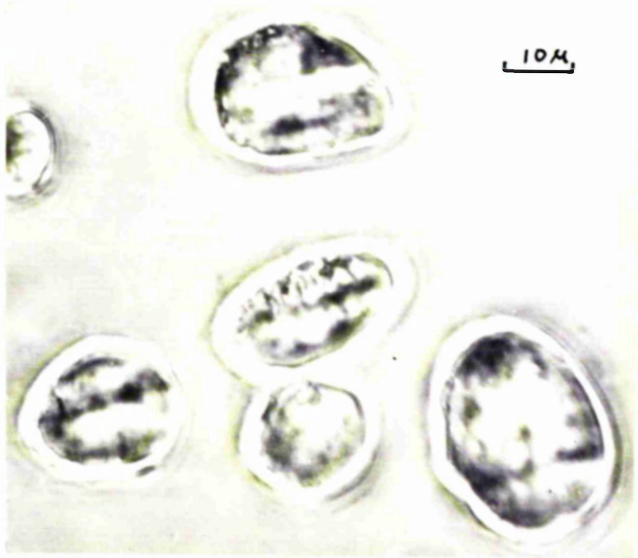


PLATE 3B

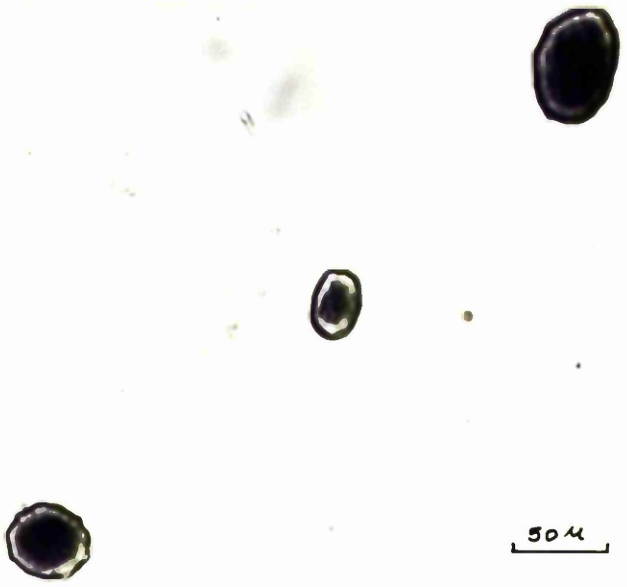


PLATE 4

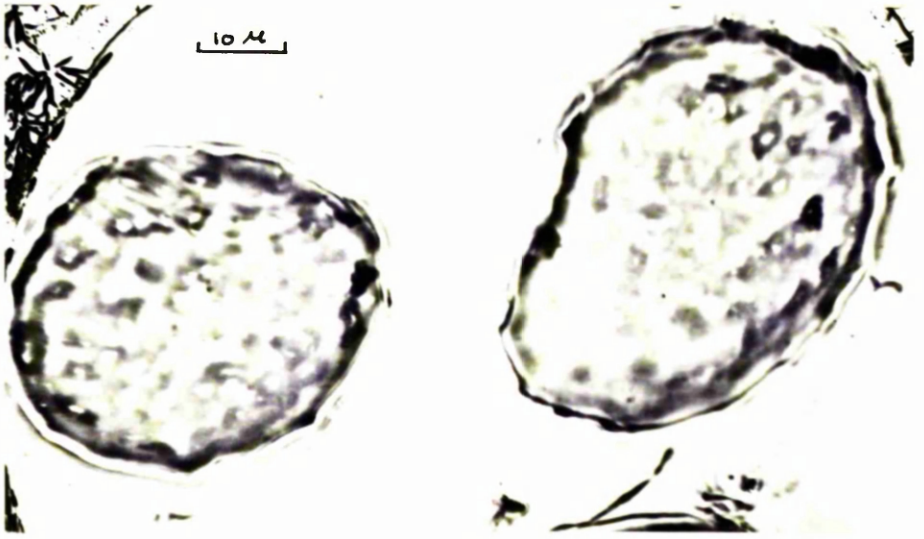


PLATE 5

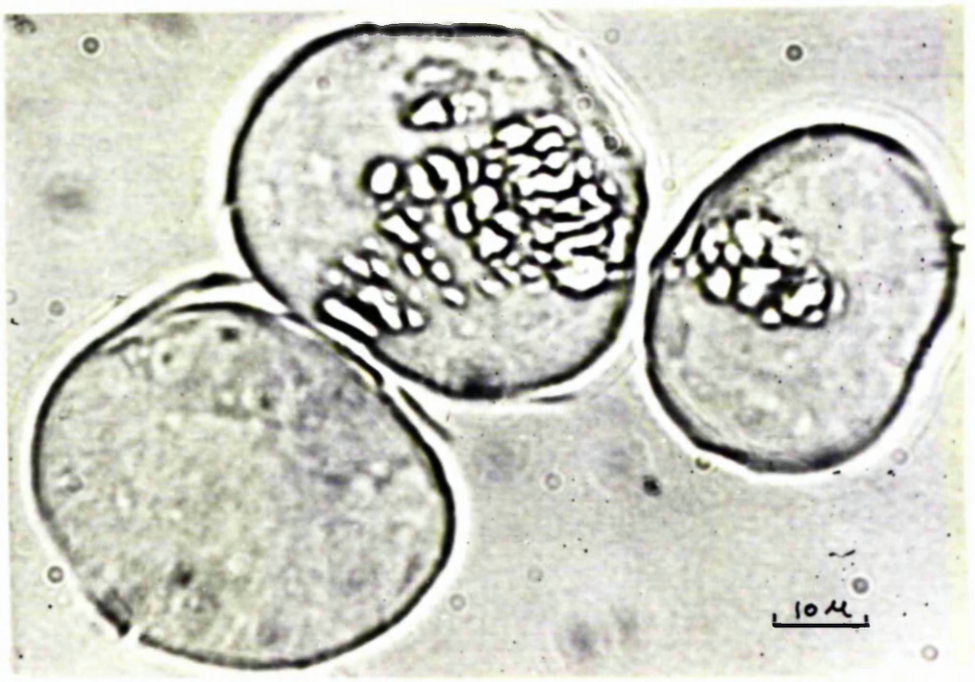


PLATE 6

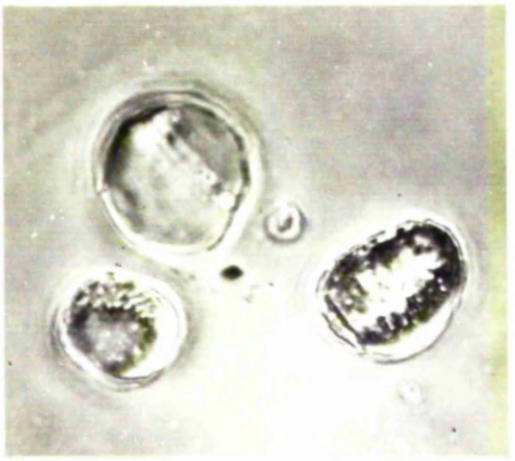


PLATE 7A

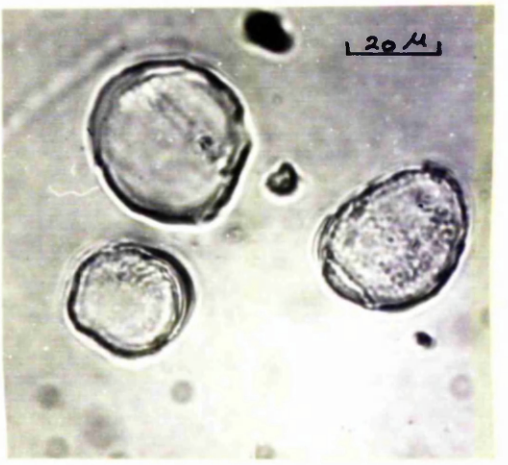


PLATE 7B

PLATE 8

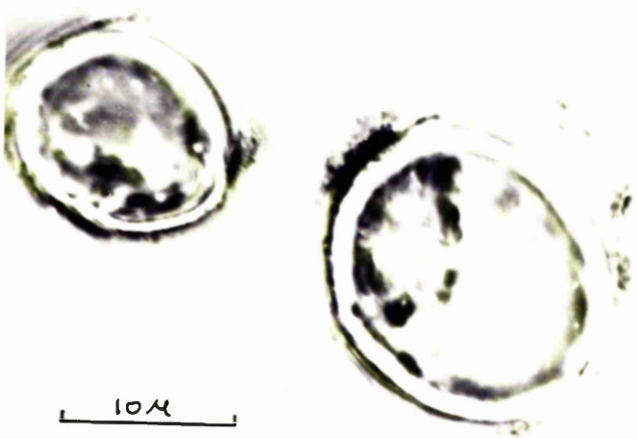


PLATE 9

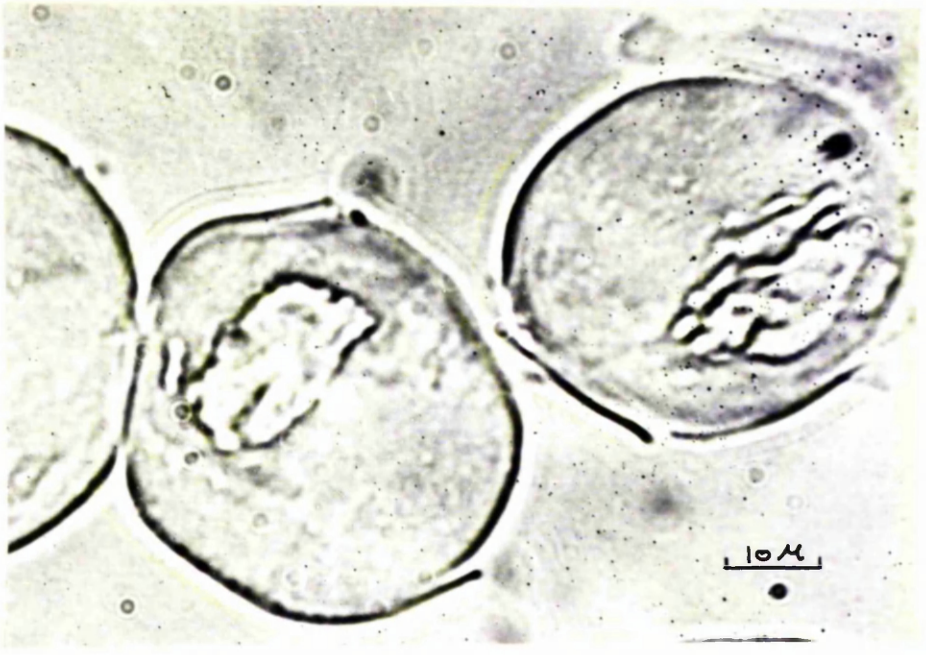


PLATE 10

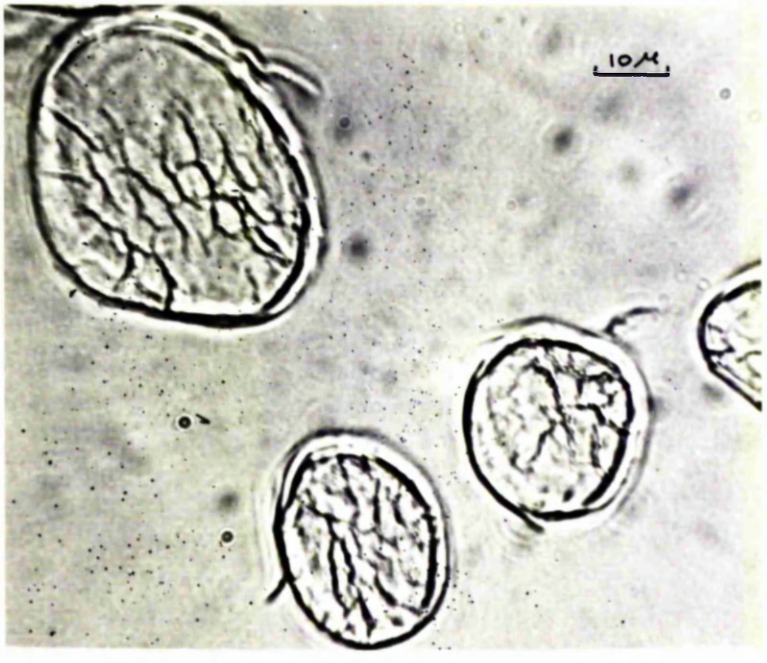


PLATE 11

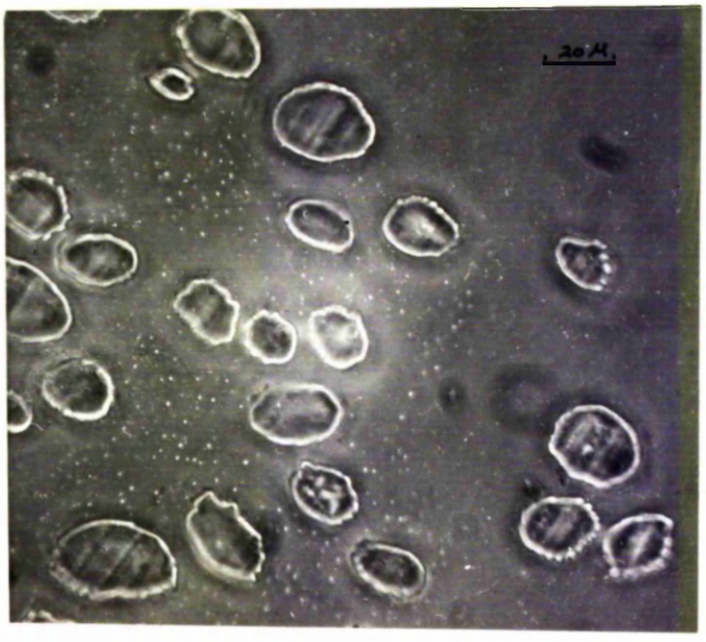


PLATE 12

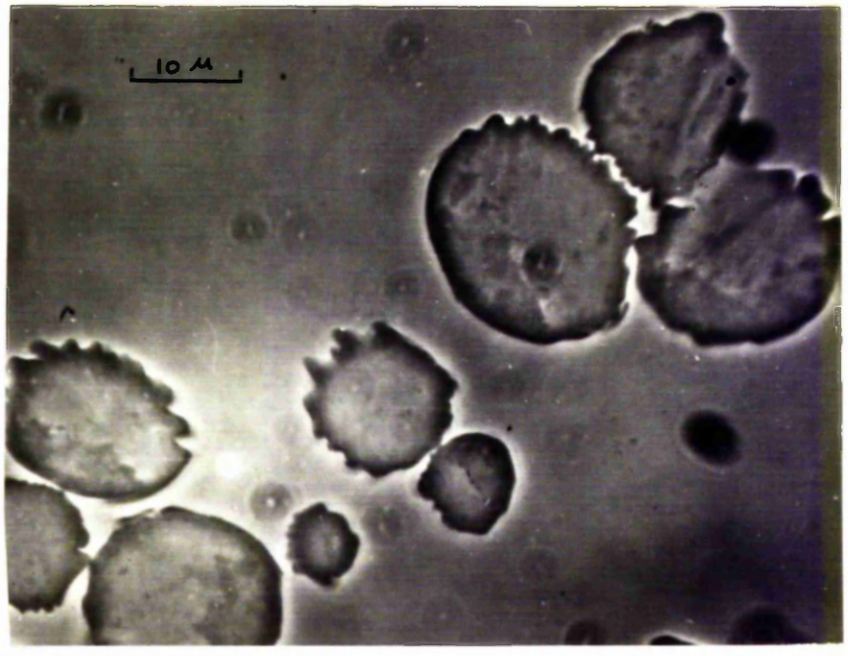


PLATE 13

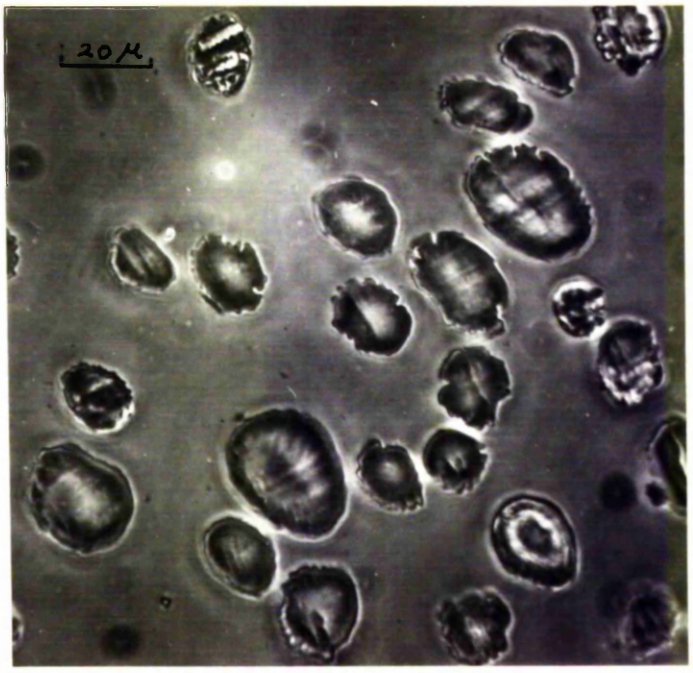


PLATE 14

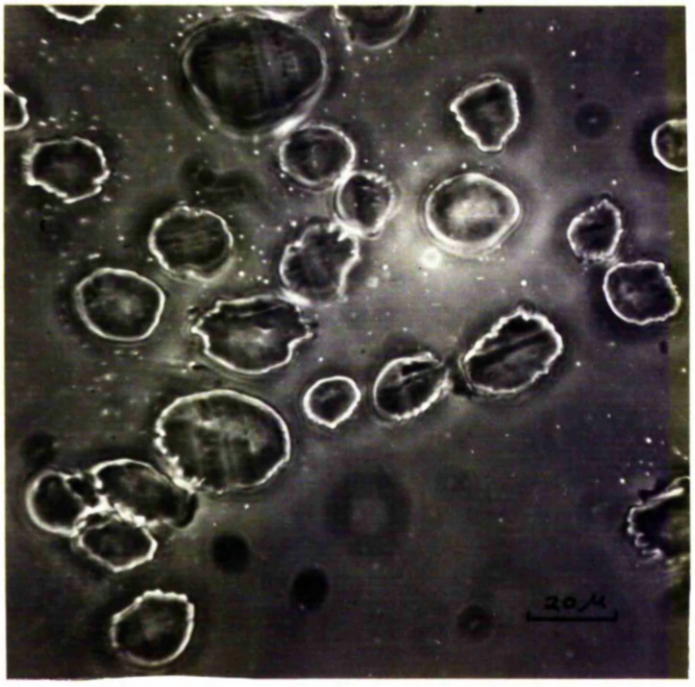


PLATE 15

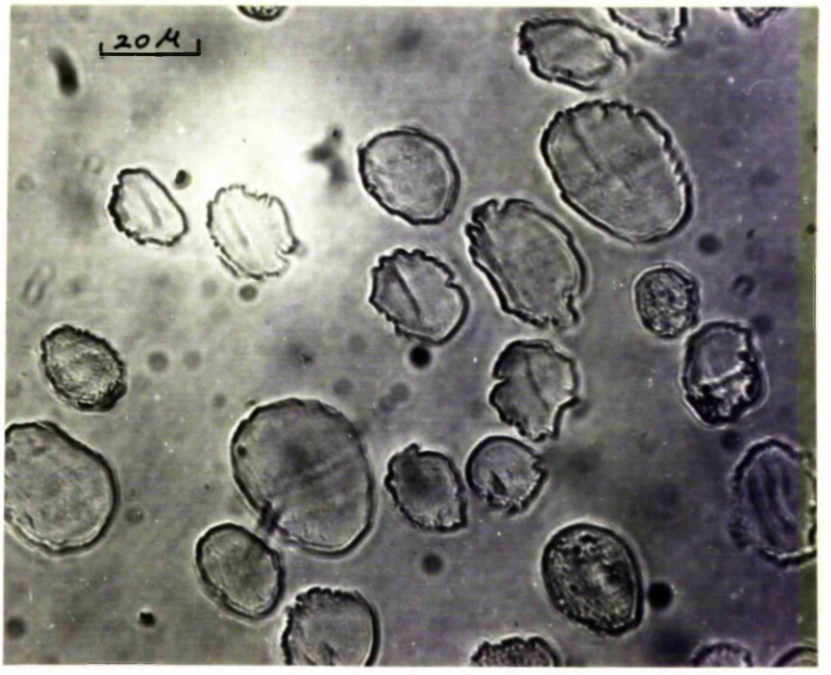


PLATE 16

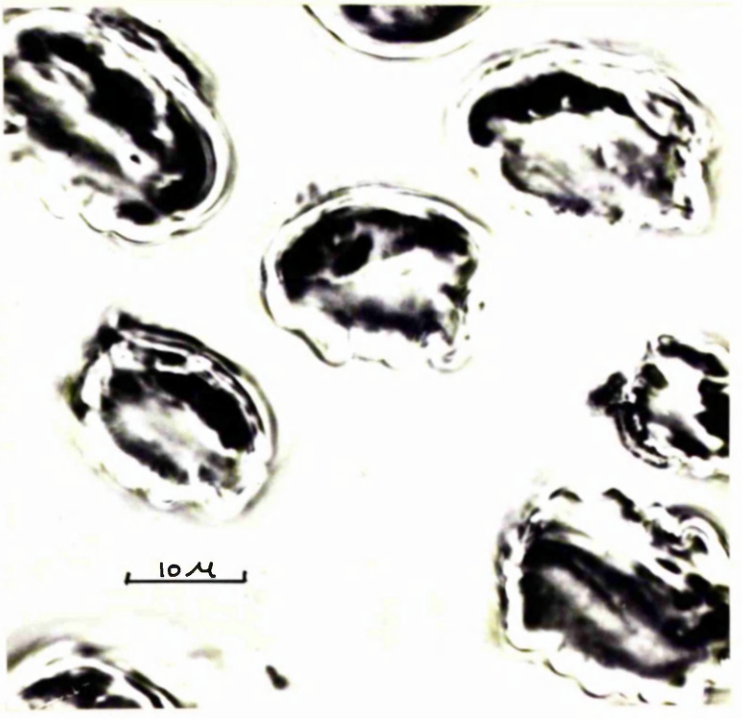


PLATE 17

PLATE 18

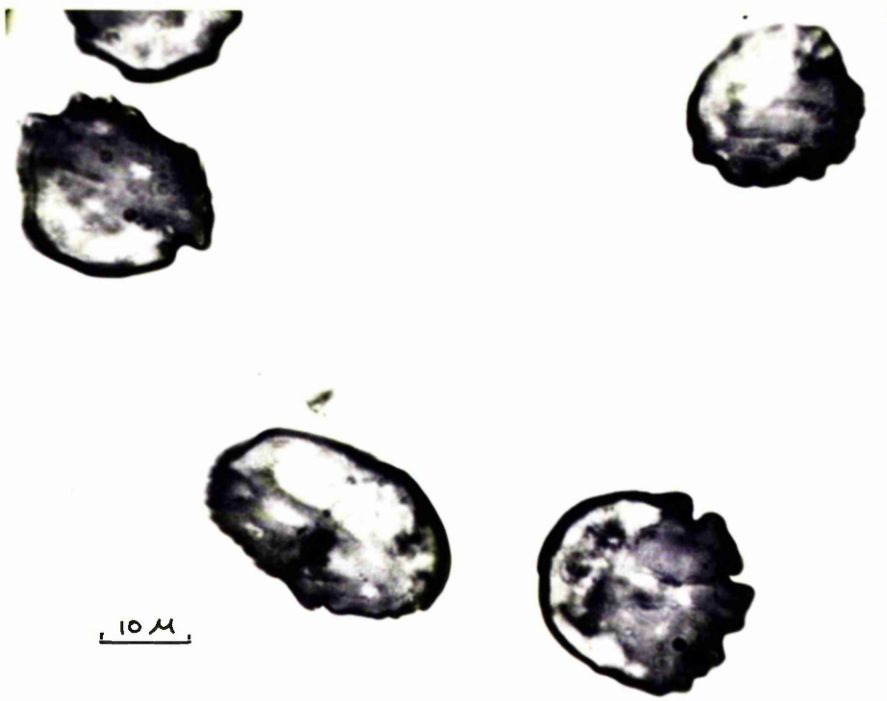


PLATE 19

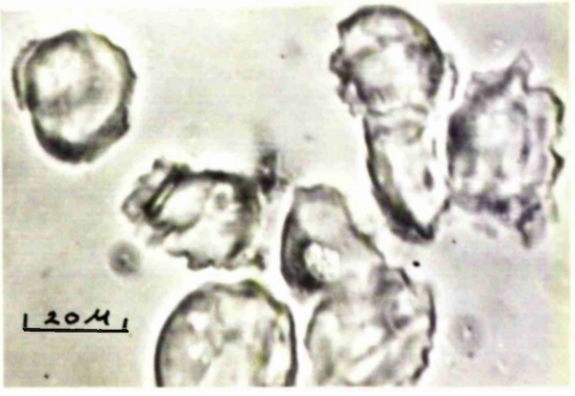


PLATE 20

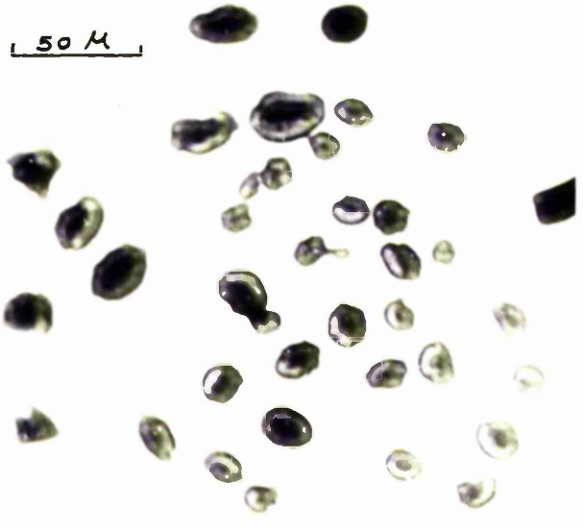


PLATE 21

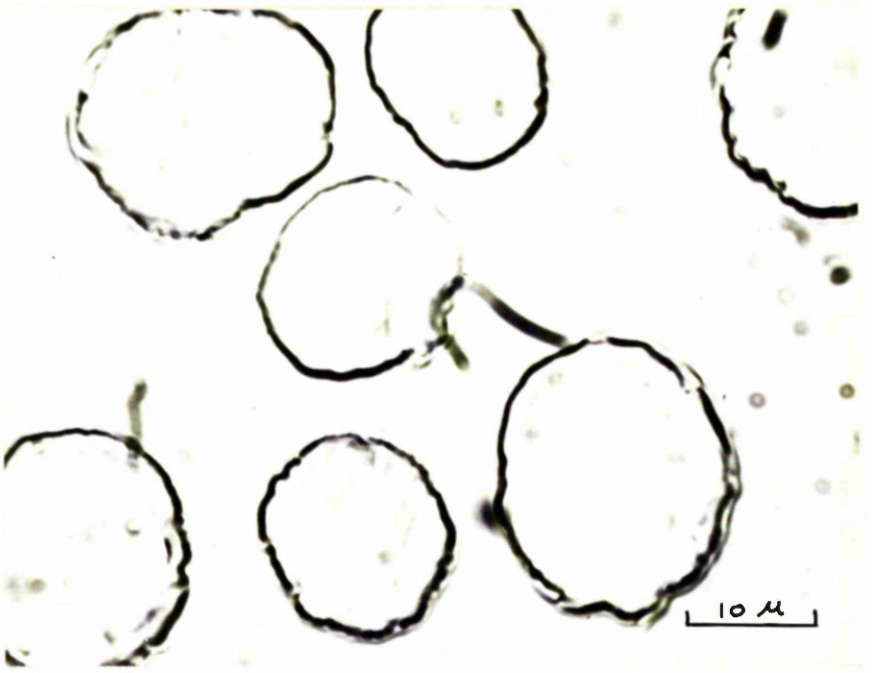


PLATE 22

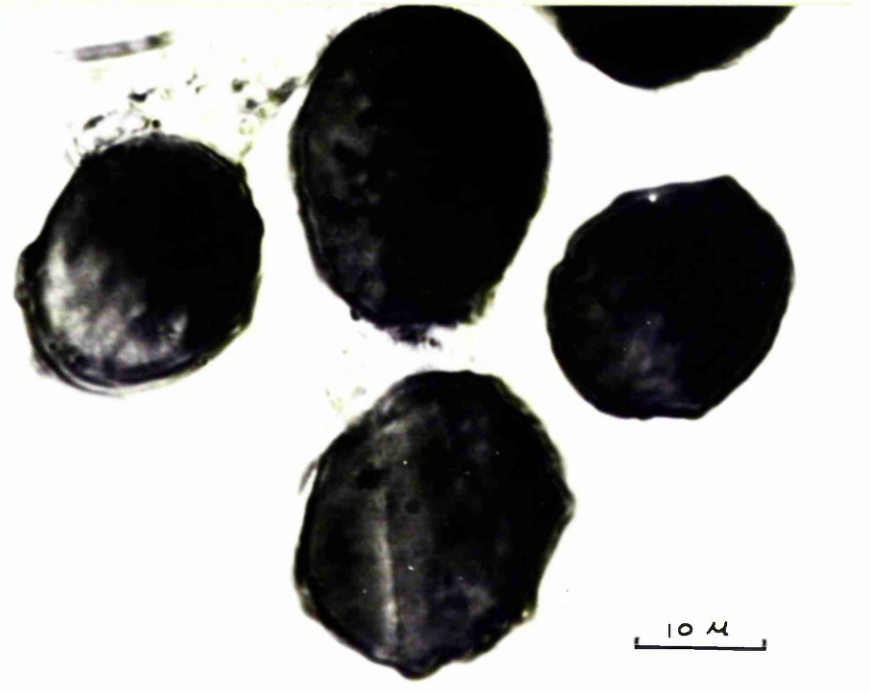


PLATE 23

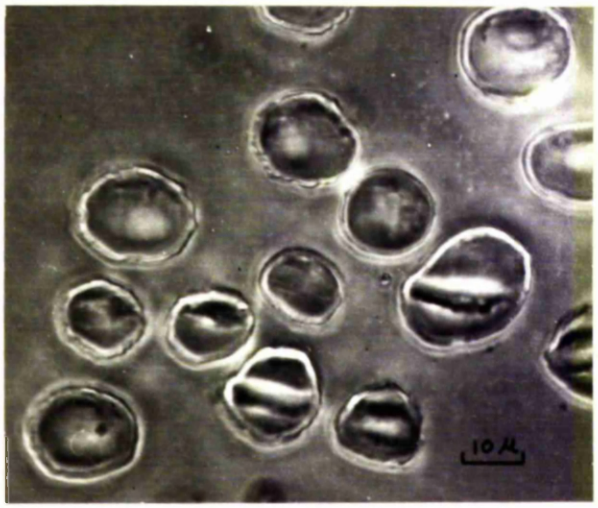


PLATE 24

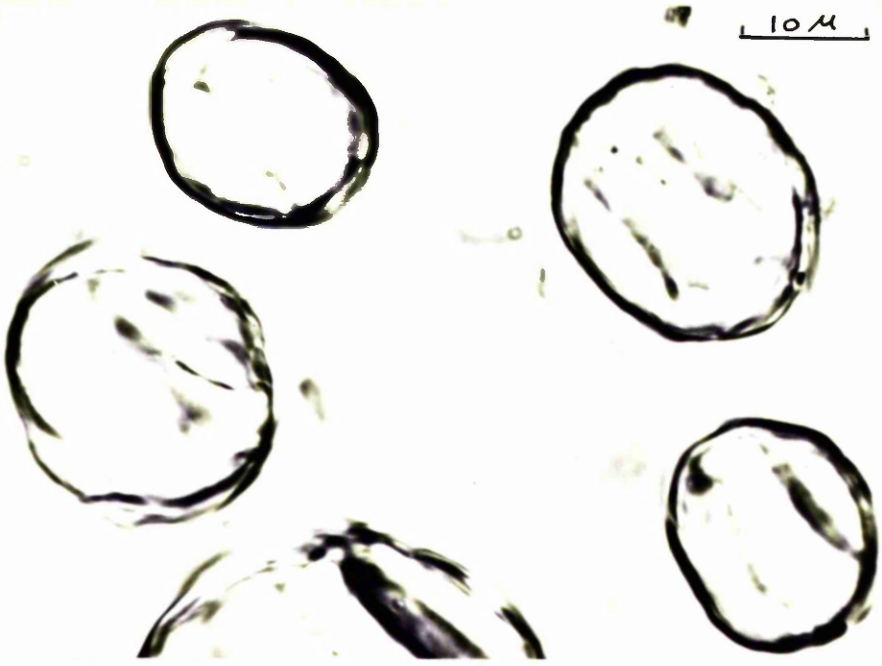


PLATE 25

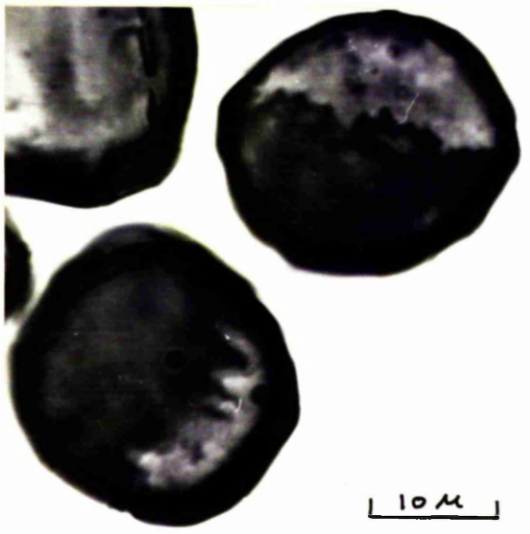


PLATE 26

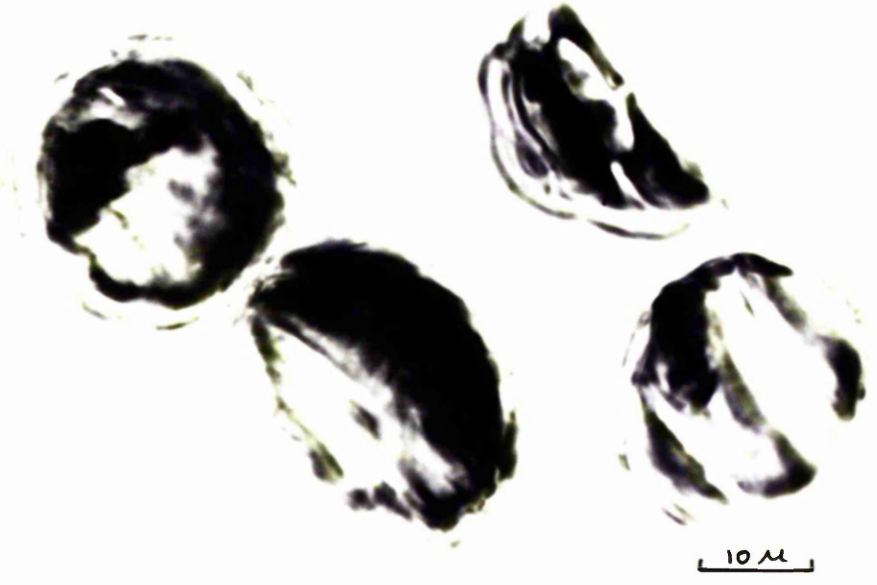


PLATE 27

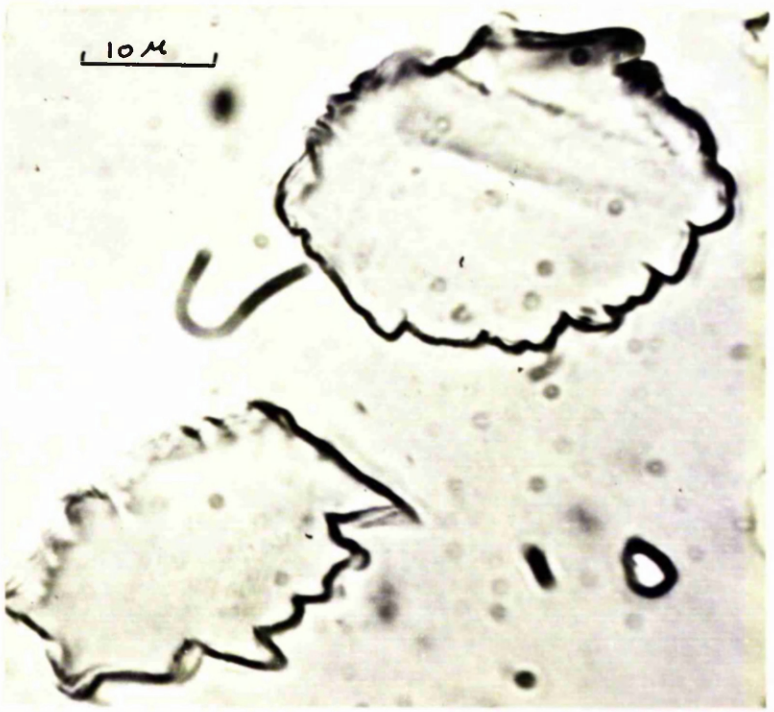


PLATE 28

PLATE 29

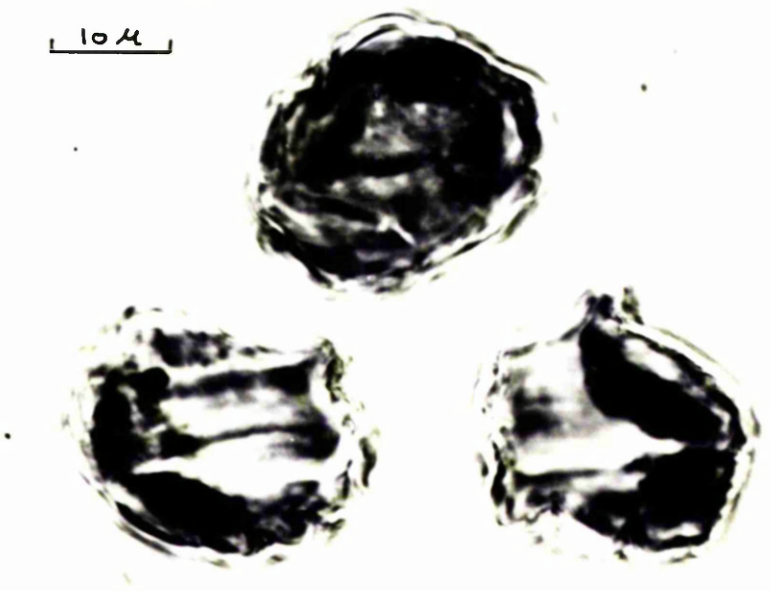


PLATE 30

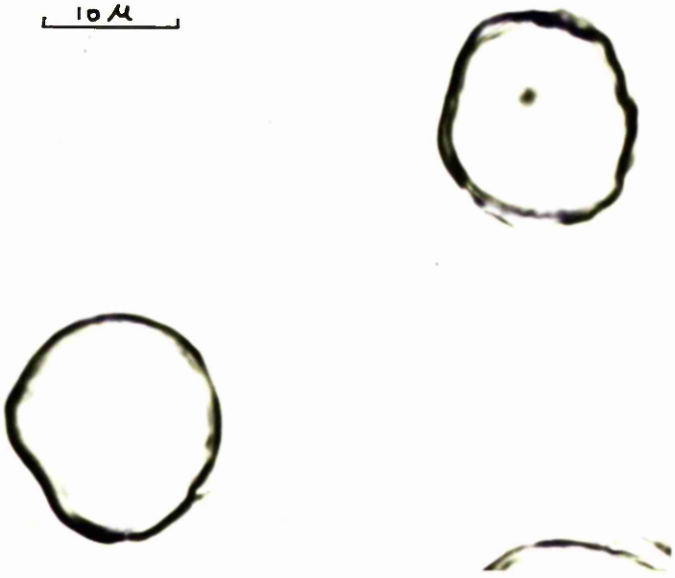


PLATE 31

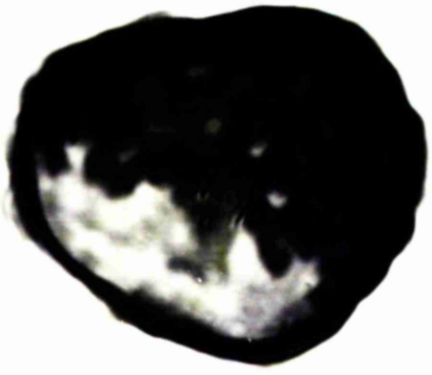


PLATE 32

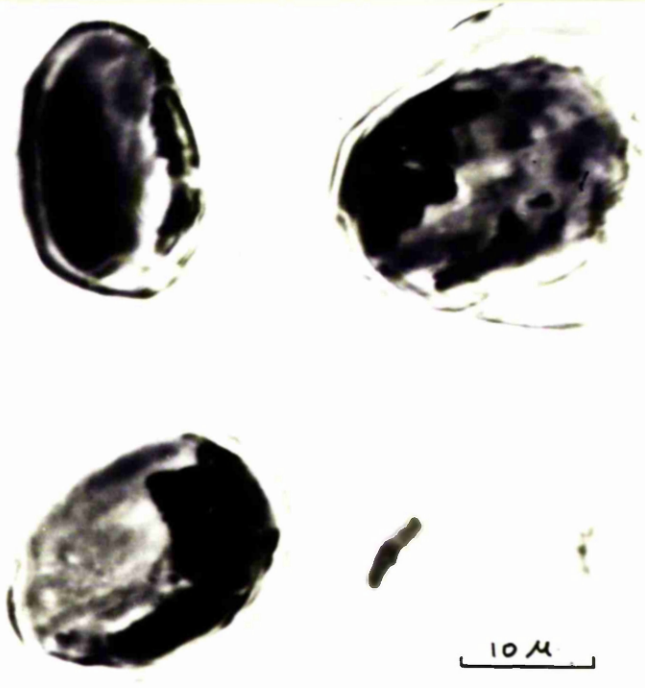


PLATE 33

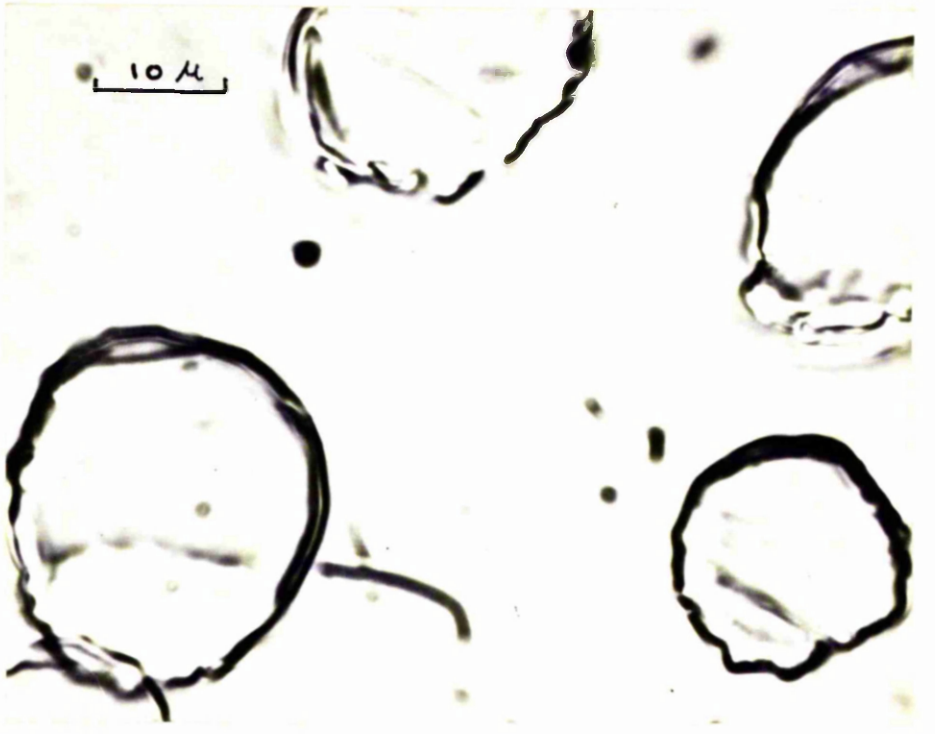


PLATE 34

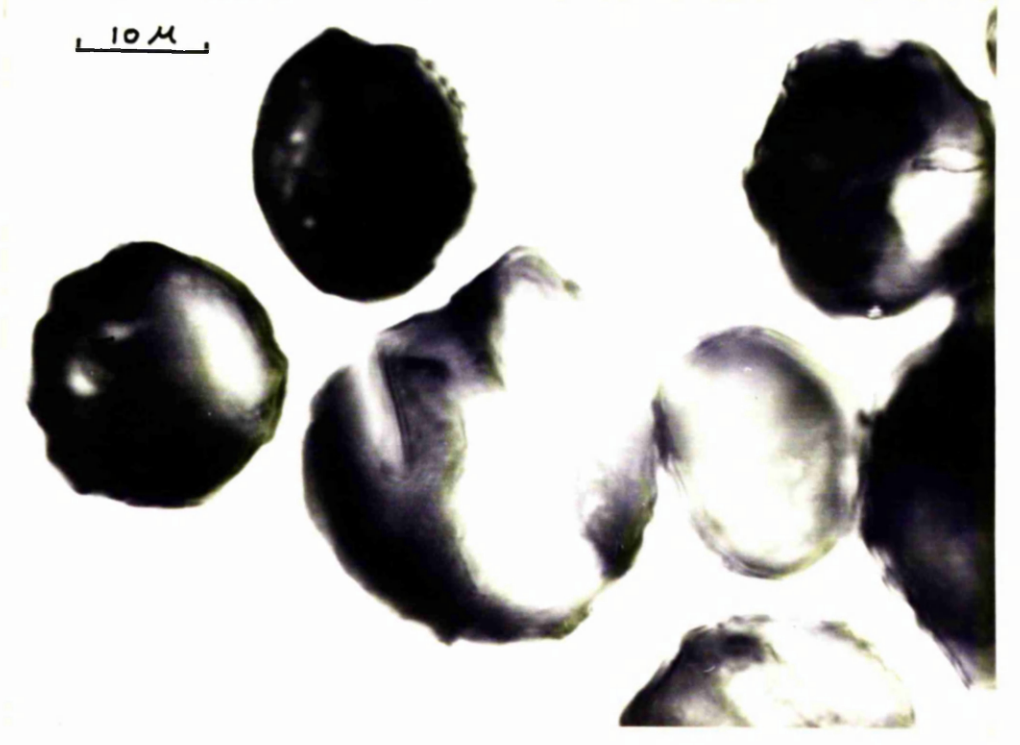


PLATE 35

PLATE 36

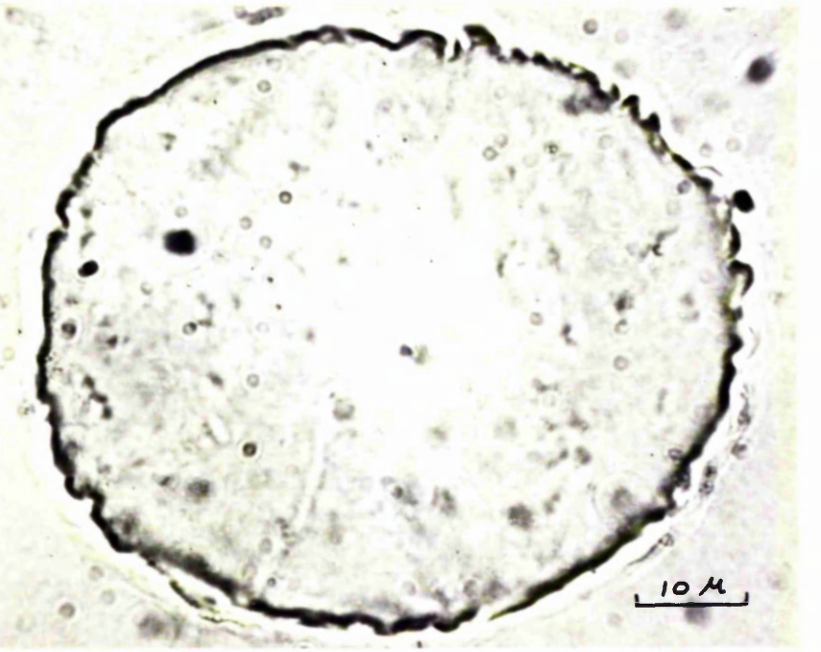


PLATE 37

PLATE 38

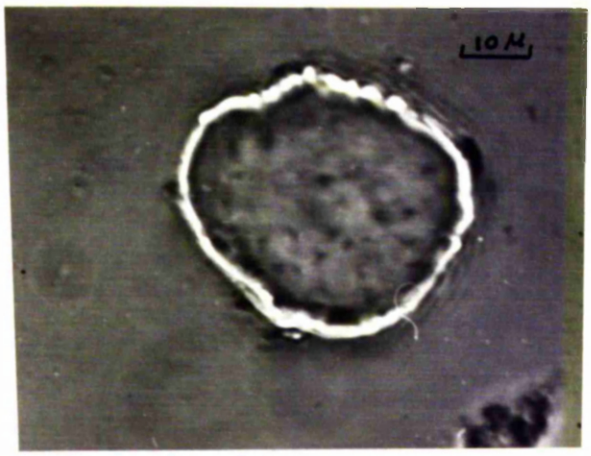


PLATE 39

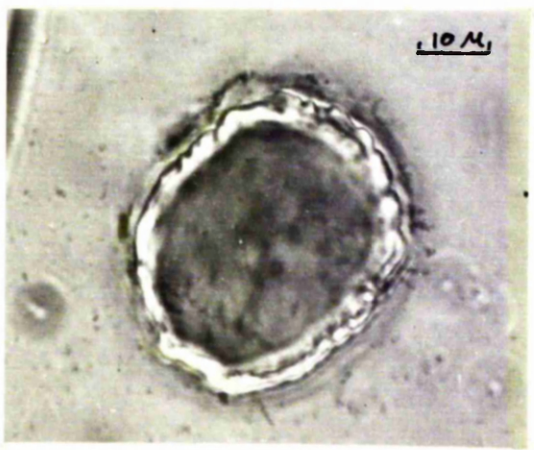


PLATE 40

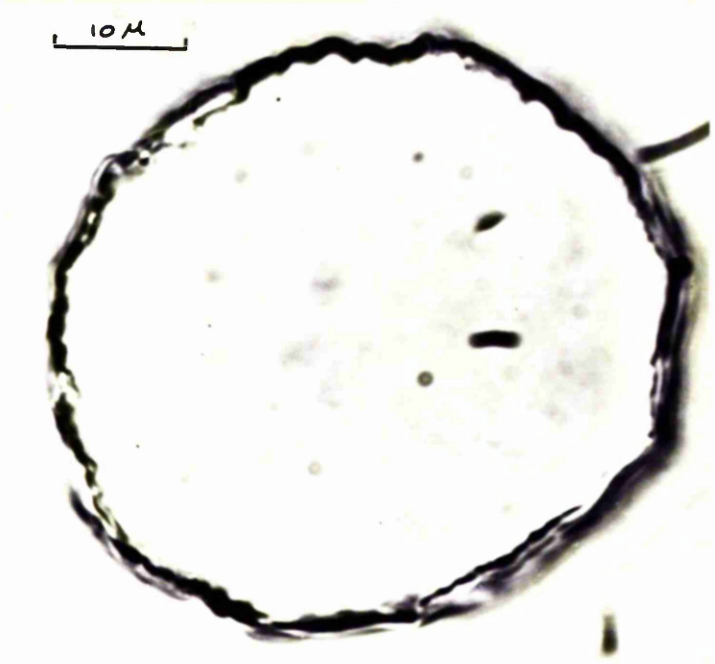


PLATE 41

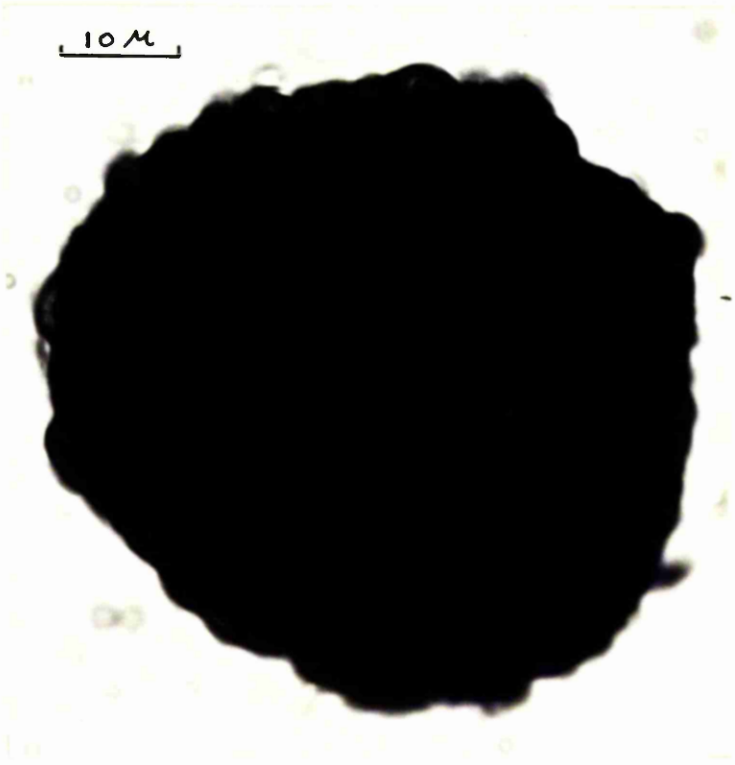


PLATE 42

PLATE 43

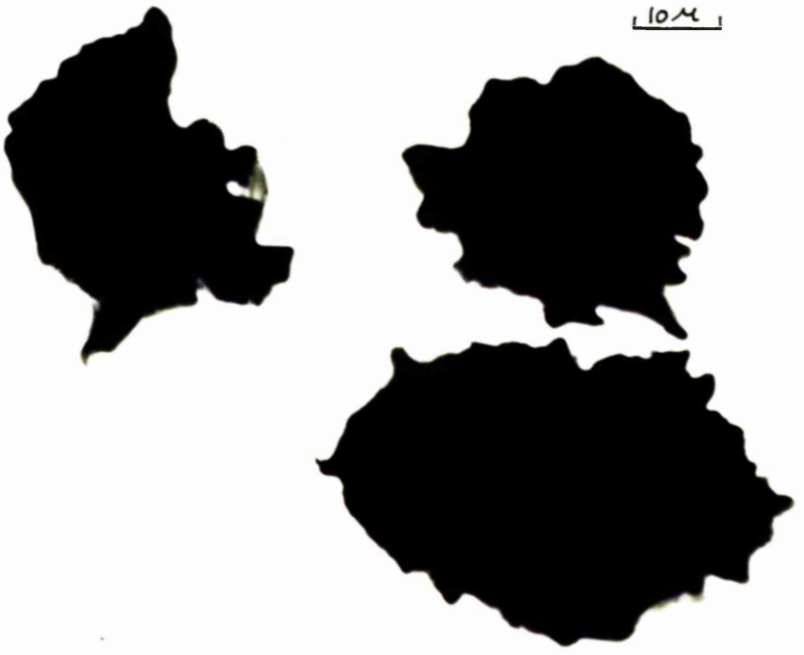


PLATE 44

PLATE 45

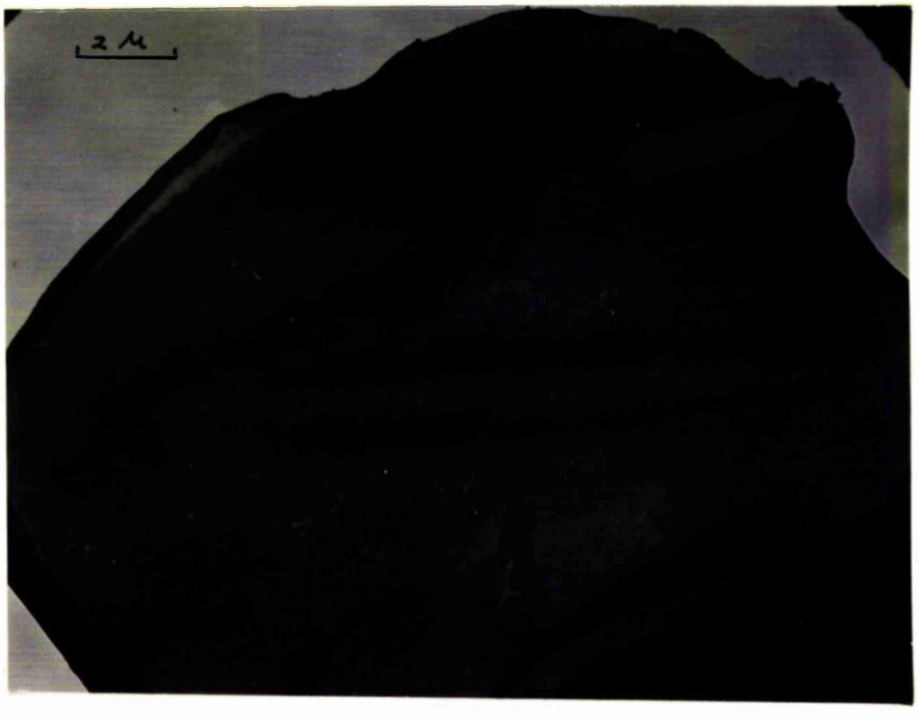


PLATE 46

PLATE 47

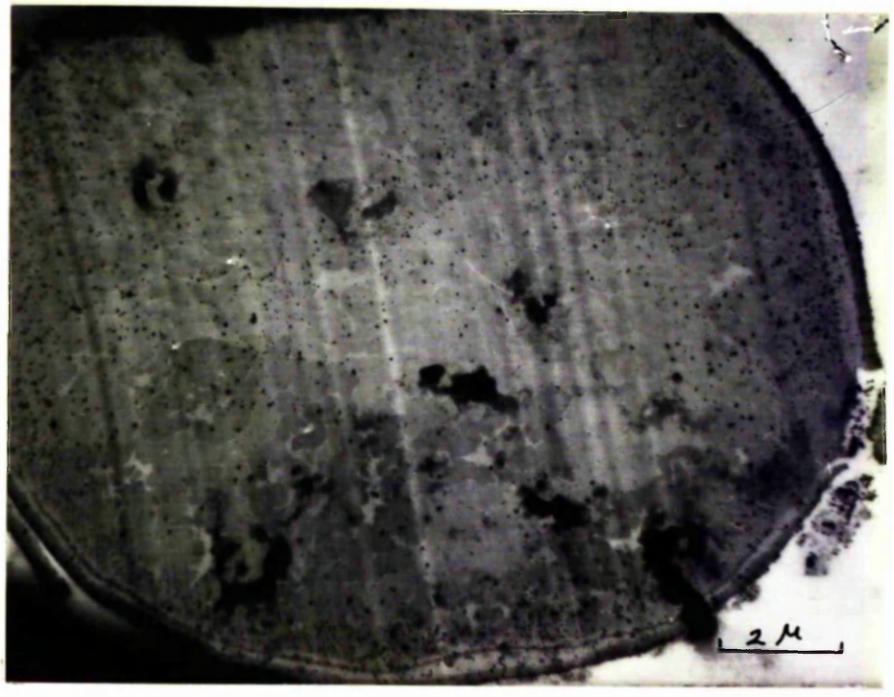


PLATE 48

PLATE 49A

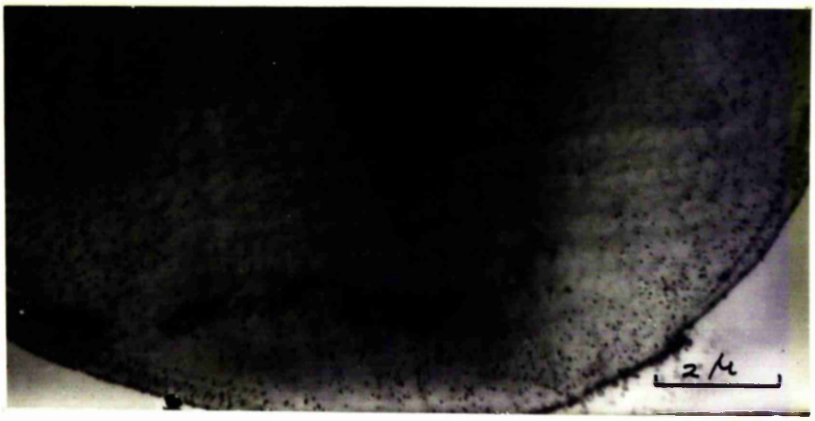


PLATE 49B

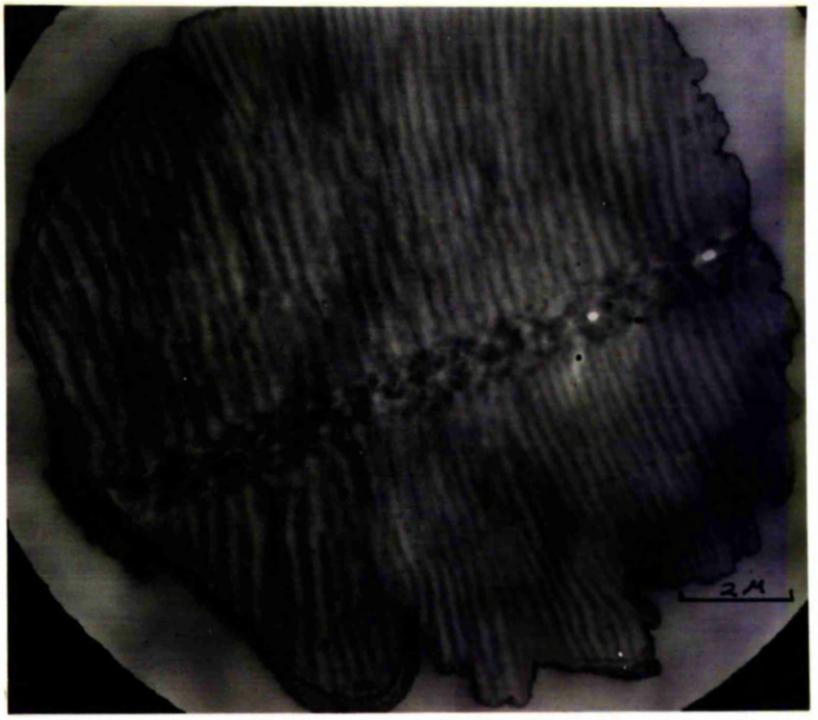


PLATE 50A

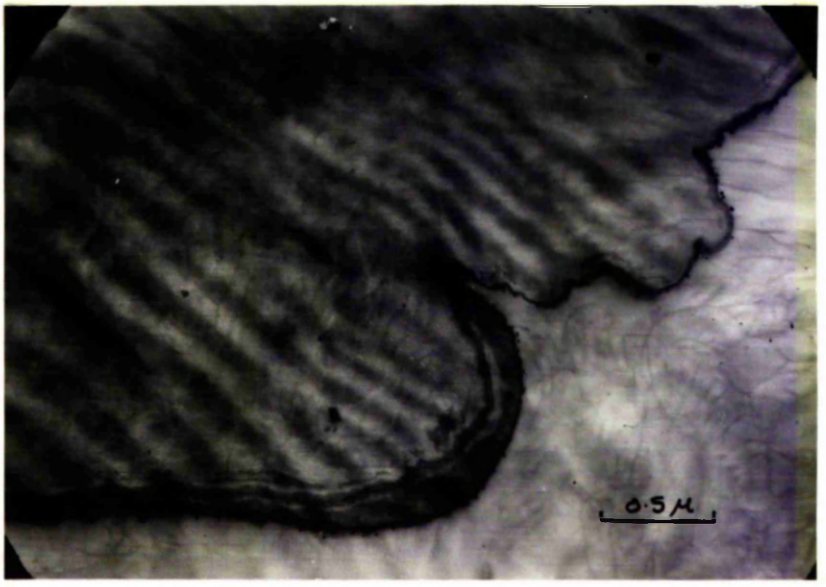


PLATE 50B

PLATE 51A

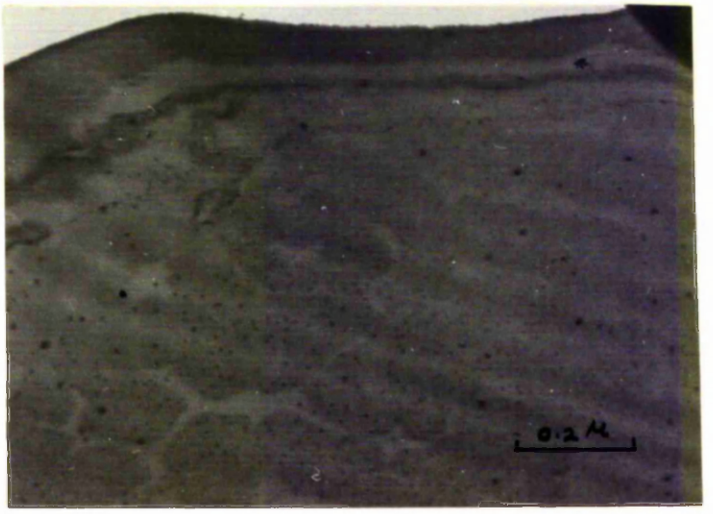


PLATE 51B

PLATE 52