MERCERISING

By the Same Author

AN INTRODUCTION TO THE CHEMISTRY OF CELLULOSE (1938)
(*In conjunction with Dr. F. C. Wood*)

MERCERISING

By

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To

R. P. FOULDS AND F. C. WOOD

AND OUR CREASE-RESISTING ADVENTURES

PREFACE

Fifty years ago a young English textile chemist, barely out of his teens, treated cotton yarn with moderately concentrated aqueous solutions of caustic soda under such conditions that the loss in length which normally occurs was restored; a great increase in lustre was observed and so modern mercerising was discovered. Almost one hundred years ago, however, it had been found that the treatment of cotton with caustic soda solutions produced great shrinkage and an increase in absorptive capacity; the chemical reactivity also increases.

Although most mercerising takes place for the improvement in lustre, those of us who are concerned with the production of new finishes for cotton on a chemical or physico-chemical basis must obviously bear in mind this simple method of turning native cellulose into dispersed cellulose or "activating" it. Hence during the research which led to the original crease-resisting process, its development and exploitation, considerable attention was paid to the mercerising phenomenon. This was also natural in view of some association with the fundamental work of Coward on the swelling of cotton during the mercerising process and the initial work of Willows on single cotton hairs.

To those who are not so conversant with the great number of publications during the past twenty years, it is hoped that the present work will prove of interest; the last book on Mercerisation to be published in English is almost forty years old, whilst the small German monographs of Gardner and of Sedlacek in 1912 and 1928 respectively, deal largely with patent specifications most of which are now obsolete.

Attention is almost entirely focussed on the treatment of cotton with caustic soda; some little space is devoted to linen and to rayon, but there is practically no reference in the following pages to mercerising with acids or with organic bases—the reader may consult "An Introduction to Cellulose Chemistry" for a brief general discussion of dispersed cellulose—as these are considered of little technical and commercial importance at present.

Thanks are due to Mr. Benjamin Leech, M.A., of Macclesfield, for some previously unpublished details of the life of Horace Lowe, to Dr. Neale for reading over the section of the book dealing with the theoretical aspects of the action of caustic soda on cellulose, to Dr. Astbury, F.R.S., for the generous gift of X-ray photographs, and for a number of helpful suggestions. Miss Alexander of the Tootal Broadhurst Lee Company has kindly provided a number of photomicrographs, whilst Mr. Sisson, of the U.S.A., generously offered some of his results on mercerising as a private communication.

Grateful acknowledgment for the loan of blocks is made to Sir Robert Pickard, F.R.S., of the B.C.I.R.A., Dr. Turner of the L.I.R.A., Professor Haworth, F.R.S., of Birmingham University, the J.S.D.C., the Textile Recorder, Messrs. Mather & Platt, Sir James Farmer Norton, Ltd., Ernest Scott & Co., J. Jaeggli & Cie., Daniel Foxwell & Sons, and Zittau Maschinenfabrik A.G.

The Controller of H.M. Stationery Office has courteously permitted the reproduction of the British Patent Specifications of John Mercer and Horace Lowe ; a number of machinery manufacturers, namely: Smith, Drum & Co., of Philadelphia, the Textile-Finishing Machinery Co., of Providence, U.S.A., Benninger of Switzerland, Messrs. Haubold and also Kleinewefers Söhne, of Germany, have kindly consented to the reproduction of some illustrations of their machines.

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PART ONE

HISTORICAL INTRODUCTION

CHAPTER ONE

JOHN MERCER

MERCERISING WITHOUT TENSION

A.D. 1850 **13,296**

Preparation of Cotton, etc.

Mercer's Specification

TO ALL TO WHOM THESE PRESENTS SHALL COME, I, John Mercer of Oakenshaw within Clayton-le-Moors in the County of Lancaster, Gentleman, send greeting.

WHEREAS Her present most Excellent Majesty Queen Victoria, by Her Royal Letters Patent under the Great Seal of the United Kingdom of Great Britain and Ireland, bearing date at Westminster, the twenty-fourth day of October (One thousand eight hundred and fifty) in the fourteenth year of Her reign, and for Herself, Her heirs and successors give and grant unto me, the said John Mercer, my ex̃ors, adm̃ors, and assigns, Her especial license, full power, sole privilege and authority that I, the said John Mercer, my ex̃ors, adm̃ors, and assigns, or such others as I, the said John Mercer, my ex̃ors, adm̃ors, and assigns should at any time agree with and no others, from time to time, and at all times during the term of years therein expressed, should and lawfully might make, use, exercise and vend within England, Wales and the Township of Berwick-upon-Tweed, my Invention of " Improvements in the Preparation of Cotton and other Fabrics and Fibrous Material " in which said Letters Patent is contained a proviso, that I, the said John Mercer shall cause a particular description of the nature of my said Invention, and in what manner the same is to be performed, by an instrument in writing under my hand and seal, to be enrolled in Her said Majesty's High Court of Chancery within six calendar months next and immediately after the date of the said in part recited Letters Patent; as, in and by the same, reference being thereunto had, will more fully and at large appear.

NOW KNOW YE that in compliance with the said proviso, I, the said John Mercer, do hereby declare the nature of my said invention and the manner in which the same is to be performed are fully described and ascertained in and by the following statement thereof, that is to say:

" My invention consists in subjecting vegetable fabrics and fibrous materials, cotton, flax, etc., either in the raw or manufactured state, to the action of caustic soda or caustic potash, dilute sulphuric acid, or chloride of zinc, of a strength and temperature sufficient to produce the new effects, and to give the new properties to them which I have hereafter described.

" The mode I adopt of carrying into operation my invention to cloth made wholly or partially from any vegetable fibres and bleached is as follows: I pass the cloth through a padding machine charged with caustic soda or caustic potash at 60° or 70° Tw.'s hydrometer, at the common temperature, at say 60° F., or under, and without drying the cloth wash it in water, then pass through dilute sulphuric acid and wash again or I run the cloth over and under a series of rollers in a cistern with caustic soda or caustic potash at from 40° to 50° of Tw.'s hydrometer, at the common temperature of the atmosphere, the last two rollers being set so as to squeeze the excess of soda or potash back into the cisterns charged at the commencement of the operation with water only, so that at the last cistern the alkali has nearly all been washed out of the cloth; when the cloth has either gone through the padding machine or through the cisterns above described, I wash the cloth in water, pass it through dilute sulphuric acid, and wash again n water.

" When I adapt the invention to grey or unbleached cloth made from the fibrous material before mentioned, I first boil or steep the cloth in water, so as to have it thoroughly wet, and remove most of the water by the squeezers or hydro-extractor, and then pass the cloth through the soda or potash solution, etc., and proceed as before described.

" I apply my invention in the same way to warps, either bleached or unbleached, but after passing through the cistern containing the alkali the warp is either passed through squeezers, or through a hole in a metallic plate, to remove the alkali, and then passed on through the water cisterns, soured and washed as above described.

" When thread or hank yarn is operated on, I immerse the thread or yarns in the alkali and then wring them out, as is usually done in sizing or dyeing them, and afterwards wash, sour, and wash in water as above described.

" When I apply my invention to any fibre in the raw state, or before it is manufactured, I first boil it in water and then free it from most of its water by the hydro-extractor or a press. I then immerse it in the alkaline solution and then remove the alkali by the hydro-extractor, or I press the alkali out with a press and then wash in water, sour in dilute sulphuric acid, wash again, then remove the water by a press or hydro-extractor as above described.

" When cloth made from vegetable fibre, cotton, flax, etc., has been subjected to the action of caustic soda or potash as above described, by padding, immersion, or any other way, and then freed from the alkali by souring and washing according to my said invention, the cloth will be found to have undergone certain changes and alterations and have acquired certain new and valuable properties; the most remarkable I here describe. It will have shrunk in its length and breadth, or have become less in its external dimensions, but thicker and closer, so that by the chemical action of caustic soda or potash I produce on cotton and other vegetable fabrics and fibres effects somewhat analogous to that which is produced on woollen by the process of fulling or milling. It will have acquired greater strength and firmness, each fibre requiring greater force to break it. It will also have become heavier than it was before it was acted on by the alkali, if in both cases it be weighed at the temperature of 60° F. or under. It will have acquired greatly augmented and improved powers of receiving colours in printing and dyeing.

" The effects of the application of my invention to the vegetable fibre in any of its various stages before it is manufactured into cloth will be readily understood by reference to its effects upon cloth composed of such fibres.

" Secondly, I employ sulphuric acid diluted to 105° Tw.'s hydrometer, and at 60° F. or under; I use this acid mixture instead of caustic potash or soda, and operate in all respects the same as when I use caustic potash or soda, except the last souring, which is here unnecessary.

" Thirdly, when I employ a solution of chloride of zinc instead of soda or potash, I use the solution at 145° Tw. and 150–160° F. and operate in all respects the same as when I use soda or potash.

" When I operate on mixed fabrics, partly of vegetable and partly of silk, woollen or other animal fibres, such as delaines or leans, etc., I prefer the strength of the alkali not to be above 40° Tw. and the heat not above 50° F. lest the animal fibres should be injured.

" I may in conclusion remark, that the description of the apparatus or machinery, and the strength and temperature of the soda or potash, sulphuric acid or chloride of zinc solution, may be varied to a considerable extent, and will produce proportionate effects without at all deviating from my invention. For instance, caustic potash or soda may be used even as low as 20° Tw.'s hydrometer, and still give improved properties to cotton, etc., in receiving colours in printing and dyeing, particularly if the heat be low, for the lower the temperature the more effectively the soda or potash acts on the fibrous material above described. I therefore do not confine myself to any particular strength, or temperature of the substances I employ, but the particular strength, heat and process here described is what I have found the best, and which I prefer.

" And I claim as of my invention the subjection of cotton, linen and other vegetable fibrous material, either in the fibre or any stage of its manufacture, either alone or mixed with silk, woollen, or other animal fibrous material, to the action of caustic soda or caustic potash, dilute sulphuric acid, or solution of chloride of zinc of a temperature and strength sufficient to produce the new effects, and give to them the new properties above described, either by padding, printing or steeping, immersion or any other mode of application."

In witness whereof, I, the said John Mercer, have hereunto set my hand and seal this fourteenth day of April in the year of our Lord, One thousand eight hundred and fifty-one.

JOHN (L.S.) MERCER.

AND BE IT REMEMBERED that on the fourteenth day of April in the year of our Lord 1851, the aforesaid John Mercer came before our said Lady the Queen in Her Chancery, and acknowledged the Specification aforesaid, and all and everything therein contained and specified, in form above written. And also the Specification aforesaid was stamped according to the tenor of the Statute made for that purpose.

Enrolled the Twenty-fourth day of April, in the year of our Lord, One thousand eight hundred and fifty-one.

* * * * * *

The publication of the above document, almost 100 years ago, with its somewhat quaint wording, disclosed to the textile industry one of the most important advances which has ever taken place. Many people are well aware that Mercer discovered mercerising—if only because his name is attached to the process—but comparatively few of us realise that his work and discovery included much more. The patent specification discloses the methods of swelling cellulose by means of solutions of sodium hydroxide at room and lower temperatures, by means of certain concentrations of sulphuric acid at room temperature and also by means of a concentrated solution of zinc chloride at a moderately high temperature. These are examples of all three classes of inorganic substances met with in any study of hydrate or dispersed cellulose.

The effects described by Mercer have undoubtedly been the direct cause of an enormous amount of scientific investigation during the present century, for the work on the action of solutions of sodium hydroxide alone exceeds in volume any other single aspect of cellulose chemistry and technology; we are still doing research work on mercerising—the process described by Mercer—and there seems to be no end to it. Further, if consideration is also given to the formation of alkali cellulose which plays such a large part in the manufacture of viscose and other cellulose derivatives, then there can be no doubt that Mercer was responsible for the biggest fundamental advance that ever took place in the chemistry and technology of the processing of cellulosic material, and is entitled to be regarded as the outstanding genius of the finishing section of the cotton trade.

What manner of man was John Mercer ?

We owe most of our information to a book by Edward Parnell, published twenty years after Mercer's death, entitled "The Life and Labours of John Mercer—the self-taught chemical philosopher." (Longmans, Green and Co., London ; 1886.)

John Mercer was born in February, 1791, at Dean in the parish of Great Harwood, a few miles from the town of Blackburn in Lancashire. At the age of nine he became a bobbin-winder, and a few years later a hand-loom weaver. When sixteen years old, Mercer was struck with the beautiful orange colour of a print dress worn by his baby step-brother and became "all on fire to learn dyeing." This was a somewhat difficult matter, for he had no book on the subject and was unable to obtain any information, for there were no dyers in the village where he worked. However, hearing that the dyers of Blackburn obtained their material from a certain druggist, Mercer went to him and obtained the names of the various materials, finally buying three pennyworth of each of nine samples. He then started to learn dyeing entirely by "rule of thumb," but by dint of his energy and powers of observation, he obtained a fair amount of useful knowledge and was able to dye in most of the colours required at that time—even indigo. In those days, the remnants which were the perquisites of hand-loom weavers represented the only cotton material to which he had access, but his experiments were so successful that he started in business as a dyer, with a partner who provided the premises. The venture was quite successful and came to the notice of Messrs. Fort, proprietors of the Oakenshaw Print Works, who invited Mercer to enter their colour-shop as apprentice. This appeared to be a good opportunity and was accepted—the apprenticeship started in September, 1809.

Unfortunately Mercer was regarded with great jealousy in the colour-shop, but during a severe depression in the calico-printing trade a year later his employers offered to surrender the indentures of all apprentices who wished. Mercer's trying position led him to accept this offer and he returned to hand-loom weaving; it was during this time that he received lessons in mathematics and science from Mr. Lightfoot. By 1813 Mercer had saved enough money to start in business as a weaver and dyer, making good use of the imperfectly spent liquors from the print-works, bought very cheaply. His methods were still empirical.

When he went to buy his marriage licence in Blackburn in 1813, he made some purchases in the market and these included a second-hand copy of "The Chemical Pocket-book, or Memoranda Chemica," arranged in a compendium of chemistry, by James Parkinson of Hoxton, 1803." This chemical pocket-book was Mercer's first book on chemistry . . . "it introduced me into a new world. I devoured it." . . . He rapidly realised the importance of chemistry to the dyer, both in seeking for new effects and in finding the reason for failures. Reading and experiment, carried out with characteristic energy, led to his first invention in 1817, of an orange colour produced by padding the cloth with a solution of antimony sulphide in sodium sulphide, followed by a passage through weak sulphuric acid. This was a great advance, and Mr. Fort of the Oakenshaw Print-works offered him a situation as experimental chemist for five years at a salary of thirty shillings per week as a start. This was accepted and in February, 1818, Mercer entered the colour-shop in somewhat different circumstances from his departure eight years before, as a disappointed apprentice.

He continued his work on antimony orange and produced many variations, including discharge styles; his main effort, however, was directed to learning the properties of the various materials with which he came into contact and he made remarkable progress.

In 1825 his services and ability were recognised by admission into partnership, which continued until 1848, and during this time the firm became very prosperous and maintained a high standard of workmanship. Mercer continued to effect many improvements in calico-printing—the list is long and difficult to classify.

Mercer always regarded his investigations into the action of alkali on cotton as his *magnum opus*, and it is ironical that what is now regarded as a fundamental textile operation in the cotton industry should have been neglected until many years after his death, while so many of his other and minor discoveries which are now obsolete and forgotten were technically and commercially successful during his lifetime. It must not be overlooked, however, that when Mercer made his observations on the effect of alkaline hydroxide solutions on cotton, caustic soda was not an article of commerce. Its manufacture appears to have started with Gossage about 1853, but quotations of price do not appear until about 1866.

Mercerising

The origin of the mercerising process appears to lie in Mercer's preoccupation with substances which are capable of forming chemical combination with water and existing in solution as definite hydrates. During the period 1843-1844 he frequently discussed his views on the differences in viscosity and mobility exhibited by solutions of differing concentrations, and even suggested passing such solutions through capillary tubes in the hope of finding a variation in flow which would agree with the extent of chemical hydration (this work was undertaken experimentally by Graham some eighteen years later).

Mercer was also keenly interested in Graham's experiments on the heat liberated during chemical combination, particularly in connection with the hydration of sulphuric acid. As the nature of solutions has an important bearing on the art of calico-printing, Mercer made a number of experiments with a view to examining the variations occurring in different strengths of solutions of the same substance. He then considered the possibility of bringing about a partial separation of different hydrates by means of slow, fractional filtration, in the course of which solutions of sodium hydroxide were filtered through cotton.

In his own words:

> "For this purpose I made a filter composed of six folds of strong, fine cotton cambric, bleached, passed three times through the calender to make it compact, and poured upon it a solution of caustic soda of 60° Tw. The filtration was very slow; the liquor which passed through was of 53° Tw. (as well as I remember). But I found my filtering cloth had undergone an extraordinary change; it had become semi-transparent, contracted both in length and breadth, and thickened or 'fulled,' as I then termed it. I then spotted bleached cambric with single drops of caustic soda of 60° Tw. and 50° Tw., and noticed that the central portion of each drop (about the size of a shilling) became semi-transparent and contracted; around this was a rim of a quarter of an inch, neither semi-transparent nor contracted, which evidently contained but little soda."

Mercer prepared a number of samples of what he termed "fulled cloth" and showed these to his partners and various friends as a matter of some interest, but his work at the Oakenshaw Works did not give him sufficient time to pursue this matter, which appears to have remained without attention from 1844 to about 1849 or 1850.

The Oakenshaw Print Works, largely as a result of Mercer's ingenuity in the field of calico-printing, had a long period of prosperity but, whilst Mercer's aim had always been the production of high class goods, commercial competition became so acute, that it was found necessary to manufacture inferior goods at a lower rate. This factor, together with the financial risk which is generally associated with keen competition, caused Mercer to dissolve partnership in 1848.

With some time at his disposal, Mercer returned to the examination of his "fulled" cotton, and in order to continue his experiments he made an arrangement with Robert Hargreaves of the Broak Oak Print Works, Accrington, who agreed to give him facilities for experiment in return for a share of the mercerising patent which was filed in 1850.

Apparently very great interest was aroused in Mercer's products at the International Exhibition of 1851, for his samples were given special commendation in the report of the Jurors of the Exhibition, and there seemed to be some evidence that if a commercial campaign had been vigorously launched about this time, then the process would have been a great success. It was unfortunate that the exceedingly keen competition in the calico-printing trade which appeared at this time made the primary consideration. one of reasonable appearance at the lowest possible cost. The price of sodium hydroxide was undoubtedly high, for the earliest quotation in 1866 for 70% NaOH was £26 per ton and the contraction of the cloth which took place during mercerising also increased the cost of the process.

Mercer's experiments led him to the conclusion that 45-55° Tw. is about the best strength of solution of sodium hydroxide at room temperature ; the characteristic changes are produced in a few minutes. In the case of lower concentrations of caustic soda, he found that a longer time was necessary, but when 10° Tw. solution was used, there was very little change produced in the cotton.

Mercer also observed that the concentration of sodium hydrate in the solution was reduced by contact with the cotton, as the sodium hydrate was preferentially absorbed ; he found that in order to maintain a concentration of 45° Tw. it was necessary to supply liquor of 60° Tw.

The effect of temperature was also noticed to be the reverse of what usually takes place in chemical reactions, i.e. when the temperature was increased, the action of the alkali on the cotton was retarded but reduction of the temperature increased the action, so that by cooling solutions which were too weak at room temperature, they could be made effective at the lower temperature.

Where the lower temperature was employed with the usual strength of solution, the cloth became stiffer and harder. The most translucent effects on paper and cotton were obtained by mixing one pint of caustic soda solution of 70° Tw. with 20 ozs. of crushed ice.

Because cloth treated with caustic soda of the necessary concentration had the alkali removed by prolonged washing with water, Mercer argued that as the washing process was greater than that which should be necessary if the alkali was merely held mechanically, it was very likely that chemical combination had taken place between the cotton and the alkali, but that the resulting compound was easily decomposed by water. A further point in favour of chemical combination was that the alkaline liquor is reduced in strength as it passes through the cotton. Mercer concluded that the compound formed consisted of single equivalents of cellulose and alkali.

When the treated cloth was exposed to solutions of various mordants and dyestuffs, it was noted that the receptive power of the cotton had become greatly increased as a result of the swelling treatment. Mercer found that this increased power of absorption was due to a mechanical change in the fibre, as the property was noted for a variety of compounds, acid, neutral or alkaline.

The shrinkage of the treated material was one of the earliest effects encountered, and Mercer found that by printing the cloth with a resist before mercerising, the protected portions did not contract during the treatment but gave a puckered effect. Further, when this material was dyed, the resisted portion resulted in a lighter shade owing to its lower affinity for the dyestuffs. The resist used by Mercer was a solution of gum. The general method was to treat the printed material with caustic soda of 60° Tw., which produced more contraction than 70° Tw.

Another important observation was that the treated material showed an increase in strength in excess of that which might be expected from mere contraction of the fibres. It is stated that this was first observed in the extra effort required to tear-off the ends of the treated pieces. Comparative strength tests on cloth showed an increase from 13 lbs. to 22 lbs. breaking load as a result of mercerising, whilst on yarn the figure rose from 13 ozs. to 19 ozs. The amount of contraction in the case of cloth is stated to have been to three-quarters of the original length and breadth ; an instance is given of a fine cotton cloth of 200 picks to the inch which became contracted to 270 picks to the inch.

Even when all the alkali had been removed from the mercerised cloth, the material weighed more than it did before treatment. This increase was found to be almost uniform and amounted to 4·5 to 5·5% of the weight of the original material.

The conclusion reached on this evidence was that the increase in weight was due to the presence of moisture in excess of the hygroscopic moisture of the original cloth and must exist in a state of feeble combination. The proportion of water required by the formula $(C_6H_{10}O_5)_2H_2O$ is 5·5% ; Mercer regarded the matter as being similar to the formation of chemical hydrates.

In addition to the work on caustic alkali, it will be remembered that Mercer's original specification contained two other examples of what we now regard as the dispersion of cellulose. The first of these methods is concerned with the use of sulphuric acid, and here again Mercer found that the action varies considerably with strength, temperature and time of reaction. When the object was merely to increase the affinity for dyestuffs of the cotton, Mercer considered the best strength of acid to be 108° Tw. at 60° F. The cloth should be absorbent in order to be responsive to the acid treatment, which should only last one minute. Sulphuric acid of 104° Tw. produced very little effect.

Mercer's observations on the action of various concentrations of sulphuric acid are as follows :

> " Three stages, or perhaps more, may be recognised in the action of sulphuric acid. The first action seems to be the expansion and rupture of the fibre ; to effect which the strength of the acid should be about 110°, at temperature about 50° F. When washed and dried, the cloth is not stiff (as is the case with stronger acid), but very soft, and feels similar to glove leather. It is not much contracted, and can

easily be stretched to its original size. It is very white, and its power of receiving colour is greatly augmented. It is to cloth of this character that my patent relates.

" The next stage is exhibited with acid of about 114° or 115°, at the same temperature. This strength causes considerable contraction of the cloth. When washed and dried under pressure between folds of bleached cloth, it is stiff and white, having the appearance of being impregnated with a dense white precipitate. It cannot be stretched to its original dimensions. If the cloth is impregnated with milk, and dried before being immersed in the acid, it looks still whiter and more beautiful.

" Sulphuric acid stronger than the above, namely, from 116° to 125° Tw. at the temperature of 50° F. produces another marked effect. With this the cloth becomes semi-transparent. It is stiff, and much contracted. If a design is first pencilled or printed with a protecting paste of albumen, solution of casein, or thick gum-water, and dried before being put into acid, the design is preserved and a very pleasing effect may be produced."

Mercer found zinc chloride to be effective in concentrated solutions of about 200° Tw. but, unlike the cases of caustic soda and sulphuric acid, a higher temperature of some 100° F. was necessary. A saturated solution of zinc nitrate was found to be without action, but certain improvements could be brought about by means of solutions of calcium chloride of 90–100° Tw. at a temperature of 200° F. A mixture of equivalent quantities of zinc chloride and calcium chloride of 165° Tw. was found to be more effective than calcium chloride alone.

Other materials which were found to produce shrinkage of the cotton fibre were phosphoric acid, arsenic acid on heating, and solutions of protochloride of tin ($SnCl_2$).

The action of sodium hydroxide solution of 20° Tw., which was too weak to be effective, gave mercerising effects when " hydrated zinc oxide " was added to it. The necessary proportions, according to Mercer, were one equivalent to two equivalents of soda, or, as we should now estimate it, $Zn(OH)_2 : 4NaOH$. This solution of 30° Tw. " acted very strongly when cold, but it did not act when hot."

Mercer also found that linen was altered in a manner similar to cotton when treated with caustic soda solution ; shrinkage was observed, but the increase in weight by absorption of moisture was not so great as with cotton. Cloths made from ramie were found difficult to wet, but the affinity for dyestuffs was increased as an effect of mercerising.

For the general treatment of cotton goods with caustic soda solution, Mercer found that the best results for improved appearance and affinity for dyestuffs were obtained on cloth which had been bleached without boiling in weak alkaline liquor—the common practice. The goods were bleached by soaking for one hour in boiling water, squeezing and washing with water five or six times, soaking in the usual chemic solution at a temperature not exceeding 170° F. and then squeezing, souring and washing as usual. Mercer regarded it as exceedingly important that the cloths should be in a sufficiently pure condition to allow the mercerising liquor to penetrate rapidly and evenly. When difficulties presented themselves, Mercer's usual practice was to soak the cloth in boiling water for about an hour, squeeze, and wash with five or six changes of water, and then treat the cloth with mercerising liquor whilst still slightly moist.

The discovery of the solubility of cellulose in cuprammonium hydrate is usually accredited to Schweizer (J. pr. Chem., 1857, *72*, 109), but according to Parnell ("The Life and Labours of John Mercer"; Longmans, Green and Co., London; 1886, page 214) the effect was first noticed by Mercer.

After considerable hesitation on Mercer's part, he was elected a Fellow of the Royal Society in 1852. John Mercer died on November 30th, 1866, at the age of seventy-six.

In view of the enormous amount of published work on mercerising and the mercerising process, it is perhaps interesting to summarise Mercer's patent and investigations in respect of the action of sodium hydroxide solutions only. The main points are as follows:

(*a*) Shrinkage in the area of cloth and the length of yarn.
(*b*) Increase in tensile strength.
(*c*) Increased hygroscopicity.
(*d*) Increased capacity for absorbing dyestuffs.
(*e*) Preferential absorption of NaOH during the process.
(*f*) Increased action at lower temperatures.
(*g*) Possible compound formation, soda-cellulose.

The silk-like lustre now commonly associated with mercerised goods and produced by mercerising under tension was not known during Mercer's lifetime, and even the caustic print or crimp-style did not appear on the market until eighteen years after his death.

Mercer always appeared to have regarded the increased affinity for dyestuffs as the most important technical aspect of his work on the treatment of cotton with caustic soda, and to have regarded the production of puckered effects or crêpe styles as of secondary importance. Nevertheless, goods in crêpe style were prepared and exhibited at the International Exhibition of 1851, and by Dr. Playfair to the British Association in the same year.

For a period of some thirty years, however, mercerisation practically disappeared, but the following generation of textile technologists made good use of the crêpe style, and goods were put on the market shortly after 1884. These were produced by local mercerisation, causing a puckered effect as the result of a printing process. The methods were protected by the patents of Depoully—chiefly D.R.P. 30,966 of 1884. Unfortunately Mercer's priority appears to have been overlooked, as the attempt to upset these specifications was made too late to be effective under the German law regarding patents, by which a patent which had not been opposed within five years of its publication became practically unassailable.

The Depoully patents contain certain points which are of historic interest. B.P. 28,696 of 1883, by Garnier and Depoully was merely a process for strengthening light cotton cloths by mercerising in order that the materials should withstand goffering without being torn. The side pressed against the cylinder received a high lustre, which was regarded as a disadvantage and obviated by interposing a cotton press-cloth between the roller and the material to be goffered. It is somewhat ironical that the first recorded mention of lustre in connection with mercerising should consider methods of avoiding it. The object of the inventors was clearly the production of crinkled cloths, as was shown by the subsequent specifications B.P. 8642 of 1884 and B.P. 15140 of 1885.

The first of these two documents dealt with two classes of goods, first, mixtures of animal and vegetable fibres, which on mercerising produced undulations (or the chemical waves of the corresponding French document) by shrinkage of the cotton whilst the wool or silk was unaffected, and secondly, cotton goods which were caused to crinkle by local printing with a thickened solution of caustic soda or by printing a resist followed by mercerising of the piece. It was even stated that the goods may be passed through the lye in a distended state, from which it appears that modern mercerising was almost discovered, particularly in view of the observation regarding lustre in the previous specification. Further, the 1884 document mentions the "elegant contrast of matt and transparent effects." It is easy to be wise after the event and too much must not be read into the actual wording of a patent specification, as many inventors are apt to give a glowing description of their process or product. The patent of 1885—B.P. 15140—dealt with the mercerising of material made from mixed yarns, either cottons and an animal fibre, or two cotton yarns, one of which has been coated with a resist to alkali. It is merely an extension to treatment of combinations of yarns with either sulphuric acid or caustic alkali to produce crimped styles.

These processes were a commercial success, being largely developed by the Lyons firm of Garnier, with which the Depoully brothers were associated, and a great variety of crimp styles was marketed. The process became very popular in England, particularly for wool-cotton unions, and some highly ingenious methods were developed. Mercer's process, therefore, only reached commercial importance thirty-five years after its discovery and nineteen years after his death.

The caustic print, crimp style or crêpon has not the same appeal nowadays, but nevertheless has not completely died out. It may be done by either direct or resist methods of printing.

In the direct style, the cloth is printed with a thickened solution of caustic soda, such as 6·5 litres of 100° Tw. NaOH solution to 3·5 litres of 35% gum senegal solution; the thickened solution usually corresponds to at least 50° Tw. NaOH solution. Almost any number of stripes may be produced, but it seems general to have at least half of the cloth printed in this manner. After printing, the cloth is run through air with the minimum of tension in order to bring about shrinkage of the treated portions; it is then dried to prevent any colours present from running in the subsequent washing process in cold water. The goods are then neutralised with dilute acid, washed, and dried. The minimum tension is employed throughout, with the result that the untreated parts of the cloth are crimped by the shrinkage of the remainder.

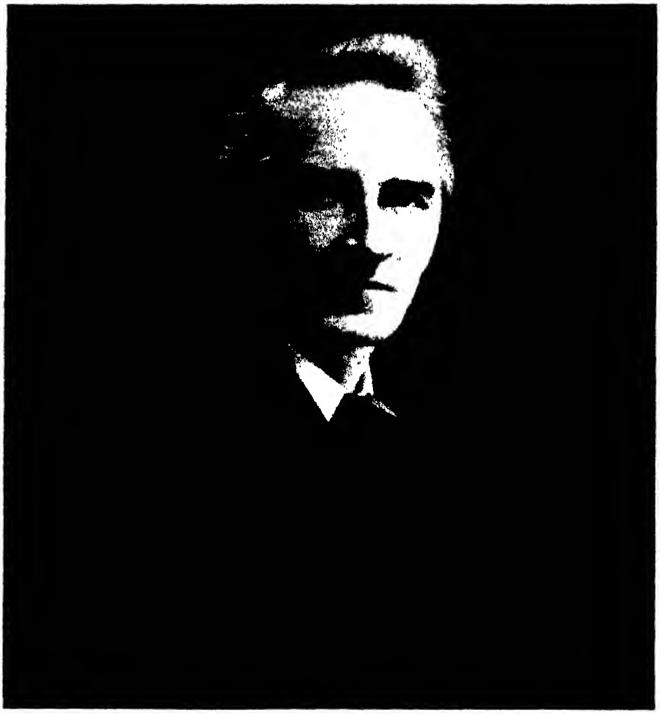
The resist method relies on the fact that thick solutions of gum senegal, gum arabic or British gum, when dry, will resist the action of the alkali. Hence they prevent the shrinkage of the cloth in the areas where they have been applied when the goods are treated without tension in sodium hydroxide solutions of 50 to 60° Tw. Recipes and details of many variations may be found in "Textile Printing," by Knecht and Fothergill (Griffin and Co., London; 1926, page 848).

PLATE I.

JOHN MERCER, F.R.S.
1791–1866

(By courtesy of Longmans, Green & Co.)

[*To face page* 16.



HORACE LOWE

1869-1930

(*By courtesy of the J.S.D.C.*)

CHAPTER TWO

HORACE LOWE

Mercerising with Tension

H. A. Lowe was the eldest of the six children of Christopher Lowe, a Manchester business man, and was born at Heaton Moor on January 22nd, 1869. He attended J. J. Robinson's boarding school at Heaton Chapel and later Owen's College, Manchester. After a short period at an engineering works, he went as chemist to Messrs. Melland and Coward's Bleachworks at Heaton Mersey in 1889, at the age of twenty.

Shortly before his appointment, the foreman dyer, W. J. Coups, had been told by an old dyer that he had found a mordant for indigo, as examination of a partly treated hank of yarn showed an increased affinity for dye in the treated portion. Investigation revealed that the hank had been treated with caustic soda, and on Lowe's arrival Mr. Coups showed him the experiments, in which he became deeply interested. Trials were made by Lowe with a view to avoiding the shrinkage which made the process of little value from the commercial standpoint. With the assistance of W. E. Barr, an apparatus was devised whereby the yarn could be treated and washed while stretched. Single threads were tied to the pan of a balance, weighted until taut, and then treated with NaOH solution. Weight was then added until the original length was restored, the yarn was then washed with water, dilute sulphuric acid, and water again, tension being maintained until the thread was dry.

According to Barr (J.S.D.C., 1931, *47*, 100) the brilliance was so pronounced that Lowe jokingly remarked, " I have almost converted cotton into silk."

Lowe's own account reads as follows (J.S.D.C., 1921, *37*, 136), on the occasion of the presentation of the Perkin Medal of the Society of Dyers and Colourists, March 18th, 1921) :

" My own work depends upon and arose out of that of Mercer in 1844. A recorded remark, that strong caustic soda modified the affinity of cotton for colouring matters, especially indigo, caused me to examine this effect, for I thought it singular that it was not utilised.

"I remember the amazed astonishment and interest I experienced in first witnessing the change produced in cotton. It became transparent, thickened, and contracted, and then remained as an elastic fibrous gut; when washed free from alkali a much shrunken cotton was obtained, and when dyed this manifested an extraordinary affinity for all dyes. This simple product so produced had excellent dyeing properties; and 'special features,' due to shrinkage, were obtainable for special purposes; but it did not show an improvement on the properties of cotton in every respect, and carried with it a great practical drawback in requiring a compensation for contraction by spinning higher counts and weaving wider widths—an innovation not convenient in industry.

"In certain hard spun yarns treated thus I noticed frequently minute speckles of lustre very difficult to understand, but eventually traced to their source; they were minute loops of cotton fibrils held unshrunken and bound tight in the lock of the spinning. I then turned back to a complete study of the alkali-cellulose—a plastic substance full of elastic strain and of singular physical interest—and after much thought I conceived a process to begin in this substance and to be carried over into the final product. It was this—to eliminate all the defective features due to the inward thickening of the cotton fibrils composing the spun yarn by stretching out the contracted formation, or preventing it forming at all, and while holding it in this proper state of plastic formation to fix it thus with water. This was to be effected by a tension equal to the inward tension in the alkali-cellulose and opposite in direction. I first ascertained that it did not pull out into thick and thin places when heavily strained, and that it did not burst the cotton fibrils when kept strained throughout the reaction, and that the molecular change was not affected thereby; also, that the bind and lock of well spun yarn held without slip. These doubtful features were fortunately found to hold perfectly good for the proposed test. I then procured the highest quality Sea Island yarn obtainable, and this was treated loose, then stretched to its full dimensions, and held so while becoming hydrated with water.

"This product was a great advance and manifested no defects whatever, and had increased strength, increased absorption and affinity for dyes, and greatly increased lustre and transparency."

Lowe filed two specifications, B.P. 20314 of 1889 and 4452 of 1890. The main feature of the first document was the recovery of the sodium hydroxide, but the glossy appearance of the treated material was definitely mentioned. The second patent, however, leaves no doubt as to the means of obtaining lustre by mercerising under tension and emphasises the method of stretching.

Lowe also applied for a German patent, but according to the Textile Mercury, 31/8/1901, this was refused without any reason being given.

B.P. 4452, of 1890

In the process as described in the Specification of my previous Patent No. 20,314 of 1889 the material is impregnated with a strong solution of an alkaline hydrate, preferably sodium hydrate, which combines with the constituent cellulose, producing a transparent elastic material but, at the same time, in the case of spun and woven fabrics, great shrinkage occurs and this shrinkage I eliminate by keeping the material mechanically stretched whilst subjected to the action of or treatment by the sodium hydrate or by subjecting it to a stretching process or operation after the sodium hydrate bath, but necessarily before the fabric has lost its temporarily pliable condition. This pliable state only occurs when the combination of the soda-cellulose is broken up—previous to that point the material if stretched out returns again (when the stretching agent is removed) to its shrunk dimensions —it is " elastic," not " pliable," this " elasticity " vanishes at the point in the process indicated, but " pliability " remains (but only for a limited period of time during which it gradually decreases and providing the fabric be not dehydrated by hot-drying, etc.). It is whilst in this peculiar and transitory state of pliability that I recover the dimensions and yet retain the other properties induced by the combination with the soda above described.

In carrying out the process the material is immersed in a bath containing a concentrated solution of sodium hydrate of a density of from 25° to 75° Tw. for a period of from 1 to 15 mins., according to the texture of the material and the density of the solution.

The action of the soda on the fibre modifies the cellulose contained therein and causes the fibre to shrink very considerably, and although by subsequent washing all traces of the sodium hydrate may be eliminated the altered condition of the fibres and the shrinkage remains.

The material when it emerges from this bath and throughout the remainder of the process is in a very pliable and elastic condition and the shrinkage can all be recovered by stretching the material either throughout the bath and maintaining it in that stretched condition until it has passed through the washing process and has thus set, or during the subsequent operation of washing to remove the soda, or after washing is complete before the material had dried or begun to set. I find that it is better in treating yarn in hanks to carry out the stretching process during the whole treatment ; that in treating heavy cloths and warp yarns the stretching process is better applied while the operation of washing is proceeding ; and that for ordinary cloth and yarn in the cop the stretching process is best carried out after the breaking-up of the combination by washing is complete, but before it is " set " by standing or by hot-drying.

When removed from the sodaizing bath the material is thoroughly impregnated or rinsed with water (preferably warm). The washing operation is conducted in such a manner as to reverse the combination of the soda and extract the soda (in the form of sodic hydrate) with the least possible dilution of the wash waters. To effect this a number of sprays of warm water may be directed against the fabric or it may be washed in baths or troughs with minimum volumes of water aided by suction or pressure or by mechanical squeezing. The action of the water upon the fibre is to wash out the chemical agent and disassociate its chemical combination with the cellulose and, while reproducing the modified form of cellulose, the fibres are in a fit condition to give back the shrinkage under suitable stretching, without in any way nullifying the results produced on the fibre by the sodaizing bath, either as regards finish, or capacity for dyeing or printing.

The fibre so treated is free from soda and the last traces may be neutralised with a dilute acid solution.

The sodium hydrate eliminated from the cellulosic compound as above described is in such a state that it can be regenerated. The solution is concentrated by a multiple effect evaporator or other concentrator to a sufficient degree, viz. 70°-80° Tw., and then returned to the bath, the density or strength of which will thus be kept constant and is thus available for reproducing the same modification upon the following batches of material. If it is found that this soda solution obtained by the decomposition of the cellulosic compound contains impurities abstracted out of or taken from the fibres it may, when necessary, be filtered or purified before being returned to the process.

Thus a triple combined process is carried out, consisting in (*a*) the treating of the cellulose with sodium hydrate, (*b*) the stretching of the cellulosic fabric whilst in the pliable condition before it " sets " rigid, and (*c*) the separating of the sodium hydrate from the cellulose, recovering it from the wash liquor and returning it to the bath to react again upon the cellulose.

The material may be treated by this process in the form of woven lengths of cloth or as yarn in the hank or cop or after being warped.

Woven lengths of material or warps are treated continuously, they are passed slowly through the bath, then through rollers or squeezers which remove most of the liquor and afterwards passed on to washing tanks where, as above described, the decomposition is carried out with as little dilution as possible. And during the operation of washing or subsequent to it the material is stretched by any suitable machine such as is at present employed to stretch fabrics.

Yarn in the form of cops or hanks may be treated in machines such as are at present in use for cop dyeing and for hank dyeing or in other similar machines which may be adapted or constructed for the purpose which will allow of the time of immersion required, of the use of a minimum quantity of the decomposing agent and the subsequent recovery and regeneration of the soda eliminated by it.

In the case of hanks, however, it is desirable to keep them stretched during all the operations and until the fibres have " set " rigid.

This modified material possesses the advantages of being considerably stronger ; of having greater capacity of absorbing natural moisture ; of having a more regular close and glossy appearance, together with the property of attaining a deeper shade with the use of the same quantity of dye, and of attaining depth and quality of colour hitherto unattainable with certain dyes, the colours so dyed being faster to both chemical and actinic destruction. The stretching does not alter any of these properties attributable to the sodaizing of the fabric, while at the same time all loss of length is obviated, the thickening or increased coarseness of the fibres is reduced, and more than that, the fibres are even finer than in the fabric before treatment.

The cloth may subsequently, if desired, be finished by any of the ordinary methods with size, china-clay or other filling or loading material at present employed in the finishing of some kinds of textile materials, and may be beetled and calendered.

The claims read:

1. The process of treating cellulosic fibrous material which consists in subjecting it to a strong solution of an alkaline hydrate, preferably sodium hydrate, and stretching the alkalized fibre during or subsequent thereto before the fibres set rigid to prevent or recover shrinkage substantially as and for the purpose described.
2. The triple process which consists in treating cellulosic fibres with a strong solution of sodium hydrate, stretching the cellulosic fabric whilst in a pliable condition before it sets rigid to recover or prevent shrinkage, and separating the soda as sodium hydrate from the cellulose, recovering it from the wash liquor and returning it to the bath to again react upon cellulose substantially as described.

Lowe's observation that the application of tension during mercerising produced a high degree of lustre placed the coping stone on Mercer's work and gave us mercerising as we know it to-day—mercerising under tension.

Lowe undoubtedly recognised the importance of his discovery and made every attempt to commercialise it, but having no means of his own, he experienced great difficulty in finding help mainly on account of his youth and his retiring nature—he was not of the type to impress business men. Nevertheless a Mr. Steiner of Accrington agreed to establish a mercerising works, but unfortunately fell ill and died before anything was done. Lowe was unable to get any other manufacturer to interest himself in mercerising for lustre, although the process was shown to many people.

In 1891 Lowe went as chemist to Messrs. Ainsworth and Co. of Bolton to superintend the dyeing of aniline black, in which he effected certain improvements; he remained there for a few years, during which time he married. Lowe's patents were allowed to lapse in 1893.

He then went to Ireland in 1894 to Carse's works, Ballyclare, Co. Antrim, but at the end of a year he brought an action against this firm for breach of contract, which was settled out of court. In November, 1895, Lowe went to Nice.

About this time, Lowe's method of mercerising was rediscovered and patented by Thomas and Prevost—a Crefeld firm of dyers who were engaged in the dyeing of silk-cotton mixtures, and wishing to obtain a darker shade on the cotton made use of the known older facts of mercerisation, but applied tension in order to prevent contraction of the cotton. The material was stretched not only during its passage through the alkali, but also whilst washing. Here again, it is interesting to note that two patents were filed, D.R.P. 85,564 and 97,664 of 1895—the corresponding British specifications being 18,040 of 1895 and 20,714 of 1896.

The first of these specifications appears to have been filed in Germany on March 24th, 1895; the process was for mercerising in the stretched condition and there was no mention of lustre. On the September 4th, 1895, an additional patent was filed for the production of lustre, and this was granted on July 30th, 1898.

Mercerised yarn with a high degree of lustre was first produced on a commercial scale about the autumn of 1896, and samples were shown on Pattern Sheet No. 26 of the Journal of the Society of Dyers and Colourists in 1897 (J.S.D.C., 1897, *13*, 112).

Considerable praise is due to Messrs. Thomas and Prevost for their successful exploitation of mercerising for lustre.

In the meantime, Lowe's work had not been forgotten, and whilst at Nice he was approached early in 1897 by Fussbahn of Crefeld with reference to his mercerising process, and also by a number of English people, notably Mr. Maddocks, a retired Manchester business man living in Yorkshire. In conjunction with the Fine Spinners' Association, a works was taken at Macclesfield in 1898, the prime movers being Mr. Maddocks of Bradford, Lord Rochdale, Mr. Rivett and Mr. Ling of the Fine Spinners' Association. Lowe received a cheque for £3,000 and a salary of £600 per annum as manager of this works.

In England the first patent specification of Thomas and Prevost, B.P. 18,040 of 1895, merely claimed two features, mercerising with stretching during both the treatment with alkali and washing, and also mercerising without tension but stretching whilst still impregnated with the alkali and during the washing process. The mixtures of material contained real silk and cotton, the latter being in the form of long staple fibres for obvious reasons, and these when mercerised under tension produced a high degree of lustre which was made the object of the second patent.

B.P. 20,174 of 1896 stated that when the vegetable fibres were mercerised in a highly stretched condition, and washed in the stretched state, they acquired a magnificent silky gloss and increased tensile strength. The specification also claimed stretching beyond the original length and washing without tension. Other features included mercerising with weaker solutions of alkali but at lower temperatures, and the use of dilute acid for removal of the alkali used in mercerising.

The application for B.P. 18,040 of 1895 was opposed by Lowe, mainly on the grounds of B.P. 20,314 of 1889 and 4,452 of 1890. The Comptroller decided that all reference to alkaline lye should be removed from the specification, and this decision was upheld by the Law Officer on appeal. Subsequently, the applicants submitted a statement, signed by their opponent, withdrawing the opposition unconditionally, and applied to the Comptroller for leave to file evidence and re-open the case on the grounds that the respective inventions had not been properly understood and that a miscarriage of justice had taken place. The matter, after coming before the Comptroller, ultimately came before the Solicitor-General, Sir Robert Finlay, on April 25th, 1898, when permission for a re-hearing was refused. (See Reports on Patents Cases, 1898, *15*, 257.)

According to the Textile Mercury for August 31st, 1901, the attempted withdrawal of Lowe's opposition was in consideration of a promised share in the possible royalties from the Thomas and Prevost patents.

Meanwhile, D.R.P. 85,564 of 1895 was annulled by the German Patent Office on June 9th, 1898, mainly on the grounds of Mercer's work, and this decision was confirmed by the "Reichgericht" on January 20th, 1899. D.R.P. 97,664, therefore, became the main patent but twelve firms protested against it on the grounds of Lowe's patent in England, and also the evidence that the process had been used in Rhenish factories in 1896 and 1897. In the meantime, the patents of Thomas and Prevost had been bought by the firm of J. P. Bemberg, who were, therefore, concerned in the defence. Apparently some difficulty was caused by the fact that although the patent was supposed to run from September 4th, 1895, the necessary descriptions of the invention were not brought to the knowledge of the Patent Office until February 23rd, 1898, and many firms had mercerised cotton for lustre before this date.

About fifty civil prosecutions were pending on the decision, including the firm of Kleinewefers Söhne, which had been active in the original application for nullity. The case was thoroughly investigated by experts and on January 24th, 1901, the German Patent Office cancelled D.R.P. 97,664 on the grounds that there was no patentable invention in the means described in the specification.

On appeal to the Reichgericht, the whole case was reconsidered and Lowe gave evidence in Cologne in the autumn of 1901. He had no difficulty in proving his case, and the previous decision was upheld on February 12th, 1902. The application of Thomas and Prevost did not correspond to the patent as originally granted. Some details of the case may be found in the Deutsche Färber-Zeitung about this time. The rejection of the German patent caused its owners to allow the corresponding British patent specification to lapse.

After this action Lowe resigned his position with the Fine Cotton Spinners' Association and retired to Pontypant in North Wales; his services, however, were recognised by a cheque for £10,000 and a consultative retaining fee for some years. He also received certain sums for settlements made "out of court" and appears to have made about £14,000 out of his invention. Although it is unfortunate that his efforts did not meet with the success they deserved, yet considering that his patent specification was allowed to lapse he did not fare badly, for he was able to retire at the age of thirty-two. He later inherited a sum of about £5,000.

There is little to record of his subsequent activities in connection with mercerising, apart from his presence at the meeting of the Society of Dyers and Colourists at Bradford in March, 1921, when he was awarded the Perkin Medal. (See page 17.) Most of Lowe's time was occupied in other directions, such as photography, microscopy, organ-building, etc. In the winter of 1924-25 he went to Grenoble University, but some two or three years later he went to Nice. Ill-health prevented his personal appearance on the occasion of the award of an Honorary Fellowship of the Textile Institute in 1928. He died at Menton on December 26th, 1930, following an attack of pneumonia.

It now seems probable that his work for the cotton industry of the world is at least equal to any other single discovery, as mercerising for lustre remains an important fundamental process.

Mercerising in the U.S.A.

The American Mercerising Company was formed in 1899 to take over the sole rights of the patents of Thomas and Prevost.

These had previously been acquired by the American Thread Company from the German firm of J. P. Bemberg. The Hampton Company of East Hampton, Mass., was made the object of a test case in 1900, but for more than a year prior to this the American Mercerising Company had warned all the mercerising firms against infringement of the Thomas and Prevost patents.

The case continued until 1906, but in the meantime the original German patents had been nullified. There was some uncertainty about the American law, however, particularly in view of the fact that the specifications of neither Mercer nor Lowe were raised by the American Patent Office at the time of the filing of the Thomas and Prevost patents in the U.S.A. The patents that caused the long contest were U.S.P. 600,826 and 600,827 of 1898. As the original German patents became void owing to lack of novelty, it was argued by the Hampton Company that this action caused the American patents to expire at the same time.

It was estimated that between 1899 and 1904 the American Mercerising Company and its licensees had mercerised about 14,000,000 pounds of yarn, and had the Thomas and Prevost patents been upheld then that company would have paid some $750,000 to the German owners of the patents. These points were brought forward to show the extraordinary character of the utility and commercial success of the process.

The preparation of the case involved an enormous amount of work and the records include a very interesting statement of the art of mercerising at the time ; the situation has been well reviewed by Clark (Textile World, 1924, *65*, 793).

In demonstrating the lack of priority, evidence was brought forward to show that in both the Mercer and Lowe processes, on suitable yarns and on ordinary warp dyeing or roller-cistern machinery, the production of lustre was an unavoidable feature.

The suit of the American Mercerising Company was dismissed on August 7th, 1906, so that mercerising for lustre became open to the public.

Early Mercerising

The first mercerising experiments of Thomas and Prevost appear to have been done with cloth, but the process was soon repeated upon yarn, and the first mercerising machine appears to have been built by Gebrüder Wansleben.

For many years mercerising in Europe was practically confined to hank mercerising, the treatment of piece goods being accomplished much later. In the machine the hanks were placed on arms fixed at certain distances apart on a special framework which could be dipped into the alkaline liquor, and this type was quickly followed by machines with a series of arms for treating much larger quantities at the same time. Subsequent developments included movable arms in order to allow of various degrees of tension, and stretching arms which were placed in a horizontal position, enabling them to be swivelled for the manipulation of the hanks before and after mercerising and to be lowered into and raised from the alkaline bath. Another series of machines had arms more or less fixed and the baths were movable and could be replaced by troughs of water for washing, acidifying and rinsing.

Horizontal stretching arms were also caused to revolve round a central mechanism for impregnation, squeezing and washing on a semi-continuous basis.

Hank mercerising machinery was soon followed by the introduction of warp mercerising which, although not utilised to a very great extent in Europe, is still in common practice in the United States of America. The machines consist of a series of iron vats at the beginning and end of which is situated a pair of squeezing rollers. Each compartment contains guiding rollers and the tension between the squeezing rollers and on the guiding rollers is sufficient to allow mercerising for lustre to take place. Naturally, the washing of the material forms part of the same continuous process.

Mercerising of piece goods was attended by many more difficulties than in the case of yarn. The earliest machines were converted from three-bowl padding mangles in which the cloth passed through the alkaline liquor in the trough, but was held at width by means of pins or points on the guide roller. The squeezed cloth was then washed on a stretching machine, but it was soon found that the ordinary machine was not sufficiently long for the removal of the caustic soda, so that special mercerising stenters were produced in order to obviate this difficulty. This possessed the defect that a certain shrinkage followed during the passage of the cloth from the mangle to the stenter. The next development was to place the padding mangle directly in front of the stenter so that the cloth could be taken up automatically by the pair of endless chains to be brought to its original width before being subjected to the action of boiling water from a series of sprinklers. By means of a sufficiently long stenter, the cloth could be delivered at the end in a fully mercerised state and sufficiently free from caustic soda to permit no further shrinkage during the final washing.

It was soon found that pin stenters were not sufficiently robust to withstand the considerable forces set up by the tendency of the cloth to shrink during mercerising, and clip stenters rapidly followed, special material being necessary to avoid stains and special designs to hold the very slippery material. In a number of cases a certain degree of lustre was obtained by the use of a continuous soaping machine; this was due to the tension produced between the several pairs of squeezing rollers.

The impressions of some of the early American mercerisers of piece goods have been recorded (Textile World, 1924, *65*, 788), and refer to the period of 1898 9. A good account of the early machines is given in " Mercerisation " by the editors of " The Dyer " (Heywood and Co., London, 1903). These fall into two broad classes, those in which the cloth was allowed to shrink and was later stretched, and secondly those in which no shrinkage was permitted. The second type of mercerisation has been revived within recent years, and it is perhaps unfortunate that a simple distinction is not made between the two methods—mercerising with stretching and mercerising under tension in its true sense.

Some of the early machines prevented contraction by running the cloth on cylinders with roughened surfaces, others on corrugated rollers; a continuous system of squeezing rollers was also employed, the cloth remaining in contact with the surface of a roller until the process was completed. Pairs of conical rollers were also suggested. In another interesting machine, the cloth was held between two parallel chains by stenter clips and carried successively through the alkali and the wash-water.

PART TWO

COTTON

CHAPTER THREE

THE GROWTH AND STRUCTURE OF COTTON

THE cotton hair contains the highest proportion of cellulose, amounting to some 90%, found in the native fibres. Flax, hemp, jute and ramie are bast fibres but cotton is a seed hair, unicellular with a single solid apex, in contrast to the multicellular bast fibres with their completely enclosed bundles of tubules pointed at each end. The cotton plant requires from five to nine months to reach maturity and its full growth of about four feet in height. The fruit or boll opens about 48 days after the bud forms and may be picked two days after it has cracked. The separation of the hairs from the seed is carried out by a process termed "ginning," but after this operation there remains on the seed a residue of short hairs known as linters. These are the seed hairs which commenced growth after the bulk, and they are utilised for the manufacture of paper, guncotton, rayon and wadding, after removal by a special "delinter machine."

The cotton hair is practically cylindrical and contains a central canal known as the lumen. When the hair has been removed from the seed, the cell collapses into a flat ribbon which twists into an irregular spiral band; these twists or convolutions are not continuous in any one direction and are largely responsible for the spinning properties of the cotton. The convolutions may vary in number from 150 to 300 per inch.

The Fine Structure of Cotton

The most complete account of the growth of cotton has been given by Balls, whose work was mainly confined to Egyptian cotton. The details of his investigations are contained in two books—"The Development and Properties of Raw Cotton" (A. and C. Black, Ltd., London, 1915) and "Studies of Quality in Cotton" (Macmillan, London, 1928), together with a series of papers in the "Proceedings of the Royal Society," 1919, *B90*, 542; 1922, *B93*, 426; 1923, *B95*,

72. Anderson and Kerr of the United States Department of Agriculture have reviewed the growth and structure of cotton, utilising the Mexican variety of American Upland cotton (Ind. Eng. Chem., 1938, *30*, 48).

The cotton hair exists in the form of a single cell, about 1,200 times as long as it is wide, and is attached to the seed only at its base. Each hair originates as a growth from a single cell from the seed coat, and the first evidence of formation is the appearance on the day of flowering of a slight swelling which rapidly elongates on the following day. The diameter of the hair is established soon after it originates, but the elongation continues for some 15–20 days and then suddenly ceases.

The fibre origin is not limited to the day of flowering, but the swellings which appear after the second or third day only produce the linters, whereas the cotton hairs of commercial value all commence their growth within the first two or three days.

Primary Wall

During the period of elongation, the protoplasm is only enclosed by a thin primary wall, which is about 0·5 μ in thickness and forms the cuticle in the mature fibre. The primary wall of the young hair possesses a coherent skeleton of cellulose from the first day of its appearance, but it does not respond very clearly to the usual tests for cellulose in the early stages of development, and this has led a number of investigators to assume that the primary wall is free from cellulose, and others that the material of which the wall is composed is not actually cellulose, but some closely related substance.

According to Anderson and Kerr, these conflicting ideas are due to the fact that the cellulose in the very young fibres is associated with pectic substances, but they have found that if the young fibres are freed from pectic material a coherent skeleton of cellulose remains, which can be identified by the usual tests. This skeleton is doubly refractive, it is soluble in cuprammonium hydrate, gives the characteristic cellulose reactions with zinc chloride-iodine and with potassium tri-iodide and 70% sulphuric acid; it also shows the typical X-ray pattern of cellulose.

The fibre wall, when examined under the usual compound microscope, shows no evidence of structure, but by means of a special technique Anderson and Kerr have demonstrated that the cellulose in the primary wall forms an open mesh of very

PLATE III.

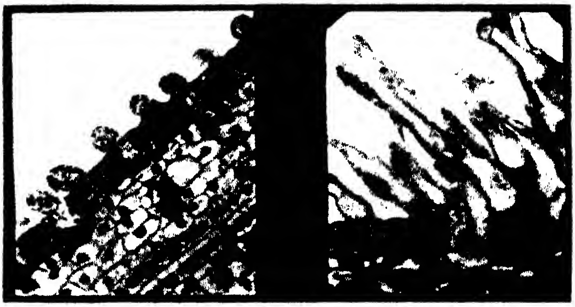


FIG. 1 FIG. 2.

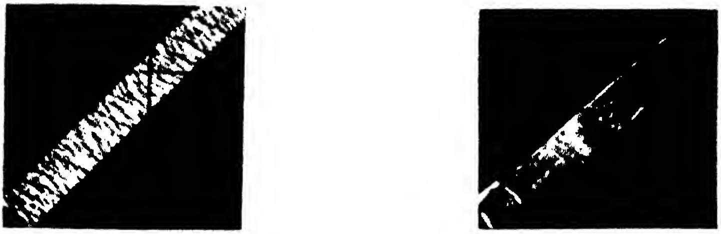


FIG. 3 FIG. 4.

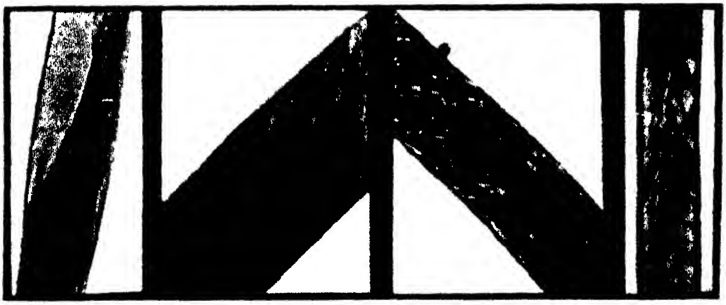


FIG. 5 FIG. 6 FIG. 7 FIG. 8.

Fig. 1 shows the cross-section of the epidermis of the cotton ovule on the day of flowering, and Fig. 2 two days later with elongation of young hairs. Fig. 3 shows orientation in the wall of a 15-day hair, and Fig. 4 transverse orientation in a 2-day hair. Fig. 5 shows the structureless primary wall of a 15-day hair. Fig. 6 shows spiral formation in secondary wall of a 16-day hair. Fig. 7 shows a reversal. Fig. 8 shows staining by zinc chloride-iodine.

(*By courtesy of Ind. Eng. Chem.*)

[*To face page* 32

Fig. 9.

Fig. 10

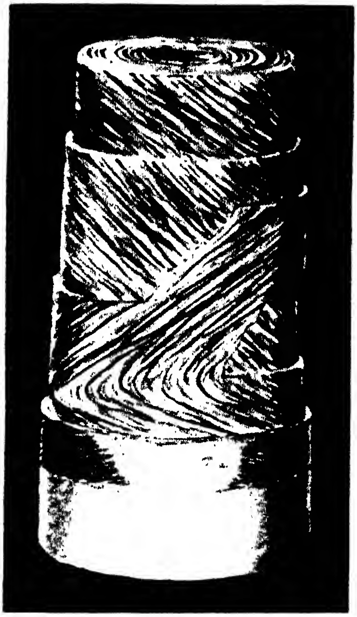


Fig. 11.

Fig. 9 shows growth rings in the hair. Fig. 10 shows absence of growth rings. Fig. 11 is a diagram of a model of the cotton hair.

(*By courtesy of Ind. Eng. Chem.*)

FIG. 12.

FIG. 14

Figs. 12 and 13.—Cotton hairs mounted in the R-O-X medium, Fig. 13 showing the furrowed appearance in greater detail.

Fig. 14 represents typical cross sections.

Magnification × 400 diameters approx.

COTTON

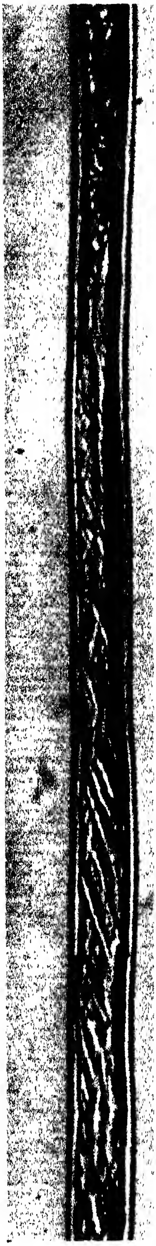
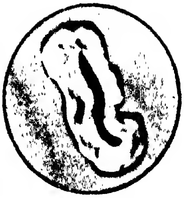


FIG. 13.

PLATE VI.

FIG. 15.

FIG. 17.



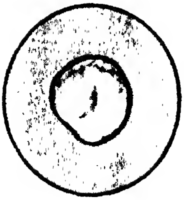


FIG. 18.

Figs. 15 and 16 are photographs of unmercerised and mercerised cotton hairs respectively, immersed in methylene iodide.

Magnification × 400 diameters approx.

Figs. 17 and 18 represent typical cross sections.

Magnification × 700 diameters approx.

Figs. 12 to 18 are from photographs supplied by Dr. W. Kling of Böhme-Fettchemie Gesellschaft, m.b.H., Chemitz.

COTTON.

FIG. 16.

[To face page 33.

fine thread-like structures with anastomosis (i.e. they have a branching habit, like arteries). The primary wall was stained with Congo Red or zinc chloride-iodine and then examined between crossed nicols. The colouring matter is directionally adsorbed on the surface of the cellulose and the double refraction of the orientated colouring matter, in addition to the double refraction of the cellulose, makes the cellulose strands appear prominently. This method was first employed by Balls on young cotton fibres about ten days old; it was observed that there were present two opposing systems of fine, spirally wound, threads of cellulose at an angle of about 70° to the long axis of the fibre. Anderson and Kerr have confirmed this observation and extended it to hairs only two days old. The cylindrical form of the young hair makes it possible to prove that the two systems of spiral threads exist in the same wall. Both right and left-hand spirals were seen when the microscope was focussed on the upper wall; they disappeared in the upper wall as the focal plane was lowered and appeared in the lower wall when the focus was established there.

A third arrangement of the cellulose in the primary wall appeared when the stage of the polarising microscope was rotated so that the long axis of the fibre made an angle of about 45° with the planes of the nicols; a system of transverse strands of cellulose became visible and these too anastomose. These three systems of strands which make the cellulose framework of the primary wall seem to be uniform over the entire surface and there is no evidence of the change of direction of the spiral which is so common in the secondary wall.

Secondary Layers

When viewed under the usual compound microscope, the second deposition of cellulose stands out in strong contrast to the structureless primary wall and even the first deposition of cellulose inside the primary wall is quite distinct when stained with zinc chloride-iodine. The branching and rebranching strands wind in a steep spiral round the inner surface of the primary wall. The spiral makes an angle of 20–30° with the long axis of the fibre as compared with 70° for the spirals of the primary cellulose. The first secondary depositions appear quite suddenly.

One of the characteristic features of the first layer of secondary cellulose is the reversal of the spirals; there are areas in the wall where the cellulose threads change from right-hand to left-hand spirals, or vice versa. The number of such reversals varies considerably, but it is quite common to find fifty or more on a single hair ; close double reversals are not uncommon. One type of reversal is that in which one set of spiral strands ends and a second system running in the opposite direction begins ; the ends of the strands overlap at the reversal. The commonest method of reversal is a simple change in direction by bending in the form of an arc.

The second layer of secondary thickening does not necessarily follow the pattern produced on the previous day. The points of reversals are at different places and the direction of the spiral is often exactly the reverse of that in the first layer of the secondary wall. In many places, however, the pattern of the second layer conforms to that of the first layer.

It is difficult to follow the course of the subsequent deposition of cellulose, but in view of the behaviour of the hair on drying and also the result of swelling agents, some sort of pattern is established which is broadly followed by the later layers. The anastomosing character of the early depositions must be emphasised, for although the fibrils have a definite spiral path, they branch and rebranch with each other. The threads which form the spiral vary in length and also in diameter.

The deposition of cellulose continues for at least twenty-five days until a few days before the boll opens. When this takes place, the fibres dry and the walls become twisted ; the direction of these twists, or convolutions, conforms to that of the spiral in the greater part of the cell wall. Where a reversal takes place in the spirality, then a similar reversal or convolution occurs. There seems to be little doubt that the convolutions in the dry fibre are determined by the arrangement of the micelles in the cell wall.

Growth Rings

One of the characteristic features of the section of the cotton hair is that when it is swollen, growth rings appear much in the same way as the annual growth rings in trees. The presence of these lamellæ has been known for many years, but Balls was the first to correlate them with the actual number of days during which the wall of the hair increased in thickness. He observed that the cotton plant ceased to grow during the hot afternoon period and assumed that the deposition of cellulose also stopped at this time and resumed during the night and morning. The lamellæ were, therefore, regarded as a sign of discontinuous periodic growth.

These growth rings may be used to distinguish between cotton hairs which are produced early in the season and those which are produced later. Anderson and Kerr have observed that bolls developing from flowers that open in the early summer matured in about forty-five days, the fibre growing in length for sixteen days and thickening for about twenty-five days. Bolls that developed from flowers opening later in the summer required about seventy days for maturing; the period of elongation of the cell was only a day or two longer than normal, but the period of secondary wall formation was enormously increased.

In the earlier fibres, the growth rings are relatively broad and may occasionally reach a diameter of 0·3 μ, but the rings formed in fibres which develop later in the season are much thinner and rarely exceed 0·14 μ in diameter. It may be remarked that there is considerable variation in the growth ring diameter, even in hairs from the same boll, but in general, the early fibres have fewer and wider rings in contrast to the larger number of narrow rings on the hairs appearing later in the season.

Kerr has confirmed the observation regarding correlation between the number of lamellæ and the number of days during which secondary thickening takes place, but, in contrast to Balls' hypothesis of intermittent growth, Kerr has suggested that the deposition of cellulose is a continuous process which varies in its rate according to temperature.

When cotton is grown under constant illumination and at a constant temperature of about 30° C., no growth rings appear. When the temperature is varied under conditions of constant lighting, then growth rings appear. Similarly, when the temperature is maintained constant and the artificial lighting is turned on and off at twelve hour intervals,. then indistinct growth rings appear.

One important feature of this investigation is that although it is possible to control the growth ring pattern by the above means, yet it has not been found possible to control either the pattern of the spirals, or to influence the reversals.

Further work (*ibid.*, 1939, *9*, 325) showed that fibres produced under constant illumination are finer and of lower breaking load than normal cotton hairs; the intrinsic strength, however, is the same.

Summary

The fine structure of the cotton fibre may be summarised as follows :

1. A primary wall contains cellulose and pectic substances. The cellulose micelles in this wall are grouped into delicate anastomosing threads which have at least two systems of orientation : (*a*) a flat right-hand spiral, (*b*) a flat left-hand spiral, and probably also (*c*) a transverse position. All three systems seem uniform over the entire surface of the fibre cell.
2. A secondary wall is composed of many lamellæ of cellulose. The lamellæ are not separated from one another by non-cellulosic substances but represent dense and less dense areas of cellulose. The layers are formed of systems of spirally wound branching threads, and the direction of the spiral is reversed at frequent intervals.
3. Frequently the pattern of spirals first appearing in the secondary wall is not similar to that in subsequent layers of the wall. Most of the layers of the wall, however, follow a pattern that is established soon after secondary thickening has begun.

General

A number of important microscopical observations on the structure of plant fibres have been made during the last hundred years ; the existence of fibrils in cell walls was reported by Meyen in 1838, whilst in 1852 Agardh was able to separate the spiral lines and demonstrate the fibrillar nature of the structure. Striations on the surface of the fibre and stratifications in the cross sections were observed by Nageli in 1877, whilst Wiesner in 1886, by means of a treatment with acids at fairly high temperatures, was able to obtain from fibres fine particles which he termed dermatosomes.

During recent years investigations have been directed more towards the isolation of the structural unit, as only a superficial observation is possible on the intact cell wall. Ritter (J. Forestry, 1930, *28*, 533) isolated a number of structural units from wood fibre, first, the fibrils and bundles of fibrils, and secondly, smaller spherical units.

Farr & Eckerson (Boyce Thompson Inst. Contrib., 1934, *6*, 189 and 309), in their study of the development of the cotton hair demonstrated the presence of small particles of uniform size which were present in bead-like strands and considerably larger in size than Ritter's spherical units. These particles in chain formation appear to form a single fibril in the cell wall and they may be separated even from the mature cotton fibre. The question of these "particles" being the structural unit of cellulose is still under consideration as they are considerably larger than the micelles. Farr and Eckerson believe them to be the fundamental, biological, structural unit, but the question is one which must await further investigation. The chemical dissection of the cellulose wall of the cotton hair into fibrils, and the further dissection into dermatosomes, fusiform bodies, etc., is only accomplished as the result of severe chemical treatment so that some caution must attend the reconstruction of the hair from data of various investigators who have employed different materials and variations in experimental method. In any case it is not possible to obtain an accurate knowledge of the structure of native cellulose owing to the gap which exists between the X-ray region of measurement and the smallest particles visible by microscopy.

It is possible to examine the anatomical structure of the cotton hair by the use of strong swelling agents such as cuprammonium hydrate or caustic soda and carbon disulphide, when the microscope shows that the swelling is not uniform but characteristically irregular. The hair assumes the shape of a distended tube tied at intervals, like a string of beads, and these constrictions are caused by parts of the cuticle which has elsewhere been ruptured by the strong swelling forces (Figs. 19 and 20). The swollen cellulose protrudes through the burst cuticle in the form of globules and the walls of the central canal may also be seen when the cellulose is on the point of dissolution. *Mercerised cotton hardly shows this effect.*

There is considerable variation in the dimensions of cotton hairs according to type as shown on page 41. A general average length is one inch, with a diameter of 0·001 to 0·0005 ins.; the hair is some three to four times as broad as it is thick and the longest hairs (about 2·5 ins.) have the smallest diameter. The breaking load of the cotton hair lies between that of silk and wool, varying from 3·5 to 10 g., but is considerably below either of them in showing only some 4% extension at break.

Mercerised Cotton

The appearance, under the microscope, of cotton mercerised in the loose state was first described by Crum (J.C.S., 1863, *16*, 406).

> " The action of the soda completes the cylindrical form of the fibre, filling up almost entirely the central cavity. The twisting of the fibre is also much increased and there is a consequent shortening of it, sufficient to account for the shrinkage in length and width and the thickening of any woven fabric which is made to undergo the mercerising process. Diagonal lines are sometimes seen in these ripe mercerised fibres, giving the impression of a spiral structure ; but they are evidently the creasing or corrugating effect of extreme twisting."

The increased twisting of the fibre is probably accounted for by the observations being made on hairs taken from woven cloth, for the most characteristic feature of mercerised cotton hairs is the absence of convolutions ; cotton hairs mercerised in the loose state lose their flat ribbon like form and appear much rounder—the surface of the hair appears smoother and more uniform, although strong magnification enables many lateral creases or wrinkles to be seen. The broad lumen of the unmercerised hair becomes greatly contracted and often appears alternately wider and narrower at different places along the length of the hair. In unmercerised cotton, the section is usually an irregular oval—kidney bean or ear-shaped—but after mercerising without tension the sections are of a more strictly oval form and the lumen or central canal appears as a narrow slit branching occasionally towards the periphery.

The first description of cotton mercerised under tension was made in 1898 by Lange, whose description and photomicrographs formed an appendix to Thomas and Prevost's patent application. When mercerised under tension, the cotton hair appears almost perfectly cylindrical—a smooth rod—and the lumen is so contracted as to appear very frequently as a central point rather than a slit. The cross section of cotton hairs which have been mercerised under tension are characterised by an almost accurate circle, compared with the oval of hairs mercerised without tension. In unmercerised cotton, circular cross sections practically never occur and the oval shape is very rare. The surface of cotton hairs mercerised under tension is more free from irregularities, such as folds and creases, than the surface of hairs mercerised loose. A relatively simple microscopic method of determining the suitability of a particular cotton for mercerising for lustre has been described by Herzog (Chem. Zeit., 1914, *38*, 1097). A number of short lengths of about 0·5 mm. are cut from ten different places in the raw yarn under consideration and each length is placed in a drop of mercerising liquor on a micro-

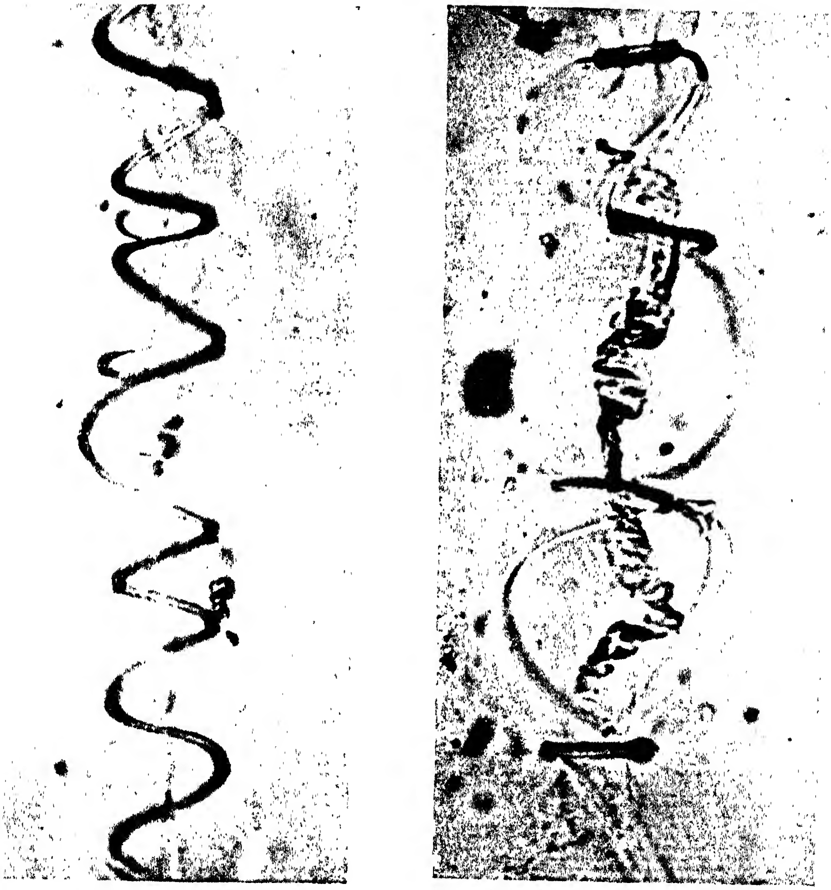


FIG. 19.

FIG. 20.

The cotton hair swollen with CS_2 and NaOH.

(Bright; B.C.I.R.A.)

[*To face page* 38.

FIG. 21.—Cotton hairs swollen with sodium zincate solution, and showing extrusion of the cellulose at the ends.

FIG. 22.—Fragments of cotton hairs swollen with 30° Tw. NaOH solution, and exhibiting a "dumb-bell" effect due to the restrictive action of the cuticle.

(*By courtesy of Miss Alexander*)

[To face page 39.

scope object glass. One hundred fragments are selected at random in each drop and the number of these which is observed to be swollen is a measure of the suitability of the cotton for the mercerising process.

Effect of NaOH

The effect of various concentrations of sodium hydroxide solution on the cotton hair has been examined in some detail by Pope and Hübner (J.S.C.I., 1904, *23*, 404), and the results are tabulated below.

BEHAVIOUR OF THE COTTON HAIR.

0–15° Tw. NaOH	No change.
16–18 . . .	Incomplete untwisting during 1 sec.
20 . . .	Rapid initial untwisting continuing slowly.
26 . . .	Rapid untwisting during 5 secs.
35 . . .	Untwisting followed by swelling.
40 . . .	Untwisting and swelling together.
60–80 . . .	Swelling precedes untwisting.

Great importance was laid on the fact that up to a concentration of about 17·5 % NaOH, the swelling action of the alkali follows the uncoiling, whereas at higher concentrations, the reverse is the case. As the concentration of 17·5 % NaOH is the lowest at which any substantial increase in lustre was observed, the authors concluded that the production of lustre is connected with the occurrence of uncoiling after or simultaneous with the swelling. This view is supported by the further observation that when cotton hairs were brought into contact with 22·5 % NaOH solution at 90° C. they uncoiled immediately and swelling only began when the uncoiling was complete, while the lustre was much less marked than that produced at lower temperatures. It was suggested that during mercerisation under tension, the uncoiling of one part produces some sort of convolutions in other parts, so that the final appearance is that of a straight cylindrical rod which carries a series of spiral ridges on its surface ; the lustre is due to the reflection of light from the smooth rounded surfaces of these ridges which are not formed if uncoiling precedes swelling or if there is no uncoiling.

Pope and Hübner further stated that the existence of the superficial spiral ridges is clearly seen by microscopic examination of sections of the mercerised hairs ; it is difficult to reconcile this with the usual description of a cotton hair which has been mercerised under tension.

Harrison (J.S.D.C., 1915, *31*, 198) agrees with Lange's view that the lustre of cotton hairs mercerised under tension is mainly due to increased surface smoothness, for he found that no lustre was produced by washing cotton hairs which had been mercerised under such restraint that they shrank only enough to remain straight without any application of tension. If, however, the hairs were mercerised without removal from their holders and stretched to the original length before washing, then a lustrous appearance may be observed ; it is difficult to explain this on the basis of Pope and Hübner's theory.

The Lustre of Cotton

An important contribution to the knowledge of lustre in cotton was made by Adderley (J.T.I., 1924, *15*, 195), who pointed out that practically all previous theories of the lustre of cotton had been based on visual estimates of that property and not on actual measurement. He designed an apparatus to be used in the following manner.

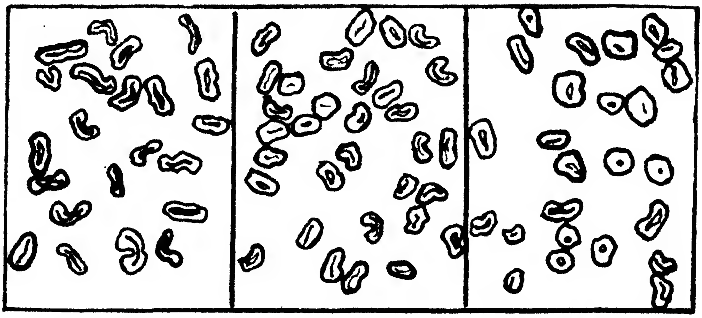
> Cotton was carefully combed and mounted across a rectangular slot in the edge of a piece of cardboard, under slight tension, in sufficient quantity to form a smooth pad, which was then covered with a black paper mask carrying a slit. The carrier of cardboard was then placed at the front of a box and directly below a slit in the box of similar dimensions to that in the cardboard. The slit in the box was situated immediately in front of a piece of ground glass illuminated by a movable lamp inside the box. The pad of cotton was illuminated by a fixed lamp of the same type connected in parallel. A suitably placed telescope will receive the light which is specularly reflected from the fixed lamp by the cotton surface and at the same time the light from the movable lamp which appears through the slit in the box. The two images in the telescope may be made to appear equally bright by moving the lamp inside the box, and the value of the lustre of the cotton under examination was found to be proportional to $1/d^2$, where d is the distance of the movable lamp from the ground glass when equality of brightness has been obtained. Several readings were taken for each variety of cotton and the results based on an average of fifty readings.

Adderley then proceeded to correlate these lustre values with the various physical properties of the cotton hair.

There was no connection between such properties as length, hair weight per centimetre, diameter or convolutions, but a close connection was found with the shape of the cross section ; cotton hairs which tend to be circular in section have a higher

LUSTRE OF COTTON.

COTTON.	ORIGIN.	Diagram reference.	Lustre.	Length in mm.	Diam. in mm.	Weight per cm. (mg.)	Ratio of axes, a/b
American, F.G.M.	Card sliver from mill	A	5·7	23	0·026	0·0023	3·07
Peruvian	From Brit. Cotton Growing Assoc.	B	6·7	27	0·025	0·0025	2·62
Queensland	Card sliver from mill	C	6·7	25	0·026	0·0024	2·53
Sakel S.	From Brit. Cotton Growing Assoc.	D	7·1	29	0·020	0·0015	2·37
St. Kitts, Sea Island	,, ,, ,,	E	7·7	41	0·022	0·0015	2·23
289 F.	Grown in India from Amer. seed	F	7·8	23	0·022	0·0014	2·43
Surat	Commer. Surat from bale	G	7·8	21	0·031	0·0029	2·37
U.S. 12, Sea Island	Pure strain	H	7·9	39	0·022	0·0018	2·15
Abassi	From Brit. Cotton Growing Assoc.	I	8·0	29	0·024	0·0021	2·21
Texas	,, ,, ,,	J	8·1	27	0·027	0·0027	2·22
Barbados, Sea Island	,, ,, ,,	K	8·2	33	0·022	0·0012	2·17
St. Lucia ,, ,,	,, ,, ,,	L	8·3	39	0·019	0·0011	2·20
V.135, Sea Island	Pure strain	M	8·7	49	0·019	0·0012	2·07
Sakel C.R.	Card sliver from mill	N	8·8	29	0·022	0·0016	2·07
M.	Grown in Peru from Egyp. seed	O	9·0	27	0·025	0·0019	2·11
Antigua, Sea Island	From Brit. Cotton Growing Assoc.	P	10·7	31	0·021	0·0012	1·91
Mercerised from	8/2 Supercombed White	Q	12·2	...	...	...	1·60
Mercerised from	3/2 Supercombed White Egyptian	R	12·9	...	...	...	1·64
Mercerised from	5½/2 Combed white	S	13·9	...	...	...	1·47



Low-lustre raw cotton. Ratio: a/b = 2·95

High-lustre raw cotton. Ratio: a/b = 2·00

Mercerised cotton. Ratio: a/b = 1·60

FIG. 23.—Ratio of axes.

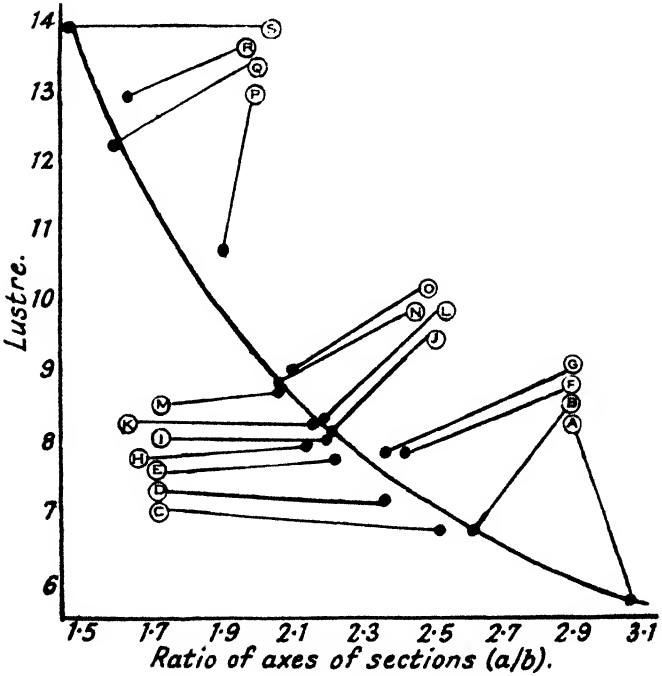


FIG. 24.—Lustre and ratio of axes.

lustre than those whose sections are flattened. The shape of the sections is difficult to express in figures, but a fair index was obtained by means of the ratio of the two axes—the longest possible straight line through the section and a line intersecting this at right angles and passing through the centre of the portion intercepted by the hair. A large number of readings was necessary and the average figures given were derived from measurements of about 400 sections for each variety. From the smoothness of the curve in Fig. 24 it appears that the variation in lustre is intimately associated with shape of the cross sections. This is also in agreement with the views of Lange (Färber Z., 1898, *9*, 197) and Massot (Leipzig Monat. Text. Ind., 1903, *18*, 446), who observed that cotton hairs mercerised under tension are more nearly circular in section than hairs mercerised without tension.

In the early days of mercerising for lustre, it was thought that only certain types of cotton and certain yarn formations would respond to the treatment. In defending their patent during the legal dispute, Thomas and Prevost considered that its novelty lay in the use of certain types of cotton spun under certain conditions. There were two extreme cases for consideration, first, a loosely spun yarn of short-staple cotton and secondly, long-staple cotton in a hard twisted yarn. The cotton in the first case required little force to stretch it to its original length after shrinkage in the alkali and there was no appreciable lustre. The second case required considerable force, involving the use of new and powerful machinery, and in this case a high lustre was said to result. The suggested explanation was that with loosely spun yarn of short staple cotton, the cotton hairs are readily displaced along the yarn and when tension is applied they slip and shrink, thus producing no improvement in lustre. On the other hand, hard twisted yarns of long staple cotton do not permit the hairs to slip when tension is applied, so that the yarn tends to shrink as a whole and requires considerable force to maintain the original length. Under these conditions a high degree of lustre was stated to be produced. The experimental work in connection with the patent dispute failed to substantiate these views, and it is now common knowledge that even with long staple cotton, a high degree of twist renders it very difficult to obtain good lustre. It was further found, according to Gardner (Mercerisation und Appretur; Berlin, 1912) that even staple length was not an absolute essential in the matter of lustre; the short combings

(20 mm.) and the long combings (36 mm.) of Egyptian cotton when spun into yarn and mercerised gave equally lustrous results.

It is now generally recognised that the lower the twist, the better the lustre, provided that sufficient turns are given to prevent the hairs slipping when tension is applied. In actual fact this means that the long staple cottons are more suitable for mercerising, because they require less twist to give a yarn of sufficient cohesion than the short-staple cottons. Staple-length is not the sole criterion for potential lustre as Adderley has shown (see page 41), but it so happens that in general the best shape of cross-section is found in the long-staple cottons. Mecheels (Textilber., 1932, *13*, 646) has given an interesting case of 2/60 yarn made from Mako and from Louisiana cotton and mercerised under tension.

LUSTRE AND STAPLE LENGTH.

Cotton.	Staple length.	Lustre unmercerised.	Lustre mercerised.
Mako . . .	19–20 mm.	25·3	70·0
Louisiana . . .	18–19 mm.	17·8	39·3

From these data it appears that factors other than staple length influence the lustre; both the nature of the cuticle and the wall-thickness must be taken into consideration.

Thomas (J.S.D.C., 1936, *52*, 325) found that certain dyeing difficulties occurred with mixtures of Australian and American cottons, as even after mercerising the latter had the advantage in affinity for dyes by a margin varying from 20 to 50%. A critical concentration of 22-24° Tw. NaOH was essential to give equal dyeing capacity and a mild bleach was also necessary. The Australian cotton has the same original width as American cotton, but swelled to a lesser extent, which indicates a thinner wall. There also appeared to be more foreign matter in Australian cotton.

CHAPTER FOUR

CONVOLUTIONS

ONE of the characteristics of the mercerising process is the untwisting of the cotton hair by the removal of the convolutions which normally exist in the native material. This deconvolution is an important factor in the matter of lustre as the approach to a circular cross-section of the fibre is accompanied by an untwisting so that the hair tends to become cylindrical—the smooth rod of the early investigators.

Some of the convolutions in cotton are temporarily removed on wetting, for Collins and Williams (J.T.I., 1923, *14*, 287) found that the initial increase in length which takes place when the hair is immersed in water or a dilute aqueous solution is associated with deconvolution; in general, the greater the number of convolutions removed the greater is the observed extension. The diameter change, however, is small. The behaviour of the cotton hair in the mercerising liquor is quite different for the degree of untwisting is much greater, it is permanent, and is accompanied by contraction in length. The uncoiling has already been mentioned on page 39.

The deconvolution of cotton hairs has been suggested as a test of the mercerising process by Calvert and Clibbens (J.T.I., 1933, *24*, 233). The method consists in cutting a large number of hair fragments 0·2 mm. long, mounting them in liquid paraffin on a microscope slide, and counting the proportion of fragments free from twist or convolution; the result, expressed as a percentage, is called the *Deconvolution Count.*

The chief practical value of the test lies in the detection of local irregularities in mercerised goods, particularly in the case of irregularities due to imperfect wetting of the cotton by the mercerising liquor. The method may also be employed, within certain limits, for deciding whether the goods have been subjected to the mercerising process or not; it is a quantitative development of the qualitative test in which a visual estimate is formed of freedom from convolution by examination under the microscope. This method has its limitations, as the extent of deconvolution is very greatly influenced by the maturity of the cotton and by the structure of the material, i.e. the twist of the yarn or the weave of the cloth. It has also been observed in the case of cotton which has been severely attacked by chemical reagents before mercerising, that the deconvolution count is much lower than the count for unattacked cotton. The test is mainly of value for purposes of comparison and must not be regarded as a measure of the characteristics which constitute successful technical mercerising, for goods cannot be classified as good or bad according to the deconvolution count. Factors such as the concentration of the liquor, the amount of shrinkage and the twist of the yarns affect the deconvolution in the same general way as they affect the absorption and reactivity ratios, but the maturity, which has a great effect on deconvolution, is without influence on the reactivity or absorptive capacity of the mercerised material.

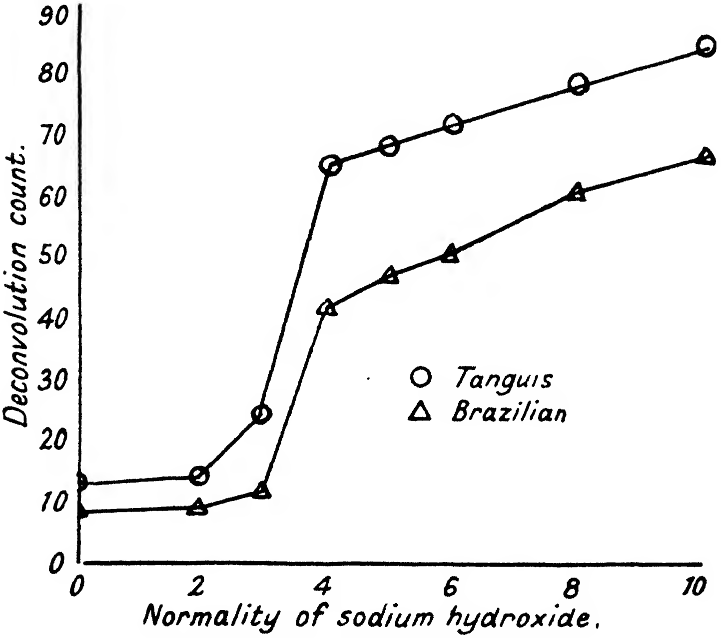


FIG. 25.—Deconvolution with NaOH.

The effect of the concentration of the sodium hydroxide solution is shown in Fig. 25.

When the deconvolution count was taken for three different types of cotton, mercerised as yarn, as bundles of hairs, and as hair fragments (0·2 mm.), the following results were obtained:

DECONVOLUTION COUNTS AFTER MERCERISING.

Cotton samples.	Yarn.	Hairs.	Hair fragments.
Uppers . .	79	82	81
Texas . .	45	71	79
Zaria . .	28	56	68

The results may be explained by consideration of the external resistance to deconvolution; yarn resists deconvolution more than unspun hairs, which in their turn resist more than hair fragments. The tendency to deconvolution is greatest in the most mature cotton (Uppers) and is little affected by structural variations, but in the case of immature cotton (Zaria) there is less tendency to hair deconvolution so that its extent is greatly affected by structural variations.

The effect of twist in yarn from the same variety of cotton is shown by the following figures:

DECONVOLUTION COUNT.

Twist . .	12·1	20·7	23·0	35·7	38·9	46
Deconvolution count . .	69	58	53	41	35	30

For woven structures, the problem of constraint is more complex; warp yarn mercerised without tension in the woven piece gave a deconvolution count of 20, whereas similar yarn mercerised as yarn but under tension gave a figure of 46, compared with 60 when full shrinkage was allowed. It has frequently been suggested that some of the difficulties of technical mercerising are due to inefficient penetration of the alkali, but even after a prolonged treatment with mercerising liquor, it is possible to show that the hairs near the surface of a mercerised fabric are more completely deconvoluted than those embedded in the cloth owing to the constraint imposed on the latter. Surface hairs may be differentiated from embedded hairs by dyeing with Primuline, diazotising and exposing to sunlight for a few minutes; decomposition of the diazotised colour results according to the depth of the hairs in the fabric, and subsequent development with β-naphthol produces the deep red coloration only in the interior of the material.

Shrinkage also affects the deconvolution count which drops if shrinkage is prevented. However, differences in shrinkage which produce great differences in lustre and in affinity for dyes have hardly any effect on soft-twisted yarns in respect of the deconvolution count.

The effect of the washing temperature is small and differs according to the shrinkage.

EFFECT OF TEMPERATURE OF WASHING.
(Hosiery yarns.)

	Mercd. with shrinkage.		Mercd. without shrinkage.	
	Washed cold.	Washed hot.	Washed cold.	Washed hot.
Sakel cotton .	82	74	55	65
Arizona cotton	31	24	20	18

The deconvolution count of unmercerised cotton is never zero, i.e. a certain proportion of hair fragments 0·2 mm. in length, cut from any unmercerised cotton will always be free from convolutions. The range varies from 2·5 to about 16; if the figure is over 20 it may be assumed that the hairs have been mercerised and if below 10 the material is unmercerised. Variation in the unmercerised cotton is probably due to wall thickness, for a thick walled hair cannot collapse on drying when the cotton boll bursts, so that there is little convolution. Thin-walled hairs exert slight twisting influence and again show few convolutions before mercerising. The original number of convolutions is therefore small for both abnormally thick-walled and abnormally thin-walled hairs.

Deconvolution, Reactivity and Absorption

The effect of the concentration of the mercerising alkali upon the mercerised quality of the cotton is the same, whether the quality is measured by the deconvolution count, the chemical reactivity or the absorptive capacity. When the concentration of alkali is plotted against deconvolution or reactivity to hypobromite oxidation (page 275), or absorption of alkali from dilute solution (page 386), or absorption of water vapour from an atmosphere of constant humidity (page 357) the curves obtained all resemble each other and may be regarded as the typical " Mercerisation Curve " as for example in Fig. 25.

The effects of variable twists on the properties of yarns and of the restriction of shrinkage during mercerising are also qualitatively similar as is seen in the following results. Series 1 to 5 represent increasing two-fold twist in a direction opposed to that of the single yarn, whilst series 6 to 9 refer to increasing two-fold twist in the same direction as that of the single yarn.

DECONVOLUTION, ABSORPTION AND REACTIVITY.

Sample.	Deconvolution.		Alkali absorption.		Reactivity.	
	No shrinkage.	With shrinkage.	No shrinkage.	With shrinkage.	No shrinkage.	With shrinkage.
1	45	50	1·67	1·91	1·47	1·47
2	45	56	1·63		1·42	
3	38	52	1·58		1·47	
4	31	48	1·62 (?)		1·30	
5	26	40		1·76		1·39
6	37	54	1·61		1·37	
7	17	42	1·25		1·28	
8	14	20	1·24		1·17	1·37
9	9	15	1·26	1·66	1·12	
Unmercd.	11		1·00		1·00	

The three measurements are affected in the same direction by increasing yarn compactness and by the application of tension during the mercerising process. Quantitatively, the effect of these two factors varies according to the method of estimation. The two most highly twisted samples, 8 and 9, mercerised with shrinkage, do not differ greatly from unmercerised cotton in deconvolution count, but are much higher in alkali absorption and reactivity ratios. There are also large differences in the effect of tension on the various properties, e.g. sample 8 allowed to shrink, yields as high an absorption ratio as sample 1 mercerised without shrinkage, whilst the deconvolution count varies from 20 to 45. The results are evidently controlled by the structural resistance to swelling and deconvolution.

The variety of raw cotton has little effect on the absorption or reactivity ratios.

EFFECT OF VARIETY OF COTTON.

Cotton.	Deconvolution count.	Reactivity ratio.	Alkali absorption ratios. NaOH	$Ba(OH)_2$.
Tanguis . .	73	1·43	1·64	1·66
Uppers . .	66	1·46	1·57	1·61
Peruvian . .	65	1·45	1·68	1·66
Sakel . . .	63	1·38	1·57	1·57
Brazilian . .	51	1·42	1·62	1·70
Arizona Pima .	23	1·34	1·62	1·70

The last two samples were immature cottons.

There is obviously an important difference between the methods of describing mercerised quality based on deconvolution and those based on chemical or physico-chemical tests.

The difficulties of interpreting Deconvolution Counts as a measure of the technical requirements of a mercerised finish are illustrated by an interesting experiment of Calvert and Clibbens. A high quality poplin cloth was singed, scoured, mercerised, bleached and dried without calendering—equal lengths being distributed over five different works.

The results are shown in the following table ; it must be remembered that the original composition and structure of the five samples were in all respects identical. The bending lengths of the materials are measures of the stiffness which increases as the value rises (J.T.I., 1930, *21*, 377) ; it will be noticed that samples 1 and 2 represent technical extremes in handle and lustre, the stiffest cloth having the highest lustre and vice versa. In spite of this they do not differ significantly either in deconvolution count or the shrinkage on remercerising without tension as shown in the last column. They are not significantly different in moisture absorption ratio and only differ to a minor extent in alkali absorption and reactivity ratios. The factors which comprise a successful mercerised finish from the commercial and technical standpoints appear to have little bearing on the measurements of mercerised quality, so that it is undesirable to describe any single measurement as the " degree of mercerisation."

COMPARISON OF WORKS' MERCERISING.

Sample No.	Deconvolution count.		Moisture absorption ratio.	Baryta absorption ratio.	Reactivity ratio.	Bending length.	Order of lustre.	Order of dyed shade.	% Warp shrinkage.
	Warp.	Weft.							
1	55	31	1·25	1·75	1·50	1·79	5 (low)	2	12·7
2	51	28	1·24	1·88	1·65	2·92	1 (high)	4	12·7
4	49	22	1·24	1·70	1·50	2·52	Inter.	1 (dark)	13·5
5	47	21	1·14	1·49	1·28	2·01	Inter.	5 (light)	13·1
3	25	15	1·12	1·53	1·30	1·90	Inter.	3	15·4

The Deconvolution Count has been found most useful in the examination of mercerised hosiery yarns, which in general are soft-twisted two-fold material giving a high deconvolution count. This has been dealt with by Clibbens and Geake (J.T.I., 1933, *24*, 255), and is discussed again on page 441.

CHAPTER FIVE

GENERAL CHANGES IN DIMENSIONS

BEFORE considering the changes in dimensions which take place during the mercerising process, it is advisable to be aware of the effect of water on cotton. The amount of swelling depends to some extent on the variety of cotton; with a bleached American sample, for example, Haller (Kolloid Z., 1917, *20*, 127) observed an increase of 16% in diameter when air-dried hairs were immersed in cold water. There is also a slight increase in length when cotton hairs are immersed in water or dilute aqueous solutions, due to deconvolution and associated with the number of convolutions in the hair (see page 31). On the other hand, according to Hübner and Kaye (J.S.C.I., 1922, *41*, 94) there is a slight contraction and a decrease in total volume when yarns are immersed in water. The contraction in length in the case of yarn may be due to the elastic recovery effect in removing the inevitable extension placed on the hair during the spinning processes. Some data bearing on this subject have been given by Collins (J.T.I., 1930, *21*, 316).

The changes which take place in the cotton hair are due to two causes, first, the true swelling or extension into space, and secondly, change of shape arising from the release of mechanical strain in the hair itself and the anisotropy (directional property) associated with the spiral fibrils.

Measurements on Cotton Hairs

The first quantitative examination of the mercerisation of cotton hairs was made by Willows, Barratt and Parker (J.T.I., 1922, *13*, 229). The changes in dimensions of yarns are due, to a large extent, to the relative positions of the hairs in the yarn, so that a measurement of yarn contraction, for example, is affected by slip or other accommodation of the hairs in the yarn. Hence it follows that measurements on single cotton hairs are a more reliable index of dimensional change due to mercerisation.

The material used was combed Egyptian sliver which had been boiled for 60 mins. in a 2% aqueous solution of sodium carbonate. Single hairs were taken from this sliver and separately mounted in the Barratt Fibre Balance (see J.T.I., 1922, *13*, 17), where the load was applied by a solenoid, and the change in length magnified about 200 times. A constant load of 50 mg. was applied to keep the hair taut, but as the average breaking load was between 6 and 7 g. the hair was regarded as practically free from tension. With suitable illumination, a magnified image of the hair was projected on a screen and the length measured before and after immersion in the liquid whose effect was under examination.

A preliminary piece of work was necessary in order to establish the necessary time for completion of the action of the mercerising liquor. In general works' practice for mercerising of piece goods, the cloth is only exposed to the action of the alkali for from 20 to 90 secs., during which time the liquor is required to penetrate yarns and hairs ; Willows and his co-workers found that for all except the strongest solutions, the complete change in length required about 3 mins.

Some interesting effects were observed, including the rapid penetration into the hair and the great contraction produced by solutions of NaOH of 30 to 35° Tw. The change in action of the alkali commences at about 22° Tw., but with the 60° Tw. solution commonly used for technical mercerising, penetration is slow, and as it is difficult to wet yarn with alkali of this concentration, it follows that works' practice cannot ensure complete mercerising within the time allowed, unless further action takes place during the washing process. The small effect of the strongest solution (86° Tw.) is very noticeable, probably due in some measure to the high viscosity.

The time of three minutes' immersion was allowed in the case of a large number of hairs, but measurements were made with a fresh solution for each hair. At the end of the period, each hair was well washed with cold water and the new length observed. The changes in length are expressed in the following curves as percentages of the original lengths of the dry hairs ; the line curve gives the changes produced by the alkali alone and the dotted curve represents the changes for mercerisation followed by washing.

The relation between change in length and concentration is not simple according to these results.

The hairs possess their maximum length in solutions of 10° Tw.—a fact which may be due to the softening of the hair and the straightening of the convolutions, as a similar but smaller extension occurs in water. Mercerisation commences rapidly at 22° Tw., a fact which had previously been observed, and there is a maximum contraction at 30° Tw. NaOH.

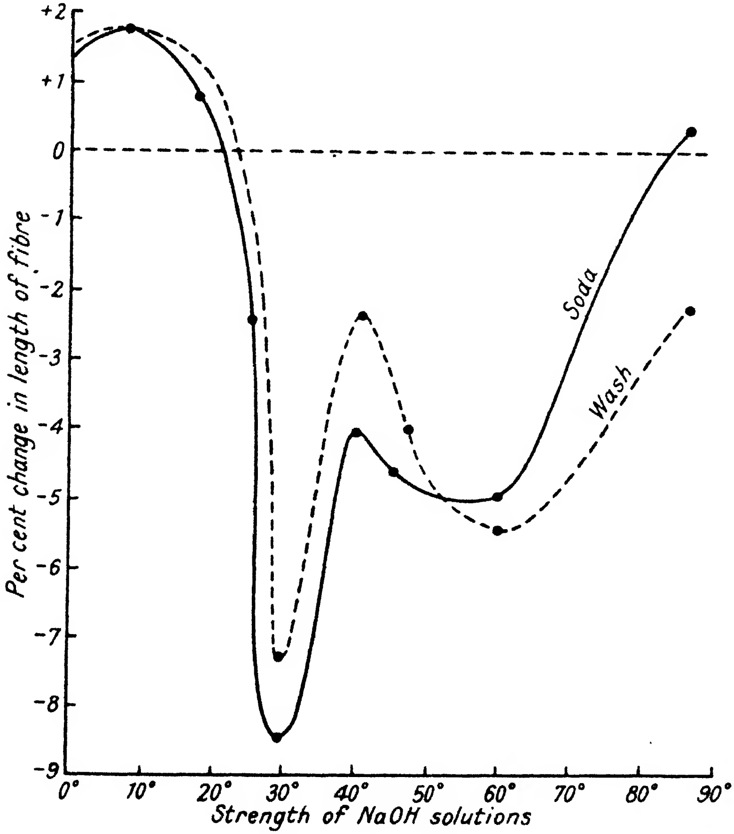


FIG. 26.—Changes in length of single cotton hairs (scoured) placed in single solutions of NaOH. (50 mg. tension.)

As the concentration of the solution rises from 30 to 68° Tw., there is, apparently, a minimum contraction of the hair at 40° Tw., but this is not confirmed by later work.

The effect of washing is interesting; hairs treated with concentrations of NaOH up to 52° Tw. and then washed show an extension compared with their length when still in the alkali, but if stronger solutions are used, there is a contraction additional to that produced by the alkali. For instance, with 86° Tw. NaOH, there is practically no effect, but after washing there is a contraction of 2%.

The effect of the temperature of the alkaline liquor was not examined in great detail, but it was found that a decrease in temperature caused a greater contraction above 22° Tw. and the maximum effect was produced with weaker solutions. For example, at 0° C. the maximum contraction was produced by 25° Tw. NaOH solution.

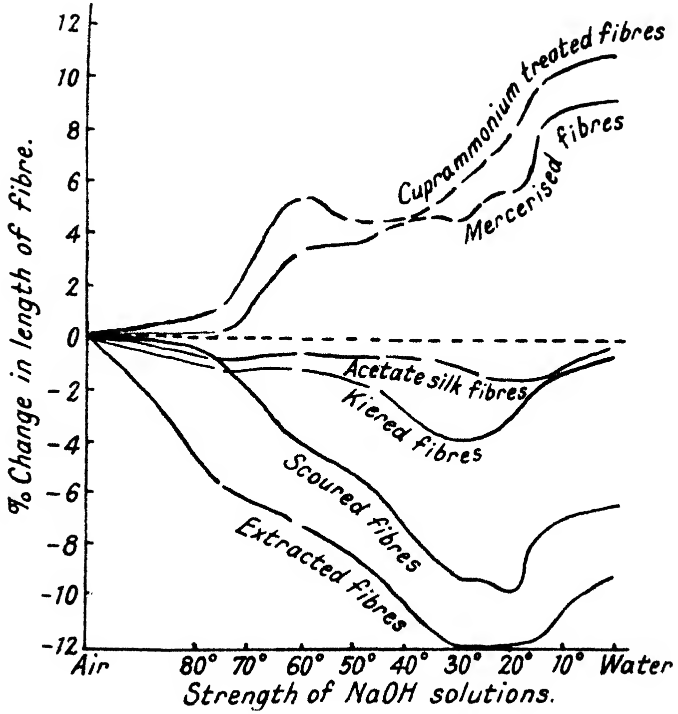


FIG. 27.—Change in length of cotton hairs in NaOH solutions of decreasing concentration.

The observation that the strongest solutions of NaOH have comparatively little action, but that contraction takes place during washing, is explained if the effect of dilution is to reach a concentration where the action of the alkali is more vigorous. This point was examined in further detail by exposing the single hair to the action of sodium hydroxide solutions of decreasing concentrations, followed by washing the hair free from alkali by means of cold water. Fig. 27 shows the results when the strongest solution was 77° Tw. approx. If the case of scoured fibres is examined, the large amount of mercerisation produced during washing is clear, the maximum contraction not being reached until the concentration was reduced to 20° Tw.

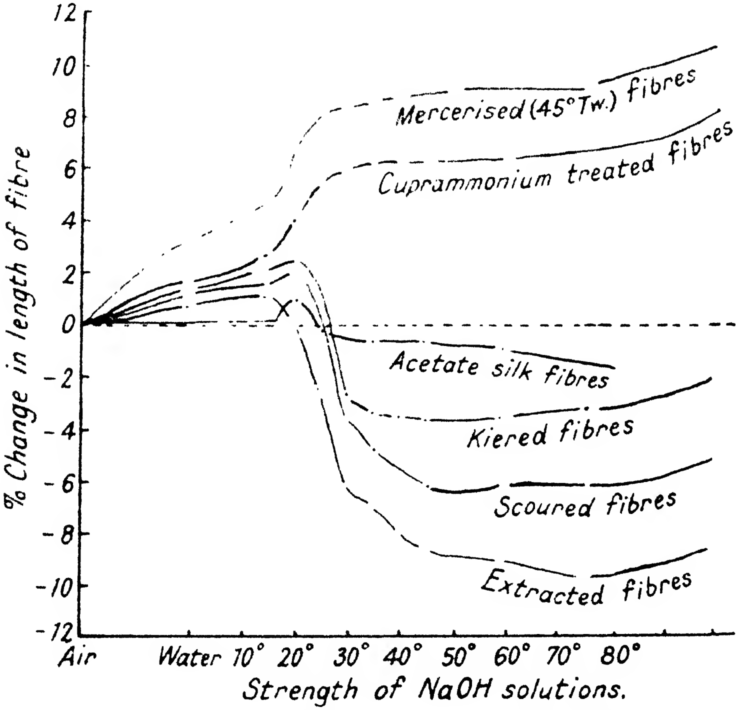


FIG. 28.—Change in length of cotton hairs in NaOH solutions of increasing concentration.

It will be remembered that in mercerising, a decrease in length of the cotton hair is accompanied by an increase in diameter. The washing effects shown in the graph, Fig. 27, were supported by observations of the change in diameter, which increased until the concentration was reduced to 15° Tw. NaOH, then remained constant until 5° Tw. was reached, and after that it decreased rapidly. The increase in diameter caused by washing amounted to 40 %. Now as an increase in diameter or a decrease in length of the hairs will cause shrinkage of the yarn containing them, *it is necessary, in technical mercerising, to wash mercerised material until the strength of the liquor in the cotton is less than 15° Tw.* before relaxing the tension, as otherwise shrinkage will take place on subsequent washing.

A further series of experiments with solutions of increasing concentration on the same cotton hair gave the results shown in Fig. 28.

In the case of the scoured fibres, it will be noticed that the line of the curve after 30° Tw. is altogether different from that given in figure 26 (see page 53). The maxima and minima at 30, 40 and 50° Tw. do not appear and the fullest mercerising is not reached until 45° Tw. and is not changed by immersion in stronger solutions.

The last two figures also deal with the possible effect of the cuticle. The three lower curves represent different degrees of purification and are parallel. The upper curves relate to cellulose which has been dispersed; the action is, therefore, quite different, but it is interesting to note that, in the case of the "cuprammonium treated" fibres, the cuticle had been ruptured and destroyed. The question of the effect of the cuticle will be referred to later (see page 58).

It is not easy, quantitatively, to measure the change in diameter which follows the mercerising process, but Willows and Alexander (J.T.I., 1922, *13*, 237) evolved a neat method by tracing of the outlines of a number of sections of cotton hairs as projected from the microscope stage on to sheets of smooth paper. The tracings, which were recognisable at every stage, were cut out and weighed so that changes in area were easily calculated.

By combining these results with those obtained for the changes in length already mentioned, it was possible to estimate the change in volume of cotton hairs, as shown in Fig. 29.

In the observations on the increase in area of the sections, the results from different sections were noticed to vary by more than 100%. Investigation of these irregularities led to the conclusion that they were not due to experimental error, but rather to a difference in the ripeness or development of the hair.

Volume Estimations

Additional information on the swelling of cotton hairs in solutions of sodium hydroxide was obtained by Coward and

Spencer (J.T.I., 1923, *14*, 32) in the course of their examination of the absorption of caustic soda solutions by cotton (see page 307). The method employed was based on the use of a suitably designed centrifuge, whose performance was described (*ibid.*, 28); from a comparison of the rates at which various liquids were removed from cotton hairs and from glass wool fibres, it was deduced that a few minutes centrifuging with a centrifugal acceleration of the order of 2,000 times that of gravity sufficed to reduce interfibrillar liquid to within 5 or 10% of the weight of the fibres, except in the case of extremely viscous liquids. Cotton was found to retain water to about 50% of its weight and caustic soda solutions up to nearly 300% of its weight; the weight of liquid retained after centrifuging substantially represented the extent to which these liquids were held within the body of the cotton hairs.

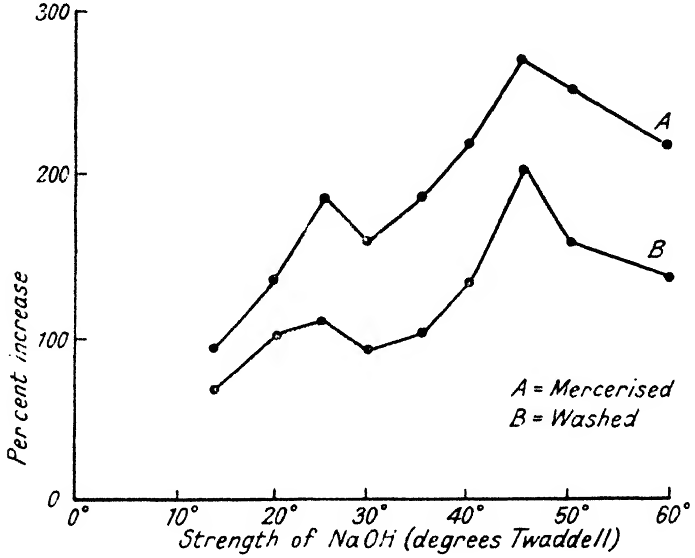


FIG. 29.—Changes in volume of cotton hairs on mercerising.

The amounts of sodium hydroxide and water removed from the solutions of various compositions were calculated from determinations of the weight of the cotton (dry), the weight of the total centrifuged mass, and of the NaOH in it as determined by titration. The results are shown in Fig. 195, page 311. The rate of absorption of the solution increases rapidly with increasing concentration, but this ends at about 14 % NaOH—the minimum strength to give well-defined mercerisation in technical practice. In order to determine whether the calculated volumes represent the overall swelling of the cotton hairs in the various solutions, comparison was made with the swelling of cotton hairs described by Willows and Alexander (J.T.I., 1922, *13*, 237). The results are shown in Fig. 19б, from which it was established that agreement is not close, although the figures are of the same order of magnitude. This is probably due to the fact the volume changes measured were based on the changes in length of whole hairs and the changes in area of sections which, after cutting, were immersed in the solutions of NaOH.

Now in the region of the points X, Y, and Z Willows and Alexander (*loc. cit.*) observed that the cut sections showed a pronounced " dumb-bell " shaped extrusion of the cellulose which had no parallel in the case of the complete hairs.

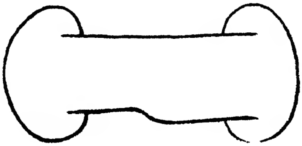


Fig. 30.—Extrusion of cellulose from ends of hair fragments swollen in 30° Tw. NaOH. (*See* also Plate VIII.)

This may be regarded as evidence of the restrictive action of the cuticle, for in stronger solutions the cuticle is more extensible as the diameter of the swollen hair is greater and there is no bulging. When the cuticle has been damaged as with chemical tendering, there is no " dumb-bell " formation.

Coward and Spencer conclude that the swelling may be represented by the calculated volume of the absorbed solution. Hence with solutions whose concentration rises from 14·3 % NaOH up to 48·8 % NaOH (practically a saturated solution) the increase in volume of 100 g. of cotton is constant at 177 ± 8 cc. This suggests that the cuticle of the cotton hair sets a definite limit to the swelling of the cellulose which it encloses and resists the osmotic forces in the stronger solutions.

Shrinkage in Successive Solutions

The work of Willows, Barratt and Parker (*loc. cit.*) contains two series of investigations, first, that in which one hair was placed in one solution, and secondly, that in which a hair was treated with a series of solutions of rising or falling concentrations. The work of Collins and Williams (J.T.I., 1923, *14*, 287) also followed the swelling of cotton hairs when immersed in a series of solutions. The change in length was measured by means of an instrument designed on the lines of Justin-Mueller's turgometer (La Turgometrie ; Paris, 1917) and the

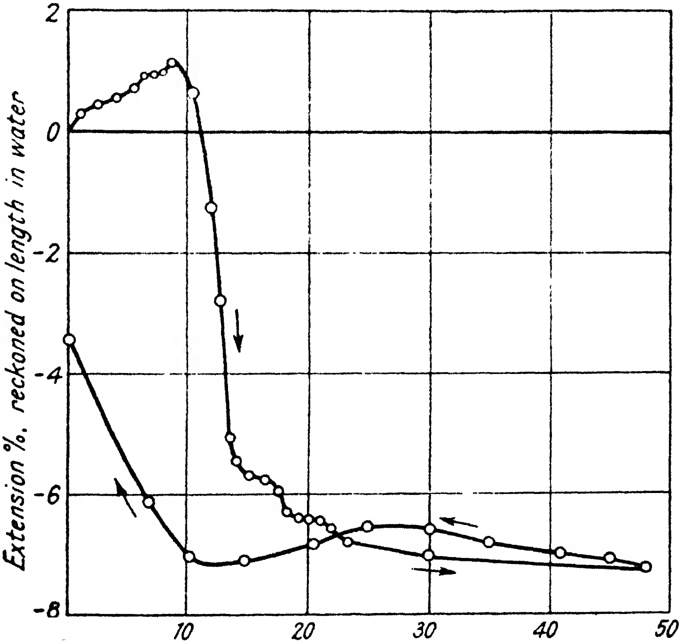


FIG. 31.—Changes in length of cotton hairs on treatment with a series of solutions of sodium hydroxide.

cellulosic material examined was Trinidad Native cotton, which had been boiled in water and soda. The hairs were successively treated with forty-three different solutions, containing up to 48·2% NaOH, and the curve connecting length and concentration was of the same general form for all the hairs examined. The results, together with those showing the change in length on gradually reducing the concentration of the alkali around the hair, are shown in Fig. 31. It is clear that the process is not reversible.

The original length in water was the basis for calculating the percentage contraction, and it will be noticed that this original length (in water) is never regained. A hair which has been treated with solutions of NaOH up to 48·2% concentration, afterwards behaves in an almost reversible manner, but the changes in length are not as great as those indicated in the first part of the above curve. The general shape of the above curve resembles that obtained for kiered and scoured hairs, by Willows, Barratt and Parker (*loc. cit.*), as shown in Fig. 26, page 53, but whereas these authors observed an extension after 30° Tw., Collins and Williams found that the cotton

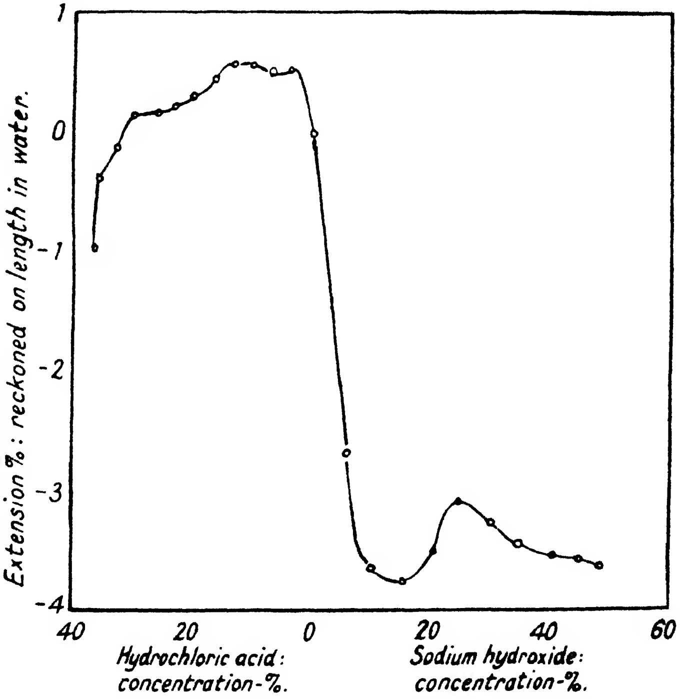


FIG. 32.—Change in length of cotton hairs in NaOH—water—HCl.

continued to contract up to 102° Tw. (48·2%). Further experiments confirmed this result and indicated that hairs treated successively with distilled water, 15·2% NaOH, 35·1% NaOH and water, or with water, 15·2% NaOH, water, 35·1% NaOH and water contract more than hairs treated with either 15·2% or 35·1% NaOH alone. It is possible that this is due to the cotton employed or to the fact that Collins and

Williams used a smaller load (10 mg. compared with 50 mg. of Willows and his co-workers).

A number of hairs of a second cotton, American Upland, were boiled in water and soda as before and treated with solutions of sodium hydroxide of 15·2, 35·1 and 48·2% concentration. They were then immersed in solutions of NaOH of decreasing concentration, next in water and finally in solutions of hydrochloric acid of increasing concentration; the extensions were calculated on the length in water after mercerisation. The results are shown in Fig. 32, from which it appears that minimum swelling, which is presumably associated with maximum extension of the mercerised cotton, takes place in a 10 % solution of HCl.

Diameter

Observations were also made of the change in diameter relative to the value in water. The volume of the hair was estimated on the formula $LD^2/4$, where L is the length and D

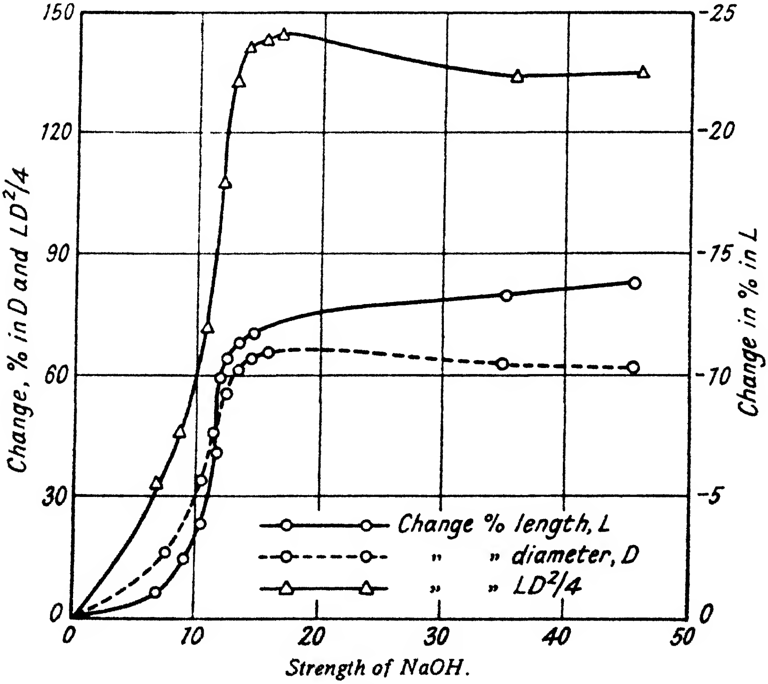


FIG. 33.—Dimensional changes in the cotton hair on treatment with solutions of sodium hydroxide.

the diameter of the hair, and the percentages changes plotted against the concentration of alkali. The results are shown in Fig. 33, and from this and Fig. 32 it appears that maximum swelling takes place near a concentration of 14·5% NaOH. (This concentration is very nearly a solution of maximum specific conductivity at 18° C.) The figure also agrees with that of Coward and Spencer (J.T.I., 1923, *14*, 32), who found a fairly constant swelling in all solutions containing more than 14·3% NaOH. Immersion in more concentrated alkali causes contraction of the hair unaccompanied by increase in diameter, so that *decreased length is not always a measure of an increase in volume.*

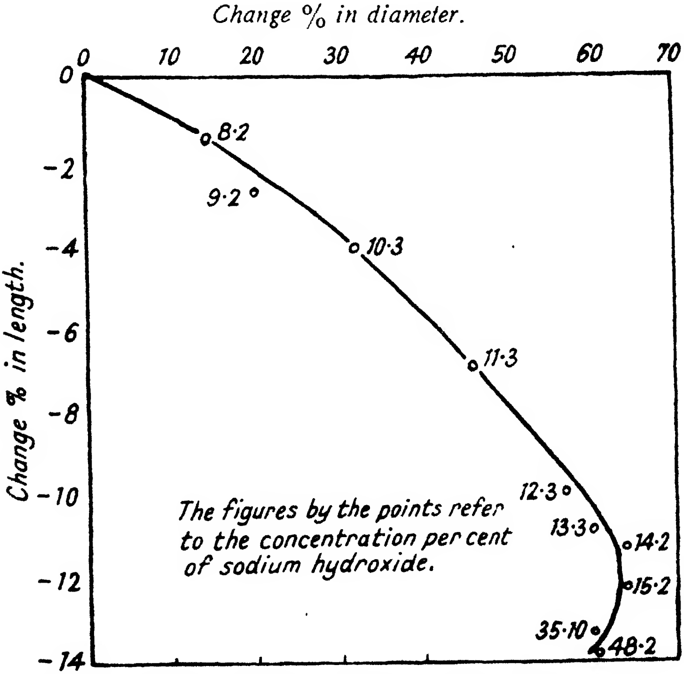


FIG. 34.—Relation between changes in length and diameter.

The relation between mean diameter and length is shown in Fig. 34, and indicates that the diameter increases five times as fast as the length decreases.

Several hairs appeared to have a limiting value of the mean diameter, which may be due to the constricting influence of the cuticle (*cf.* Willows and Alexander, and Coward and Spencer).

It would appear from the work described in these three papers relating to the swelling of cotton hairs, that for maximum swelling there is no advantage in the increase in concentration of the alkali solution above 15 %, i.e. 34° Tw. NaOH. The observations of Collins and Williams on the change in diameter, combined with those of length, show that a *maximum swelling occurs in a 15 % solution of NaOH,* and that hairs which have been immersed in the complete range of solutions up to 48 % NaOH, on immersion in more dilute solutions also show a maximum swelling in 15 % sodium hydrate solution.

The Bast Fibres

There is comparatively little information on the mercerisation of bast fibres. Some of the physical changes which flax fibres undergo have been described by Herzog (Textilber., 1920, *1*, 136) ; Marshall (J.S.D.C., 1922, *38*, 293) has described the effect of mercerising ramie, mainly in respect of lustre.

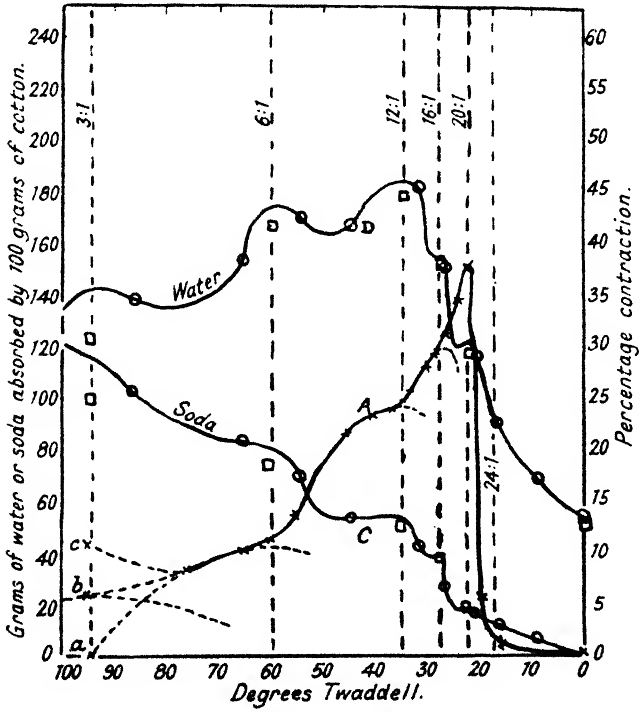


FIG. 35.—Linear contraction of ramie in NaOH

The first quantitative examination of the effect of caustic alkali was made by Nodder and Kinkead (J.T.I., 1923, *14*, 133).

Ramie fibres are very suitable for estimation of changes in length as they are frequently 8 inches long as compared with 2 or 3 inches for flax. The material used was obtained from de-gummed and bleached ramie ; the diameter varied considerably, being 50 to 60μ on the average in the widest part. The length of fibre was as much as 20 cms., but this was cut down to 9 to 14 cms. where necessary. The load under which measurements were taken was 6 mg. and the temperature 15° C. Each measurement was made in a fresh solution and the time for complete contraction varied from 10 mins. to 3 hours, according to the strength of solution.

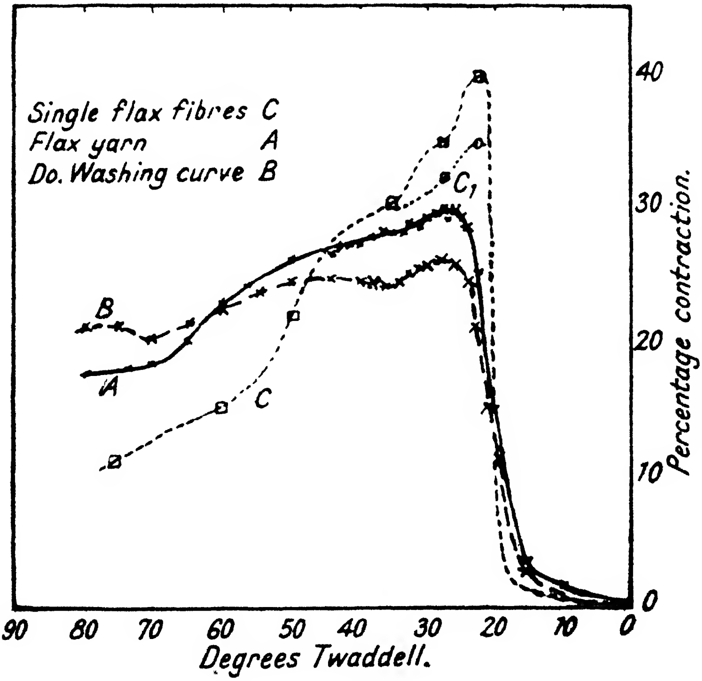


FIG. 36.—Linear contraction of flax in NaOH.

Measurements were also made on yarn contraction, and in order to have as close a comparison as possible fibre measurements were made on material taken from the yarn. The percentage contraction, calculated on the length in water, was found to be very uniform, and generally no more than 20 measurements were necessary to obtain a figure of sufficient accuracy. The results are shown in Fig. 35, *A*, and also in Fig. 37, *C*, where percentage contraction is plotted against strength of caustic soda expressed in degrees Twaddell.

The most striking feature of the curve *A* in Fig. 35 is the exceedingly well-marked maximum contraction obtained in a 22·2° Tw. (10 %) solution of NaOH.

At this point, a contraction of almost 38 % was observed, whereas a solution containing only 1·5 % less NaOH (i.e. 18·5° Tw.) caused a contraction of less than 2 %.

Curves *C* and *D* represent the amounts of soda and water absorbed per 100 g. of cotton, according to Coward and Spencer (J.T.I., 1923, *14*, 32).

The flax fibres were joined together by means of rubber solution and the contraction measured under a load of 2 mg. ; this allowed for the difference in area of cross-section as compared with ramie.

The curve is shown in Fig. 36, *C*, and in Fig. 37, *G*. The points indicated by circles in Fig. 36, represent the contrac-

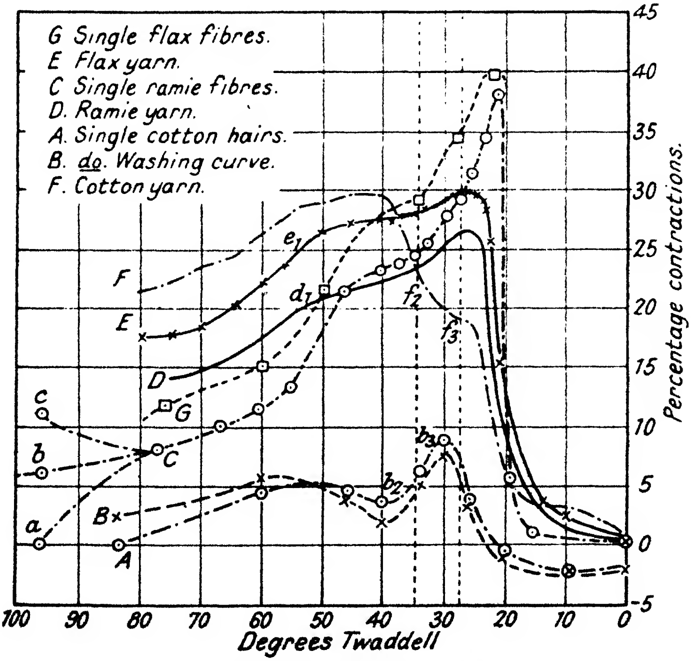


FIG. 37.—Shrinkage of flax, ramie and cotton.

tions found when a weight of 6 mg. was used as with ramie. In the region of maximum contraction at 22° Tw. the fibre is very sensitive to small changes in tension. The maximum contraction was almost 40 %.

The shape of the curve is very similar to the curve for ramie and lies a little above it at all points. The curves shown in Fig. 37, *D* and *E*, represent the contraction produced by NaOH solutions on ramie and flax yarns respectively; the curves for ramie fibres and ramie yarn are related to each other in much the same way as the corresponding curves for flax fibres and yarn.

The above data have been combined with those obtained by Willows, Barratt and Parker (J.T.I., 1922, *13*, 229) for cotton hairs and by Hübner and Pope (J.S.C.I., 1904, *23*, 404) for cotton yarn. The results are incorporated in Fig. 37.

The prominent maximum at 22° Tw. on the curves for single bast fibres does not appear in the yarn curves; the reason may be that the fibres are very sensitive to tension in this region and this is supplied by the constraint exercised by the yarn. The curve for ramie yarn shows a more prominent maximum at about 28° Tw. than does the flax curve; this may be explained by the greater length of fibre, as shorter fibres have a better chance of sliding over neighbouring fibres without increasing the gross contraction of the yarn.

Comparison of cotton hairs and bast fibres is difficult, but it is safe to comment on the different maximum swelling concentrations of alkali. The effect of tension is important, for in the case of cotton the load for a given area of cross section was about 50 times that employed by Nodder and Kinkead.

Potassium Hydroxide and Cotton

Collins and Williams (J.T.I., 1924, *15*, 149) investigated the effect of solutions of potassium hydroxide on cotton hairs. Previous work with KOH had been limited to the papers of Ristenpart (Textilber., 1921, *2*, 130) and Knecht and Harrison (J.S.D.C., 1912, *28*, 224), who confined their measurements to yarns. The material used by Collins and Williams was Trinidad Native cotton, both in the raw state and after boiling in water and in soda. Each hair was immersed in water, then in solutions of potassium hydroxide of increasing concentration, solutions of decreasing concentration and finally in water.

The changes in cross section are shown in Fig. 38.

In calculating the mean sectional area, circular section was assumed for simplicity, so that the values in solutions less concentrated than 20 to 25 % may be too high.

Changes in length are shown in Fig. 39, in which is incorporated Knecht and Harrison's measurements on yarn contraction.

Fig. 38 indicates that the prepared hair increases more in diameter than the raw hair, whilst Fig. 39 shows that the

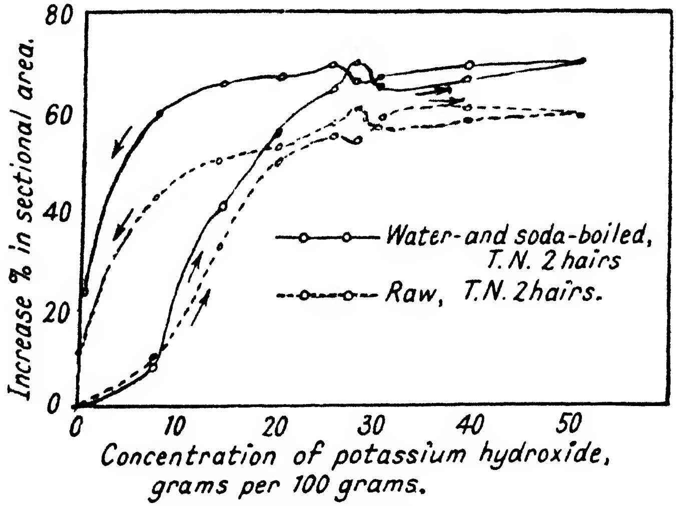


FIG. 38.—Increase in area of cotton hairs in KOH.

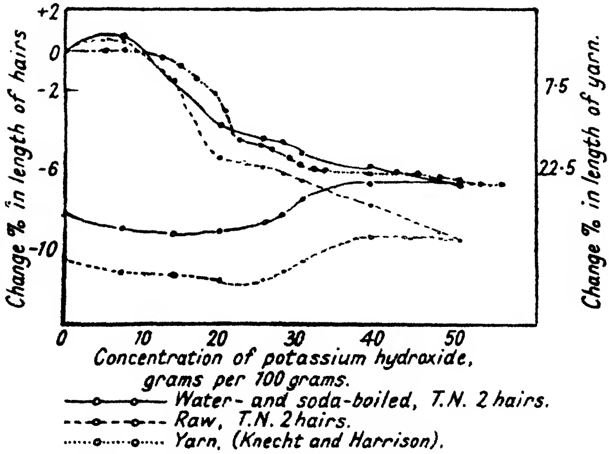


FIG. 39.—Linear contraction of cotton in KOH.

greater increase in diameter is accompanied by a smaller contraction in length, contrary to expectations. Maximum swelling takes place in 28% KOH, the concentration of maximum specific electrical conductivity.

A comparison of the action of NaOH and KOH at the same molar concentrations emphasised the independence of swelling on the total molar concentration.

The contraction in length was found to be of the same order of magnitude in solutions of NaOH and KOH, but the increase in diameter in the KOH solutions was less than half that attained in the solutions of NaOH, showing that changes in length alone should not be used as a measure of swelling in different solutions. This difference indicates that cotton material mercerised with solutions of potassium hydroxide should dye less deeply and have a handle less full than similar material mercerised in caustic soda.

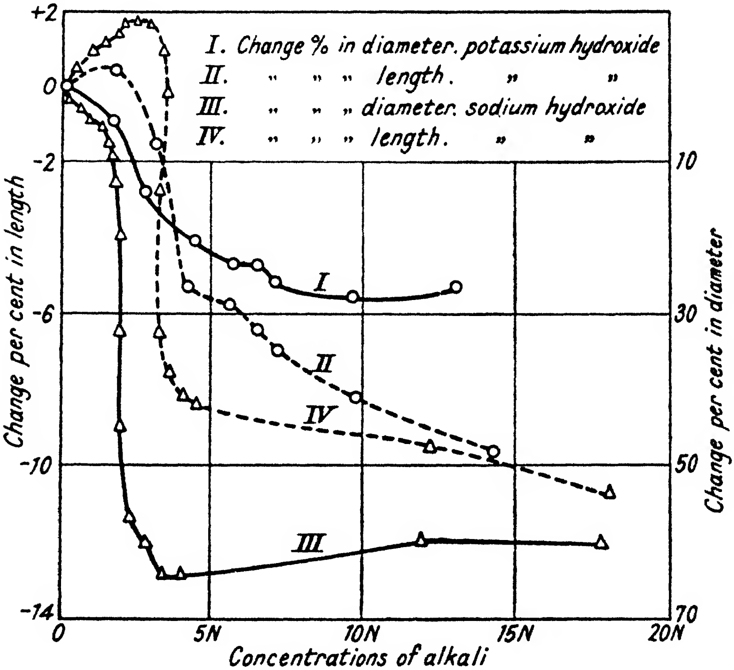


FIG. 40.—Comparison of KOH and NaOH.

The increase in diameter in 19·6% KOH is in good agreement with the value given by Haller (Kolloid Z., 1917, *20*, 127)

—24 % compared with 23 %. The concentrations for maximum swelling are 28 % for KOH and 15 % for NaOH, which correspond to molecular ratios of 1·44 : 1 as compared with Ristenpart's estimate of 1·5 : 1 (Textilber., 1921, *2*, 130).

Action of LiOH, RbOH and CsOH

The effect on the dimensions of single cotton hairs of treatment in solutions of lithium, rubidium and cæsium hydroxides has also been examined by Collins (J.T.I., 1925, *16*, 123). The procedure was the same as that described in the previous papers by Collins and Williams (J.T.I., 1923, *14*, 287; 1924, *15*, 149), changes in the length and diameter of single hairs of raw Trinidad Native cotton being examined in a small plane-faced glass cell under the microscope. No tension was applied, and the results are related to the value in water. When the dimensional changes for the five alkalis were plotted against normalities or molar fractions, no regularities were apparent.

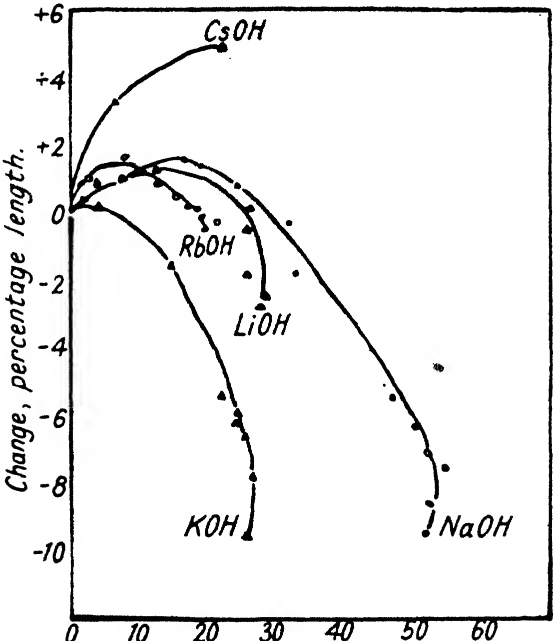


Fig. 41.—Relative change of diameter and length in five alkalis.

The relative change of diameter against length is shown in Fig. 41.

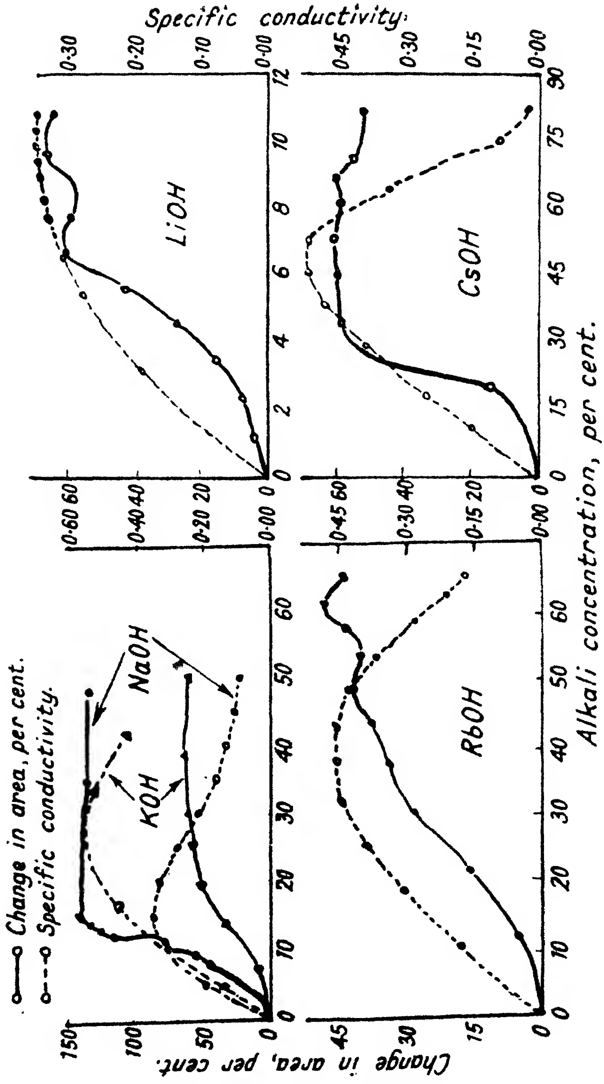


FIG. 42.—Change in area of cotton in five alkalis.

With lithium, rubidium and cæsium hydroxides, the contraction of the hairs is much less than with NaOH or KOH; the hairs only extend in concentrated solutions of cæsium hydroxide. In the case of diameter changes, sodium hydroxide stands apart, the increase being as much as 55 % compared with less than 30 % for the other hydroxides.

Investigation of the effect of NaOH and KOH had suggested the association of maximum swelling with maximum specific electrical conductivity of solutions, and perhaps also with the maximum heat of formation in the case of NaOH. This idea received attention in the examination of the other alkali hydroxides. There was, however, no strong indication of the coincidence of maximum swelling and maximum electrical conductivity (see Fig. 42). It seems that the *solutions corresponding with the fully hydrated ion are solutions for maximum swelling* in the case of the hydroxides of lithium, sodium, potassium and rubidium.

The lithium ion is believed to attract 17 water molecules, for example, and one swelling maximum occurs at 6·6% LiOH where the composition of the solution is $LiOH : 17H_2O$. The solutions corresponding in the case of the other hydroxides are

15·5% NaOH	or	$NaOH : 12H_2O$
38% KOH	or	$KOH : 7H_2O$
49% RbOH	or	$RbOH : 6H_2O$

The most striking feature of this work is the emphasis on the swelling powers of sodium hydroxide.

About the same time, Heuser and Bartunek (Cellulosechem., 1925, *6*, 19) also examined the action of various alkaline hydroxides on the cotton hair. These authors, however, did not treat each hair with a successive series of solutions, but adopted the method of one hair in one solution. The results are shown in the following graph (Fig. 43).

The swelling is measured in terms of volume percentage of the dried fibre. The maximum swelling concentrations of the various alkalis were found to be as follows:

SWELLING IN ALKALINE SOLUTIONS.

Swelling of cotton hair. %	Concn. of alkali. (g. per 100 cc.) %	
97	9·5	LiOH
78	18	NaOH
64	32	KOH
53	40	RbOH
47	40	CsOH

From these results, which show good agreement with those of Collins (*loc. cit.*), it again appears that *the swelling of the* *cotton hair in aqueous solutions of alkaline hydroxides depends on the degree of hydration of the alkali ion.* For any one alkali those concentrations which show maximum electric conductivity also cause the greatest swelling.

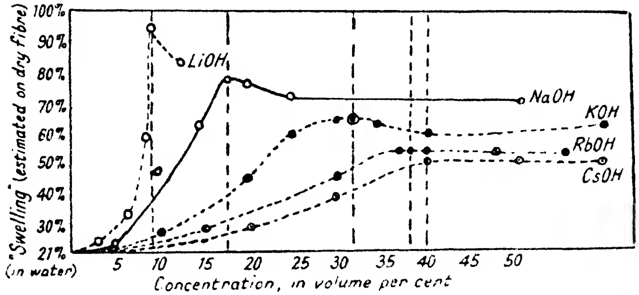


FIG. 43.—Change in volume of cotton hairs in five alkalis.

The work of Lottermoser and Radestock (Z. angew. Chem., 1927, *40*, 1506) was concerned with the loss in weight and degree of swelling of various bleached and unbleached forms of pulp of different degrees of fineness, when mercerised with lithium, sodium or potassium hydroxides.

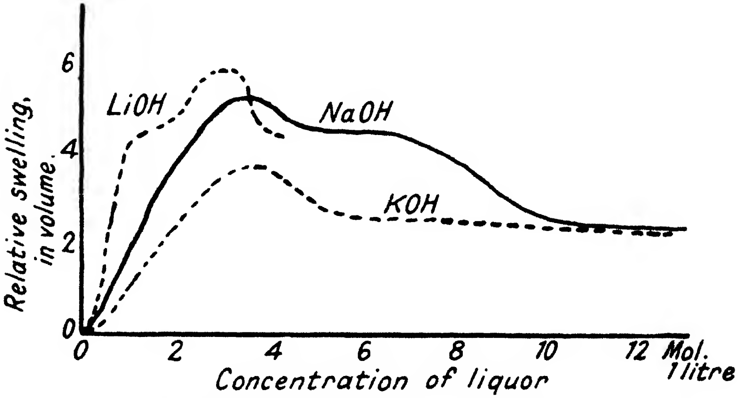


FIG. 44.—Swelling of cellulose pulp in LiOH, NaOH and KOH.

A specially designed volumenometer, containing mercury, was utilised for determining the degree of swelling. Of the three alkalis examined, lithium hydroxide gave the highest degree of swelling and potassium hydroxide the least, but the curves drawn with molecular concentration of alkali as abscissæ and degree of swelling as ordinates are different in the three cases. With lithium hydroxide the curve has a maximum at a concentration of 2·6 mols./litre with a horizontal portion at each side; with sodium hydroxide, the maximum is at 3·15 mols./litre and is followed by two horizontal portions; and with potassium hydroxide the maximum is at 3·8 mols./litre and is followed by one long horizontal portion.

It appears reasonable to assume, on the evidence at present available, that the metallic ion of the alkaline hydroxide exerts a specific action which is in the direction of the lyotrope series. This agrees with the views expressed by Herzog and Beck (Z. physiol. Chem., 1920, *111*, 287) and by Williams (J.S.C.I., 1921, *40*, 221) on the solvation of cellulose by salt solutions, $NH_4 < K < Na < Li$. The sodium ion, for example, is more hydrated than the potassium ion and aqueous solutions of sodium salts are more viscous than corresponding solutions of potassium salts.

The X-ray data of Susich and Wolff (Z. phys. Chem., 1930, *B8*, 221) on the mercerising action of various alkaline hydroxide at 20° C. show that it is necessary to utilise minimum concentrations of 9% LiOH, 12% NaOH and 17% KOH, for ramie fibres.

CHAPTER SIX

CRITICAL EXAMINATION OF CHANGES IN WIDTH

EXAMINATION of the process of mercerisation in respect of the cotton hair had for its object a more fundamental study than could be obtained from yarn or fabric. Whilst this method avoided the complications introduced by the additional forces and conditions existing in yarn structures, it was not suggested that the unit of the cotton hair was a simple structure; indeed it is known that the arrangement of the cellulose in the hair is highly complicated. A full explanation of the mercerisation process must take into consideration the morphological structure of the individual cotton hair. This was emphasised by Calvert and Summers (J.T.I., 1925, *16*, 233). The question of obtaining from a seed, which contains some 8,000 hairs, or from a bale of millions of hairs, a truly representative sample is naturally of fundamental importance to any study of dimensional changes in the hair. Further, there is the doubt which arises in applying the data obtained for one variety of cotton to another.

Effect of Mercerising

In the case of raw cotton, immediately before the boll bursts, the individual hairs are tubular in form; there are no convolutions and the transverse section is elliptical. The cellulose layer is not shrunken but completely hydrated; it encloses the central canal, and is in its turn enclosed by the definite external skin of the cuticle. On exposure to the atmosphere, the hairs quickly dry to form the collapsed and convoluted hairs of the cotton bale. The degree of collapse depends on the original diameter of the hair and the wall thickness. It is clear that there are large measurable variations between the hairs of one type of cotton; Calvert and Summers (supra) also showed that the average variations between one cotton and another are equally great. The degree of variation in width of the mature hair becomes increased when the hairs collapse, so that uncollapsed hairs of the same diameter may collapse to give different hair widths owing to differences in wall thickness; conversely, uncollapsed hairs of different diameters may give the same collapsed hair width. The method adopted was to measure the width of each hair across the widest portion between two convolutions near the middle of the hair. The distribution of hair width in the bale was investigated and it was found that about 250 hairs were sufficient. In the case of the more regular Sea Island cotton 150 hairs were adequate. The range of hair widths was

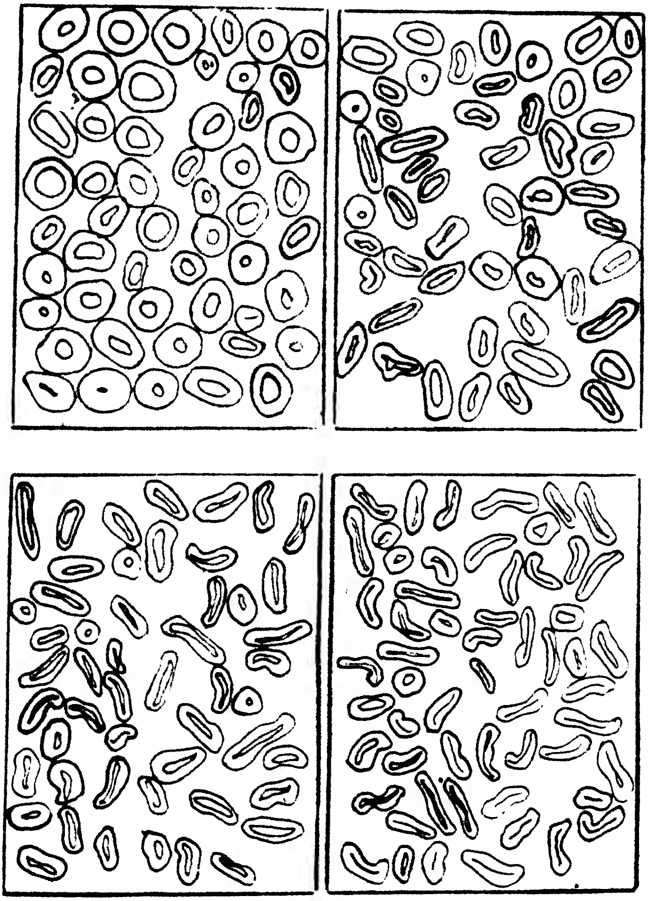


FIG. 45.—Transverse sections of Sea Island cotton hairs, ½, 1, 2 and 15 minutes after exposure to the atmosphere.

found to be 7 to 25μ in the case of a fine cotton such as Sea Island, but 10 to 30μ for Peruvian Full Rough.

When a cotton hair is brought into an aqueous solution of sodium hydroxide of 40° Tw. (18 %), the cellulose begins to swell immediately and in a few seconds the hair is elliptical in section. On further swelling, the section rounds off and the major axis of the ellipse is at least 25 30 % greater than the hair width of the corresponding collapsed hair. The cellulose of the wall swells inwards until the lumen is practically eliminated. These changes are shown in the following figure (Fig. 46, 1–5). When the hair is transferred to water and well washed, shrinkage begins (stage 6), and on drying at room temperature a further and final shrinkage occurs (stage 7). During the last three stages, the hair retains the same form of section, but shrinkage proceeds uniformly towards the centre and the lumen does not recover its original size.

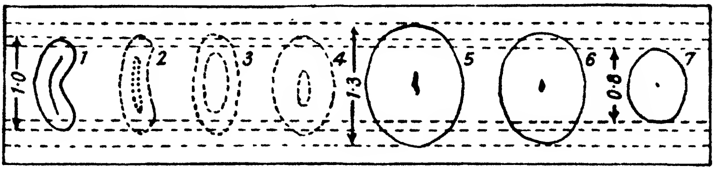


FIG. 46.—Changes in section of cotton hair during mercerising.

The distribution of hair width was different at each of the last three stages from that in the collapsed sample—see Fig. 47.

Hair-width Ratio

The ratio of the mean mercerised to the mean collapsed hair width of four cottons is shown below and illustrated in Fig. 48.

RATIO OF MERCERISED TO COLLAPSED HAIR WIDTH.

Cotton.	Ratio.
Sea Island	0·83
Jannovitch	0·82
American	0·80
Peruvian F.R.	0·81

The closeness of this ratio led to the examination of thirty-eight cottons, from which it was established that the ratio for the whole series varied from 0·77 to 0·89, the mean being 0·82, although for three cottons alone the ratio was as large as 0·87. There appears to be a striking tendency for the ratio to approach a standard value. It is also clear that the hair width of the collapsed hair cannot form an accurate standard on which to base percentage changes in diameter. The mercerised hair width, however, does form such a standard.

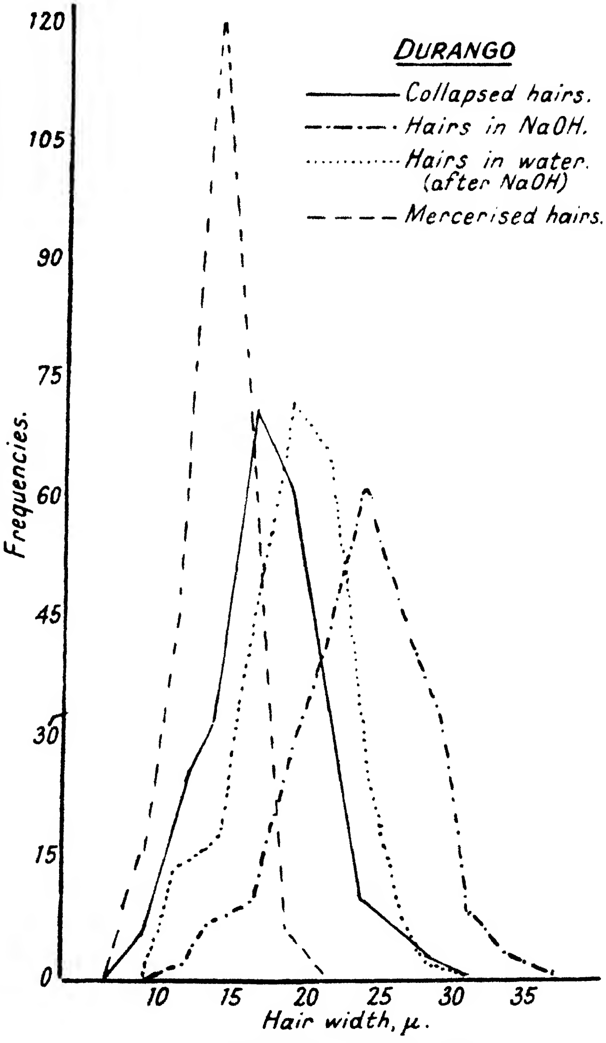


FIG. 47.—Distribution of hair width.

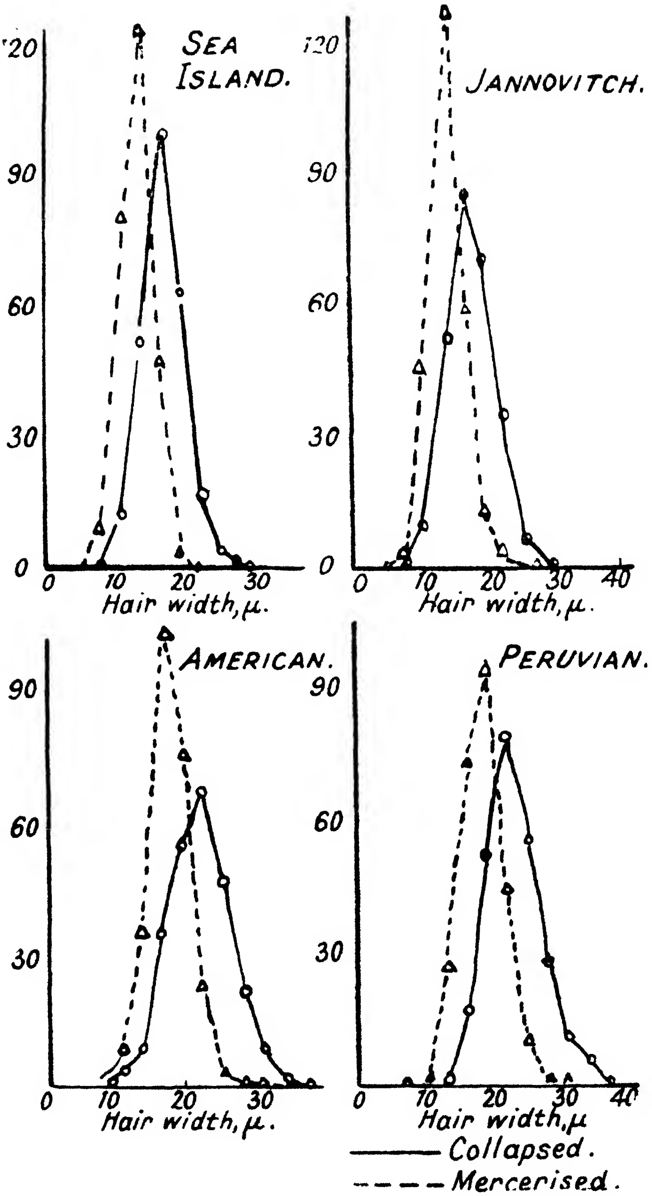


FIG. 48.—Distribution of hair width for four widely differing cottons.

A comparison was made of the hair width changes during mercerisation of eleven typical cottons.

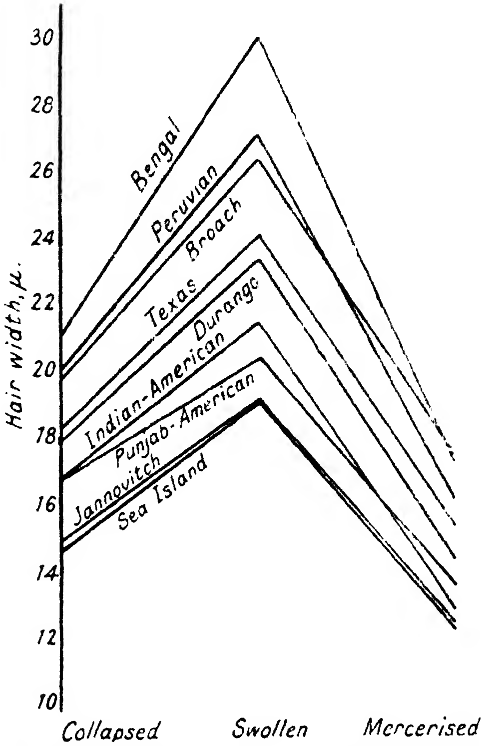


FIG. 49.—Regularity of swelling process as shown by different cottons.

HAIR WIDTHS.

Cotton.	Mean hair width (μ)				Hair width ratio			
	Col-lapsed	NaOH 18%	Water	Dried	Col-lapsed	NaOH 18%	Water	Dried
Sea Island . .	14·75	10·98	16·32	12·12	1·00	1·00	1·00	1·00
Sakel . . .	14·16	19·19	16·75	11·62	0·97	1·01	1·02	0·96
Jannovitch . .	14·86	19·01	16·82	12·24	1·02	1·00	1·03	1·01
Punjab-American .	16·64	20·47	18·07	13·49	1·14	1·08	1·10	1·11
Indian-American .	16·75	21·48	18·86	12·78	1·15	1·13	1·15	1·05
Durango (annual) .	17·61	23·98	19·84	14·00	1·21	1·26	1·21	1·15
Durango (ratooned)	17·86	23·35	19·98	14·29	1·22	1·23	1·22	1·18
Texas . . .	18·18	24·02	21·47	15·24	1·25	1 27	1·31	1·25
Peruvian F.R. .	19·92	27·17	22·83	16·06	1·36	1·43	1·32	1·32
Broach . . .	19·66	26·46	24·36	17·42	1·35	1·39	1·49	1·44
Bengal . . .	20·93	30·07	25·29	17·27	1·44	1·58	1·55	1·43

In the last four columns, advantage is taken of the regularity of Sea Island cotton to express the mean hair widths of the remaining ten varieties, at each of the four stages of swelling, as multiples of the corresponding Sea Island hair width.

The data of the above table are reproduced in Fig. 49. It would appear, therefore, that consideration of all the data for the special case of swelling in sodium hydroxide solution of 40° Tw. (18·0 %) points to the swelling of the cotton hair and its subsequent shrinkage during the mercerisation process as perfectly regular.

Concentration of NaOH

These conclusions were based on the assumption that the hair width is at a maximum in 40° Tw. (18·0 %) NaOH. The assumption appears to be justified in view of the work of Collins and Williams (page 59), but in view of the relatively small number of hairs examined and the unsatisfactory nature of the collapsed hair as a basis of reference, Calvert and Summers decided to confirm this point. This appeared to them to be all the more necessary in view of the fact that Willow, Barratt and Parker (page 53) when investigating changes in length found these to behave in an anomalous fashion between 22° Tw. (9·9 %) and 85° Tw. (39·2 %).

The curve obtained for the relation of percentage decrease in length to concentration of alkali showed minima at 30° Tw. (13·5 %) and at 55° Tw. (24·8 %) with an intermediate maximum at 40° Tw. (18·0 %). It was obviously important that the question of such maxima and minima for width changes should be investigated. It is difficult to understand these anomalies unless there should be some secondary complication at 40° Tw. There is, however, the complication of the cuticle as shown by Willows and Alexander (page 58).

Calvert and Summers established that in NaOH of 40° Tw. the cellulose is capable of swelling to a greater degree than is possible when surrounded by the cuticle. This was observed with hairs taken direct from the boll when they were placed under the microscope and a slight cut made in the cuticle both before and after irrigation with 40° Tw. NaOH. In both cases extrusion of the cellulose occurred showing the existence of tension within the cuticle, as observed by Willows and Alexander.

Examination of change in width of 250 hairs in various solutions of NaOH (one hair—one solution) failed to reveal any significant difference from 35° Tw. onwards, however.

A limiting factor is apparently introduced near 35° Tw. which prevents further swelling beyond this point.

Evidence from the work of Collins and Williams (page 59) confirms that the form of the upper curve of the above figure correctly represents changes in hair width. It should be the characteristic curve for all varieties of cotton if the swelling powers of the cellulose and the elastic properties of the cuticle are the same throughout. Quantitatively, the position is different owing to variations in the cottons, more especially in respect of hair width and wall thickness. The following table shows the percentage changes in hair width, reckoned on the collapsed hair width, of the same cottons mentioned on page 79, when immersed in 40° Tw. NaOH.

CHANGE IN HAIR WIDTH.

Cotton.	Increase in hair width. %
Punjab-American	24
Jannovitch	28
Indian-American	28
Sea Island	30
Durango (ratooned)	31
Texas	32
Sakel	35
Broach	35
Durango (annual)	36
Peruvian F.R.	36
Bengal	43

As all these cottons behave similarly while swelling and on shrinking in water and air, the swelling curves of the lowest ten may be diagrammatically represented in Fig. 50, and the absence of minima at 30° Tw. (13·5%) and 55° Tw. (24·8%) regarded as established. This is supported by the fact that Collins and Williams (J.T.I., 1924, *15*, 149) obtained a similar curve for KOH.

The qualitative observations of Hübner and Pope (J.S.C.I., 1904, *23*, 404) have been combined with the observations of Calvert and Summers and incorporated in Fig. 50 by these authors.

From 0 to 15° Tw. (6·75%) the increase in hair width is entirely due to the change of cross section from the bean shape to elliptical. No measurable swelling of the wall takes place nor is the change sufficient to remove all the convolutions. Between 15 and 20° Tw. (9·0 %) the wall thickness increases and the occurrence of some inward swelling slows down the rate of increase in hair width. These two interacting phenomena proceed until about 25° Tw. (11·3 %), when the hairs are fully swollen in so far as elimination of the lumen is concerned. At this point the cuticle is not fully extended, for additional swelling outwards takes place in more concentrated solutions until maximum swelling occurs at about 30° Tw. (13·5 %).

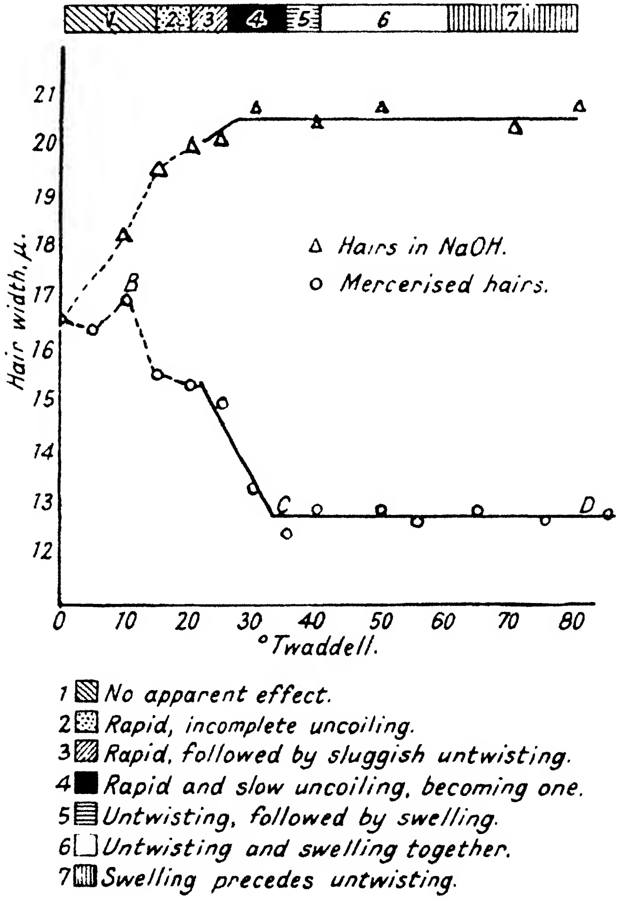


FIG. 50.—Changes in cotton hairs immersed in NaOH solutions.

In the higher concentrations of NaOH there is no difference to be remarked, except the increasing slowness of penetration as emphasised by Hübner and Pope. The bursting of hairs observed by the latter is regarded as an accidental occurrence by Calvert and Summers, who found this to be the invariable sign of a damaged cuticle.

The lower or mercerised curve of Fig. 50, received the following interpretation: Between 35 and 85° Tw. the hairs in the swollen condition are quite uniform in section, i.e. they have swollen inwards as much as possible and have almost eliminated the lumen, whilst in the outward direction the cuticle is fully extended. The remarkable feature is that whereas the cuticle has reached its limit of extension, under pressure from the contained cellulose which would continue to swell if possible, yet it is able to follow the cellulose in its uniform shrinkage towards the lumen which remains unaltered in size after once being reduced.

Between 5° Tw. (2·5 %) and 25° Tw. (11·3 %) the presence of a lumen in the swollen hairs leads to the shrinkage being combined with collapse or flattening of the section so that the measured hair width is artificially enlarged. The interaction of shrinkage and collapse begins near the turning point in the curve, probably close to 30° Tw., where the section in the swollen condition has assumed the maximum thickness of cell wall and minimum lumen. This is the point where Hübner and Pope report the first disappearance of twist in the hair. The degree of flattening increases with the size of the lumen in the swollen hair, and as between 20° Tw. (9·0 %) and zero the lumen retains its normal size, the variations in hair width are due to different degrees of unfolding during swelling which give rise to fresh and larger hair widths on shrinkage. The hair width which is generally regarded as a measure of swelling does not become truly so until a concentration of about 30° Tw. is reached, changes below this concentration are merely indications of these form changes.

The introduction of a limiting factor at 30° Tw. (13·5 %) flattens out the swelling curve immediately. Coward and Spencer (page 311) gave a curve of similar form for the relation between the volume of liquid absorbed per 100 g. of cotton and the concentration of the alkali, and this volume is a fair representation of the swelling. The data for length and width changes given by Collins and Williams (page 62), together with the above data, support the deduction that in concentrations of NaOH above 30° Tw., the external hair surface is constant, but Coward and Spencer's work suggests that the total absorbing surface is constant. Consequently there appears little doubt that there is a definite limit at 30° Tw. to the swelling—the limiting factor lying outside the swelling process and being probably imposed by the cuticle.

Morphological Comparisons

There have been some interesting speculations as to the form assumed by the swollen cotton hair. Coward and Spencer (J.T.I., 1923, *14*, 32) suggested that the observed limit of swelling is attained when the fibre, under the action of hydration induced by the alkali, has resumed the dimensions which it possessed while still hydrated in the seed pod. Clegg and Harland (J.T.I., 1924, *15*, 14) stated that by treatment with sodium hydroxide solution of 40° Tw., it is possible to restore the hair to something like its original conformation. In the absence of any direct evidence on this point, it was investigated by Calvert and Summers (J.T.I., 1925, *16*, 233), using the different cottons available from the greenhouse of the Shirley Institute (B.C.I.R.A.). The ripe boll was broken open, part of the contents immediately placed in water, part in sodium hydroxide solution and part allowed to dry. In order to obtain the hair width of the uncollapsed hair, an examination was made without removing the material from the liquid. The hairs which were allowed to dry were later swollen with NaOH solution and the hair width measured.

Some of the results are shown below:

MEAN HAIR WIDTHS (μ).

Cotton.	Uncollapsed.	Uncollapsed in 40° Tw. NaOH.	Collapsed.	Collapsed in 40° Tw. NaOH.	Mercerised.
Sea Island .	15·6	16·2		16·8	
Egyptian .	21·2	22·2	19·3	22·9	15·3
American .	21·9	21·5	17·5	21·7	13·6
Indian . .	21·8	21·6		22·3	

The agreement appears to be sufficiently close to justify the conclusion that dimensional change in transverse section is negligible and the cuticle does set a limit to swelling. The complete assumption about dimensions, however, is not borne out by observations in respect of length.

The following data refer to the mean length obtained from a random sample of 200 hairs, expressed as percentages of the original uncollapsed length in the boll.

HAIR LENGTHS.

Percentage of uncollapsed hair length.

Cotton.	Uncollapsed.	Collapsed.	Collapsed in NaOH.
Sea Island . . .	100	95	75
Indian	100	90	80
Upland	100	99	80
Egyptian . . .	100	88	70

The swelling of the cellulose in the collapsed hair is more than is necessary to restore the original wall thickness, for at no stage of development is the lumen filled to the extent shown in the swollen hair, although the hair width of the uncollapsed hair remains unchanged in NaOH, yet the wall thickness is changed by swelling of the cellulose to fill the lumen.

Inward swelling and longitudinal contraction proceed simultaneously and their resultant controls hair width. At the narrower hair widths, inward swelling fills the lumen and then proceeds to eliminate the numerous irregularities, but at the wider places the cellulose wall is unable to fill the lumen by swelling alone ; contraction in length combined with inward swelling produces a resultant pull on the wider intermediate portion, which tends to decrease the external width until swelling equilibrium is reached.

If the cuticle is injured, however, tension is relaxed and there may be local and very great increases in hair width, often greater than the original semi-perimeter of the uncollapsed hair.

Calvert and Summers point out that it is difficult to imagine that the elastic properties of the cuticle, which are imperfect during swelling, should be perfect during contraction, so that in the latter process there is likely to be some degree of folding or wrinkling, in which case the behaviour of the cuticle is based more on structural characteristics than physical properties. Microscopic examination has shown the presence of striations, which are flat spirals formed by elevated bands alternating with depressions. During swelling, the cellulose of the hair presses outwards against the cuticle and the spiral bands open somewhat and approach more closely owing to the longitudinal contraction, causing the cuticular depressions also to contract. After this point, through washing to drying, contraction in length is inconsiderable, but the perimeter of the section shrinks about 33%, and it is suggested that this may be due to the cuticle following the shrinkage of the cellulose by a coiling of the spiral bands, which is sufficiently intense to eliminate the depressions. This theory would account for the presence of the oblique striations so frequently observed on the surface of mercerised hairs.

(N.B.—The statement that 40° Tw. NaOH solution is equivalent to 18% NaOH is in keeping with modern practice; more precisely, of course, it is the density of 17·81% NaOH solution.)

CHAPTER SEVEN

FREE AND RESTRICTED SHRINKAGE

CALVERT (J.T.I., 1930, *21*, 293) investigated the shrinkage of single cotton hairs under a wider range of conditions than those previously described. The data are not related to those of Collins and Williams (page 59), where hairs were given successive treatments with alkali solutions of increasing or decreasing concentration, but rather to the work of Willows, Barratt and Parker on the basis of one hair—one solution. The apparatus employed resembled that used by the above-mentioned authors, except that a "chainometric" arrangement replaced the electro-magnetic method of Barratt (J.T.I., 1922, *13*, 17).

The cotton hairs were examined under various conditions, and included raw hairs, scoured hairs (six hours in 1 % NaOH solution at 20 lbs. pressure), extracted hairs and also raw hairs which had been subjected to friction with emery paper until staining with Congo Red (J.T.I.,1926, *17*, 396) showed partial or complete stripping of the cuticle. The conditions of measurement comprise shrinkage under no load, i.e. free shrinkage, shrinkage under loads applied after free shrinkage, and restricted shrinkage where the load was maintained throughout the shrinkage.

Whilst the free shrinkage measurement relates to the unrestricted contraction of the cotton hair, the actual measurement was made under a small load applied subsequently in order to straighten the hair, but from a number of observations under small but different tensions it was possible to determine by extrapolation the free shrinkage under no load. It is also important to realise the difference between the free shrinkage under, say, a 10 mg. load, and the restricted shrinkage under the same load. In the former case there was no restriction on the shrinkage, but measurement was made under a 10 mg. load, whereas in the latter case the shrinkage took place against a 10 mg. load and the measurement was made under the same load.

Free Shrinkage

Fig. 51 shows the free shrinkage of two sets of cotton hairs under no load, the full curve refers to Egyptian Sakel which had been scoured, whilst the dotted curve relates to another Egyptian cotton taken direct from the seed and scoured. There is a maximum well-marked shrinkage at 13·3 % NaOH, but the shrinkage is less in the case of the second type of cotton.

Curves are also given for free shrinkage of the first cotton measured under various loads (Fig. 52*a*), from which it will be seen that the maximum shrinkage becomes less pronounced as the load increases and the addition of a load has least effect in the most concentrated solution. Further work by Calvert showed that the rate of loading does not greatly affect the final shrinkage.

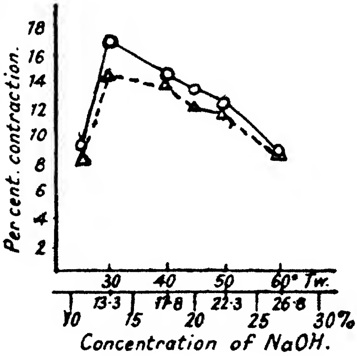


FIG 51.—Free shrinkage of two types of scoured cotton.

The shrinkage of two cottons under no load is compared in Fig. 54, where the full curve refers to raw cotton hairs and the dotted curve to the same material after alkali boiling. The shrinkage of the raw hairs is much less than that of the scoured hairs in the region of maximum swelling concentration and the maximum swelling at that point for scoured hairs is not present in the curve for the raw hairs.

The pronounced difference in shrinkage under no load between raw and scoured hairs is a most important feature.

The free shrinkage curves for raw cotton measured under various loads is shown in Fig. 52*b*; there is a gradual flattening of the curve as the load is increased, as in the case of the scoured hairs in Fig. 52*a*.

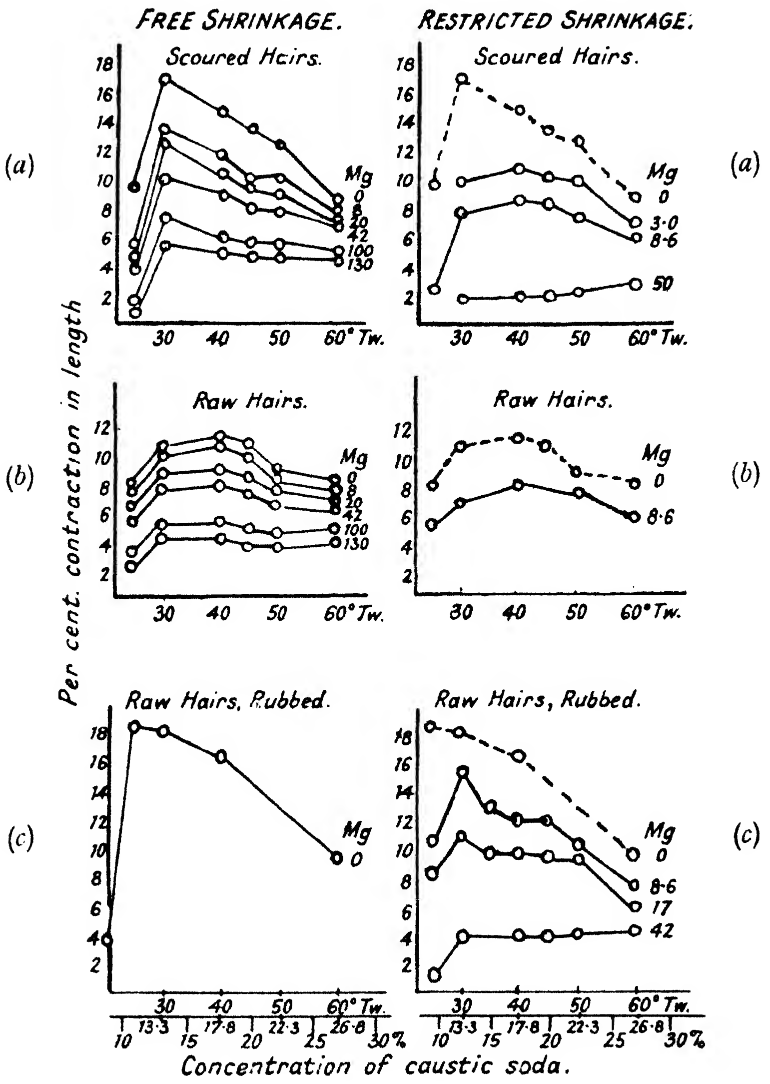


Fig. 52. Fig. 53.

Free and restricted shrinkages of scoured, raw and rubbed hairs.

Restricted Shrinkage

Restricted shrinkage curves were obtained by allowing the hairs to shrink against a constant load and measuring the change in length under the same load. Fig. 53*a* shows the restricted shrinkage curve for scoured cotton under various loads, whilst the dotted curve gives the free shrinkage under no load, for purposes of comparison. The restricted shrinkage curves naturally fall below the curve for free shrinkage under no load, but it is very remarkable that, if free shrinkage is not allowed, a load of 3 mg. per hair is capable of removing the characteristic peak. It is also interesting that the curves are similar in form to those for free shrinkage of raw hairs (Fig. 52*b*).

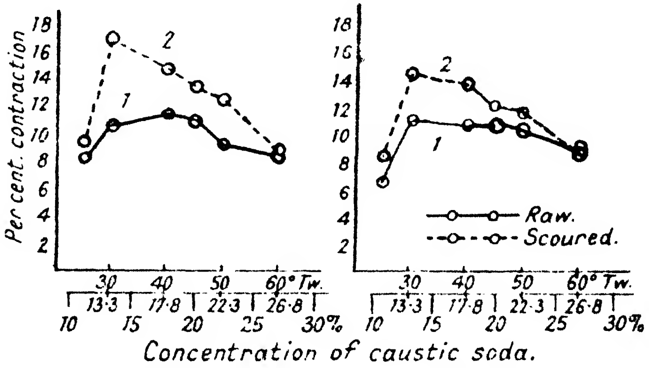


FIG. 54. FIG. 55.
Free shrinkage of two different cottons, raw and scoured, under no load.

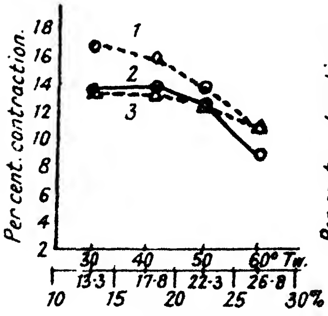


FIG. 56.
Restricted shrinkage and free shrinkage.

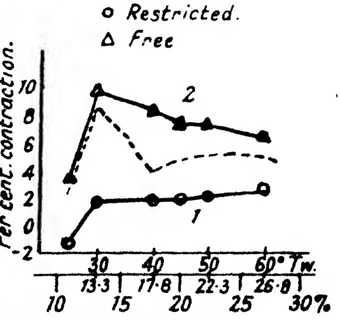
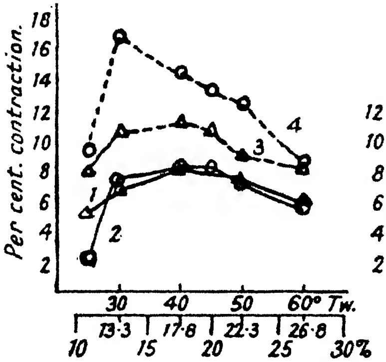


FIG. 57.
Free and restricted shrinkage under 50 mg. load.

Fig. 56, curve *2*, shows the restricted shrinkage of scoured cotton under a load of 3 mg. compared with no load in curve *1*. The shrinkage of the former is approximately constant over a range of concentrations from 13·3 to 22·3% NaOH, and the shrinkage values, except in 26·8% solution, are identical with those for free shrinkage of raw hairs under no load in curve *3*.

There is obviously a great difference between the restricted shrinkage under a load and the free shrinkage measured under the same load. This is clearly illustrated by Calvert in Fig. 57, where observations are recorded on scoured cotton with a load of 50 mg. The dotted curve is taken from the work of Willows, Barratt and Parker (page 53), who used 50 mg. under conditions of restricted shrinkage.



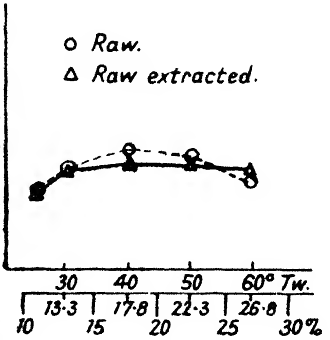


FIG. 58.
Free and restricted shrinkage of raw and scoured hairs.

FIG. 59.
Restricted shrinkage (8.6 mg.) of raw and extracted hairs.

It is well known that the tension necessary to prevent the shrinkage of cotton yarns and fabrics in caustic soda is much less than that necessary to restore the original dimensions where shrinkage has once been permitted, and the similar behaviour in the case of the cotton hair is illustrated in Fig. 57. For example, in 13·3% NaOH solution, a load of 50 mg. only allows 2% shrinkage, but if the hairs have been allowed to shrink in the same concentration of alkali, a load of 50 mg. results in a final contraction of 10%. (See also page 101.)

Fig. 58, curve *1*, shows the restricted shrinkage of the raw cotton and curve *2* of the scoured cotton under a load of 8·6 mg., whilst curves *3* and *4* in broken line are the curves for the raw and scoured cottons under no load. It would appear that there is some restriction which is present in the case of raw hairs, but from which scoured hairs are free, which has the same effect on their behaviour as the direct application of a load on the behaviour of scoured hairs.

Fig. 59 shows the curve for restricted shrinkage under a load of 8·6 mg. of a raw cotton after extraction with chloroform. The curve for the same cotton before extraction is shown by the broken line—shrinkage is not increased by the removal of wax. Calvert also examined the effect of the severity of the scour, and found that water-boiled hairs showed a shrinkage as high as that given by hairs from yarn boiled under pressure in alkaline liquor.

Effect of the Cuticle

Some of the most interesting data are concerned with the shrinkage of " rubbed " hairs, which had been so treated with emery paper that subsequent staining with Congo Red showed that the cuticle was partially or completely stripped. The free shrinkage under no load of the raw hairs after rubbing is shown in Fig. 52*c* and in Fig. 60, curve *1*, while curve *2* shows the free shrinkage of the raw hairs before rubbing, and curve *3* the free shrinkage of scoured hairs.

This mechanical treatment has exercised a great effect on the behaviour of the raw hairs, the shrinkage in 13·3% NaOH is almost doubled and is more than doubled in concentrations of 11·1% NaOH. The maximum, which occurs at 13·3% NaOH for the scoured hairs, is nearer 11·1% for the mechanically treated raw hairs.

Fig. 53*c* shows the restricted shrinkage curves of the rubbed hairs under various loads ; here, as in the case of the scoured hairs, the effect of a load of 8·6 mg. is remarkable, the peak at 11·1% being entirely removed, and the curve is similar in form to the curve for free shrinkage of scoured hairs under no load as in Fig. 52*a*. The restricted shrinkage of rubbed hairs under a small load is comparable with the free shrinkage of scoured hairs under no load, whilst the restricted shrinkage of scoured hairs under a small load is comparable with the free shrinkage of raw hairs under no load. These observations support the view that there is some structural resistance imposed on the shrinkage of raw hairs which is also present to some extent with scoured hairs, although they are freer than the raw hairs. It is natural to assume that this restraint is imposed by the cuticle, particularly in view of the work of Willows and Alexander (J.T.I., 1922, *13*, 238) as mentioned on page 58.

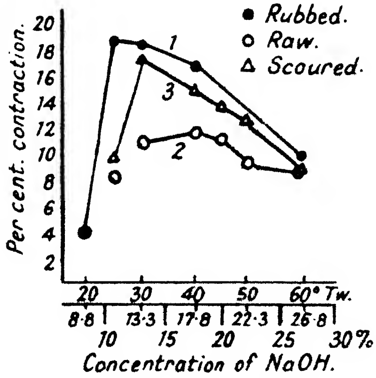


FIG. 60.—Free shrinkage of rubbed, raw and scoured hairs.

The action of the cuticle has also been examined and demonstrated by Calvert and Summers (J.T.I., 1925, *16*, 233), and comments upon its restrictive action have been made by Coward and Spencer (*ibid.*, 1923, *14*, 32) and by Collins and Williams (*ibid.*, 287) as mentioned on page 62.

Calvert has also examined the changes in width of raw, scoured and rubbed cotton hairs. The results for two different cottons are plotted below.

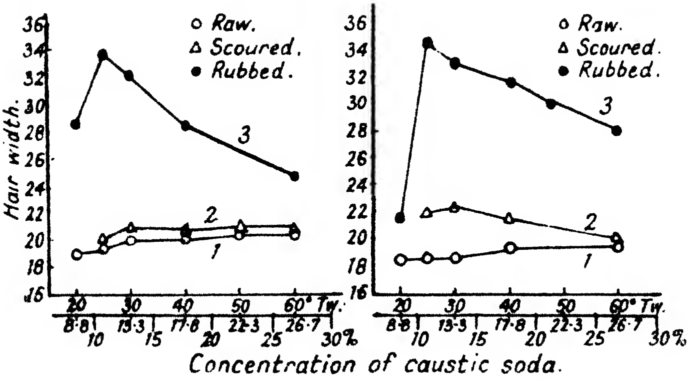


FIG. 61. FIG. 62.

Hair widths of two different cottons.

The curve relating to the width of the rubbed hairs again shows a maximum at 11·1% NaOH, and also in all concentrations a great increase in width over that of the untreated and of the scoured hairs in the same concentration of NaOH. Hence there is every indication that both for change in width and in shrinkage, the behaviour of the hair is greatly influenced by mechanical treatment, which removes the restriction to swelling normally present and probably in the form of the cuticle. The observation of Nodder and Kinkead (J.T.I., 1923, *14*, 133) that bast fibres, devoid of cuticle, exhibit maximum swelling in a concentration of NaOH lying between 8·8% and 11·1%, helps to confirm this point. (See page 65.)

General

The data of Calvert on the free and restricted shrinkage of cotton hairs are of interest in connection with an observation of Coward and Spencer (J.T.I., 1923, *14*, 32) that there is a great difference in the volume of liquid absorbed by fibre and by fabric as shown in Fig. 197, page 312.

This difference was not attributable to any difficulty in wetting of the yarn, which was found to be well penetrated on examination under the microscope. The conclusion is that in a fabric there is a considerable mechanical resistance to the swelling of its individual hairs. This agrees with the general possibility of obtaining better results in technical practice by mercerising yarn rather than cloth. (See also page 47.)

Further, the difficulties encountered in works' practice in dealing with fabrics containing hard twisted yarn is not entirely due to difficulties of penetration, but also to the impossibility of obtaining full swelling of the fibres in such a yarn. The production of a high lustre in cloths containing soft twisted yarn involves other factors as the swelling is less limited, but there is a greater possiblity of hair slippage when tension is applied during the mercerising process and the consequent derangement of the hairs in the dried cloth contributes to loss of lustre.

PART THREE

THE MERCERISING PROCESS

CHAPTER EIGHT

YARN MERCERISING

THE first authoritative information on the mercerisation of cotton yarn is due to Herbig and was published in Gardner's book "Die Mercerisation der Baumwolle" (Berlin; 1898). A table of results is given on page 99, from which it appears that mercerisation starts at 10° Bé. (15° Tw.) and increases up to 35° Bé. (64° Tw.), but any further increase of the mercerising action is relatively slight between 30 and 40° Bé. (52 to 76° Tw.). It also appears that the temperature should not exceed 15 to 20° C., and that, if good penetration is assumed, the factor of time within the stated limits is of less importance at the higher concentrations of alkali.

The experimental range was not great and some of the conclusions are open to revision; for example, it is now accepted that the onset of mercerisation takes place in 20° Tw. NaOH solution (13° Bé. or 8·78% NaOH), as shown by fibre measurements, X-ray evidence and deconvolution. Mercer mentioned 20° Tw. NaOH in his patent specification.

Shrinkage

A more important point, however, is that at which the maximum contraction takes place, and this was first observed by the examination of cotton yarns on treatment with various strengths of alkaline liquor. Many investigators found a maximum contraction in the region of 20% NaOH solution (45° Tw. or 26·5° Bé.) at room temperatures. The changes in length of yarns are not a reliable measure of the mercerising effect, as a great deal must depend on the structure of the yarn; in addition, the changes observed in yarns are the resultants of the changes in the length and thickness of the cotton hairs complicated by slipping or other forms of rearrangement during the mercerising process. Nevertheless, the concentration at which the maximum change occurs is of greater importance than the extent of that change, which in certain circumstances may be very great indeed. Shrinkage effects have been recorded by Lindemann (Dissertation, Dresden, 1909), Krais (Z. angew. Chem., 1912, *25*, 2649), Kirchbacher (*ibid.*, 1910, *23*, 2269), and Ristenpart (Farb. Zeit., 1912, *23*, 93).

The work of Hübner and Pope (J.S.C.I., 1904, *23*, 404) is of particular interest in this connection, for in addition to measuring the extent of the shrinkage of a bleached two-fold yarn in various concentration of alkali they made an estimate of dyestuff affinity as shown in Fig. 63.

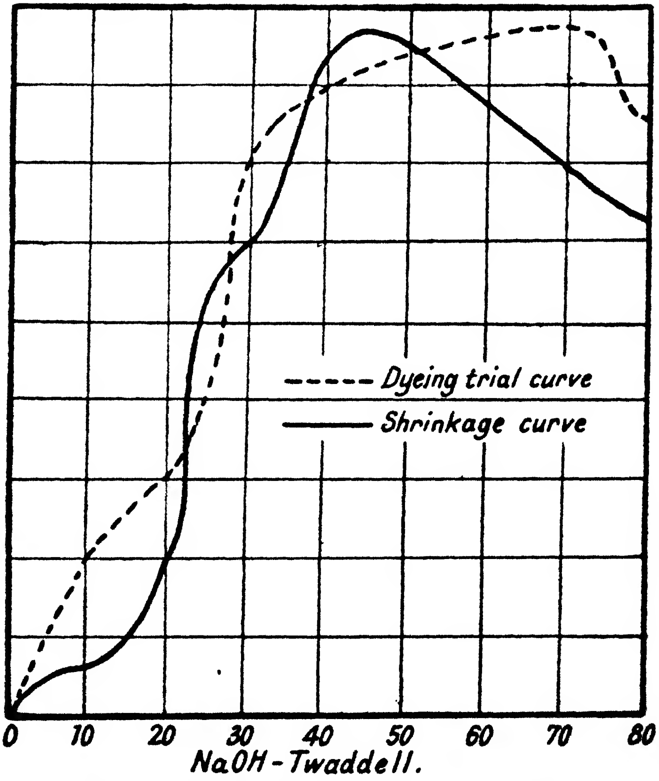


FIG. 63.—Shrinkage of cotton yarn in NaOH.

The results of Knecht and Harrison (J.S.D.C., 1912, *28*, 224) are also of importance, for they observed a reversal of the shrinkage effect with temperature; solutions containing 25% NaOH and less produce a greater contraction at room temperatures than at 80° C., but the reverse effect is stated to occur with solutions containing 50% NaOH.

Contraction Per Cent. of Cotton Yarns on Mercerisation

Temp. ° C.	Density of Sodium Hydroxide Solution														
	10° Bé. 6·5 per cent.			15° Bé. 10 per cent.			25° Bé. 19 per cent.			30° Bé. 24 per cent.			35° Bé. 29 per cent.		
	Duration of Mercerising in Minutes														
	1	10	30	1	10	30	1	10	30	1	10	30	1	10	30
2	1	1	1	12·2	15·2	16·8	19·2	20·1	21·5	22·7	22·7	23·5	23·5	23·0	23·0
18	0	0	0	8	8·8	11·8	19·2	20·1	21·1	22·5	22·5	22·5	23·5	23·0	21·0
30	0	0	0	4·6	4·6	6·0	19·2	20·3	19·0	19·8	19·8	19·8	20·7	20·5	20·1
80	0	0	0	3·5	3·7	3·8	13·7	14·2	15·5	15·5	15·5	15·5	15·5	15·5	15·4

Tension

The above results refer to the mercerisation of yarn in the free state, i.e. without tension, and in these conditions there is no improvement in lustre. Most cotton yarn is mercerised to increase the lustre—it is mercerised under tension. The effect of various amounts of tension has naturally received a great deal of attention in the literature, and Herbig's results may be summarised as follows :

1. Mercerisation without tension gives no lustre, while even a small amount of tension gives some increase in lustre.
2. Maximum lustre is obtained when the tension is sufficient to bring the material back to its original length and any increase in tension above this does not increase the lustre further.
3. The lustre obtained by impregnating and washing under tension is the same as impregnating loose and washing under tension, but more force is required in the second case.
4. The lustre obtained by impregnating and washing loose and then stretching is much inferior, and the tension required is very great.
5. Yarn made of long-staple cotton produces the highest lustre.

The effect of tension has also been examined by many other investigators ; Skinkle and Hale (A.D.R., 1931, *20*, 547) established that the amount of tension exerts a considerable effect on the rate of absorption of the alkali and also on the rate of its removal. There appears to be no advantage in a higher degree of tension than is necessary to restore the original length of the yarn in so far as strength and absorptive properties are concerned.

Schramek (Leipz. Monat. Text. Ind., 1934, *49*, 257) has given some interesting data on the variation in lustre with the extent of stretching cotton hairs in 15 % NaOH solution ; the stretched length of the unmercerised fibre was 14·8 mm. and the total shrinkage in the alkali was 2·65 mm.

LUSTRE AND STRETCHING.

Stretching as % of shrinkage.	Lustre No.
0%	4·3
40%	5·7
70%	6·5
100%	7·8
Lustre of raw hair	3·5

Most modern mercerising processes allow the material to shrink in the alkali, in order to assist thorough penetration, and then apply the tension later, either before or during the removal of the caustic soda. The forces required in the various methods are not the same ; Herbig (loc. cit.) has stated that the yarn can be maintained at its original length in alkali by a third to a quarter of the force required to restore the original length even when the shrunk material still contains the mercerising liquor. Willows, Barratt and Parker (J.T.I., 1922, *13*, 229) observed that a force of 0·16 g. was necessary to maintain the length of a cotton hair during mercerising, but that 0·32 g. was necessary to restore the length after contraction. Herbig also noticed that the smallest force is required to stretch the shrunk yarn when the rinsing or washing is actually in progress ; the restoration of the original length of the fully washed material requires twice the force necessary for yarn still in contact with the alkali.

Measurements of the contractive force have often been made and vary with the twist of the yarn, but the following results of Edelstein (A.D.R., 1936, *25*, 458) are of interest as showing the variation of the contractive force on a particular yarn (see page 115) with the concentration of the NaOH solution. The results broadly confirm those of other workers.

CONCENTRATION AND CONTRACTION.

Concentration of mercerising liquor, deg. Tw.	Force to prevent shrinkage, in lbs.
10·3	0·0
15·0	0·0
21·8	2·5
25·5	15·0
30·5	22·5
35·5	24·0
39·0	25·0
45·0	27·5
52·5	32·5
55·5	37·5
60·0	40·0
65·0	40·0
70·0	42·5
80·0	42·5

It is often assumed that the maximum contractive tendency shows the conditions for optimum lustre, which is impaired, for example, by the presence in the alkaline liquor of alcohol or inorganic salts, which restrict shrinkage. However, this relation between shrinkage and lustre has been questioned by various observers, such as Beltzer (R.G.M.C., 1902, *6*, 25), Hübner and Pope (J.S.C.I., 1904, *23*, 404) and Knecht and Harrison (J.S.D.C., 1912, *28*, 224)—the two latter observed that in the case of 16 *N* KOH heating to 80° C. decreased the shrinkage and increased the lustre. (This is different from the effect of NaOH where increasing the temperature reduces the lustre.) Mecheels (Textilber., 1932, *13*, 645) has suggested that rate of shrinkage is more important than total shrinkage in determining lustre, i.e. the improvement in lustre on mercerising under tension is related to the velocity of shrinkage rather than to the total tendency to shrink in the alkali.

Langer (Textilber., 1934, *15*, 165) made a series of determinations on 2/40s cotton yarn which had been hank-mercerised under various conditions of tension. Two series of experiments were done; in one series the yarn was boiled under pressure and then mercerised, in the second the grey yarn was mercerised in caustic soda containing Mercerol. The original length of the hank was 137 cms. and the tension was graded to produce various mercerising lengths from 132–141 cms. in one cm. stages.

2/40s. PRESSURE BOILED AND MERCERISED.

Hank circumference.	Breaking load.			Extension.		Reduction.
	Grey.	Mercerised.	Increase.	Grey.	Mercerised.	
	g.	g.	%	%	%	%
132	404	586	45	6·4	6·1	5
133	386	572	48	6·2	6·1	2
134	401	560	40	6·4	5·9	8
135	412	566	37	6·4	5·7	11
136	396	560	41	6·1	5·2	15
137	401	577	44	6·3	4·9	22
138	405	545	35	6·3	4·8	24
139	388	569	47	6·1	4·5	26
140	407	560	38	6·6	4·3	35
141	383	553	44	6·0	3·9	35

2/40s. Mercerised With NaOH and Mercerol.

Hank circumference.	Breaking load.			Extension.		Difference.
	Grey.	Mercerised.	Increase.	Grey.	Mercerised.	
	g.	g.	%	%	%	%
132	384	537	40	6·5	6·8	+ 5
133	423	560	32	6·1	6·4	+ 5
134	411	554	35	5·8	6·2	+ 7
135	384	563	47	5·6	5·8	+ 4
136	392	543	39	6·0	5·6	− 7
137	374	537	44	6·4	5·2	− 9
138	381	531	39	6·6	5·1	−23
139	365	521	43	6·1	4·6	−25
140	359	525	46	5·8	4·5	−22
141	338	515	52	5·8	4·3	−26

Langer (*ibid.*, 1935, *16*, 507) also measured the breaking load of fibres taken from these yarns, and the results expressed as a percentage increase in strength on the breaking load of the original fibre are given in the following table :

Increase in Hair Strength.

Hank circumference.	Scoured and mercerised.	Mercerised in NaOH and Mercerol.
cm.	%	%
132	28·9	33·4
133	44·8	31·2
134	47·3	41·0
135	44·8	42·4
136	35·2	40·1
137	28·0	29·1
138	24·2	28·5
139	20·9	21·1
140	30·5	26·5
141	43·5	24·4

The increase in fibre strength of the scoured and mercerised material was 34·8 % compared with 31·8 % in the case of fibres from yarns mercerised in caustic soda containing Mercerol.

The fibre length was also examined ; yarns which were scoured and mercerised gave a contraction of 1·4 % in fibre length when minimum tension was exercised on the yarn, compared with 3·9% extension under maximum tension. Comparative figures for fibres from yarns treated with Mercerol were 2·9% contraction and 1·9% extension respectively.

The fineness of the fibres also showed a difference. In the case of minimum tension there was 2·8% increase in thickness, compared with a 8·4% decrease in thickness for maximum tension ; the corresponding figures for fibres from the yarn in the mercerised experiments were + 2·6 and — 8·2% for minimum and maximum tensions.

Midgley (Textile World, 1937, *87*, 1382) examined some 2/40s yarn before and after mercerising according to commercial practice and found that the fibre diameter had increased by 4%, but that the yarn diameter had decreased by 18%, in agreement with an observation previously recorded by Lowe (J.S.D.C., 1921, *37*, 296). This means that in so far as covering power is concerned, yarn of 2/60s count is equivalent to mercerised yarn of 2/40s count.

From these data it appears that the increase in strength of mercerised yarn is due to an increase in strength in individual cotton hairs and increased cohesion between them ; the closer embedding of the hairs in the yarn not only increases the strength of that yarn but makes it more uniform in strength and less in diameter.

Temperature

As previously stated (page 11) one of the effects of a reduction in temperature of the alkaline liquor is that the mercerising action takes place with lower concentrations of NaOH, but there appears to be no advantage in this method. The best effects are obtained with the solutions of usual concentration at room temperatures ; as the temperature increases the mercerising effect diminishes in the case of NaOH. This has been shown by Beltzer (R.G.M.C., 1902, *6*, 25 and 34) and is illustrated in Fig. 64, from which is also observed a characteristic change in passing from 15° Bé. to 25° Bé. NaOH (23 to 42° Tw.).

Although the lowering of the temperature of the caustic soda solution may be beneficial in the case of the lesser concentrations, it is not general practice for the ordinary mercerising concentrations—say 20 to 25% NaOH. The lowering of the temperature to 0° C. has little or no effect on the lustre, the handle is apt to be harsh, and although great shrinkage is obtained in the absence of tension, this is not reflected in the reactivity ratio or absorptive properties as shown by Birtwell, Clibbens, Geake and Ridge (J.T.I., 1930, *21*, 85)—see also page 279.

Special effects due to the use of low temperatures have been described and patented by Heberlein. (See page 134.)

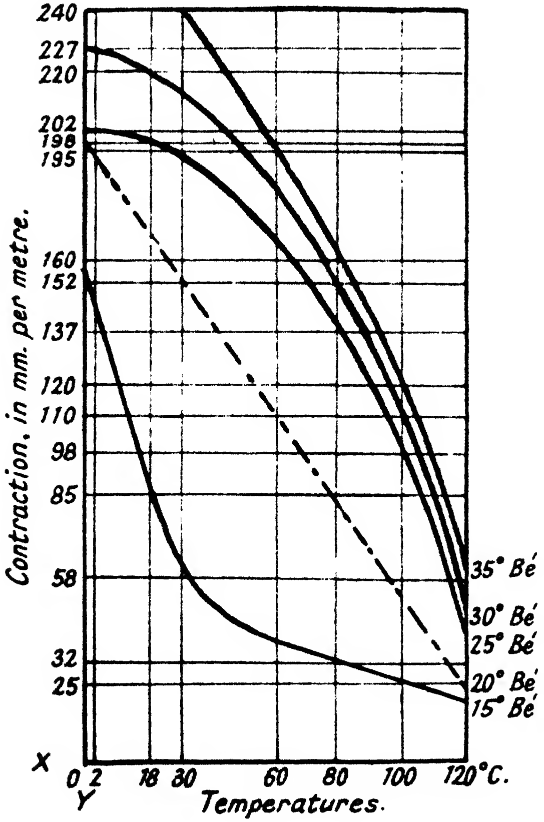


FIG. 64.—Contraction of yarn in NaOH of various concentrations and temperatures.

Cooling, as distinct from refrigeration, is common practice, for although the heat developed in the mercerising of bleached material is not sufficient to warrant special cooling devices, this is not so with grey yarns where the amount of heat developed is considerable, more especially in the mercerisation of grey cloth, where the presence of sizing material produces an additional heat effect. Water-cooling is, therefore, employed to maintain the alkali at room temperatures.

It is common experience that the temperature of the caustic soda solution should not exceed 18° C. and Mecheels (Textilber., 1932, *13*, 645) has given some quantitative results on mercerising at different temperatures with 30° Bé. NaOH solution.

EFFECT OF TEMPERATURE.

(2/100s.)

Temperature.	Lustre No.	Breaking load.	Extension.
7·5° C.	76	302·2 g.	4·11%
17	71	276·6	3·07
30	57	253·5	3·00

(3/30s.)

Temperature.	Lustre No.
18° C.	13
30	12
70	9

The concentration of the alkali was then varied at a constant temperature of 8° C. and the following results were obtained:

EFFECT OF CONCENTRATION AT 8° C.

Concn. of NaOH		Lustre No.	Breaking load.	Extension.
Bé.	Tw.			
16	25	49	247 g.	2·85%
21	34	57	287	2·99
27	45	71	288	3·13
30	52	76	302	4·11
33	59	64	282	2·97
2/100s Egyptian (untreated)		28	229	3·42

The optimum concentration of NaOH appears to lie between 46 and 54° Tw.

A similar set of determinations was made at a temperature of 18° C.

EFFECT OF CONCENTRATION AT 18° C.

Concn.	Lustre No.	Breaking load.	Extension.
15° Bé.	34	229·6 g.	3·08%
20	51	267·7	2·94
27	70	265·9	3·16
30	73	270·8	2·70
33	61	285·2	2·80

Here again the optimum concentration of alkali lies in the range of 46 to 54° Tw., and within this range there is not sufficient improvement in lustre to warrant the cost of refrigeration.

It might be thought that the fact of mercerising with lower concentrations at low temperatures would effect a reduction in the amount of NaOH absorbed by the cotton and so enable economies to be made ; the difference in absorption, however, is not appreciable.

Tensile Strength

The increase in tensile strength of mercerised cotton was first noticed by Mercer, who commented on the sore hands of boys employed to separate pieces of mercerised cloth by tearing ; these goods, of course, were mercerised without tension.

Experience has shown that mercerisation under tension also causes an increase in tensile strength, but there are so many factors to be taken into consideration that most of the data have little comparative value. Even in the case of the cotton hair there is conflicting evidence. Barratt (J.T.I., 1922, *13*, 17) found that when scoured Egyptian cotton hairs were mercerised without tension in 20% NaOH solution there was a decrease in breaking load, which fell from 7·2 g. to 6·7 g. ; the extension at break rose from 7·4% to 12·2%. Greenwood (J.T.I., 1919, *10*, 274) found no conclusive evidence in the case of hairs taken from yarns mercerised both before and after bleaching.

HAIR STRENGTH.

Single hairs from :	Breaking load in grams.	
Grey yarn	6·77	6·83
,, ,, mercerised without tension	6·87	6·35
,, ,, mercerised with tension .	6·60	6·30
Bleached yarn	5·32	5·82
,, ,, Mercerised with tension previously .	5·79	5·40

The results of Clegg (J.T.I., 1924, *15*, 6) on mercerising hairs without tension in 40° Tw. NaOH solution, however, showed not only an increase in breaking load, varying from 11·8 to 49·2%, but a greater uniformity. (See also page 103.)

The results on yarn depend on the construction of the yarn as well as on the mercerising conditions ; some typical results of interest are shown in the following table :

INCREASE IN YARN STRENGTH.

Observer.	Yarn.	Treatment.	Increased strength %
Bantrock (Cross and Bevan, Researches on Cellulose, 1895 (1900, p. 25)	2/40	no tension	68
		tension	35
Hübner and Pope (J.S.C.I., 1903, *22*, 70)	2/50 Egyptian	no tension	40
Smith (J.S.D.C., 1902, *16*. 55)	2/38 Sea Island	tension	12·4
Bowman (Structure of Cotton Fibre, 227)	2/60 Egyptian	tension	49
Greenwood (J.T.I., 1919, *10*, 270)	2/80 Egyptian	no tension	23
	,,	tension	20
Lowe (J.S.D.C., 1921, *37*, 206)	2/60	tension	10–40

Lindemann (Dissertation; Dresden, 1909) found that in the case of cotton yarns treated without tension in various concentrations of NaOH solution, the breaking load fell to a minimum first of all and then rose to a maximum in 22 % NaOH solution with a breaking load 16 % above the original figure.

Mercerisation of yarn for maximum breaking load has been investigated by Wilkie (A.D.R., 1933, *22*, 217) with interesting results.

The yarns were spun from middling Peeler cotton and varied in count from 10s to 90s, though most of the data refer to 80s, both single and two-fold. One of the important facts which emerged was the increase in tensile strength which took place as a result of a thorough preparation of the yarn; this broadly followed the well-known method of Corey and Gray (Ind. Eng. Chem., 1924, *16*, 853) for the preparation of standard cellulose, and involves extraction with alcohol and with ether, followed by a six-hour scour in 1 % NaOH solution. In these circumstances, increases in breaking load amounting to between 11 and 100 % of the grey yarn were observed, depending on the character of the yarn. The great increases were encountered in the case of 10s of low twist and are probably due to a true break as against fibre slippage, the scouring process bringing about a closer embedding of the hairs in the yarn. The lower figure is more likely to apply to yarn normally intended for mercerising. *Low twist appears to be essential for maximum increase in strength,* the highest figures being obtained from yarns spun with twist factors of 2·2 to 3·0. The observations on the concentration of NaOH confirmed previous work, but there was little difference in the yarns mercerised at various temperatures between 95 and 20° C., but below room temperatures a further increase in breaking load was noted—27 to 28 lbs. as against 23 to 25 lbs. per 100 ends. There was no improvement with time of mercerisation over 30 seconds, although Wilkie recommends a period of 5 mins.; the amount of tension should be such that the yarn does not contract more than 3% compared with the original length.

It appears to be common knowledge in mercerising for optimum tensile strength that twist is the chief factor.

Effect of Twist

Corser and Turner (J.T.I., 1923, *14*, 332) made a survey of 2/60s yarn spun from fine Sakellaridis cotton. A 60s singles was spun twist way with three different twist constants (2, 3 and 4, respectively; S, M, H), and then each singles was doubled weft way with three doubling twist constants (3, 4·5 and 5·6, respectively; S, M, H). This gave nine types of two-fold yarn, which are marked in the table as SS, being soft singles twist, soft two-fold twist and HH as hard singles twist, hard two-fold twist, etc.

The yarns were scoured by boiling for five minutes in 2° Tw. caustic soda solution and 2% olein oil, after which they were mercerised in two sets; those marked M2 were given a works' treatment in which the hanks were allowed to shrink during the process and were extended to the original length before washing, whilst those marked M1 were mercerised on a laboratory machine, which maintained the yarn at tension during the whole treatment. 55° Tw. NaOH solution was used at room temperature and the hanks were revolved for ten minutes. The laboratory experiments were done under conditions of over-stretching, as the greater the tension, the greater was the strength of the mercerised yarn, but extensions of 7% brought about yarn breakages in all except the softest yarns. The actual extensions were 3% for MM and HS, 3·5% for SH and MH, and 3·8% for SM and 4·0% for SS, MS, HM and HH.

It was found that the most lustrous yarns were those which were doubled with the softest doubling twist, indeed a doubling twist constant of three is often used in commercial practice; the most lustrous yarn of all was that with medium singles twist and soft doubling twist.

SUMMARY OF RESULTS FOR TWO-FOLD YARNS.

State of yarn.	Type of yarn.	Count.	Baer single-thread strength.	Moscrop single-thread strength.	Lea strength.	Extensibility.
			ozs.	ozs.	lbs.	%
Grey . .	SS	29·5	13·75	13·53	107·3	6·4
	SM	29·8	15·59	15·65	120·3	6·25
	SH	28·7	17·57	17·90	126·6	7·3
	MS	30·3	14·16	14·40	103·7	5·55
	MM	29·6	16·43	15·62	117·0	6·5
	MH	29·3	16·48	17·08	120·0	7·35
	HS	30·6	15·36	15·04	108·2	6·35
	HM	30·1	15·90	15·78	117·3	7·1
	HH	29·6	16·73	15·79	119·4	7·6
Mercerised . (M1)	SS	31·7	18·86	19·69	138·0	3·55
	SM	31·1	18·04	17·77	122·6	3·75
	SH	30·5	17·35	18·13	115·7	4·35
	MS	33·4	18·06	18·32	122·1	3·65
	MM	30·6	19·61	18·87	126·5	3·95
	MH	30·4	18·02	18·28	117·5	4·35
	HS	31·4	17·95	18·72	121·2	4·25
	HM	33·1	17·37	17·38	115·1	4·3
	HH	31·1	17·49	18·00	105·6	4·15
Mercerised . (M2)	SS	30·7	17·58	17·05	128·4	3·8
	SM	29·5	18·10	18·57	125·8	5·1
	SH	29·6	17·33	18·36	114·7	4·5
	MS	30·5	18·49	18·21	125·3	4·5
	MM	29·7	18·88	19·13	120·9	4·5
	MH	30·1	17·21	17·98	116·4	4·95
	HS	30·6	18·74	18·04	119·2	4·4
	HM	29·9	18·26	18·24	114·6	4·9
	HH	29·5	17·76	18·14	110·1	4·4

It was found that the strength of two-fold yarns of soft twist in doubling is more sensitive to tension during mercerising than that of similar yarns of harder doubling twist. For two-fold yarns of a given singles twist, the maximum strength is obtained by using soft doubling twist, but this sometimes requires excessive tension, and the best compromise appears to be obtained with a medium doubling twist.

The general conclusions to be drawn from these data are that the gain in strength of two-fold yarns increases up to a certain point with increase in the mercerising tension, and for singles yarns with a given twist, the tensile strength in the unmercerised state increases up to a point with doubling twist, but decreases with doubling twist for mercerised yarns. In order to obtain the most lustrous and strongest yarns after mercerising, it appears advisable to use grey yarn with a soft doubling twist.

Mercerising under such tension as to ensure the original length of the yarn does not affect the twist of the material; if shrinkage is allowed, then the number of turns per inch is affected proportionately. In many processes of hank mercerising there is a slight shrinkage which gives an increase in twist of 3 or 4%.

Twist and Lustre

In general it is not possible to produce such a high degree of lustre on singles as on doubled yarns so that practically all yarns mercerised for lustre are doubled yarns. This has been explained by Bourcart (R.G.M.C., 1902, *6*, 34), who argues that as the tension is applied in the direction of the length of the yarn and not necessarily in the direction of the individual hair length, the single yarn is at a disadvantage, as the angle between yarn direction and hair direction is greater, the greater the twist. This is obviated in the case of a two-fold yarn with a doubling twist in the reverse direction to that of the singles.

At one time it was common for tables of doubling twists to be compiled as a guide to the production of maximum lustre. Adderley and Oxley (J.T.I., 1925, *16*, 167) made a survey of a series of two-fold yarns ranging from 2/12s to 2/140s and established that *maximum lustre is obtained when the doubling twist is seven-tenths of the original twist of the component singles.* The condition for maximum lustre is obtained when the cotton hairs are parallel to the axis of the folded yarn.

TWIST AND LUSTRE.

Yarn.	Singles twist.	Doubling twist (maximum lustre).
2/60 unmercerised	19·8	14·0
2/60 mercerised	19·8	13·0
2/80 unmercerised	22·7	16·0
2/80 mercerised	22·7	16·0
2/100 unmercerised	24·7	17·0
2/100 mercerised	24·7	17·0
2/140 unmercerised	24·4	18·5
2/140 mercerised	24·4	16·0

DOUBLING TWIST AND LUSTRE. (*Kurtz.*)

50s singles.		Unmercerised.					
		2/50		3/50		4/50	
Twist factor.	Lustre No.	Doubling turns.	Lustre No.	Doubling turns.	Lustre No.	Doubling turns.	Lustre No.
3·59	13·6	19·8	19·1	15·1	16·5	14·3	14·7
		23·1	19·1	19·5	13·4	18·5	10·2
		27·9	16·2	24·4	10·2	20·0	11·1
4·16	12·5	19·7	22·7	15·0	19·1	14·0	14·9
		23·1	19·3	18·7	15·1	18·2	13·6
		27·3	17·1	23·8	15·1	18·8	17·6
4·96	9·8	19·3	18·2	14·3	15·3	14·4	17·8
		22·5	20·0	18·9	16·4	18·2	13·6
		26·8	16·4	23·8	17·3	19·0	16·0
		Mercerised.					
3·59	13·6	19·4	55·6	15·1	52·0	14·3	37·8
		22·6	48·2	19·6	40·6	18·6	24·7
		27·8	37·3	24·4	23·4	20·2	20·4
4·16	12·5	20·5	55·8	15·0	56·0	13·9	38·7
		22·6	54·7	18·9	39·4	18·2	32·4
		26·4	44·4	23·9	33·6	19·4	28·9
4·96	9·8	18·2	61·3	14·5	49·4	13·5	36·9
		22·4	51·3	19·2	41·1	18·3	34·7
		27·5	47·8	24·0	32·9	19·9	28·4

Kurtz (Leipz. Monat. Text. Ind., 1935, *50*, 219) has made a series of lustre measurements on 2-, 3- and 4-fold yarns, prepared from combed Egyptian cotton with various singles and doubling twists, before and after mercerising under tension. The results are shown on page 112, from which it will be seen that the highest lustre is obtained with mercerised soft-twisted 2-fold yarn from soft to medium twisted singles. The lustre of the mercerised yarns falls with increase in folding number and with increasing hardness of the doubling twist.

Effect of Mercerisation on Count of Yarn

Some data have been given by O. Mecheels and G. Stuhmer (Textilber., 1933, *14*, 463-464). Yarns of different count were scoured in a solution containing 0·5 g. of sodium carbonate and 2 g. of Turkey Red oil per litre and then mercerised so that the original length was maintained.

From the table it will be seen that scouring (for 60 mins.) raised the counts by 2 %, while mercerising produced an increase of 6 %.

VARIATIONS IN COUNT.

Nominal count.	Actual count.	After scouring.	After mercerising.
2/30	30·2	30·7	31·8
2/50	50·6	50·9	53·5
1/60*	62·5	63·4	64·5
2/70	70·1	71·3	72·8
2/90	88·4	88·7	90·5
2/100	99·0	100·9	105·0
2/120	120·0	120·5	121·0
2/130	130·6	131·7	135·6

* This is apparently a typographical error for 2/60.

In another series of experiments, the mercerisation, which allowed 5 % shrinkage, produced a decrease in count of 5 %, whereas a 5 % increase in length during mercerisation brought about an increase in count of 10 %.

EFFECT OF TENSION ON COUNT.

Count.	Count after mercerising. Stretching. −5%	0%	+5%
2/30	29	31·5	32·5
2/90	88	91	92
2/100	96	105	114

The shrinkage of yarn in the alkali and the lustre of the mercerised cotton both decrease with increasing temperature of alkali. For a series of soft twist yarns, it was found that the shrinkage in the NaOH solution diminished as the counts became higher, but the relation between shrinkage and counts was not obtained where yarns of different twist were compared. It was also observed by Mecheels that a high tendency to shrink does not necessarily imply high lustre, for the yarns with the highest lustre after mercerisation are those with the highest initial lustre. If, however, two yarns have the same lustre before mercerising, then that with the highest tendency to shrink shows the higher lustre after mercerising.

General Comparisons

Useful details are to be found in papers published from time to time on mercerising, which mainly confirm previous experiments, but provide more information, for instance, of the effect on more than one or two properties of variations in a single factor. Kurtz and Kurtz (Leip. Monat. Text. Ind., 1935, *50*, 165) have examined the effect of tension, particularly in respect of "over-stretching," on a series of 2-, 3-, 4- and 5-fold yarns. The results are shown on page 115. In each series the strength and lustre increase and the extensibility decreases with increase in the amount of stretching. The highest lustre is obtained for the 2-fold yarn by 9% over-stretching, and it is also interesting to note that a 2-fold yarn mercerised with little or no over-stretching has as good a lustre as a 4- or 5-fold yarn which has been over-stretched in mercerising. The influence of stretching on breaking load decreases with increasing folding number, and it must be remembered that a high breaking load is not the sole criterion

EFFECT OF STRETCHING DURING MERCERISATION. (30° Bé. NaOH.)

Yarn.	Treatment.	Resultant count.	Doubling turns.	Breaking load.	Extension.	Lustre No.
2/50	Untreated	27·2	7·81	347 g.	4·8 %	...
2/50	Mercerised without tension	22·8	9·56	451	14·9	24·2
2/50	Mercerised at original length	26·8	7·79	460	5·9	72·0
2/50	3% over-stretched	26·8	7·72	464	4·0	80·6
2/50	5% „ „	27·2	7·68	460	3·6	80·2
2/50	6% „ „	27·7	7·94	453	3·2	85·6
2/50	9% „ „	28·0	6·80	531	3·2	94·8
3/50	Untreated	17·6	6·60	613	5·4	24·3
3/50	Mercerised without tension	14·2	8·30	729	16·1	20·4
3/50	Mercerised at original length	17·3	6·27	761	5·5	55·8
3/50	3% over-stretched	17·6	6·71	741	4·8	62·0
3/50	6% „ „	18·0	6·04	750	4·3	68·8
3/50	9% „ „	17·7	6·48	771	4·0	70·0
4/50	Untreated	12·9	5·40	701	6·5	21·3
4/50	Mercerised without tension	10·7	6·82	1041	18·6	19·1
4/50	Mercerised at original length	12·3	5·21	1090	7·0	48·8
4/50	3% over-stretched	13·2	5·14	1039	5·5	65·4
4/50	6% „ „	13·8	5·07	1035	4·5	73·0
4/50	7% „ „	13·9	5·03	1052	4·6	75·0
4/50	9% „ „	13·5	5·11	1113	4·4	80·0
5/50	Untreated	9·9	4·48	1117	7·0	18·3
5/50	Mercerised without tension	8·4	5·44	1291	18·6	19·1
5/50	Mercerised at original length	10·1	4·62	1347	6·8	45·8
5/50	3% over-stretched	10·4	4·47	1347	6·0	48·3
5/50	5% „ „	10·6	4·40	1328	5·3	57·4
5/50	6% „ „	10·3	4·32	1350	4·9	68·0
5/50	9% „ „	10·6	4·11	1372	5·0	75·3

The singles yarn was made from Mako cotton (combed) with a twist factor of 2·55.

of strength in textiles. The above data, whilst undoubtedly of great value, must be applied with caution as generalisations ; Corser and Turner (J.T.I., 1923, *14*, 354) have shown that some yarns cannot be over-stretched by more than 5 %, and Mecheels (Textilber., 1932, *13*, 645) states that cotton loses strength if stretched more than 5 % during mercerisation. Obviously, much depends on the actual material investigated.

In considering the published work on mercerising it is often difficult to correlate the results of one worker with those of another as the conditions are rarely the same in respect of the type of cotton, the yarn, the concentration of the alkali and the tension applied during the process.

Edelstein (A.D.R., 1936, *25*, 458 and 724) has published results which were confined to the treatment of 2/40s yarn, spun from Mississippi Delta cotton of 1 in. staple and having 13 doubling turns per inch. Samples were mercerised in caustic soda solutions of varying concentrations at 27° C. The force required to keep the yarn at constant length was measured, and found to increase with the concentration of the alkali up to 70° Tw. ; the lustre was also found to increase with the concentration and appears to be related to the force necessary to prevent shrinkage. The first noticeable increase in lustre occurred in 25·5° Tw. NaOH—approximately the concentration where shrinkage starts. On the other hand, properties such as tensile strength, moisture absorption, dyestuff absorption, baryta number, etc., increased with the concentration of sodium hydroxide only up to 30° Tw. and samples mercerised in stronger solutions showed very little change in these properties. It must not be assumed that the lustre is necessarily the highest that could be obtained in a particular concentration, for the samples were all maintained at the same length. Shrinkage measurements under no load in NaOH showed a rapid increase up to 35° Tw., after which there was a decrease ; in the case of washed samples there was no decrease above 30° Tw. (For baryta number, see page 401.)

The effect of tension was examined for similar yarn under three different conditions of tension in five different concentrations of alkali. The hanks were then washed, neutralised, washed, dried and wound on cones.

It was observed that there is no noticeable effect on the tensile strength, but the extension at break is decreased by high tension.

EFFECT OF TENSION.

Concn. of NaOH	Maximum tension. Strength.	Maximum tension. Extn.	135 lbs./30 g. hank. Strength.	135 lbs./30 g. hank. Extn.	No shrinkage. Strength.	No shrinkage. Extn.
Tw.	lbs.	%	lbs.	%	lbs.	%
25°	156	3·8	157	5·0	158	5·2
30	181	3·5	163	4·2	162	4·5
35	168	3·5	154	4·1	165	4·7
50	162	3·8	165	4·2	168	4·5
60	172	3·8	163	4·6	181	5·2

The unmercerised yarn had a breaking load of 125 lbs. and an extension of 5·2%.

When the lustre of the yarns was examined, it was found that application of the same tension to yarn mercerised in NaOH solutions stronger than 30° Tw. produced approximately the same result. The greater the tension applied to a yarn in a particular solution, the greater was the lustre and the less the absorption of dyestuffs. In all samples mercerised in the weaker solutions, there was a tendency to unevenness as shown by the dyed material.

These data confirm the general experience that it is not possible to obtain maximum dyestuff absorption and maximum lustre under the same conditions of mercerising ; the greatest lustre is obtained at the highest tension which affects the dyeing power and the extension at break. In mercerising for lustre it is advisable to use 50 to 55° Tw. NaOH, but the maximum affinity for dyestuffs was obtained in solutions of 25 to 30° Tw. NaOH, where the stretching force was only half that required in the higher concentrations.

2/40s Mississippi Delta cotton was also used in experiments on the effect of temperature (A.D.R., 1937, *26*, 427). The skeins were maintained at constant length during the mercerising process, and it was found that for any particular solution of sodium hydroxide, the lower the temperature of the solution, the greater was the force necessary to prevent the yarn from shrinking. The affinity for dyestuffs and also the barium number of the mercerised yarn increased with decrease in temperature of the mercerising liquor. The extension at break was not influenced by the temperature of the alkali, but the breaking load of yarn mercerised at 15° C. in all cases was higher than that of yarn mercerised in the corresponding solutions of alkali at the higher temperatures.

The effect of temperature is largest on breaking load, barium number and lustre with solutions of 30 and 35° Tw. NaOH, the yarn mercerised at the lowest temperature having the highest lustre, but in solutions of 50 and 65° Tw. NaOH, the temperature only exerts a slight effect.

EFFECT OF TEMPERATURE OF NaOH SOLUTIONS.

NaOH.	Temp.	Force to prevent contraction.	Breaking load.	Ba. No.	*Lustre No.
Tw.	C.	lbs.	lbs.		
30°	15°	67·5	167	160	231
	32	52·5	165	142	219
	43	37·5	150	131	194
35°	15	75	168	160	230
	32	67·5	166	152	224
	43	52·5	160	137	214
50°	15	97·5	180	162	229
	32	90	170	162	233
	43	67·5	170	159	226
65°	15	102·5	160	165	228
	32	97·5	168	163	233
	43	81·5	170	160	227

* The lustre number is the ratio of light reflected when the sample is illuminated at 45° to that when illuminated at 90° as measured by the photoelectric photometer described by Ransom and Edelstein (A.D.R., 1937, ***26***, 432), and must not be confused with the lustre numbers of the German workers.

Solutions of sodium hydroxide of 30° Tw. appear to be very critical, in that small variations in concentration and temperature cause considerable variations in the properties of the mercerised material—on the other hand solutions of 50° Tw. NaOH are not very sensitive and are, therefore, to be preferred for practical mercerising. It appears that some properties of mercerised cotton change more rapidly with mercerising temperature above 32° C. than below.

Wetting Agents

A criterion of successful mercerising is rapid and even wetting of the cotton by the sodium hydroxide solution. If mercerisation is attempted on goods which have not received any preparation, then penetration is irregular and the results uneven. At one time double mercerising was commonly practiced in order to avoid these defects, but recently a number of wetting agents have been produced which may be added to the mercerising liquor enabling it to penetrate the cotton rapidly.

In this manner it is possible to mercerise grey yarn or cloth without previous preparation in the way of wetting. In the case of yarn treatment, this eliminates a process and permits a softer handle to be retained than with yarn which is scoured before mercerising. With piece-goods mercerisation, the requirements of the cloth itself, or of the arrangement of the works, often decide the state in which the material is mercerised, but the use of wetting agents gives greater latitude in this respect ; for instance, delicate material may be mercerised in the loom state by means of efficient wetting agents in the mercerising solution.

The time of impregnation of cotton cloth is rarely sufficient for maximum swelling of the cotton, so that even with the mercerisation of bleached cloth, the use of wetting agents is advantageous ; further, their presence is a safeguard against uneven penetration.

Most ordinary wetting agents cannot be used in the mercerising process as they are not sufficiently soluble in moderately concentrated sodium hydroxide solution. Phenolic compounds, such as cresylic acid, form the basis of most of the successful wetting agents for mercerising, but the wetting power may be increased by the addition of solvents such as cyclohexanol. Sulphonated acids of high molecular weight, sulphuric esters of aliphatic alcohols, etc., have also been suggested as additions to the phenolic wetting agent.

The amount of wetting agent required for the maximum effect rarely exceeds 2 % and 0·5 to 1 % is frequently sufficient.

The two main features of a good wetting agent are that it should possess a high wetting power and enable the alkali rapidly to swell the cotton ; in addition, it should disperse perfectly, its effect on the mercerising liquor should be permanent and it must be readily removed from the goods by washing.

A number of tests have been suggested for the efficiency of wetting agents, including the rate of capillary rise, observations of weight or volume absorbed in a given time, and "sinking time." The latter method necessitates the sample being kept below the surface of the liquor by means of a bent wire (Landolt ; Textilber., 1928, *9*, 759) or a sinker (Draves ; A.D.R., 1931, *20*, 201). For the specific use in mercerisation, however, the rate of swelling of the cotton is the important feature, and this may be measured either through the rate of contraction under constant tension or the rate of increase of tension at constant length ; the former method is commoner.

Landolt's original apparatus has been subjected to slight modification in the hands of other workers, but the basic method remains unchanged. A graduated burette is adapted for the measurements, and it is possible to hang in this a 50 cm. length of yarn under a load of 1 or 2 g. according to the type of yarn. The alkali and wetting agent are then admitted and the contraction noted after 15 seconds contact. A second determination of maximum contraction, and the time necessary to effect this, is also made. The results are then calculated to a percentage of the entire submerged length. Minor modifications of this method include a double length of yarn gripped at each end in order to avoid any untwisting of the yarn.

An apparatus is also provided by Schopper where the yarn is held horizontally in two clips one of which is attached to a pointer which reads the amount of contraction on a graduated scale when a small bath of mercerising liquor is raised to impregnate the yarn. The amount of shrinkage is determined after 15 seconds and also the total contraction and the time necessary for its accomplishment.

The results of tests on wetting agents as recorded in the literature are sometimes contradictory, but it now appears that the concentration of any particular wetting agent may need adjustment for maximum activity according to the concentration of alkali. Mercerol, for instance, shows its optimum effect in 52° Tw. NaOH solution, Inférol M special at 57° Tw. NaOH, Inférol M in 57 to 66° Tw. NaOH, and Inférol M extra in concentrations exceeding 66° Tw. NaOH.

Another point which requires attention in the use of wetting agents is that some of them are disproportionally absorbed during mercerisation, so that the returned liquor is weaker in respect of wetting agent ; periodic checking is advisable.

Apart from the requirement that the wetting agent should exert the maximum effect in the minimum time, questions of stability also arise. It is advisable to measure the rate and extent of contraction of the alkali containing the wetting agent

WETTING AGENTS.

Amercit N and C	Cresol and cyclohexanol.
Arburol	Cresol and methylhexalin.
Créstxyl	Cresol and solvent.
Dyonil NC	Cresol, methylhexalin and diethyleneglycolbutyl ether.
Elvétol	Cresol, cyclohexanol and tetralin.
Flerhenol	Sulphonated oil, cyclohexanol and cresol.
Floramine MC and AMC	Similar to Elvétol.
Florhanit L 140	Cresol and a solvent.
Eumercerine A	Cresol and methylhexalin.
Humectine M	Cresol and methylhexalin.
Inférol M	Cresol and a solvent.
Leophen M	Sulphuric ester of an alcohol (*b.p.* 120–160° C.).
Mercerol (C)	Cresol, cyclohexanol, xylene and a gylcol derivative.
Mercirane N	Cresol and cyclohexanol.
Moistine	Cresol and a solvent.
Perminal Merc.	Cresol, pine oil and olein oil.
Præstol oil BM	Highly sulphonated oil.
Shirlacrol	Phenolic mixture from tar fractions *b.p.* 205/290°.
Synalcal	Sodium cresylate.

(See also page 298 of Textilhilfsmittel by Chwala-Springer; Vienna; 1939.)

every day over a period of some ten days The stability of the solution requires testing also, for the range of mercerising liquor may vary from 66 to 40° Tw., or even lower in the case of semi-mercerising ; the range of mercerising temperatures also may lie between 0 and 25° C. There should be no separation of the wetting agent as shown by turbidity, separation of an oil, or crystallisation within the range of temperature and concentration likely to be encountered in works' practice over a period of about ten days.

There is a comprehensive literature on wetting agents in general, but the data on page 121 are mainly compiled from a review of the patents literature by Sisley (R.G.M.C., 1933, *37*, 340).

Preparation

The materials which give the best lustre after mercerising under tension are those which start with the highest lustre ; this point has already been mentioned and applies to cotton hairs, cotton yarns and the cloth itself. In the mercerising of yarn, therefore, it is essential not only to start with a cotton which is already lustrous, but also to ensure that the yarn is so constructed that the lustre of the cotton is developed to the highest degree ; this means that yarns for mercerising are made from either carded or combed cottons, sometimes triple-combed cotton. With certain varieties of cotton, the effect of combing is only a little superior to that of carding.

The yarn should be singed or " gassed " before mercerising, in order to remove those hairs which are not twisted into the yarn structure, but project from the surface ; if these hairs were not removed they would shrink under the action of the alkali and so be devoid of lustre. Further, it is essential to the full development of lustre that the yarn should have a smooth and clean appearance and approximate to a cylinder ; the presence of a " fuzz " of projecting shrunk hairs would take away from the lustre of the mercerised yarn.

This question of shrinkage of various parts of the yarn is one of the utmost importance, for it is probably the chief cause of irregular dyeing in mercerised yarn. With this end in view, it is necessary to pay attention to such details as the even winding of the hank and the provision of generous tie-bands. The latter are not under tension and may, therefore, shrink to an extent sufficient to prevent thorough mercerising of that part of the hank on to which they contract. Watkins

(Textile Colorist, 1924, *46*, 582) has given instances where a tie-band arranged in figure-eight fashion only shrank 7% during mercerising, compared with 24% shrinkage of a tie-band passing once round the hank. Some mercerisers avoid all possible trouble by using previously shrunk tie-bands.

Raw cotton is practically waterproof and very difficult to wet with the mercerising liquor of fairly high viscosity. The use of wetting agents for mercerising has been developed to a surprising degree during recent years and is discussed on page 119. Prior to their use there were sharp divisions of opinion on the question of preparation for mercerising, but for yarn the question of mercerising after bleaching scarcely arises. With the exception of some special sewing and embroidery cottons, it is common practice to mercerise yarns in the grey state. A great deal of mercerised yarn is used in weaving and the cloth produced has to be bleached later, so that there is no point in bleaching before mercerising, particularly as weaving is not a spotlessly clean process.

The preparation of yarn for mercerising is directed to making it wet readily and evenly with the caustic soda solution. Although modern wetting agents enable mercerising to be carried out on the raw yarn, the present tendency is towards their use with material which has already been purified to some extent. The wash-water from grey mercerised material contains many impurities from the raw cotton and is difficult to concentrate and re-causticise in a satisfactory manner.

Nevertheless it is held by many mercerisers that better results are obtained by " dry-mercerising " in presence of a wetting agent. As against mercerising the yarn in the dry state, it is general practice to mercerise in the wet state, after a preliminary wetting or scouring operation. In this case it is obvious that the greater part of the water must be removed from the yarn before mercerising as this would dilute the alkali to an excessive extent and render it inefficient. *It is essential that the water should be evenly removed*, as any local excess would bring about local dilution and affect the subsequent dyeing affinity. It is usual to centrifuge the yarn very thoroughly before mercerising and also to cover the material whilst awaiting the mercerising operation, so that local drying is avoided.

There are a number of different methods of purifying the yarn before mercerising and each of them has it own protagonists—some hold that a thorough scour or " bottoming " is apt to give harsher results than a light scour. The effect of the degree of scour on lustre has been examined by Mecheels (Textilber., 1932, *13*, 646) with interesting results.

EFFECT OF SCOUR ON LUSTRE.

Scour.	Lustre No.
Untreated	28
Boiled 4 hours in 0·3% NaOH (3 atmos.) . .	21
,, ,, 0·4% Na_2CO_3 (1 atmos.) .	23
,, ,, soft water (3 atmos.) . .	26

These figures relate to the mercerised yarn, and it appears that the best results are given from material which has not been scoured, and after that the yarn which has only been scoured in water.

This effect was confirmed in the case of three different yarns of another type of cotton.

EFFECT OF SCOUR ON LUSTRE.

(2/80s Sakel)

Scour.	Lustre No.		
None	76	83	74
Four hours in 0·3% NaOH (3 atmos.)	50	83	60
,, ,, 0·4% Na_2Cl_3 (1 atmos.)	69	87	65
,, ,, soft water (3 atmos.)	75	84	74

The preparation of the yarn is reflected in the feel or handle of the mercerised product. A scouring process, as distinct from a wetting process, is directed to the purification of the cotton, including the removal of the cotton wax. It is well recognised that there is a connection between the amount of wax left in the cotton and the handle of the mercerised yarn, so that from the standpoint of handle alone it is preferable to avoid a thorough scour before mercerising. The softness of the product runs parallel to the wax content even when the mercerised yarn has been bleached, so that from the standpoint of both lustre and handle it is preferable to give the lightest scour which is consistent with thorough and even wetting.

In so far as subsequent processes are concerned it must be realised that mercerising itself removes some of the cotton wax, thus facilitating the bleaching operation where this follows the mercerising process, as is common with yarn treatment.

There are many individual requirements to be met, and the final decision must be reached in a manner which will satisfy the customer for whom the yarn is intended. A very common practice is to give the yarn a light scour on poles in a beck containing hot water and a wetting agent such as Turkey Red oil or a proprietary wetting agent, taking care to avoid any excess over the required amount ; the material is then centrifuged thoroughly and mercerised in the wet state in the mercerising liquor to which has been added a specific wetting agent for mercerisation.

General

A great deal of trouble may be caused if the process of mercerising is not standardised in every detail and the faults arising from variations are not those of lustre but affinity for dyestuffs. The variation in shade is not apparent in the dyed hank, but when the yarn is knitted into hose or garments it so happens that " patterning " occurs through the light or dark parts of the yarn being brought together as described on page 439. Slight variations in shrinkage are the chief cause of dyeing variations. It may happen that although every hank is evenly wound when received and also is mercerised to a standard girth, yet during the wetting process prior to mercerisation some hanks or parts of hanks shrink more than others. This will affect the degree of shrinkage during mercerising and the shade in dyeing, although the degree of stretch was standardised. In general, the process of wetting on sticks in a beck is more uniform than light kiering.

The yarn must be mounted evenly on the rollers of the mercerising machine, for any unevenness will produce irregular shrinkage ; the turning of an edge of a hank with a figure-eight tie-band is a common source of trouble, producing a kind of selvedge which lies on the rest of the hank.

Variation in the concentration of the NaOH is not a common error as it is readily observed and controlled ; within the range of 50 to 60° Tw. a few degrees does not appear to produce serious consequences. The temperature of the alkali is also capable of control, but it must be remembered that washing with hot water has the effect of heating the iron rollers on which the hanks are rotated and the temperature may rise as much as 6 to 10° C. during a few hours. The variation in shade of the dyed mercerised material is more acute where the temperature of the caustic soda solution is below 15° C. A separate supply tank with a large volume of circulating solution and cooling arrangements is standard practice in most works. It is hardly necessary to comment on the purity of the NaOH and the avoidance of appreciable amounts of sodium carbonate, the presence of which gives a fictitious value to the density determinations of the sodium hydroxide.

Variation in tension may be due to uneven wetting of the yarn if part of it has been allowed to dry, if it is not uniform as it comes from the centrifuge or if the squeezing roller is not perfectly true. The rotating rollers must be parallel, as otherwise the outer hanks will finish at a lower girth than the inner hanks. The biggest variation in dyeing occurs with the lowest stretch and with the lowest concentrations of NaOH solution. Within the range of 40 to 60° Tw. there are many points in favour of the common use of the higher density liquor. It may not be appreciated at first thought that a low amount of stretch should ever be given in mercerising for lustre where tension plays such an important part in developing this property, but a great deal of hosiery yarn is mercerised to finish less than the original length. It is quite common to finish 54 inch hanks at 52 inches.

In many processes it is usual to wash the yarn before or during the final stretch and it is possible for variations in tension to come from the fact that some hanks or parts of hanks receive the final tension when in contact with alkali of various concentrations; in the extreme case part of the material may be in contact with water and part with alkali of mercerising strength. One of the grosser errors would be to remove the material when it still contains a high proportion of alkali and thus shrink freely in subsequent washing or souring. Many machines apply water to both the inner and outer surfaces of the rotating hanks and so avoid some of these difficulties.

Most hank mercerising machines reverse the direction of rotation of the rollers at frequent intervals during impregnation and washing, this not only assists in obtaining uniform results, but avoids breakage of individual threads.

As previously stated, it is common practice to employ NaOH solution between 50 and 60° Tw. at room temperatures and to circulate it through the trough from a separate supply tank.

The yarn leaves the hank-mercerising machine containing traces of alkali, which it is necessary to remove by "souring" with dilute sulphuric or hydrochloric acid. The concentration of the acid is determined by the amount of alkali which has to be neutralised, but about 2° Tw. is commonly employed. A gross excess of acid merely involves a longer washing process to remove it ; the traces of acid may be removed by washing with copious amounts of water, but sometimes the yarn is "sweetened off" by treatment with dilute sodium carbonate solution or dilute ammonia, followed by washing.

The drying of the mercerised yarn requires great attention, for high temperatures produce harsh results. A uniform temperature is essential, for the absorptive capacity of the freshly mercerised material is very sensitive to both temperature and rate of drying. This point is dealt with on pages 380 and 408.

Warp Mercerising

Warp mercerising relates to the mercerising of long lengths of yarn in a truly continuous manner as distinct from hank mercerising ; it must not be confused with the weaver's warp, although these have been mercerised on slashing machines.

Warp mercerising is current practice in the U.S.A., not only with yarn intended for warps, but also for knitting. It is claimed that mercerising is carried out in a positive and uniform manner with little chance of variation ; the lustre may be less than with hank mercerising, but the effect is more even and this is of great importance for material which has to be dyed.

The machines are all the same in principle and resemble the ordinary warp-dyeing machine—a series of boxes or compartments which may be as many as eighteen, each of which is fitted with guide rollers and squeeze rollers. The latter hold the yarn at the proper tension as it passes from one bath to the next.

The number of ends in the ball-warps depends on the spinning arrangements of the mill from which they came, but American practice appears to favour 378 ends, of about 6,000 yards in length. Naturally, the yarn must be of good quality cotton, well combed, and gassed before preparation. This type of mercerising is not limited to doubled yarns and is a very satisfactory method of treating singles yarn. The number of warps brought together on the machine is determined by the type of yarn, but is it usual to combine the warps in sets or drafts of three, so that the weight of a draft is about 90 lbs. per 1,000 yards.

Skinkle (A.D.R., 1931, *20*, 323) has pointed out that yarns of opposite twist should not be combined in a draft on account of the tendency to roll or twist together during the mercerisation. Yarns of different folding numbers should also be kept in separate drafts ; singles yarn should never be mixed with doubled yarn. Sets can be composed of two warps of 2/20s, three warps of 2/30s, six warps of 30s, twelve warps of 60s, etc., so that all the sets are of uniform thickness, otherwise a thicker draft will be gripped to a greater extent by the rollers than a thinner draft, which will be pulled through the rollers by the shrinkage of the yarn, with detrimental results. Even with a number of uniform drafts there are certain other matters to be considered. Thin drafts enable the process to be carried out more quickly in respect of wetting, shrinkage, washing, etc., and the machine may, therefore, be run at a higher speed, but less tension must be applied on account of the risk of breakage and the lustre suffers. Thick drafts are difficult to penetrate and unevenness is apt to occur.

According to the width of the machine, from 12 to 16 drafts may be run side by side, the former number being common practice for 36 inch machines, so that from 36 to 48 warps are mercerised together.

Prior to treatment the warps are supported by iron bars in a frame so arranged as to have several warps one over another. Each warp goes over rollers and through guides to the binding machine, where they pass through hollow spools holding a cone of strong waste yarn. The spools revolve and run a spiral of yarn round the warp. A pitch of 10 to 12 inches is usual for this " water-band," the object of which is to prevent entanglement of any broken ends with the rest of the material and to avoid roller-lapping.

In the mercerising process, the warps first pass through two or three compartments or boxes, where they are boiled in a suitable solution such as dilute caustic soda and Turkey Red oil or one of the newer scouring assistants ; the liquor is usually heated by closed steam-coils and should be boiling briskly. Some mercerisers use boiling water only. It is possible to replace the boiling process in favour of a compartment containing a wetting agent for mercerisation. If the warps have been boiled they must then pass through a box which contains cold water for purposes of cooling as well as rinsing. The warps are then squeezed and pass into the first of three boxes containing caustic soda solution of mercerising strength. It is usual to give from two to five minutes contact with the alkali, the flow of which may be arranged on the counter-current principle. The upper guide rollers are raised in some machines to a height of a few feet to give a longer period of contact with the alkali without reducing the speed of the machine or increasing the number of compartments. The alkali is at room temperature as usual, and is provided from an external source, usually a tank in the floor from which it is pumped. After the first impregnation it is possible to have slightly more tension on the yarn, as the strength will have increased owing to the action of the alkali. Penetration is assisted by the rubber-covered rollers, the speeds of which determine the amount of tension applied to the yarn.

The washing is done in three or four compartments, which are generally arranged to give counter current washing, starting with hot dilute alkali of 10 to 12° Tw. and finishing with cold water. The washing is done with the warps under tension and the initial temperature is about 50 to 60° C.; spurt pipes supplement the supply in the boxes.

A good squeeze is given to the warps, before they enter the souring compartment, in order that the caustic liquor should be removed to the greatest possible extent and so economise in the use of acid. The warps are allowed to relax from the tension previously applied, as they enter the souring compartment where the residual alkali is neutralised with dilute acid, usually sulphuric or hydrochloric of from 3 to 7° Tw. The concentration of the acid should be checked periodically by titration and not by specific gravity measurements. A period of at least one minute is given in the souring compartment, but a longer time is necessary for thicker drafts. Owing to the flexibility of the arrangements for warp mercerising it is possible to have more souring compartments and to start the neutralising with more concentrated acid. The final washing arrangements are designed to remove the acid, and usually consist of about five or six compartments with a water supply increasing in temperature up to 50° C. It is also possible to neutralise the last traces of acid by means of sodium carbonate solution or dilute ammonia, followed by a further wash. Economies are possible by leading the wash-waters from the last souring compartments into the box before the first souring compartment, similarly the wash-water after the soda-ash compartment may be led to the box in front. It is essential that all traces of acid should be removed before the yarn is dried.

Air-driers are preferable to cylinders, as the latter are apt to give harsh results. After drying, the water-band is removed from the warps, which are split up and wound as required.

It will be seen that warp mercerising is essentially a large scale process ; in America the mercerising of yarns as fine as 2/100s and 2/120s is undertaken, but 2/60s is probably the finest count of yarn mercerised in very large quantity.

CHAPTER NINE

THE MERCERISATION OF CLOTH

It has already been shown that in the case of cotton yarns the highest degree of lustre after mercerising is obtained with material which is already constructed to give the maximum lustre; yarns must be made with the hairs lying parallel to each other and to the yarn axis as far as possible. This approximation to a pad of parallel cotton hairs holds in the case of cloth also, and the most lustrous materials are those in which this condition is fulfilled, as for instance in the satin or sateen weave, with the characteristic arrangement of "floats." A surface which responds to the mercerising process may also be produced by a preponderance of either warp or weft yarn, usually the former, without departing from the plain weave. In woven satin stripes the effect of yarn arrangement for lustre is most striking, but even in plain cloths a well-mercerised material has a peculiar charm owing to the "pin-head" or "peaky" nature of the lustre, as discussed on page 423.

Combed yarns are to be preferred in cloths to be mercerised for lustre, but soft singles yarn may be used, as there is not the same danger of disintegration as in hank-mercerising. Shorter staple cottons may also be employed successfully.

Although the majority of cloths are mercerised for lustre a considerable quantity of goods are treated to improve their affinity for dyestuffs. The highest degree of absorbency produced by mercerising has also been suggested for the anti-crease process in B.P. 304,900 where the goods are maintained in the wet and swollen state during impregnation with the lightly condensed product which later forms the synthetic resin.

It is customary to singe all cloths which are to be mercerised and so remove any loose projecting hairs, otherwise these shrink during the process and produce a "fuzz," which would detract from the lustre produced on the rest of the surface which had been mercerised under tension. Practically all goods are de-sized before mercerising, for otherwise the heat of reaction would necessitate cooling, the alkali would become contaminated more quickly and difficulties would arise in its recovery.

The question whether to mercerise in the grey or bleached state is one which requires careful consideration and may be decided by the nature of the cloth itself; with fabrics of low tensile strength it is sometimes expedient to mercerise in the grey state, so that the strength of the material is increased at the earliest possible opportunity and thus facilitate subsequent treatment in rope form.

Where goods are mercerised in the grey state it is not generally necessary completely to remove the alkali by washing or acidification, for the cloth may go forward to the kiers saturated with the residual sodium hydroxide solution which is then utilised in the scouring operation; this process requires milder conditions where the cloth has already been mercerised. There is some evidence to show that a softer handle is obtained on goods which are mercerised in the grey state compared with those mercerised after bleaching; this is more apparent with yarn than cloth.

The fundamental argument against mercerising in the grey state was the difficulty of rapid and even penetration by the sodium hydroxide solution during the 30 to 50 seconds interval between the impregnation and washing processes. The use of special wetting agents for mercerising, as discussed on page 119, has removed this objection to some extent, but even under the best conditions modern high-speed mercerising of piece-goods is apt to err on the side of incompleteness. Coupled with high output is the question of cost, and it is here that the main argument against grey mercerising is to be found; where the output is such that recovery of the alkali is undertaken, the contamination of the caustic soda will make this more difficult and expensive.

In some cases it is usual to give the goods a preliminary boil in water or in dilute alkali, and then mercerise them in the wet state in order to facilitate wetting by the alkali. This procedure not only dilutes the sodium hydroxide solution, but also entails risk of uneven mercerising; the goods must be evenly expressed before mercerising and all danger of local drying must be avoided. It is doubtful whether these factors compensate for the cost of a modern wetting agent.

Bleached or half-bleached material is usually mercerised dry so that the danger of irregularities is avoided ; the pure and clean fabric gives more uniform and satisfactory results and the subsequent dyeing is invariably better. It is an open secret that the best results in commercial practice are obtained by mercerising bleached cloth. Careful workmanship avoids any staining, although the easier removal of stains in kiering grey goods is an advantage sometimes claimed for grey mercerising.

The contact with the alkali should be long enough to swell the cotton hairs and make them assume a cylindrical shape, and owing to the vicosity of the mercerising solution the chief difficulty is poor penetration. Further, when the external hairs of the yarn commence to swell some constriction is placed on their neighbours, and owing to the limitations of yarn and cloth structure the possibility of free swelling is considerably restricted. An absorbent material and the presence of an efficient wetting agent are obvious means of assuring rapid and even treatment. The high pressures exerted by modern mercerising mangles also assist rapid penetration, but where the latest development in the way of " padless machines " is utilised it appears necessary to rely entirely on the absorbency of the goods and the rapid wetting powers of the mercerising liquor.

The actual condition of the cloth prior to mercerising must be decided by a number of other factors, including the experience of the works, the arrangement of the plant, the mercerising range, the routine of works' procedure, the preferences of the customer and manager, and finally the cost.

Before dealing with the usual process of mercerisation where sodium hydroxide solutions of 55 to 65° Tw. are utilised at room temperatures as with yarn, there are two main variations which are of interest.

Semi-mercerisation

Semi-mercerising or " caustic prepare " is concerned mainly with the treatment of goods intended for dyeing or printing in heavy shades, and makes use of the increased absorbency of mercerised cloth for dyestuffs. The work of Hübner and Pope (see page 98) showed that between 20 and 30° Tw. NaOH the affinity for dyestuffs increased more rapidly than the shrinkage of the yarn, but above 30° Tw. NaOH the rate of colour absorption decreases. This observation is the basis of semi-mercerisation where concentrations of 25 to 30° Tw. NaOH are employed sometimes without stretching the cloth to restore the original dimensions. In this manner a better exhaustion of the dyebath may be obtained and economies of up to 25% may be realised. This is an important matter with the expensive vat colours where heavy shades are required. Better results are also obtained with aniline black on goods which have received a semi-mercerisation. Poor quality goods may also have their dyeing affinity improved in this manner, and the irregularities due to neps and dead or unripe cotton are less conspicuous.

The Heberlein Processes

From the early investigations of the variation in temperature of the alkali it has been broadly established that the effect decreases as the temperature rises and increases as the temperature falls. Where concentrations of caustic soda of 50 60° Tw. are employed, temperature has no great effect on the extent of mercerising, but where more dilute alkali is used, which has little effect at ordinary temperatures, mercerising may be improved by reducing the temperature and becomes equivalent to the use of the stronger concentrations at ordinary temperatures. In other words, the same mercerising effect may be obtained with alkali of the usual concentration at room temperature and by more dilute alkali at a lower temperature.

In B.P. 108,671 it was shown that special effects could be obtained by cooling alkali of the usual concentration, i.e. 50° Tw. to below 0° C. For instance, if cotton fabric was impregnated for one minute with a caustic soda solution of 30° Bé. (53° Tw.) at a temperature of −10° C., it acquired a transparent appearance which was not lost even after washing and drying. This effect may be enhanced by a further treatment with sulphuric acid of at least 108° Tw. The concentration of the alkali, the temperature and the duration of the action may be varied according to the quality of the material and the desired degree of the effect.

B.P. 191,203 disclosed that the transparent appearance obtained by the action of cold caustic soda could be improved if the material is mercerised in the ordinary manner, either before or after treatment with the cold alkali. In this way it is possible to produce a transparent and lustrous effect.

(*a*) Normal mercerisation—cold lye.
(*b*) Cold lye—normal mercerisation.
(*c*) Normal mercerisation—cold lye—normal mercerisation.
(*d*) Cold lye—normal mercerisation—cold lye.

This treatment may also be followed by treatment with 108° Tw. H_2SO_4.

These processes form the basis of the well-known Swiss finish and are mainly applied to cloths such as voiles and organdies, although a similar effect has been obtained in one operation by the use of 55–65 % sulphuric acid containing 0·5–1·0 % of 40 % formaldehyde, as described in B.P. 200,881.

The peculiar transparent appearance when the usual concentrations of NaOH are employed at −10° C. is in some measure determined by the construction of yarn and cloth. In B.P. 192,227 it is stated that as the yarn becomes coarser the transparency disappears until it is replaced by a linen-like effect which is also fast to washing. It is not possible to draw a sharp boundary between the transparent effect and the linen-like effect, but in general yarns of 80s count and finer show transparency, whereas the coarser yarns give the typical linen appearance. This is qualified to some extent by the quality of the cotton and the construction of the cloth.

These effects are produced by mercerising with caustic soda of 50–60° Tw. Temperatures from 0 to −10° C. give a peculiar lustrous effect and a considerable increase in tensile strength.

A further specification of Heberlein is of interest, although it does not concern the low range of temperatures described above. In U.S.P. 1,717,315 it is stated that the use of 15° Bé. (23° Tw.) NaOH solution at temperatures between 2 and 6° C. gives a stiff effect which is permanent to washing. The treatment in the alkali is of 20–60 secs. duration, but the effect does not appear if the temperature is as high as 8° C. This finish is stated to be beneficial in the cases of mock voiles or 2-ply loosely twisted material in order to give them the firmer handle and crispness associated with higher quality voile productions.

Mercerisation

As previously stated, it is customary to mercerise at room temperature with 55 to 65° Tw. NaOH, and the period of treatment is generally 30 to 50 seconds.

There are two broad general methods of mercerising cloth :

(*a*) shrinkage and subsequent stretching ;

(*b*) continuous tension, i.e. without shrinkage.

The latter is the latest development in mercerising practice, and although rarely encountered in England and America, it is fairly common in Continental Europe.

The commonest form of mercerising utilises one or two mangles for impregnating the cloth with sodium hydroxide solution, followed by a machine for washing out the alkali while the cloth is being stretched ; this may be done by a stenter device or by a system of rotary expanders where weft extension is brought about by warp tension.

For most cloths it is advisable to use two mangles for impregnation, although one may be sufficient for light cloths such as lawns and handkerchief material. A counter-current system of impregnation (see page 162) may be adopted to avoid the difficulty of a first contact with cold alkali of high viscosity. Between the two mangles, or alternatively between the mangle and the stretching device, it is usual to have a set of iron cylinders which support the impregnated cloth and give the alkali additional time to penetrate the cotton ; these cylinders also prevent curling of the selvedges. Where two mangles are employed it has been suggested by an anonymous writer (Textile Mercury, 1936, *95*, 464) that the alkali in the first should be at a temperature of about 40° C., which will produce good penetration, even if the mercerising effect is less at the higher temperature, for this may be counteracted by the cooling which takes place during the passage over the cylinders and the further impregnation in the second mangle with alkali at room temperature or even lower.

Complete penetration rarely takes place with one mangle, and after the single impregnation with a heavy squeeze the cloth is not thoroughly saturated owing to the swelling of the hairs as the goods pass over the cylinders.

The use of two mangles and a set of drums also permits of variations in treatment according to requirements. It is possible to run the second mangle faster than the first and so exercise warp tension which may be desirable in a cloth with a warp face ; alternatively if the second mangle runs at a lower speed the cloth will shrink and so absorb the alkali better when it enters the second mangle box.

During the process of impregnation the cloth will shrink, and it is necessary to pull it out again during the removal of the alkali ; it is usual to mercerise to " grey width " in order to produce maximum lustre. The amount of stretching is therefore considerable, for a cloth which was 39 inches wide on the loom may shrink to 36 inches during the preparation for mercerising and to 30 inches when in contact with the alkali.

In the case of stenter-washing, it is usual to extend the weft and have the warp under tension. This may be done by running the stenter at a slightly higher speed than the mangle. The cloth is stretched while in contact with the alkali and washing starts when the cloth has been pulled out—usually after a distance of some 15 to 20 feet along a stenter of 50 to 75 feet in length. Various arrangements for washing are described on page 164, but the simple spurt pipe is not satisfactory as the holes are too far apart and apt to become blocked. If the washing is uneven, the mercerising is uneven and the subsequent dyeing will also be uneven.

Goods containing wool, for instance in the selvedges, need rather careful treatment during washing after mercerising. Wool is not harmed by a short immersion in cold 50° Tw. NaOH, but is attacked by lower concentrations during washing, particularly at higher temperatures. Rapid washing with *cold* water, the use of suction devices and immediate souring enable possible damage to be avoided, without recourse to a pre-treatment with formaldehyde solution to render the wool immune to alkali attack.

It is most essential that sufficient alkali be removed from the goods to prevent subsequent shrinkage ; this means that the concentration must be reduced to below 15° Tw. NaOH by the end of the stenter. The actual concentration is determined by the efficiency of the counter-current system of washing and whether recovery of the alkali is practised. If the cloth leaves the stenter whilst containing alkali of mercerising strength it is possible to remove this later, without tension, and then stretch the cloth to the desired width, but it will shrink on the first wash. The dimensions of the cloth are more or less fixed at those where the alkali concentration is reduced to below 15° Tw. NaOH ; the concentration of the external liquor, of course, is not that of the liquor in the cloth.

The use of expanders for stretching the cloth was first suggested by Heberlein in 1909 for embroidery cloths without selvedges. " Arched rotatable rollers " such as Mycock expanders were caused to revolve by the pull of the fabric and pushed it laterally from the middle to the edges. This idea has been developed during the past ten years, but the expanders are driven. The two chief advantages of this arrangement are that it is possible to run cloths superimposed and it is easy to run materials of different widths consecutively.

The operation of the machines used in the mercerising of cloth is described in Chapter XI ; in most cases it is customary to couple the various machines in tandem fashion to form a range. This ensures even treatment of the material and avoids any unnecessary handling of the goods.

A typical mercerising range consists of

(1) the impregnating machinery ;
(2) the stretching and washing machinery ;
(3) the recuperator ;
(4) the neutralising and washing machine.

Where expanders are used instead of a stenter—the so-called chainless system—there is a considerable saving in space. The recuperator and neutralising machine are not always included in the range and in some cases a recuperator is omitted from the sequence of operations. Its function is described on page 177, and is concerned with the further removal of the alkali by steam. The use of a complete range enables many economies to be made by utilising the counter-current system of washing.

Where mercerisation is effected with continuous tension, as described on page 174, sections (1) and (2) of the range are combined in one complete unit. Impregnation is not assisted by special mangles, but by passage between a series of rollers whose contact prevents shrinkage ; the excess alkali is removed by mangling, and the washing takes place as the cloth passes over a second series of rollers. The machine is very compact and as no shrinkage is permitted it does not require as much power as where stretching the shrunk material has to be undertaken. Here again, it is possible to run cloths superimposed and there is no necessity to adjust the machine for consecutive pieces of different widths.

The chainless and padless machine is very suitable for the mass production of mercerised cloths, particularly of light and medium weight, and the relatively few factors which are capable of variation assist in the production of a standardised product. Nevertheless it would appear that thorough penetration must be difficult in the case of medium and heavy cloths and those of a compact construction where no shrinkage is permitted to assist the realisation of complete mercerisation. It has been claimed for these machines that they reduce the art of mercerising to the simplest possible treatment and avoid the scores of minor adjustments which may be made on the older chain or stenter system. The highest quality of mercerised cloths, however, is still produced on mercerising ranges which include the stenter, and the possibility of the greater number of adjustments enables each cloth to be treated under optimum conditions according to its peculiar character.

Simili-mercerisation

The term "similisage" was applied many years ago in France to the normal process of mercerising for lustre, in order to differentiate Lowe's process from that of Mercer. Simili-machine is sometimes used as a method of describing the Schreiner calender, but simili-mercerising is quite a distinct and separate process, based on the fact that the highly swollen mercerised cotton is in a receptive condition for impressions. It will be remembered that many short staple cottons do not acquire a high degree of lustre when mercerised even under the best conditions; nevertheless, they swell during the mercerising process and may be calendered in a special manner to improve their lustre.

The simili-mercerising machine is built on the basis of a Schreiner calender, but the upper bowl is plain instead of engraved. A considerable amount of skew is arranged for the lower cotton bowl, about 15 to 20 mm., and it is usual to have an upper dummy bowl to take the vertical axial pressure. The steel bowl is heated to about 200° C., and the speed of the cloth, containing about 40 to 50 % moisture, is so adjusted that it is dry when it leaves the machine; this usually means a speed of 16 to 20 yards per minute. The pressure varies according to the type of cloth, lightweight shirtings requiring about 400 lbs./sq. inch and heavy cloths 500 or 600 lbs./sq. inch.

The wet and mercerised cloth becomes flat and papery after passing through the machine and acquires a greasy kind of lustre, which is removed by steaming or passing through boiling water, when the flattened threads swell and become rounded, giving the cloth a fine silky lustre equal to that of Egyptian cotton goods.

Lace and Knit-goods

In many cases it is possible to manufacture coarse lace and net materials and then contract the fabric by mercerising without tension ; this is sometimes cheaper than producing a close structure directly. The shrinkage may be brought about by NaOH of 30 to 35° Tw. followed by very thorough washing in a winch machine.

Knitted material for glove and suede fabrics cannot conveniently be knitted as compactly as necessary, and here again it is usual to mercerise without tension in order to produce a high degree of shrinkage. Many knitted fabrics are flat, with the result that the selvedges curl or roll in to the centre when wet, making impregnation difficult. Open-width treatment in the padding mangle is practically impossible. The usual method is to produce a tubular fabric by sewing the selvedges together, and run this through the impregnating trough with the assistance of a stainless steel internal stretcher, generally made from tubing. This stretcher inside the tubular fabric comes immediately before the " nip " of the mangle and so avoids the material running into a rope through the mangle with all the attendant results of rope-marks, crease-marks and streaky dyeing later. After impregnating in 50 to 55° Tw. NaOH the material is piled in moist containers for some hours, protected from light and currents of air, in order to shrink to the fullest extent. Subsequent washing, souring and washing take place as usual but with minimum tension in order to preserve the fully-shrunk effect.

Caustic Soda Recovery

The question of the recovery of the caustic soda from the mercerising plant is largely decided by the type of works in which the mercerising is done. It must be remembered that in many works there are opportunities of utilising the dilute alkaii in a very economical manner. If the goods are mercerised in the scoured state and certainly if the mercerising is performed on bleached goods, then it is possible to use the dilute wash-waters in the kiers. Another means of utilising the dilute alkali is by the absorption of chlorine and the use of the sodium hypochlorite for bleaching purposes.

Conditions vary in different plants, but it may be possible that dyeing and printing operations find an outlet for the dilute caustic soda from the mercerising ranges. In a bleach

PLATE IX.

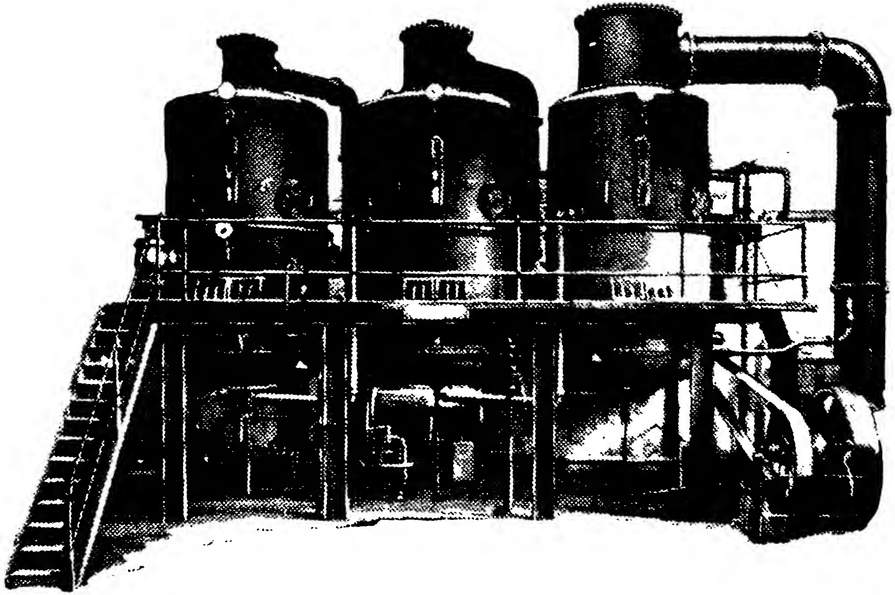


FIG. 65.—Scott triple effect vacuum evaporator using pass-out steam.

(By courtesy of Ernest Scott & Co., Levenbank, Leven, Fife and London.)

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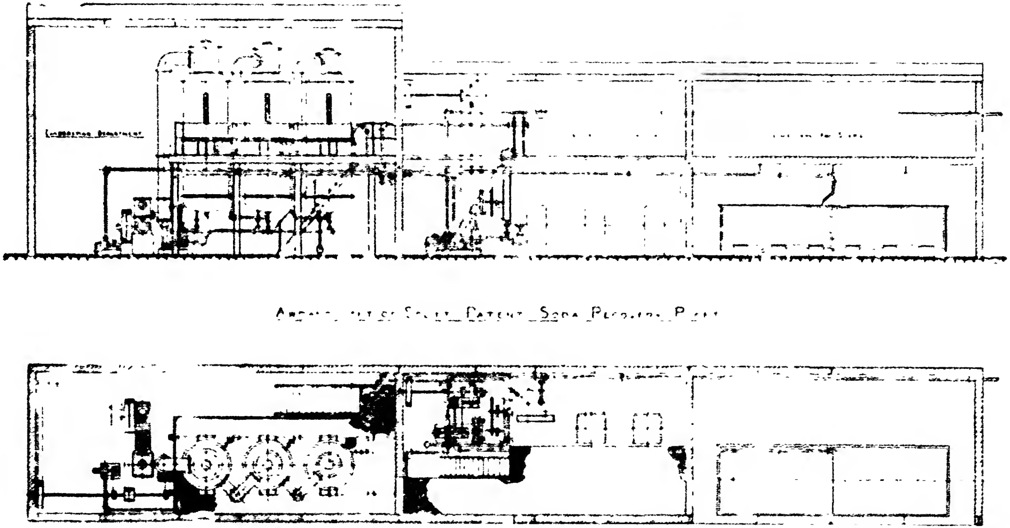

FIG. 66. Typical lay-out of complete Scott soda recovery plant.

(By courtesy of Ernest Scott & Co., Ltd., Falkirk, Leeds, Lyon and London.)

[To face page 141.

works, however, it may be taken as general opinion that the installation of special apparatus for the recovery of the caustic soda is not worth while where the output of mercerised material is only 25% of the total production. Apart from this, there are other factors to consider, such as a possible supply of exhaust steam, etc.

Where there is a large output of mercerised material the lay-out of the plant is usually arranged to include some sort of recovery, even if it is only to the extent of dissolving solid caustic soda in the wash-waters to bring them up to the required concentration for mercerising. The wash-waters are not allowed to become too dilute when running on the counter-current system, for this adds considerably to the cost of recovery.

Chase (A.D.R., 1925, *14*, 21) has given some details of an American plant with five mercerising machines which gave an output of 750,000 yards of cloth per 50-hour week. The goods were mercerised in the wet state by a three-bowl mangle and a stenter 60 feet in length equipped with spurt pipes and running at about 60 yards per minute. The concentration of the alkali was maintained at 52 Tw., necessitating a supply of 10,000 gallons of 76° Tw. NaOH per week. This is equivalent to 40,000 lbs. of solid NaOH; one pound of alkali was required for four pounds of cloth.

About 75,000 gallons of water were required to wash the cloth before it left the stenter and the wash-water was recovered at 10° Tw. NaOH; 65,000 gallons of water were evaporated, producing 10,000 gallons of 69° Tw. NaOH solution, to which 10,000 lbs. of fresh alkali were added to restore the concentration of 76° Tw.; about 75% of the alkali may, therefore, be recovered.

If the counter-current system is operated so that the wash-water is recovered at 5° Tw. then it is possible to recover 90% of the alkali, but the cost is much greater, for there is twice as much water to evaporate.

Filtration forms an essential preliminary to the recovery process, coke crushed to pea size being the common filtering medium, but iron gauze is sometimes used. The question of causticising must be decided by the type of work in hand, for the amount of sodium carbonate does not always accumulate to a serious extent; the mercerising of grey goods, however, builds up supplies of foreign matter in the alkali, and the simplest course to follow is caustification.

The common practice is to treat the recovered wash-waters with lime in a cylindrical tank or a U-tank ; after stirring and heating, the sludge is allowed to settle and the clear liquor is drawn off. Lead acetate may also be used to assist the deposition of the impurities.

Evaporation of the water is usually done in multiple-effect evaporators, either the vertical or horizontal tube type, of sufficient capacity to concentrate to the required strength. The multiple effect consists in making use of the latent heat of the vapour evaporated from one liquid to generate vapour from a liquid with lower boiling point ; in this case a reduction of the pressure in the second evaporator lowers the boiling point sufficiently below the temperature of the vapour from the first evaporator for reasonable heat transference to occur.

The evaporator usually works with steam at exhaust pressure and consists of an upper chamber for vapour and a lower circulating chamber, connected by a special arrangement of tubes surrounded by steam. The liquor is fed into the upper chamber and descends through the heated tubes where evaporation occurs ; automatic feeds are common. The machine continues to function until a sample shows that the required concentration has been reached. In some cases a further precipitation of impurities takes place necessitating further filtering.

The first caustic soda recovery system appears to have been installed in 1901 by Ernest Scott and Co., Ltd., of Levenbank, Leven, Fife, and of London.

CHAPTER TEN

YARN MERCERISING MACHINERY

THE basic method of all hank mercerising is the manipulation of the hanks stretched on rollers during the impregnation with caustic alkali and the subsequent washing process. An interesting exception to this general statement was the Centrifugal Mercerising Machine produced by Kleinwefers Söhne, in which the yarn was wound round a perforated cylinder, the circumference of which was adjusted to the length of the reel. The alkaline liquor was brought into the cylinder through a perforated pipe, and in consequence of the centrifugal force the yarn was rapidly saturated with caustic soda. Modern demands, however, necessitate machines requiring the lowest possible amount of labour, liquor and operating power.

In all cases the yarn is kept in movement by the rotation of the rollers on which the hanks are placed, and many types of machines frequently reverse the direction of rotation in order to ensure a more even treatment. Some machines maintain the yarn at tension during the mercerising and washing operations, but the great majority allow shrinkage during the impregnation process in order to bring about the utmost possible penetration by the caustic soda solution. The tension is then applied to the thoroughly impregnated yarn, either before or during the washing process in order to produce the necessary lustre under conditions which demand the minimum expenditure of power.

For instance, in one machine the hank, originally 134 cms. in circumference, is immediately allowed to shrink to about 110 cms., and then pulled out to about 132 cms. in the first minute. The hank is then allowed to shrink again to about 120 cms. and expanded to 135·5 cms. immediately before and during the washing process. In another machine, on the other hand, the hank is entered at 135 cms. and allowed to contract to about 110 cms. in the alkali; it is then pulled out to 135 cms. during the washing process.

In almost all cases the mercerised hanks are removed to a second machine for the neutralisation of the final traces of alkali by means of dilufe acid—usually H_2SO_4; this process is termed "souring," and is followed by a thorough wash with water to remove any excess of acid.

It is not possible to give a complete account of every hank mercerising machine without a considerable amount of repetition, and the following have been chosen as representative and typical examples. The early machines have been described by the editors of "The Dyer" (Mercerisation, Heywood, London, 1903), whilst a later account has been given by Hall (Bleaching, Dyeing, Printing and Finishing Machinery, Benn, London, 1926).

It often happens that a small machine gives one a clearer idea of the principles involved and the actual mechanical operation than may be obtained from consideration of a large industrial plant. Most manufacturers of mercerising machines supply small "hand" mercerising machines for use in laboratories, technical schools and testing institutes; some of these machines have a vertical arrangement of the rollers, but the modern tendency seems to be in the direction of a horizontal arrangement. A typical machine is illustrated in Fig. 68.

The yarn is laid on the rollers which are caused to revolve by a belt and pulley in connection with gear-wheels. The application and relaxation of tension are under manual control through a worm wheel and spindle. In the particular model under consideration, decreased friction on the spindle is ensured by ball-bearings. The tank for the alkali is raised and lowered by means of a handle, and the rinsing tank is brought into position by hand, covering the tank which is for the caustic solution. The alkaline lye is applied by raising the trough containing the liquor until the hanks are partly submerged. After suitable manipulation and impregnation, the yarn is squeezed by a rubber roller, which is pressed by means of a hand lever against the roller carrying the yarn. When all excess of the alkali has been removed, the trough containing the alkali is lowered and that for the water brought into position over it. The yarn is then washed with water from the spurt pipes immediately above it and tension applied in order to produce the lustre. The excess of water is then removed by the squeezing roller as in the case of the alkali, and relaxation of the tension enables the yarn to be removed for drying. A machine of this type will carry about ¾ lb. of yarn and has an output of some 70 to 100 lbs. of yarn per day.

Kleinewefers

A good example of a machine for works' production is made by the same firm (Kleinewefers Söhne), who utilise a cast block for the main machine instead of the alternative base plate and stays. This gives lightness and rigidity, and also ensures room for the driving gear in the block itself, so that these parts may be enclosed in a gear case and protected against dust, dirt and splashes by the alkaline liquor. Central lubrication is also employed. Fig. 69 illustrates this machine.

The two chief features of this machine are that it is automatic in operation and is fitted with hydraulic drive. The term "automatic" means that with the exception of the mounting of the yarn on the rollers before mercerising and their withdrawal afterwards, all the other processes are entirely automatic and eliminate the personal factor of the operative in respect of the effect produced and the amounts of alkali and water employed. The use of hydraulic pressure enables a considerable tension of an elastic nature to be applied to the yarn, for the hydraulic pump is so arranged that when the required maximum pressure is reached in the accumulator, it is automatically cut out, eliminating the possibility of excessive tension. Similarly, when the accumulator falls below a certain height, the pump starts to function again, and in this manner works between definite limits of maximum and minimum pressure. The use of hydraulic devices also makes possible fine adjustments of the tension, and the same pressure can be produced during the processing of subsequent deliveries of yarn. A pointer working on a scale indicates the exact length of the yarn. The use of hydraulic pressure permits a longer period for the penetration of the lye, relative to the other types of pressure, for over the same time for mercerising, the hydraulic device enables the tension to pass from minimum to maximum in a shorter period.

The squeezing or mangling of the yarn is also effected hydraulically, and on account of the heavy pressure thus obtained it is possible to effect considerable economies in the amount of caustic soda solution. The amount of liquor used is about 300 grammes per pound of yarn.

Another important aspect of the absence of weighted springs or levers is that the power required to work the machines remains constant.

The rollers of the machines under consideration are of particularly generous dimensions and made from special steel, so that there is no danger of any variation in tension of the various hanks along the entire length of the rollers. The absence of any supports in the front of the rollers is an advantage in respect of ease of loading and unloading. The rollers are fitted with forward and reverse drive, which is automatic, and this is of great benefit not only for the actual mercerising but also for obviating any breakages or yarn entanglements. One roller is fixed in its bearings and the other is moved in slide bars, but both are driven so that the yarn is easily moved or rotated. The rubber squeezing roller is situated above each of the fixed rollers and lies on them during impregnation and washing, thus assisting thorough impregnation. It is lifted automatically for the mounting or withdrawal of the hanks on the rollers.

During the mercerising process with this machine, the yarn is first under moderate tension and is then allowed to shrink as the alkali takes effect ; finally the full tension is applied.

Separate collecting tanks are provided for the caustic soda solution and for the wash-water from the yarns. Their movement is effected in a particularly even manner, so that there is no possibility of spilling or splashing of the alkali from its tank during the slow downward movement, during which the tanks for collecting the rinsings come in from the side and cover the tanks for collecting the alkali. Only when the latter are covered completely is the washing from the spurt pipes allowed to start.

Two models of these machines are provided for the mercerising of cotton hanks, and they give hourly outputs of 40 and 70 lbs. of yarn ; they require a driving power of two and three horse-power respectively.

In Fig. 69 it is clear from the illustration that the machines are actually twin machines ; there is another pair of rollers, tanks, etc., at the back of the machine. These machines can be arranged for the treatment of hanks of from 49 to 98 inches in circumference ; a special model on the same principle has been designed for the mercerising of staple fibre yarn and for cotton-staple fibre mixtures.

Recent developments in this type of machine include a new hydraulic system designed to work without weights and accumulator. A specially constructed regulating valve is fitted to the main pressure pipe, together with a gauge, so that the working pressure of the machine can be adjusted by simply turning a handle.

A further improvement consists in the tension control, enabling the pre-determined stretching in the alkali and the final stretching during washing to be adjusted independently, instead of bearing a fixed ratio to each other.

Bonnet

The " Bonnet " type of hank mercerising machine of Mather and Platt again comprises two pairs of tension rollers, one at each side of the machine. The cycle of operations is carried out automatically in the proper order, and the only work for the operative is to place the hanks in position before mercerising and to remove them afterwards. The machine thoroughly impregnates the yarn in the trough containing the caustic soda solution and rotates it in alternating directions during the impregnation ; tension is applied automatically and maintained during the washing process. The mechanism provides for the removal of the bath containing the caustic soda at the correct moment, and the substitution of the hot and cold washings. Extra tension is given to the hanks during the wash with hot water, and it is possible to collect the first washings separately with a view to recovery, as these are relatively more concentrated in NaOH than the later washings. Both inner and outer surfaces of the hank are sprayed.

The tension on the rollers is obtained by a powerful steel cam and roller ; it is transmitted to the yarn by means of a lever and weight. The distance between the rollers is regulated by a single handwheel in front of the machine and may be read on a graduated scale. This distance varies according to the original length of the hanks and the desired extension. Another scale with a moving pointer shows the actual degree of tension on the yarn, and when the safe maximum tension is exceeded the machine is stopped by a safety device.

The rotation of the rollers during the mercerising operation is effected by a special gearing which enables four changes in the direction of rotation to be given during each operation ; this is a somewhat important feature of modern hank mercerising machines, for not only does it help in obtaining even results, but it prevents the breakage of threads which is apt to occur. The change in rotation takes place instantaneously.

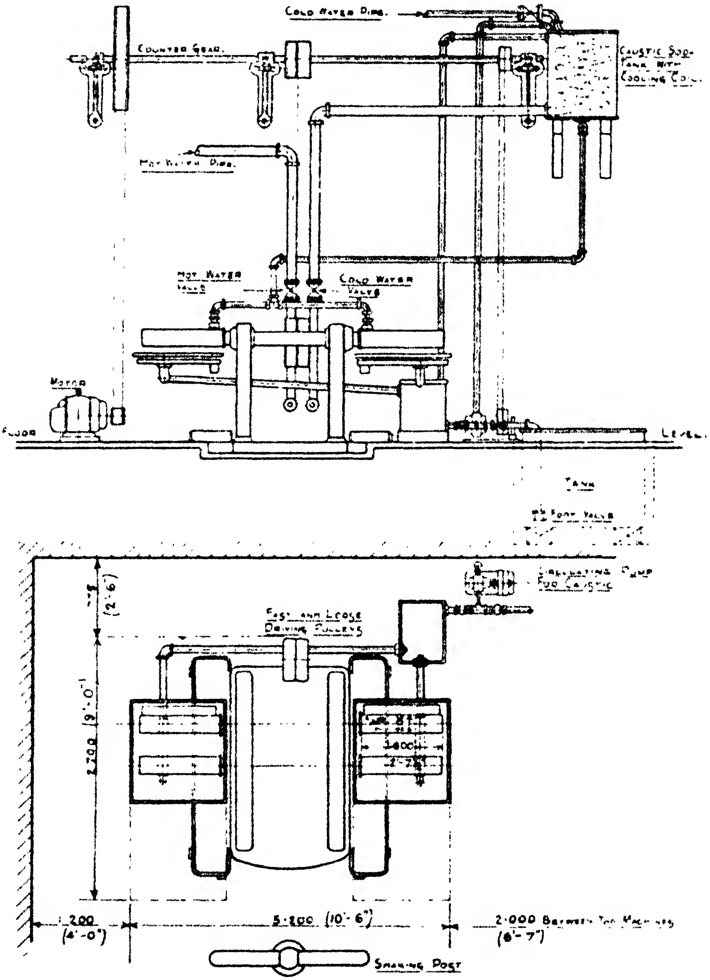

FIG. 67.—Layout of the "Bonnet" machine. (Mather & Platt Ltd.)

PLATE XI.

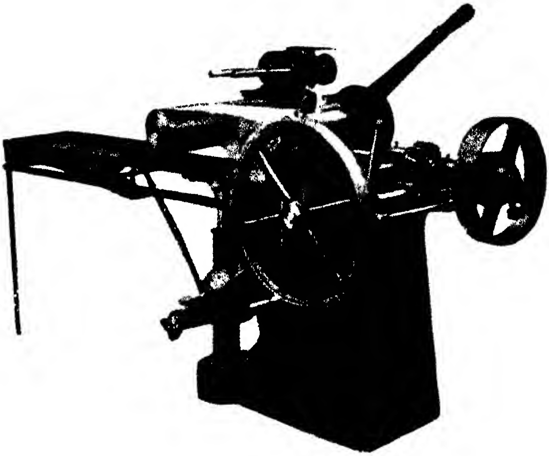

FIG. 68.—Hand mercerising machine.

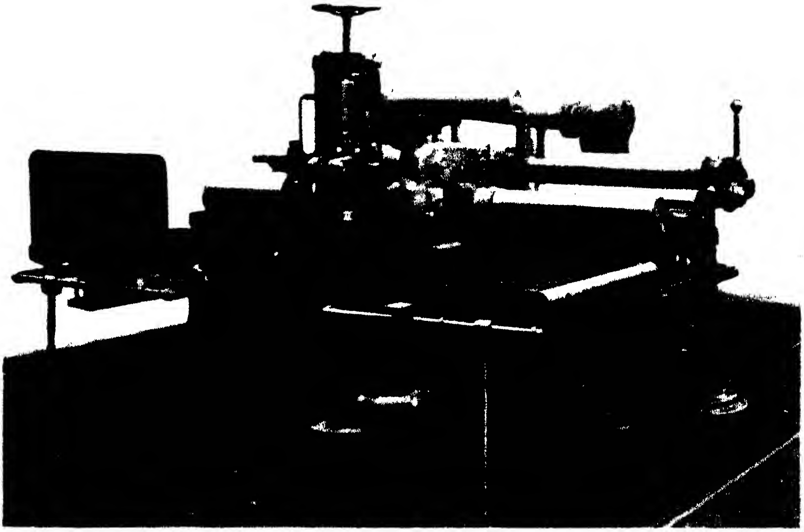

FIG. 69.—Kleinewefers machine, type N 111.

(By courtesy of Kleinewefers Sohne.)

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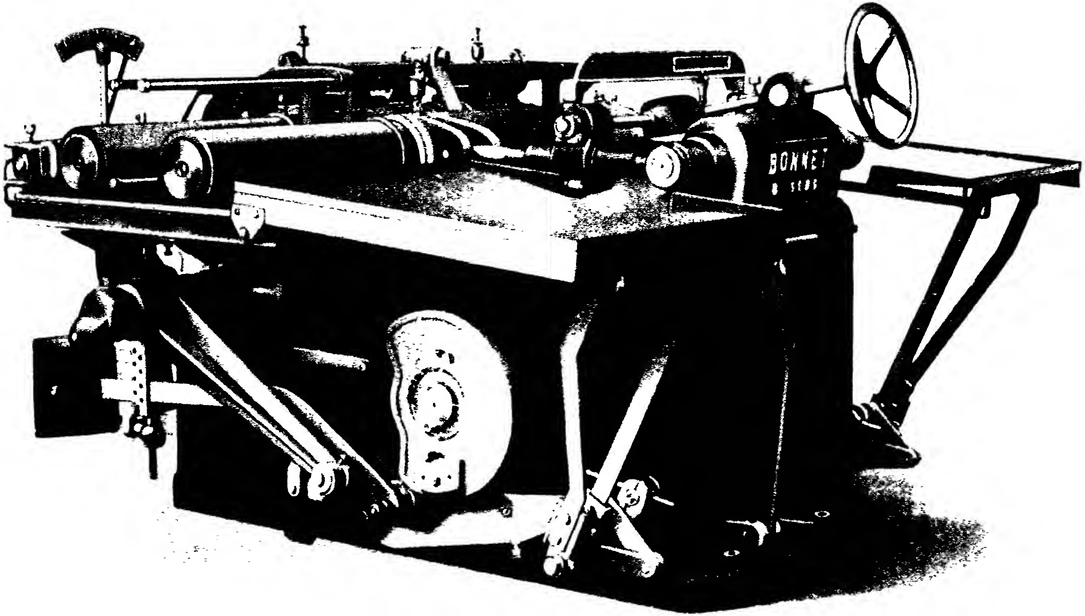

FIG. 70. The Bonnet bank-note issuing machine.

By courtesy of Mather & Platt.

The squeezing of the yarn is done by rubber-covered rollers, mounted on ball-bearings, to avoid any drag or slip on the yarn. The pressure on these squeezing rollers is regulated by steel cams, levers and weights limiting the pressure to a safe figure. A protective device, again automatic in operation, protects the fingers of the operative from the squeezing rollers. (Figs. 71, 72.)

The motions of the trough are such as to avoid any loss of the liquor. The machine is illustrated in Fig. 70.

The total time for a complete operation of placing the hanks in position, mercerising, washing, squeezing and removing the hanks is five minutes. The extent of movement of the rollers during the stretching operation is 5·9 inches and the pressure exerted by the squeezing rollers varies from 4,000 to 4,400 lbs., according to the size of the machine, of which Messrs. Mather and Platt make three types requiring power of 3·5, 4·5 and 5 h.p. The total maximum tension exerted by two pairs of rollers is 9 12 tons. The average weight of cotton hanks which may be mercerised at one time varies according to circumstances, but figures are given of 5½ to 6½ lbs. for the small machine, 6½ to 7¾ lbs. for the medium machine and 10 to 11 lbs. for the large machine (90 ins. reels).

The Bonnet machine is of French design originating from Etablissements Bonnet Ainé et ses fils, Villefranche sur Saone.

Haubold

Another type of automatic hank mercerising machine is made by Haubold, and this, too, is a double machine with a pair of rollers, a squeezing roller and the necessary tanks on each side. The movements of the troughs, the rollers and the squeezing roller are operated by hydraulic power and the pump is so constructed that any desired pressure may be set precisely and maintained ; the safe maximum pressure cannot be exceeded as a safety device stops the pump. The exact length of stretch may also be precisely adjusted ; an automatic reversing motion is fitted to the rollers. When the hanks are undergoing the caustic treatment, they are first stretched, then allowed to shrink and finally stretched again, when the rubber-covered roller presses on the yarn to assist penetration. Separate troughs are provided for the alkali and for the wash-waters.

The cycle of operations is seen from Fig. 74, Plate xv. First, the yarn is placed on the rollers whilst they are close together ;

secondly, the alkali is applied and the yarn is stretched, during which operation the squeezing roller presses on the yarn to ensure thorough penetration. Thirdly, heavier pressure is applied by the squeezing roller and the excess of liquor is collected in the trough below the rollers. Fourthly, the yarn is washed and squeezed ; the first washing is with hot water, and the dilute lye is led into a special channel for further use, after which the washing is continued with cold water. Fifthly, the rollers are brought close together to facilitate the removal of the yarn, as shown in the sixth and final operation.

Both the fixed and sliding rollers are positively driven and their free ends are supported by small auxiliary hydraulic cylinders which work in conjunction with the main cylinder. These auxiliary cylinders are of telescopic design to allow for various distances between the rollers, and ensure absolute parallelism of the rollers under all operating conditions.

The amount of yarn which may be treated on this machine varies from 2·8 to 3·3 lbs. per pair of rollers.

Vertical Machines

A typical semi-automatic mercerising machine, manufactured by Smith, Drum and Co., is shown in Fig. 75 : a machine of somewhat similar appearance is also made by Messrs. Haubold. About two pounds of yarn are loaded on to each pair of rollers, which are then caused to separate and put the yarn under tension. It is advised that this tension should be such that it is possible to press the middle of the hanks about half an inch towards each other when mounted on the rollers. The rollers are caused to revolve and the entire frame is lowered into the bath of alkali. After the yarn has been immersed for about three minutes, the entire frame is raised and the hanks are squeezed and allowed to drain ; with the rollers still revolving, the yarn is washed, first with hot water (approx. 60° C.) and then with cold water. During the washing by means of the customary spurt-pipes, the yarn becomes slack on the rollers, and extra tension may be applied either automatically or by manual control. The wash waters are prevented from going into the caustic tank under the machine by a sheet metal gutter, which automatically comes into position as the yarn rises from the tank.

A special feature of the Smith, Drum machine is that each of the poles is supported at both inner and outer ends by heavy ribbed castings, which prevent any tendency to sag under the strain of the contracting yarn.

The lowering of the frame carrying the rollers covered with yarn is an essential characteristic of this type of mercerising machine.

The Haubold machine operates by hydraulic pressure and has six pairs of rollers on each side, each pair of rollers taking about two pounds of yarn. The bank of rollers on each side enables the operative to replace the yarn on one side during the mercerising of the yarn on the other—a feature common to most hank mercerising machines. Two attendants are necessary, however, for steady uninterrupted working.

It is not possible to exceed the highest required pressure which forces the rollers apart, for in such a case the machine stops automatically. Both the fixed and movable rollers are driven and the direction of the rotation of the yarn changes periodically. The squeezing of the yarn after impregnation is effected by twelve strong iron rollers covered with rubber and ensuring a small consumption of lye. The spraying arrangements for washing are so arranged that both the inner and outer surfaces of the hanks are well washed with hot and cold water. A cycle of operations can be arranged to give periods of 8, 10, 12 or 15 mins. for the complete mercerising process. An average output for this machine is about 130 lbs. per hour, but 180 lbs. per hour can also be reached.

Revolving Machines

Revolving machines were quite common some years ago, the pairs of arms describing a circular path as they carried the hanks of yarn through the successive operations of mercerisation. The Spencer-Lord machine, for instance, consisted of pairs of vertically-arranged rollers which described a horizontal path, whereas the Dolder machine caused the pairs of rollers to revolve in a vertical plane. Mather and Platt also made a revolving machine.

Kleinewefers' revolver machine for hank mercerising has the pair of rollers arranged horizontally in a revolving head to move in a horizontal plane. The rollers are arranged in eight pairs and the separate operations of mercerising are distributed over the machine. Those rollers in front of the machine are filled with the hanks of yarn and stretched; they then move into the second position, where the hanks are partly immersed in the tank containing the caustic soda solution, the direction of rotation of the rollers being changed several times as the hanks pass through the third and fourth positions. Penetration is assisted by rubber squeezing-rollers, but in the fifth position much heavier pressure removes the excess of alkali. There is application of heavy pressure in the sixth position also, but in conjunction with a small amount of hot water which is supplied from spurt pipes; this enables a solution of about 23° Tw. NaOH to be collected separately. Copious supplies of hot water are supplied in the seventh position, followed by cold water and a final squeeze in the eighth position. The time for each stage of the process may be varied between 45 to 65 seconds according to requirements. All the rollers are driven directly and the pressure is applied hydraulically. The machine is illustrated in Fig. 77.

Jaeggli

The Jaeggli automatic hank mercerising machine contains a number of interesting features and is a "double-ended" machine. The stretching devices consist of two pairs of solid rollers, covered with rubber and running in special ball-bearings, the hydraulic cylinders and pistons, the squeezing rollers and the operating valves. The troughs for the alkali and the wash-waters are situated inside the cast-iron frame, along the back of which runs the operating shaft fitted with eccentrics. The bed-plate at the left end carries the hydraulic pump, the complete drive with hydraulic couplings for reversing and changing speed, and also the pump for the alkali with its valve for reversing the circulation.

A special type of hydraulic friction coupling is used for reversing and altering the speed at which the hanks rotate. The toothed wheels and couplings are carried by two hollow shafts, which are internally constructed to act as pressure cylinders and are fitted at their ends with nozzles for admitting the water. The plungers are located in these hollow shafts and are connected in the middle part of the couplings, giving instantaneous engagement without shock. The admittance of the pressure water is regulated by two valves operated by eccentrics on the camshaft. The hydraulic couplings ensure smooth and reliable working of the machine, and there is practically no stoppage of the rollers when altering direction and speed—a point which contributes towards uniformity of mercerisation.

A minor refinement is provided by three separate channels

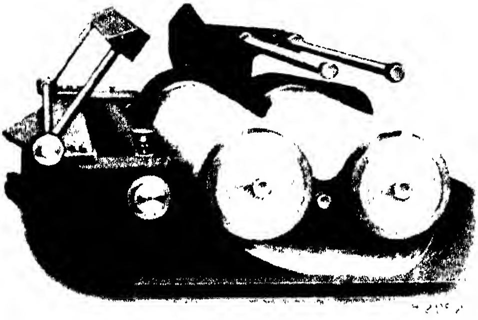

FIG. 71. The Bonnet machine with the hanks slack on the rollers, and the protective device out of operation.

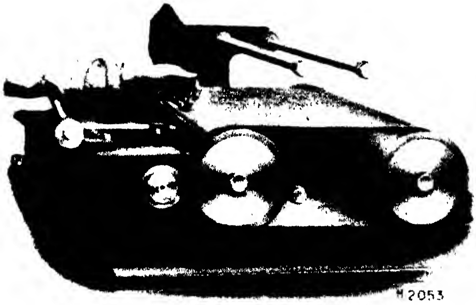

FIG. 72. The Bonnet machine with the hanks under tension, and the protective device guarding the hands of the operative from the squeezing roller.

(By courtesy of Mather & Platt.)

PLATE XIV.

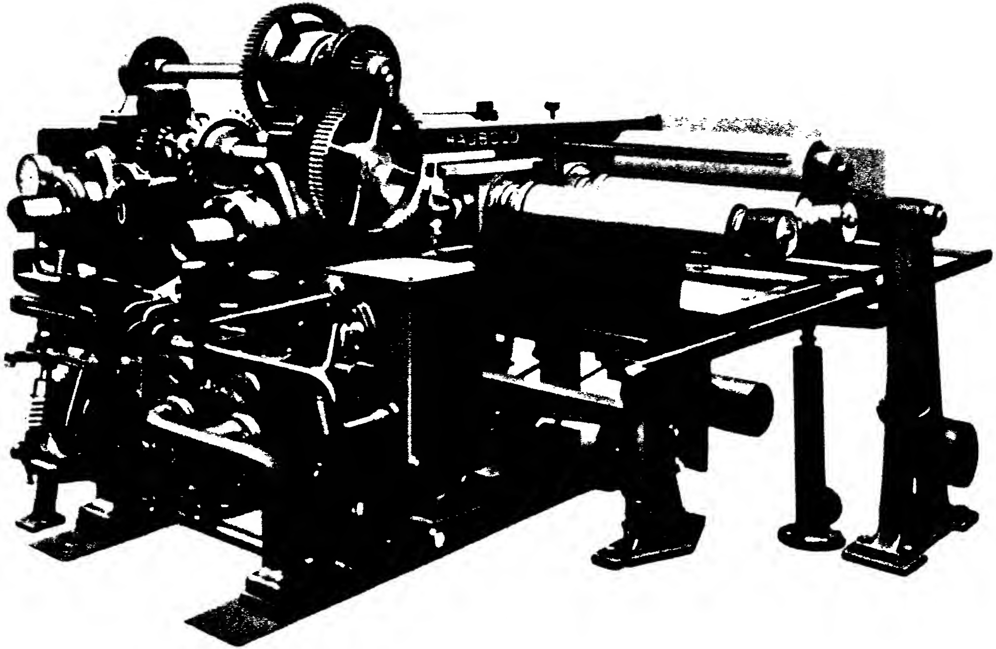

Fig. 73. Haubold hank mercerising machine.

(By courtesy of C. G. Haubold, A.G.)

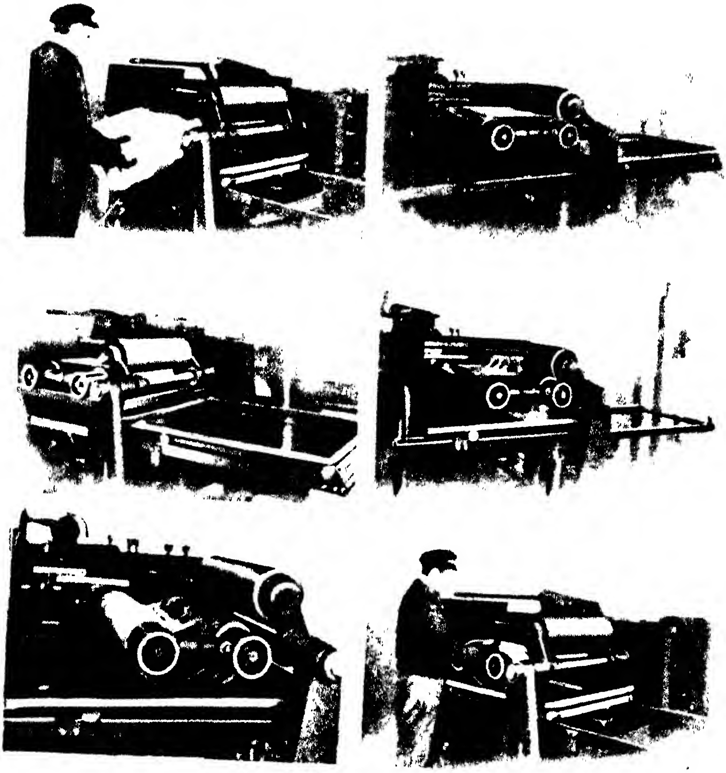

Fig. 74. Sequence of operations with Haubold mercerising machine.

(By courtesy of C. G. Haubold, A G.)

PLATE XVI.

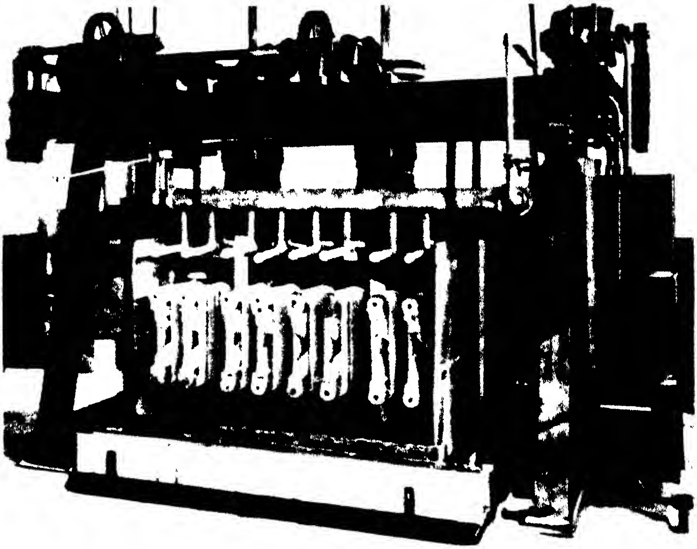

FIG. 75.—The Smith drum machine.
(*By courtesy of Smith Drum Co.*)

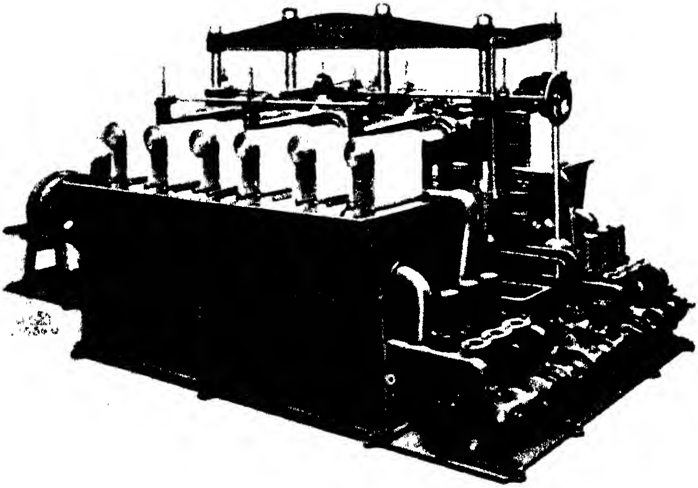

FIG. 76.—Haubold machine, type Hn.
(*By courtesy of C. G. Haubold, A.G.*)

PLATE XVII.

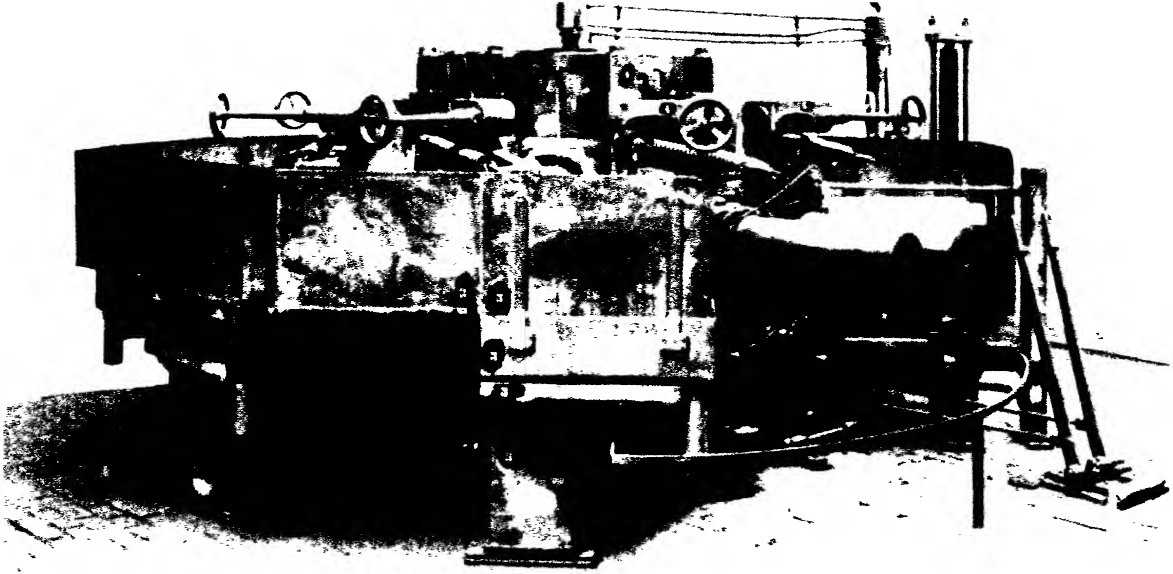

FIG. 77.—Kleineweters revolver machine, type E III.

(*By courtesy of Kleineweters Sohne.*)

PLATE XVIII.

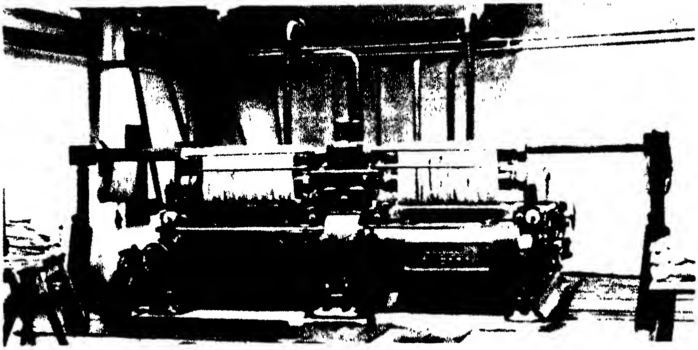

FIG. 78.—Jaeggli standard machine
(Charging position.)

FIG. 79.—Sliding the hanks on to the Jaeggli machine

(By courtesy of J. Jaeggli & Cie.)

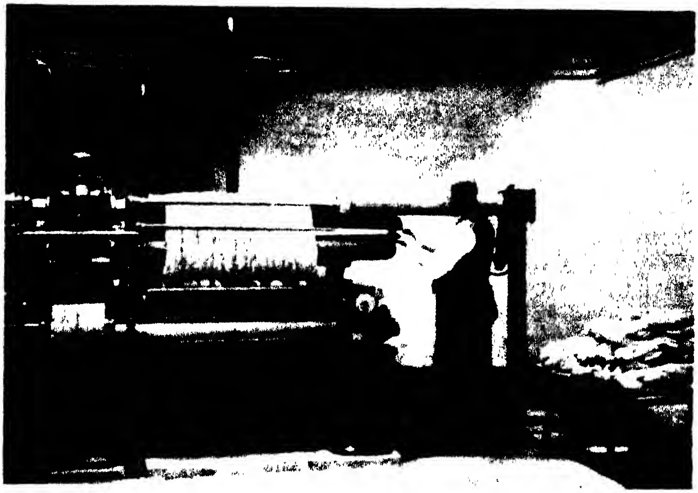

FIG. 80.—Removing the special shovels.

FIG. 81.—Removing the mercerised yarn.

(By courtesy of J. Jaeggli & Cie.)

PLATE XX

FIG. 82.—Jaeggli machine, type MM3, in charging position.

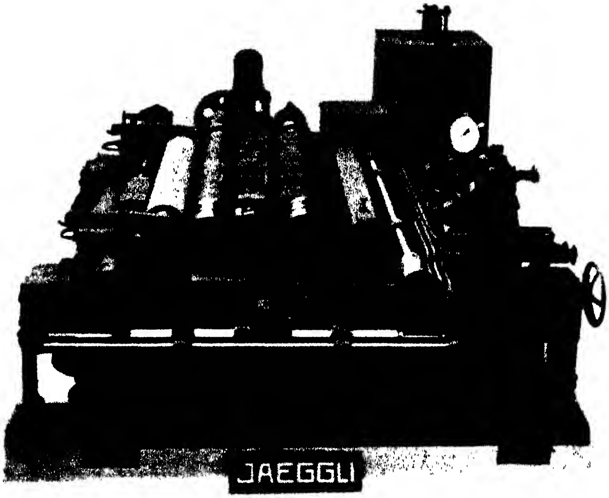

FIG. 83.—Jaeggli Machine, type MM3, in working position.

(By courtesy of J. Jaeggli & Cie.)

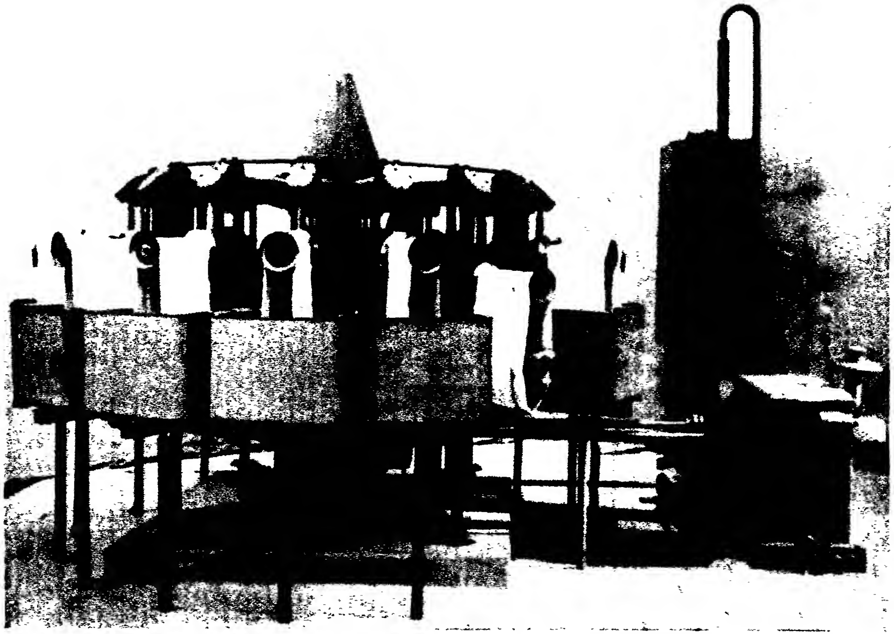

FIG. 84.—Jaeggli "Coloras" machine for neutralising and washing the hanks after mercerising.

(*By courtesy of J. Jaeggli & Cie.*)

PLATE XXII.

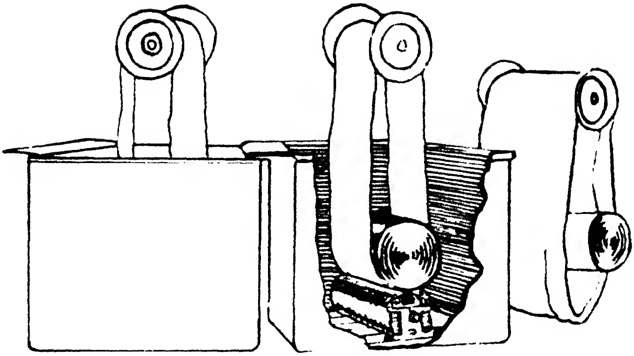

FIG. 85.—Descriptive drawing of the Jaeggli "Coloras" washing machine.

(By courtesy of J. Jaeggli & Co.)

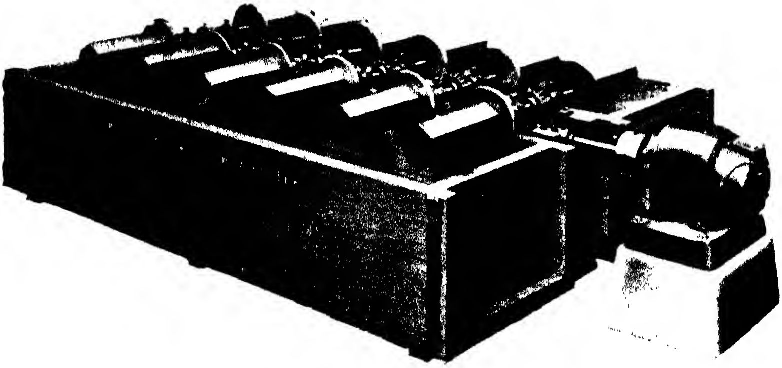

FIG. 86.—Hank neutralising and washing machine.

(By courtesy of Messrs. Mather & Platt.)

PLATE. XXIII.

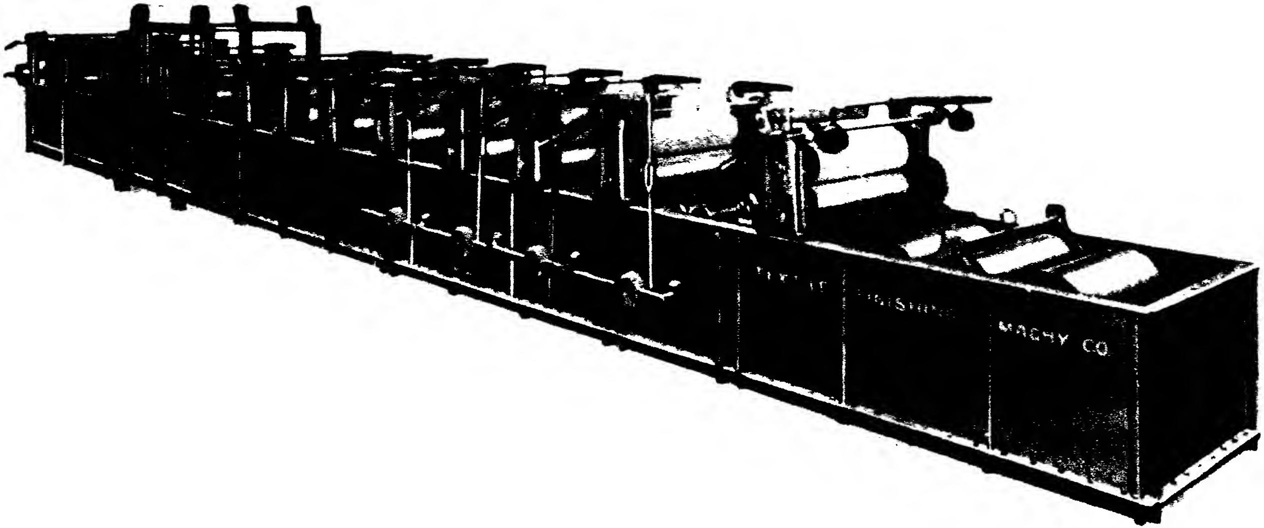

FIG. 87.—Warp mercerising machine.

(*By courtesy of The Textile Finishing Machinery Co.*)

PLATE XXIV.

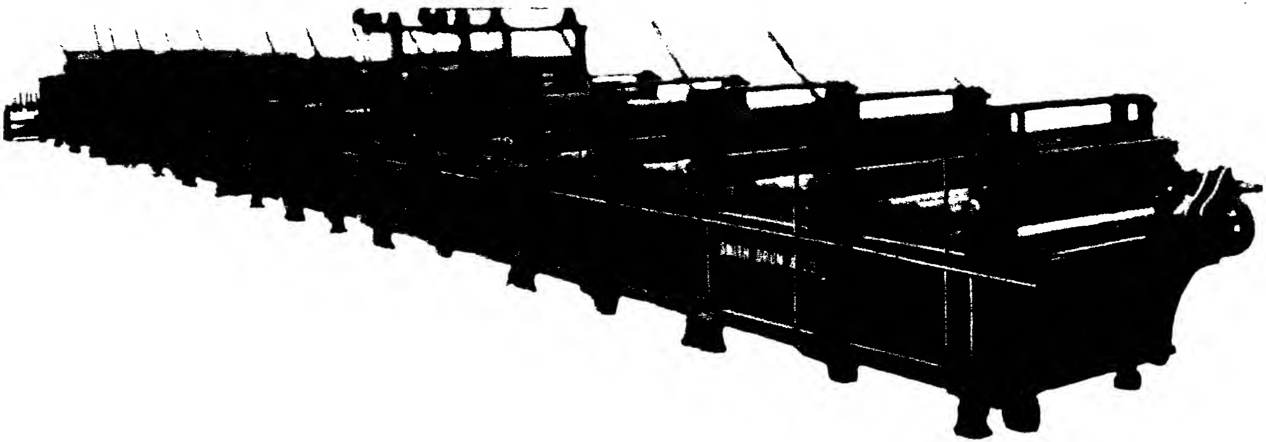

Fig. 88.—Warp mercerising machine.

(By courtesy of Smith Bros.)

[*To face page* 153.

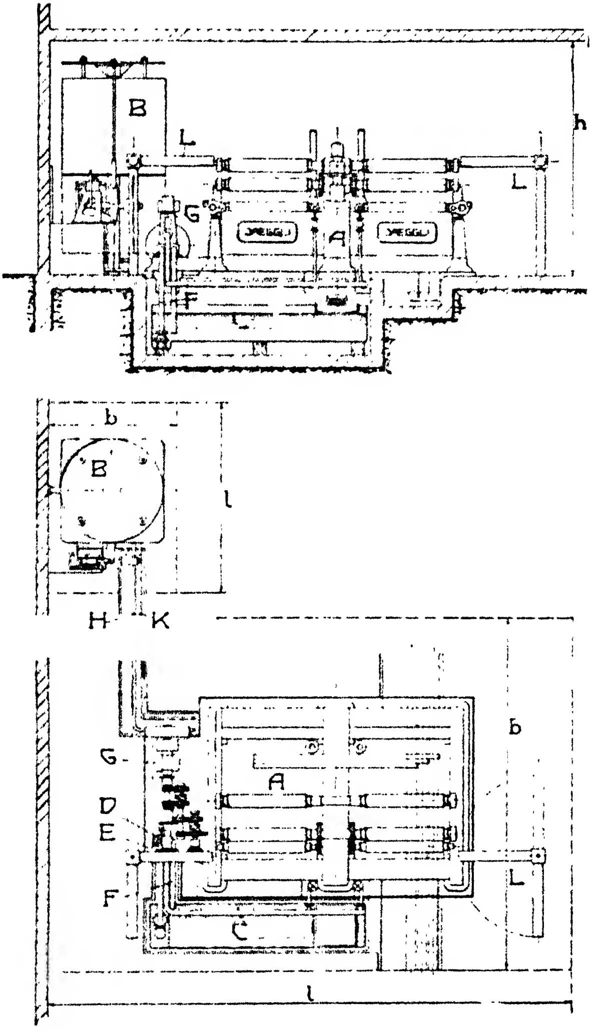

FIG. 89.—Descriptive drawings of Jaeggli hank mercerising machine, "Standard" type, and accumulator.

A Machine, *B* Accumulator, *C* Lye basin, *D* Lye pump, *E* Lye valves, *F* Lye main, *G* Hydraulic pump, *H* Pressure water piping to pressure gauge, *J* Pressure regulator, *K* Pressure water piping to machine, *L* Hank pin.

Machine space (*A*) : Length, 23⅛ ft. ; Breadth, 15¾ ft. ; Height, 10 ft. ; *Accumulator* : Length, 8½ ft. ; Breadth, 5¾ ft. ; Height, 10 ft.

for the wash-waters; the first is for the hot wash-water from the first rinse, which is relatively concentrated in NaOH and may be recovered, whereas the second hot rinsing water is more dilute in alkali but, nevertheless, may be used in scouring or dyeing. The separation of the wash-waters is automatic.

The adjustment of the machine to suit the yarn is achieved quite simply by means of a handwheel which sets three buffers according to a scale, one buffer is mounted on the middle frame and two on the end framings. A second scale at the seat of the stretching rollers serves for observing the stretch in the yarn. The machine is also fitted with a setting device for the preliminary stretching-shrinkage-tension movement; the preliminary tension shows little change, but the shrinkage is very marked and will enable the yarn to shrink completely. The pressure-regulating valve allows the yarn to be stretched properly under slow and increasing tension, but stretching beyond the desired extent is rendered impossible by the three buffers.

One of the characteristic features of the machine is the disposition of the two pairs of rollers. They are permanently supported in the middle frame and are also held in sliding supports with heavy ball bearings at both ends when in the horizontal working position; this enables high stretching pressures to be employed uniformly along the whole length of the rollers.

Figs. 82 and 83 show the oscillating movement of the pairs of rollers from the charging position (vertical and above the body) to the working position (horizontal and below the body). The useful length of the rollers is 43¼ ins. on each side, and the thickness of some seven pounds of yarn is distributed along this length, and by stretching and squeezing is so reduced as to minimise to a great extent the difference between external and internal circumferences of the hanks. The stretching force is 32 to 35 tons per machine and the squeezing pressure 4·8 to 5·4 tons. Stretching and squeezing are effected hydraulically, and the raising and lowering of the oscillating body with the pairs of rollers is carried out automatically.

The cycle of operations may best be followed from the first preliminary stretching, when the yarn is dipped in the alkali and impregnated on the whole circumference with the rollers running at high speed. The yarn is then allowed to shrink and the speed of the rollers changes to slow; the hanks are then stretched to the predetermined desired extent.

The alkali is continuously renewed in the basins or troughs during these three operations. The next step is to squeeze out the alkali with the rollers running at high speed and to lead the alkali back to the tank in the floor. The troughs for the alkali are then lowered and those for the rinsing water are brought into position. The hot rinsing water is applied from spurt pipes and the first rinsing water is separated from the rest. After washing with cold water, the hanks are squeezed with the rollers running at high speed ; they are then raised to the charging position and the distance between them reduced, the machine then stops and the yarn is removed. A fresh charge of yarn is placed on the rollers by the attendant, who slides the hanks from the swivelled arms of the hank pins at each side of the machine with the assistance of a special shovel.

In the meantime, the rinsing trough is lowered and the alkali trough raised and filled with fresh liquor. The rollers are then lowered into the working position and the preliminary stretching starts.

The mercerising cycle takes five minutes for fourteen pounds of yarn. The consumption of alkali is about 2 to 3 lbs. of NaOH per 10 lbs. of yarn.

The yarn is in contact with the alkali for about two minutes, and during the high speed rotation of the hanks during the first minute there are two changes in direction of rotation ; this assists evenness of mercerising.

A similar machine has been designed with only one pair of rollers for half the output and is seen in Figs. 82 and 83.

General

Continuous hank-mercerising machines are rarely manufactured to-day, but represent a passing development, the revolving type being a possible exception. An interesting alternative was made by Mather and Platt some years ago and consisted of a series of horizontal compartments with a trough extending the full length. Horizontal iron rollers were carried by two endless chains and as they passed through the machine the distance between them was varied by inclined planes of steel at definite distances ; this gave the necessary tension to the hanks. The rollers rotated continually and the direction of rotation was periodically reversed. The yarn was fed in at one end of the machine and withdrawn at the other ; during its passage the hanks were sprayed with caustic soda solution, stretched and then washed by hot-water sprays. The mercerising liquor and the wash-waters were collected in the troughs under the travelling hanks and returned to the tanks supplying the spurt pipe.

The modern tendency in hank mercerising machines is to bring the caustic soda solution and the wash-water to the hanks, and not the hanks to the liquids.

Washing Machines

Hank washing may be performed in any machine which is used for the washing of yarn after scouring or dyeing ; the simplest method is to treat the hanks on poles in a beck. Handling of the hanks is not as satisfactory as machine washing which may be by means of rotating winches in a vat. A superior method, however, is to use a machine with pairs of fluted porcelain rollers to carry the hanks, the rollers being mounted on ball-bearings and driven by spur-wheels. The souring, washing, etc., is effected by spurt pipes arranged so as to wash both the inner and outer surfaces of the material. Machines of this type are made by Mather and Platt, Haubold and other manufacturers. One type is shown in Fig. 86.

Circular or revolver types of washing machines are also used ; in that made by Haubold the central spur-wheel causes the radial reels to rotate. Bonnet Ainé and also Jæggli supply machines in which the yarn is lowered into tanks or troughs, rotated in the dilute acid, water or whatever solution is required, raised and passed on to the next trough. The Jæggli Coloras machine has 12 or 16 carrying arms, each with a driven press-roller and a built-in squeezing roller ; the troughs can be arranged for the counter-current principle of working. The direction of rotation of the hanks changes every 10 seconds and the rollers carrying the hanks are lifted from the troughs at intervals of from 20 to 60 seconds, moved on by 1/12 or 1/16 of their course and lowered again. The machine operates hydraulically ; it is illustrated in Fig. 84.

Warp-mercerising Machines

Machines for warp-mercerising are capable of a variety of arrangements of the fundamental unit, which is a compartment or box fitted with squeeze roller and guiding rollers ; the number of the latter may vary, but it is common to have five near the bottom of the box and four at the top. These guide rollers are generally about 12 inches in diameter and may be made of brass, except in the compartments where they would come into contact with the alkali, in which case they are made of iron. The squeeze rollers should be covered with hard rubber, as soft material would wear into grooves fairly quickly. The squeeze rollers are all mechanically driven and are 10 inches in diameter and usually 36 inches long to accommodate 12 chains or drafts. A greater number of drafts would tend to mat and longer rollers are required in this case; this is rare, for the warp-mercerising machine gives a great output.

The number of compartments varies according to the requirements of the works, but 13 appears to be the average minimum. Nos. 1 and 2 are used for boiling the yarn and No. 3 for cooling it; Nos. 4, 5 and 6 contain the mercerising liquor, while Nos. 7, 8 and 9 are devoted to washing off the alkali. Souring is done in No. 10, and the final washing with hot and cold water takes place in Nos. 11, 12 and 13. As already stated the number of compartments may be extended as desired.

The compartments containing the alkali have their squeeze rollers driven at constant speed, but the preceding and succeeding squeeze rollers may have their speed increased or decreased by two nine-speed gear boxes. The tension on the warps is adjusted by the speed of the squeeze rollers with which each compartment is fitted. The pressure is applied to the squeeze rollers by the usual system of weights and levers.

Hosiery yarns are usually mercerised at a speed of 12 yards per minute and other yarns at 8 yards per minute on account of the greater difficulty of penetration. The average production is about 5,000 to 6,000 pounds of yarn per day. The complete machine may be about 150 feet long.

Arrangements are made for counter-current supply of alkali through the boxes, counter-current washing and the usual circulation of alkali and also of the acid for souring. As already stated, some machines have raised guide rollers to give a longer period of contact without decrease in speed; this also avoids undue increase in the number of compartments. Compensators may be placed at about two places in the range of boxes in order to take up any small differences in speeds.

Certain accessory plant is also required for winding and unwinding the "water-band." In some cases the warps are plaited into boxes for drying later, but it is usual to make the process truly continuous by a continuous air-drier in tandem with the rest of the range.

CHAPTER ELEVEN

CLOTH MERCERISING MACHINERY

THERE have been some major developments in cloth-mercerising machinery during the past fifteen years, first in the use of expanders in place of the usual stenter, and secondly, the fundamental return to mercerising without shrinkage or static mercerising. As previously mentioned, mercerising without shrinkage has mainly attracted attention in Continental Europe and most of the information concerning the performances of these new machines is to be found in periodicals such as Melliand Textilberichte, TIBA and Teintex ; in particular, a useful and detailed review has been given by Colomb (Teintex, 1938, *3*, 656).

In certain cases where only a small amount of material requires mercerising, it is possible to work with a mangle alone. A production of some 1,500 yards per 8-hour day may be realised, and machinery for this purpose is manufactured by both Haubold and Zittau.

The mercerising mangle consists of a frame carrying two iron squeezing rollers, the upper of which is under lever pressure. The fabric can be rolled alternately on top or bottom rollers by reversing the drive. Below the rollers is a trough which serves as a container for the caustic soda solution during the impregnation of the cloth, and later to collect the wash-waters. Under this trough is situated a storage tank with a cooling jacket, and the alkali is circulated from this tank through the trough by a centrifugal pump.

The fabric (*f*) is drawn over the guide-rollers and stretchers (*c*) through the trough (*h*) and then wound on the top roller (*b*), under strong lever pressure. The drive is then reversed and the cloth rewound on the bottom roller (*a*) Fig. 90, where it receives a further impregnation. This may be repeated several times so that a thorough penetration is effected. The alkali is then drained into the tank (*i*) ; the drive is reversed again and the fabric rewound on the top roller, but at the same time it is washed by hot water from the spurt pipe (*e*). The washing is continued when the cloth is run on to the batch-roller (g). There is some loss in width during this method of mercerising, but a part of this may be recovered by stretching later.

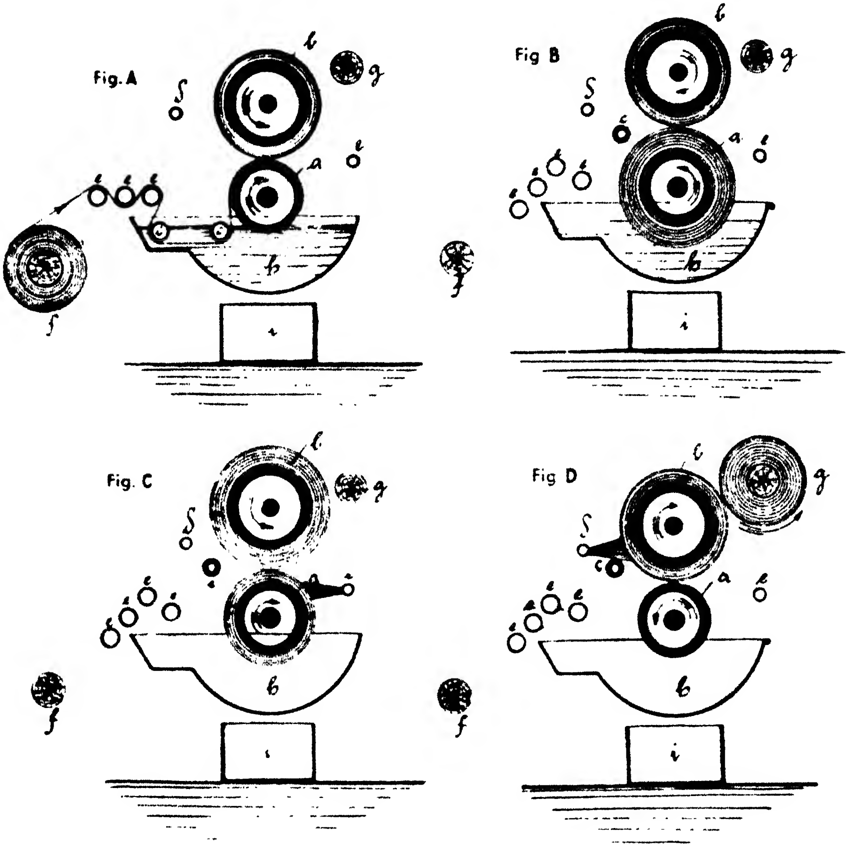

FIG. 90.—Descriptive drawings showing the use of a mangle for impregnating cloth with NaOH solution and then washing with water.

Mercerising Ranges

In general it is customary to employ a mercerising range in which the necessary sequence of machines enables a continuous treatment to be effected ; such a range embraces the arrangements for impregnation, washing under tension, removal of residual alkali, neutralising, washing, squeezing and plaiting the cloth. Variations on this arrangement are also frequent.

Occasionally the impregnation and washing under tension are not continuous ; the cloth is treated with the caustic soda solution, squeezed and then wound on a batch roller. Some time later it is washed under tension on a separate machine, and for certain heavy cloths this method has its advantages. The two parts of the process may be operated at such independent speeds as best suit the material ; ample time may be given for the alkali to act on the cotton, but it is important to avoid the formation of oxycellulose. (See page 245.)

The recuperator for removal of the residual alkali by steam is sometimes omitted from the range, where the goods are mercerised in the grey state and go forward to the kiers while still containing the residual alkali. The souring and washing apparatus in tandem with the rest of the range may also be omitted in favour of separate souring and washing, sometimes in rope form.

The simplest range is, therefore, an arrangement for impregnating the cloth and then washing it under tension, the impregnation section consisting of a mangle, a mangle followed by a number of cylinders, or two mangles with the row of cylinders between them.

Mangles and Stenter

The commonest types of mercerising range include at least one mangle ; two mangles with a set of iron drums between them is a very popular arrangement and the cylinders give time for the alkali to act on the cloth. They are driven by the passage of the cloth and are lightly mounted on ball bearings. Where two mangles are utilised it is possible to arrange the drive so that there is some warp tension between them, and this contributes to the lustre. It is usual in the two-mangle arrangement for the second mangle to have the higher expression and so economise in alkali.

Opinion is divided on the question of hydraulic mangles versus lever pressure, the former appears to be capable of a higher and more even expression than the latter, and it is also possible to repeat given pressures more easily. The lever system is less complicated and there is no danger of leaking valves and pumps.

Most mercerising mangles have three bowls, but two-bowl mangles are also found. The advantage of the three-bowl mangle lies in the better impregnation and the possibility of giving multiple impregnation with the one machine. The

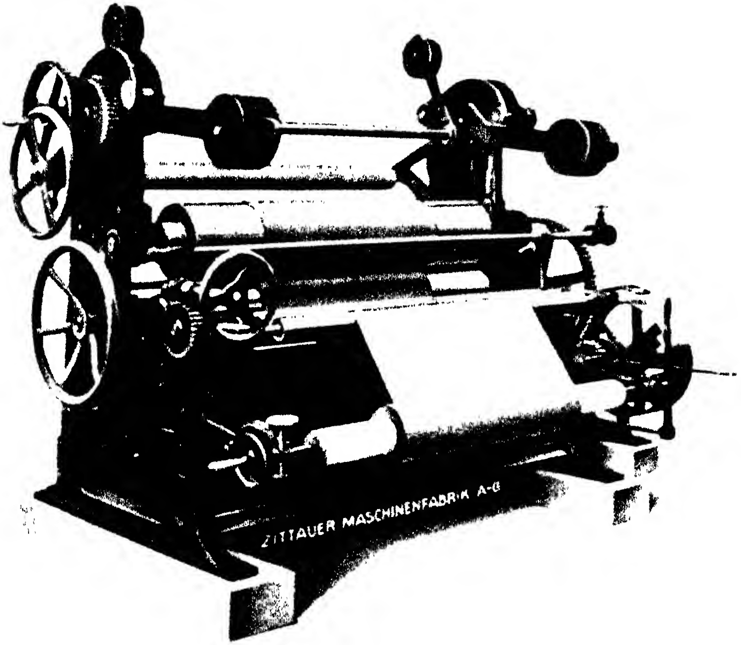

FIG. 63. Mercerising mangle as used for impregnation and washing of piece goods, as illustrated diagrammatically in Fig. 60.

(By courtesy of Zittau.)

PLATE XXVI.

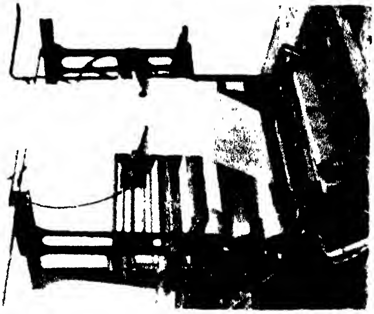

FIG. 94.—Foxwell guiders before a mercerising mangle.

(By courtesy of David Foxwell & Son.)

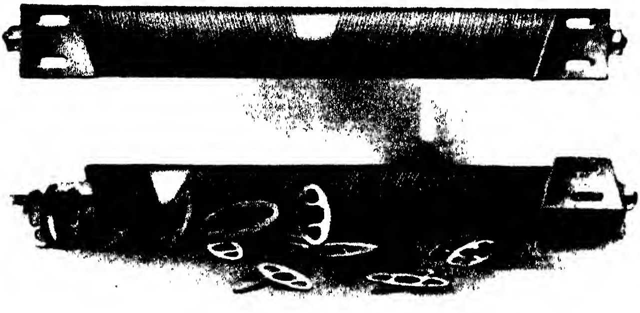

FIG. 95—Scrimp rails.

(By courtesy of Sir James Farmer Norton & Co.)

FIG. 66. Curved three bar expander

FIG. 67. Improved single bar curved expander

(By courtesy of Messrs. Mather & Platt.)

PLATE XXVIII.

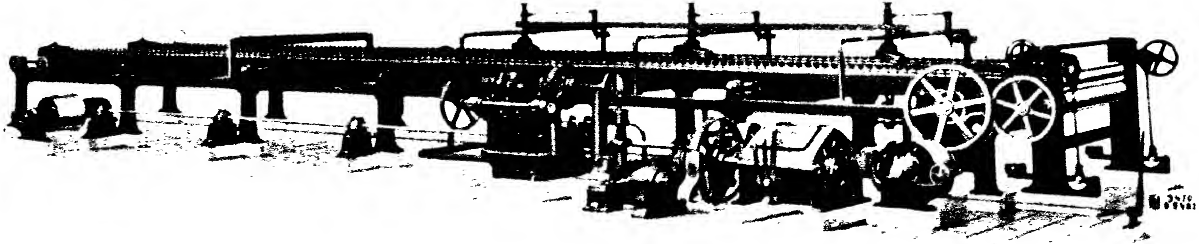

FIG. 98.—The washing frame or stenter of Messrs. Haubold, A.G.

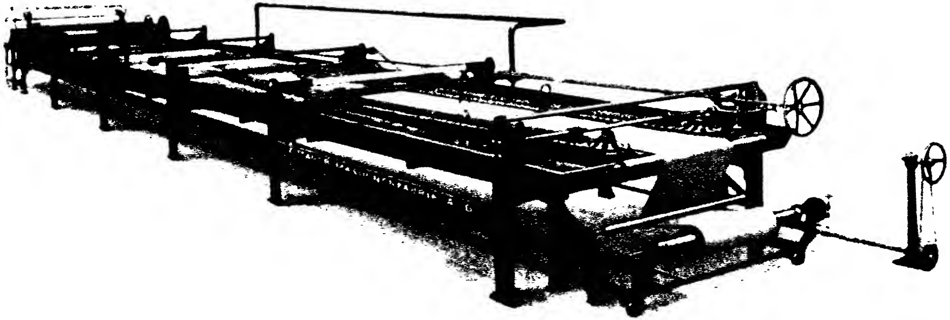

FIG. 99.—The dipping frame or stenter of Zittau Maschinenfabrik.

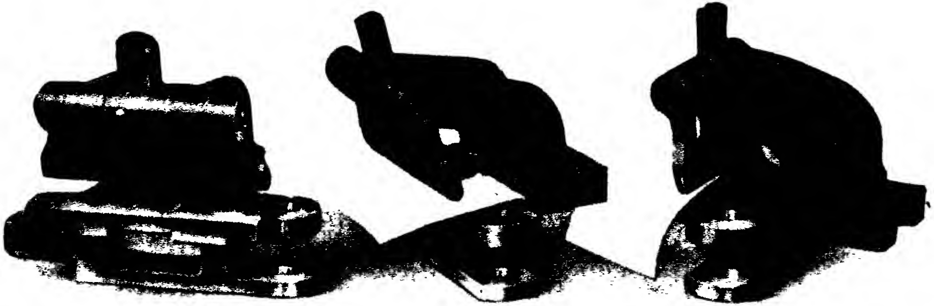

FIG. 100.—Stenter clips.

(*By courtesy of Sir Jas. Farmer & Sons, Ltd.*)

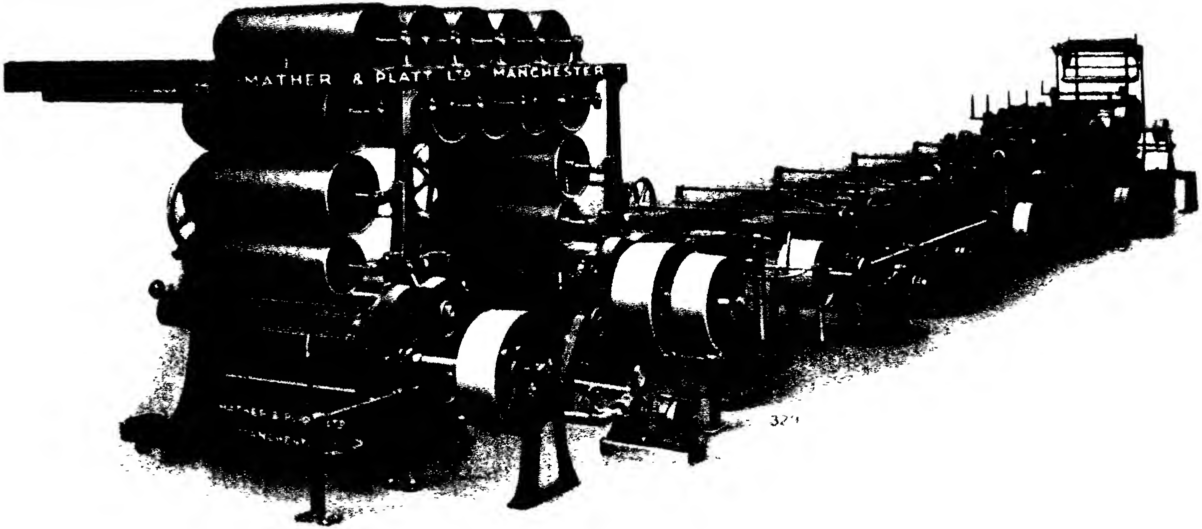

FIG. 101.—The Mather and Platt mercerising range showing mangles, stenter and washing machine.

By courtesy of Messrs. Mather and Platt.

PLATE XXXI.

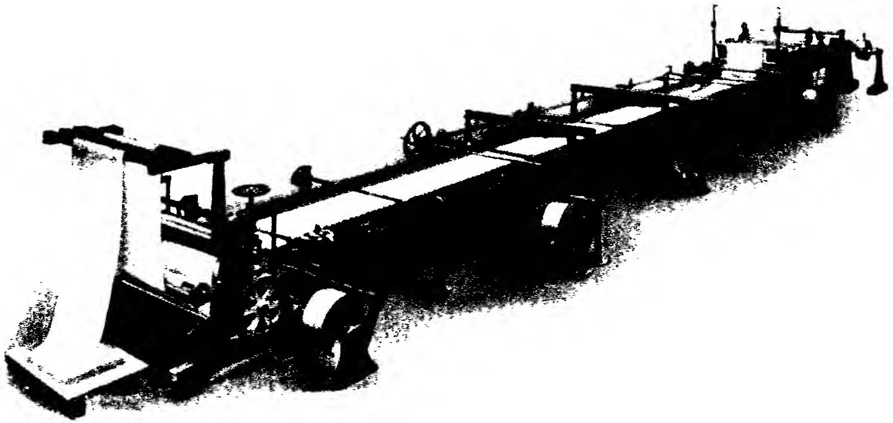

Fig. 102.—A Farmer Norton mercerising range.

(By courtesy of Sir Jas. Farmer Norton & Co.)

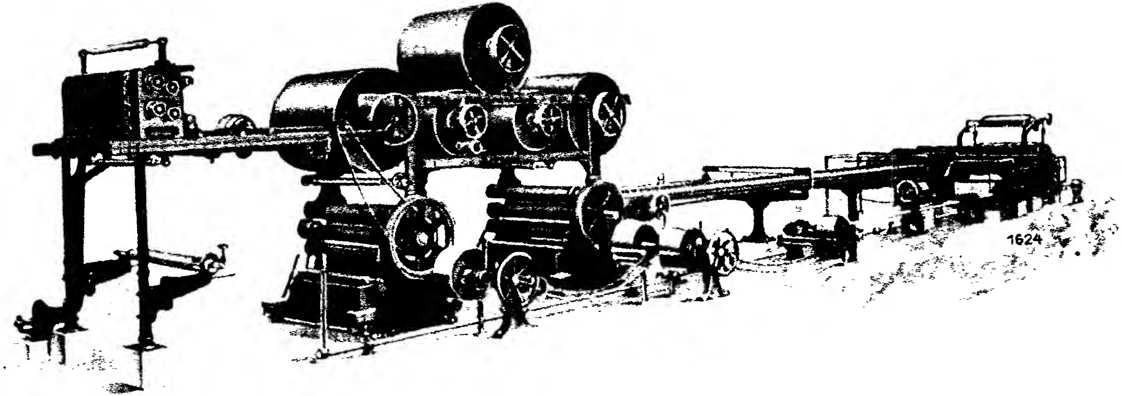

Fig. 103.—A Zittau mercerising range.

By courtesy of Zittau Maschinenfabrik.

pressure exercised by mercerising mangles is usually high and varies from 10 to 25 tons—these high pressures assist the thorough penetration of the cloth and also reduce the amount of alkali carried forward to the washing system to the minimum.

Some ingenious methods of arranging the cloth for multiple impregnation have been devised.

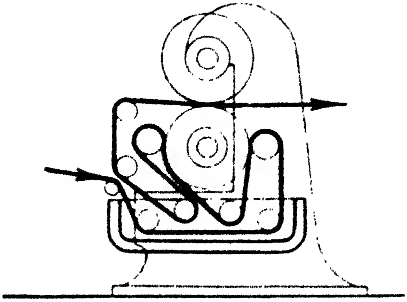
FIG. 91.

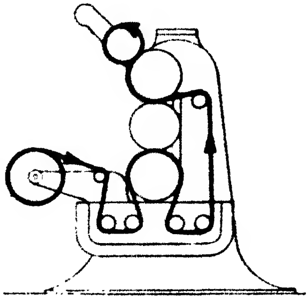
FIG. 92.

Methods of arranging for multiple impregnation on a single mangle.

Three-bowl mangles are manufactured by Mather and Platt, with two cast-iron bowls and one rubber bowl. The iron bowls are positively driven by machine-cut wheels, and the rubber bowl floats between them and is driven by frictional contact. In this method of driving there is no possibility of slip, with danger of damage to the cloth ; the life of the rubber bowl is longer in this arrangement. The pressure is obtained by compound levers and weights. The trough under the bowls is made with a cavity or jacket through which cold water or brine may be circulated in order to maintain the desired temperature of the caustic soda solution. Jacketed troughs for mercerising mangles are standard practice and may be filled with ice if necessary. For hot countries a refrigeration plant may be necessary for cooling the mercerising liquor.

Mather and Platt arrange the trough rollers for double impregnation of the cloth, each immersion being followed by squeezing. After the first immersion, the cloth passes over a patent suction pipe which contains a longitudinal slot which can be adjusted to suit the width of the goods under treatment. This pipe is submerged in the caustic soda solution and coupled to a vacuum pump, so that when the cloth passes over the slot the liquor is drawn into the fabric, displacing the air and ensuring a most thorough impregnation. The liquor is returned to the trough by the vacuum pump and the circulation continues.

Various hydraulic mangles are built by Farmer Norton; where a single mangle is required a pressure of 15 tons is adequate, but the use of two mangles enables the first to operate at a pressure of 6 tons and the second at 20 tons. The pressures may be varied to suit individual needs, and the pressure is regulated by a control valve with hand wheel, transmitting the pressure from the rotary pump to the hydraulic cylinders placed under the bottom bowl. It is claimed that the use of these high-expression hydraulic mangles makes possible an alkaline consumption of 25 lbs. of NaOH per 100 lbs. of cloth.

The ideas of multiple impregnation and a jacketed trough have been developed to a high pitch in the Farmer Norton mangles, and the cloth is impregnated in graduated steps by counter-current flow. This avoids the difficulties of the initial impregnation in liquor of high density. The tank is divided into two compartments through which the caustic soda solution flows in the opposite direction to the run of the cloth. The fresh liquor is fed into the last compartment of the second mangle and flows towards the first compartment, gradually becoming more dilute and rising slightly in temperature. When this plan is carried out with two mangles the cloth receives a series of impregnations: (*a*) 30° Tw. at 25° C., (*b*) 40° Tw. at 20° C., (*c*) 50° Tw. at 16° C., and (*d*) 60° Tw. at 12° C. Absorption is stated to take place more uniformly and quickly than in the case of cold and stronger lye. The excess of liquor from the first compartment which the cloths meet flows to a storage tank, where it is brought to its original strength (about 60° Tw.) and pumped to the fourth compartment.

Accessories

Some mercerising ranges include an instrument panel for recording the temperature and density of the alkali in the mangle boxes. The recording of temperature works on a thermocouple device in the usual manner, whilst the density is recorded by the fluctuations of floats which rise and fall in the alkali; these fluctuations are transmitted to dials and recorded, as for example, in the instrument panel made by Farmer Norton.

There are a number of accessories to the mangles, and the commonest of these is the system of rails or supports which lead the cloth from the batch roller or wagon, pass over the head of the operative and bring the cloth to the mangle. These rails may be used to impart the slight tension necessary for even running, but in the Zittau system a box containing brushes may be fixed to the overhead rails and remove any loose fibres or other materials from the cloth before it enters the mangle. This is seen in Fig. 103.

It is usual to have some form of guide immediately in front of the mangle; sometimes this is merely a pair of tension rails with a young operative in attendance to see that the cloth is as straight as possible and free from creases, particularly at the selvedges. Fabric guiders are almost standard fittings, however, and one of the commonest is the Foxwell Guider, which operates automatically. A driven rubber roller presses against a flat plate and the fabric passes between them; the inclination of the axis of the roller to the weft of the cloth draws the cloth to the sides of the machine. The plates are set to the width of the fabric and two stops are adjusted to the position in which the cloth should enter the machine. Any outward displacement of either stop releases the pressure of the roller and frees the cloth, which is then drawn to the other side by the opposite roller; the cloth is thus maintained between the stops. The rollers may be operated by compressed air, electromagnetically or by the force from a freely rotating roller in contact with the moving cloth. (See Fig. 94.)

Expanders are frequently employed in front of mangles in order slightly to stretch the cloth and free it from creases. In the Mycock type the expanding device consists of a number of grooved bobbins which interlock and are mounted on a curved shaft. The interlocking of the bobbins is loose enough for them to rotate as a whole when the cloth passes over them and is expanded. It is possible to raise alternate bars, increase the tension on the cloth and, therefore, the lateral stretching. The usual types are 3- and 5-bar; the former is shown in Fig. 96.

Scrimp rails are composed of oval metal discs, with fibre washers between them and threaded on to a square steel bar. The divergence of the discs straightens out the cloth as it runs over the rail under slight tension.

The simple curved rubber expander is formed by a rubber sleeve which covers a spring mounted on a curved bar. A later type, Fig. 97, gives maximum flexibility by supporting the sleeve by bobbins with plain rims running in ball bearings;

between each pair of bobbins is fitted a spiral spring and a number of distance pieces, the whole being supported on a curved bar.

A set of cylinders or drums is a frequently encountered subsidiary device to the impregnating plant ; they prevent the selvedges of the cloth from turning or rolling, but their main function is to permit a longer period of contact between the fabric and the alkali and so assist in thorough mercerisation.

Stenters

The function of the stenter or stretching frame is to pull the cloth out to approximately its original width and then wash out the alkali. This necessitates a very strong frame of such a length that the greater part of the alkali is removed during the passage of the cloth. It is possible to reduce the alkali concentration to the order of 10° Tw. NaOH, and higher concentrations must not be allowed to pass, for any stretching of shrunk cloth at a later stage merely results in subsequent shrinkage during laundering. The width of the material is set during the removal of the alkali.

Efficient methods of washing on the counter-current system enable shorter stenters to be used, but they still vary in length from 50 to 75 feet. The first 20 feet or so is the length of run during which the cloth is stretched to width, and where spray or weir systems of washing are employed it is usual to stretch to this full width before starting the washing. A special dipping frame is made by Zittau, equipped with obliquely placed chain-rails in such a manner that the fabric is run through a long tank filled with recovered wash-water (Fig. 99).

Washing frames involving the use of spurt-pipes are part of the mercerising ranges of Farmer Norton, Haubold and Zittau, the last-mentioned supplying a frame with spurt-pipes both above and below the cloth. It is usual, however, to have the spurt-pipes above the cloth and suction boxes below it. In some cases the floating liquor is guided to the suction box by a steel doctor immediately above and close to the fabric. The main part of the wash liquors passes through the cloth, to be collected in troughs and used on the counter-current system.

The suction boxes under the cloth are made of cast iron and have perforated lids ; the washing liquor is drawn through the cloth into the suction box by means of a pump.

Fresh water or dilute lye from the recuperator is fed to the spurt-pipe at the delivery end of the stenter, and having washed the last part of the cloth it is collected in a tank from which it is pumped to the next spurt-pipes and again collected after it has washed another part of the cloth ; the more alkaline liquor is then pumped to the first spurt-pipes which the cloth encounters, so that actually the cloth which is still saturated with the original mercerising liquor is washed in dilute alkali of diminishing concentration. The washing liquor becomes progressively stronger as it approaches the entering-end of the stenter where it is collected for use in kier-boiling, etc.

The standard washing system of Mather and Platt operates through a number of weirs, and here again the greater part of the alkali is removed while the cloth is in the stretched state—more than sufficient to ensure freedom from shrinkage. The series of weirs, suction boxes, circulation and vacuum pumps, together with piping and troughs, effects considerable economy in the consumption of water and facilitates the recovery of alkali at a reasonably high concentration. The weir is so designed that the washing liquor flows over and on to the cloth in an unbroken stream, the width of which exactly corresponds to that of the cloth ; this effects a very even wash. The initial wash-liquor is fed into the machine at the washing cistern behind the stenter at the delivery end, and overflows into a collecting trough under the stenter frame, having taken up a small amount of alkali.

The wash-liquor is drawn from the collecting trough by the first circulating pump and delivered to the weir over which it flows on to the cloth. The wash-liquor is then drawn through the cloth into the suction box in contact with the lower surface of the cloth by means of a vacuum pump, and discharged into a trough under the stenter. This operation is repeated by additional pumps, weirs, suction boxes and troughs ; the number of operations depends on the length of the stenter. From the last trough (the first in the direction of the run of the cloth) the fairly strong caustic soda solution is conveyed by a centrifugal pump to a storage tank for concentration or for use in scouring. Only one water feed is necessary for the whole washing operation.

An alternative system replaces the weirs by disc washers arranged in pairs, one disc at each end of a swivelling supporting pipe, but this cheaper arrangement is less efficient.

The troughs under the stenters are sometimes built of concrete, but cast iron is preferable.

It has already been stated that the cloth is expanded to full width during the first 20 feet or so of the stenter, before the removal of the alkali; the width of the stenter is then almost constant for the remainder of the run, but a contraction of about one inch is allowed before the cloth leaves the clips in order to avoid damage. In some cases the cloth passes through a washing cistern fitted with a mangle, in others a mangle only, and yet again, it may pass directly or via a compensator to a recuperator or to a washing and souring apparatus.

STENTER FRAME

The stenter frame is primarily a machine for the lateral stretching of cloth while it is moving along the frame, which is constructed with two side rails each of which with races for an endless chain of clips. The distance between the rails can be adjusted by screwed rods which run across the frame and are operated by power; hand-wheels are also attached and a scale is usually provided for readings of the width.

Stenter clips are produced in a variety of designs and for dealing with light and heavy cloths. In general, the clips have a tongue and a pawl; the tongue swings freely on a horizontal pin and lifts the pawl from the slotted bed-plate on which the cloth lies. The action is seen in Fig. 100.

Projecting steel bars at the ends of the chain races make contact with the tongue of the clip as it passes round the sprocket wheel; the tongue is pushed back and lifted from the base plate, allowing the cloth to enter. As the clip leaves the sprocket wheel the tongue falls but the cloth is not gripped, as the pawl does not sink into the slots. As the side rails diverge the cloth gradually recedes from the clip, uncovering the slots into which the pawls fall so that the tongue of the clips grips the cloth at the selvedge only. At the delivery end of the stenter the tongue is forced back again and the cloth released.

The clips must be made from material which withstands the action of caustic soda; they are usually made of iron with nickel or nickel-iron alloy plates. They must be sufficiently strong to withstand the great tension of the cloth.

The divergence of the rails of the first section of the stenter extends the cloth to the required degree; the remaining sections are parallel and the cloth passes through them under constant tension.

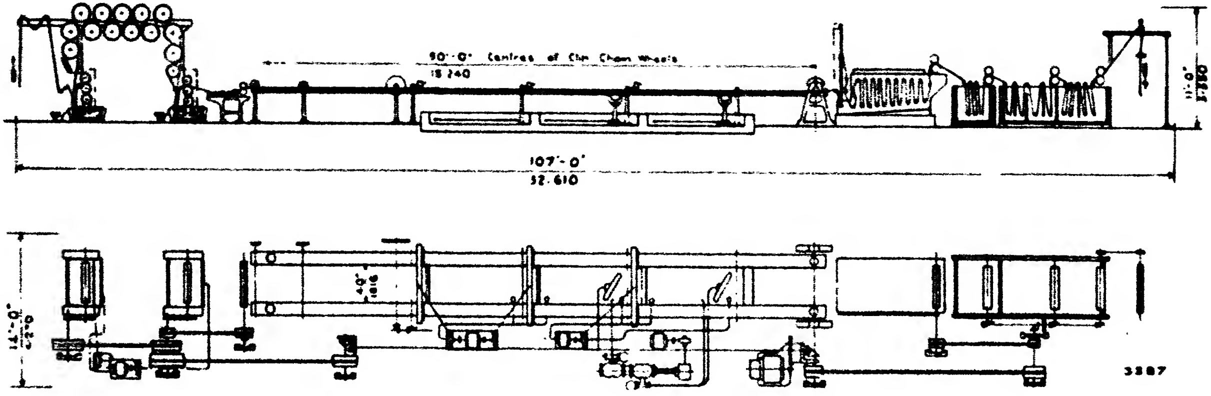

FIG. 108.—Descriptive drawing of a Mather and Platt Mercerising Range, with mangles, stenter, recuperator and washing machine.

Pump Motors.

1–4 H.P., 1,000 r.p.m. for wet vacuum pumps.
2–3 H.P., 1,000 r.p.m. for centrifugal and rotary vacuum pumps.
1–1·5 H.P., 1,000 r.p.m. for centrifugal pump.

Mercerising Range.

Production per minute . .	50 yds.
Horse-power	35.
Speed of motor	1,000 r.p.m.
Gross weight	750 cwt.

Chainless Machines

The Benninger chainless machine, type O.M., operates with either one or two mangles, with or without a series of drums; the pressure of the mangles may be varied from 1 to 15 tons, higher pressures not being advisable. The absorption of caustic soda solution is determined, not only by the expression of the mangle, but also by the degree of saturation of the cloth. For instance, if the first mangle gives an expression of 80% with a pressure of 13 tons, the second mangle with a higher pressure of say 17 tons may give an expression as much as 50% higher.

According to the speed of the machine, it is possible to arrange for from 30 secs. to 1·5 mins. contact with the alkali before the impregnated material is washed. In a machine with one mangle only, and without cylinders, it often happens that the cloth is only subject to the action of the alkali for about 10 secs., which is inadequate for proper mercerisation, even with specially prepared cloth in contact with caustic soda containing wetting agents. Where two mangles are employed it is general to drive the first a little faster than the second, so that the cloth enters the second mangle trough under only slight warp tension, sufficient to keep the cloth under control from the standpoint of smooth and even running. In this manner a better absorption of alkali takes place in the second mangle. In all chainless mercerising machines the warp tension must not be applied too soon, but preferably in conjunction with the stretching of the weft. An exception may be made with heavy cloths and material in which the warp predominates where the longitudinal contractive force is high.

Owing to the curvature of the rollers in the washing and stretching compartment of the mercerising range, it is possible to exercise a force more than ample to restore the cloth to its original width. The range of twelve rollers is capable of dealing with shrinkages in width of 50 to 60%, and there is not the slightest difficulty in restoring the average contraction of about 30%. It is possible two deal with to and sometimes three cloths superimposed, according to the thickness, and there is no difficulty in mercerising cloths of different widths consecutively.

An important fundamental point in the working of a chainless mercerising range is that the width of the goods is determined by the tension on the warp. An apparatus is fitted for

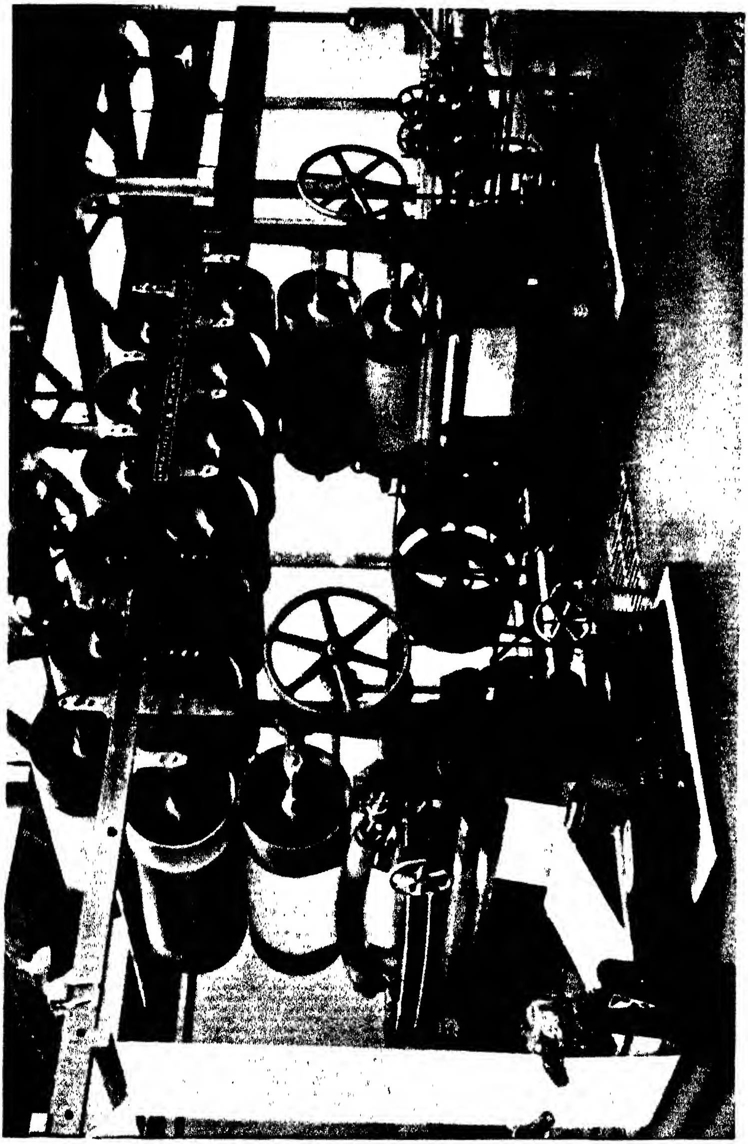

FIG. 104.—Entering end of mercerising range, showing two impregnating mangles, drums, etc., with cloth passing through.

(*By courtesy of Messrs. Mather & Platt.*)

PLATE XXXIV.

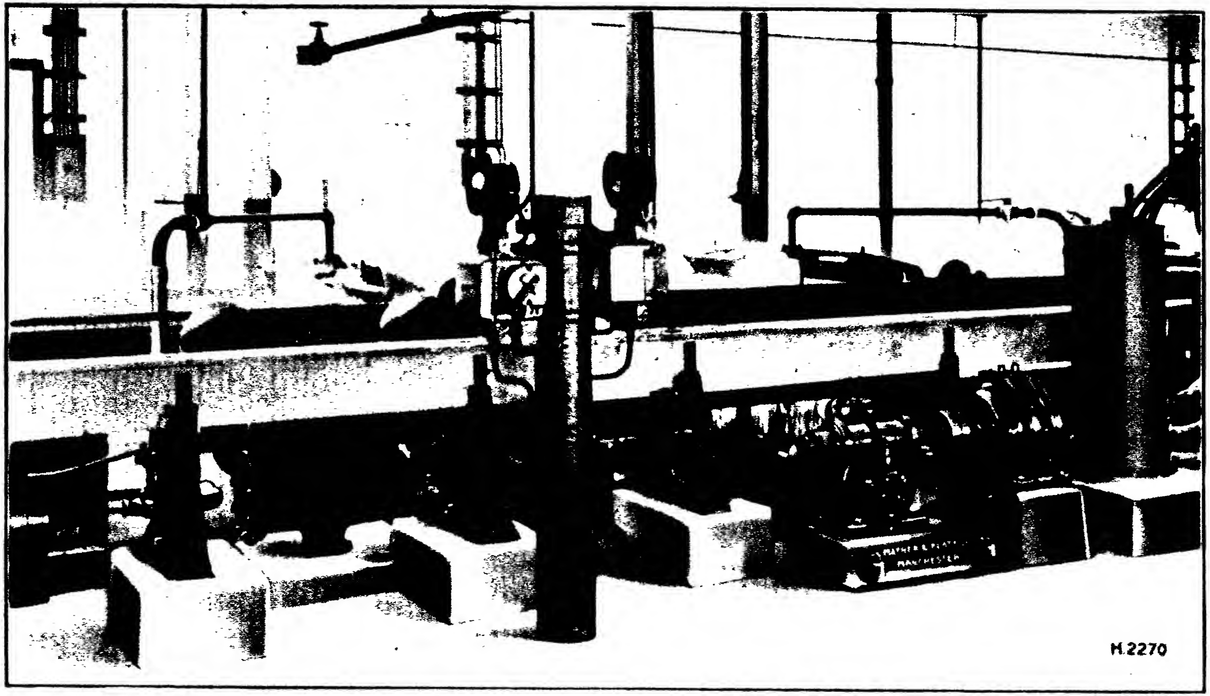

FIG. 105.—Part of mercerising range showing washing apparatus with weirs and pumps, on the stenter.

(By courtesy of Messrs. Mather & Platt.)

PLATE XXXV.

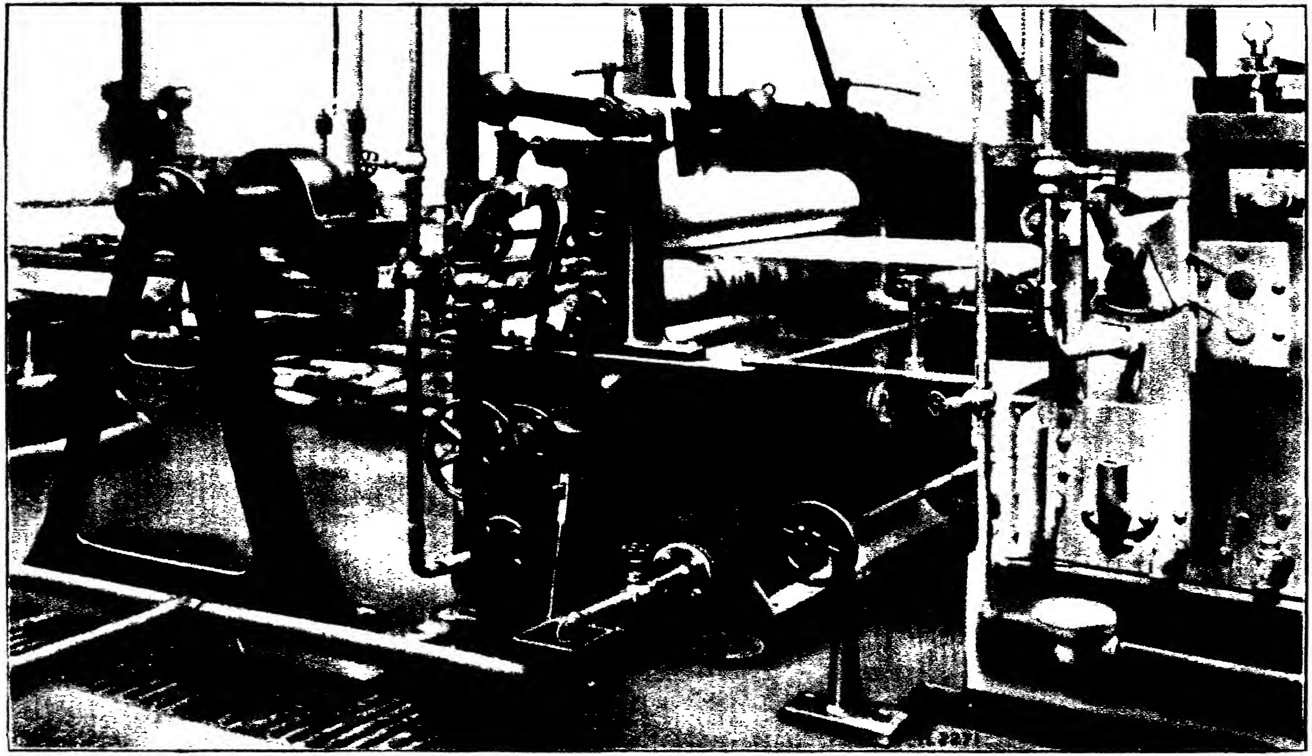

FIG. 106.—Delivery end of mercerising range, showing end of stenter, washing cistern and squeezing mangle.

(By courtesy of Messrs. Mather & Platt.)

PLATE XXXVI.

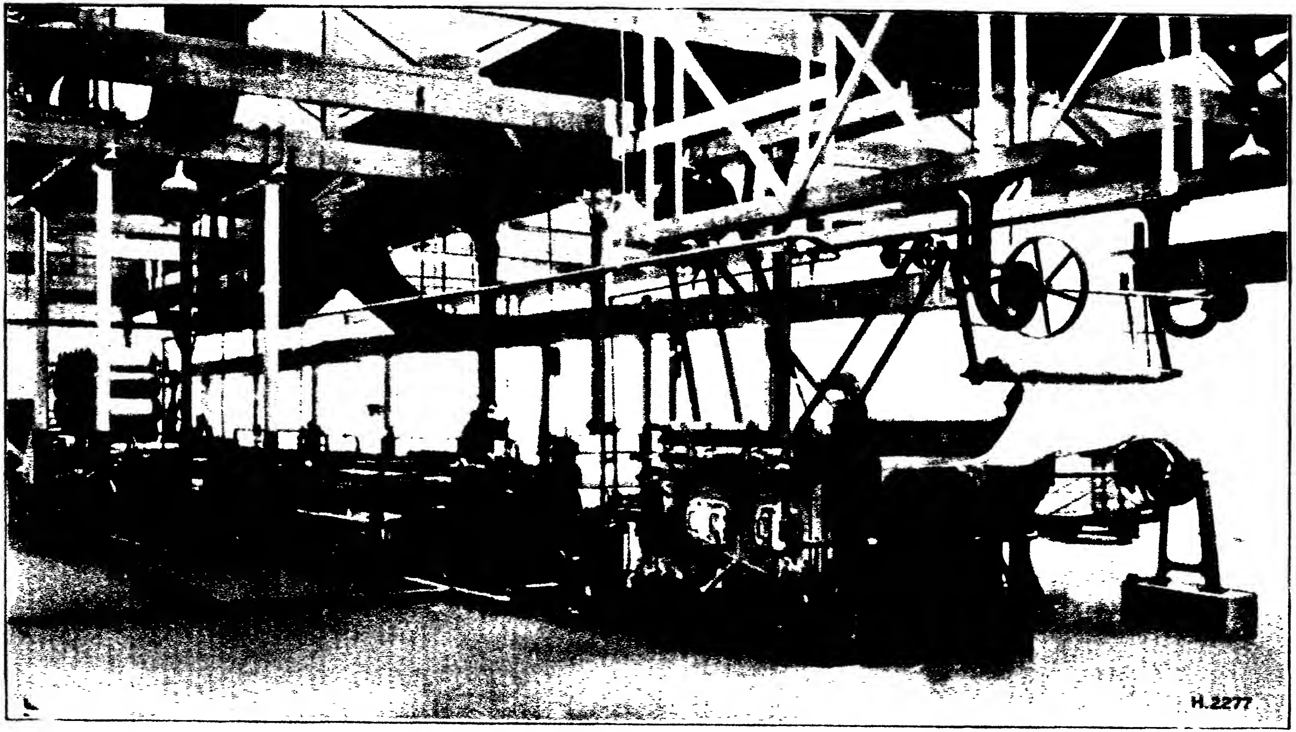

FIG. 107. Mercerising range with two mangles, drums, stenter, washing apparatus with weirs, suction boxes and pumps, and a recuperator.

By courtesy of Messrs. Mather & Platt.

PLATE XXXVII.

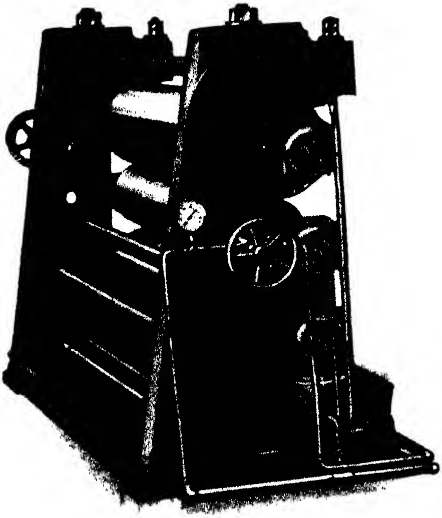

FIG. 110.—Mercerising mangle.

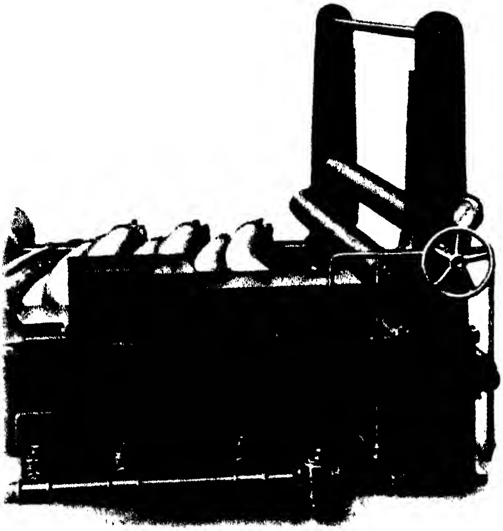

FIG. 111.—Hydraulic tension regulator and curved expanders.

(*By courtesy of Sir James Farmer Norton & Co.*)

PLATE XXXVIII.

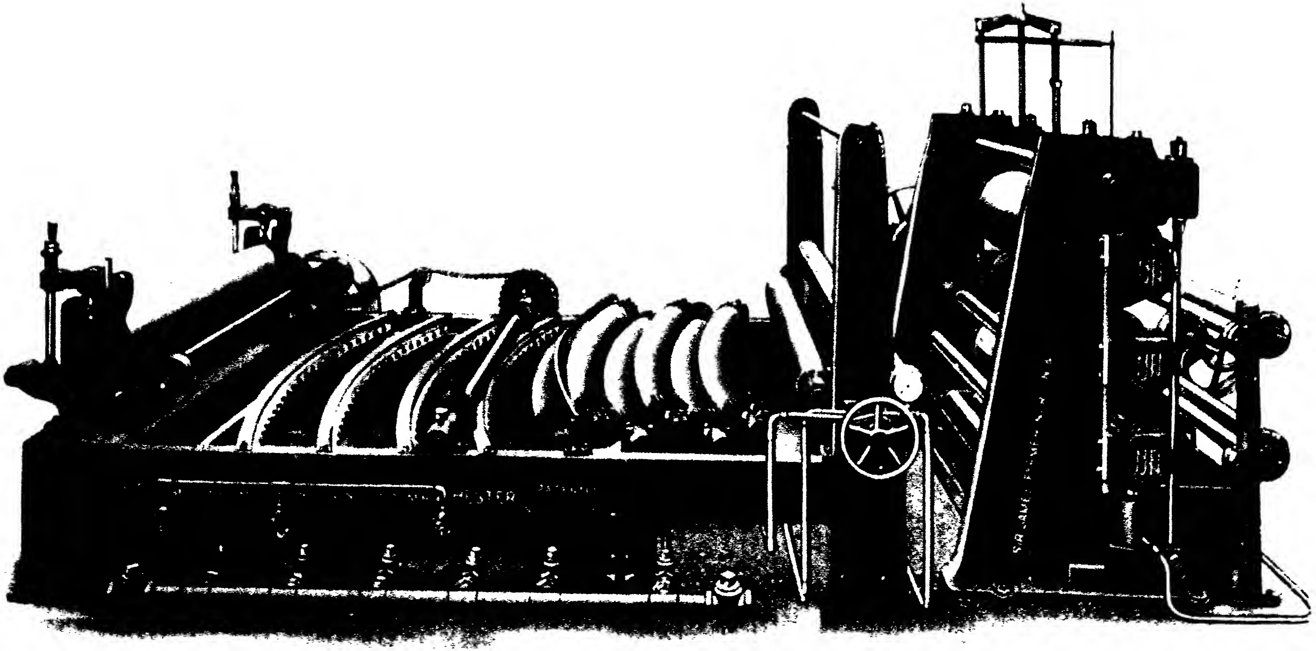

FIG. 112.—Chainless mercerising machine with single mangle.

(By courtesy of Sir James Farmer & Sons, Ltd.)

PLATE XXXIX.

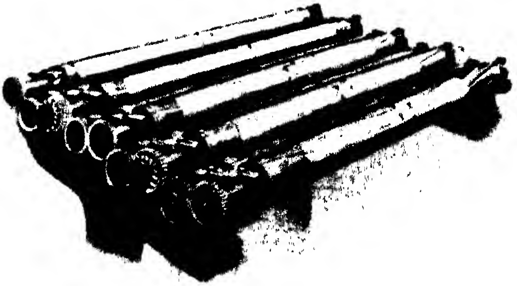

FIG. 113.—Screw-shaped expanders of Messrs. Haubold.

(*By courtesy of Messrs. Haubold, A.G.*)

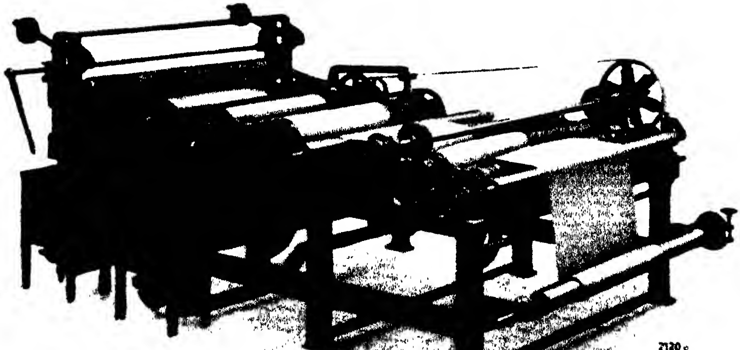

FIG. 114.—Zittau machine, type V.C.

(*By courtesy of Zittau Maschinenfabrik.*)

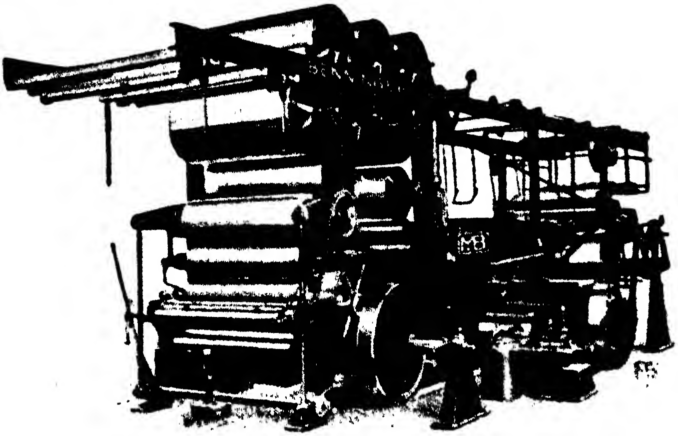

FIG. 115.—Benninger chainless mercerising machine, type OM.

(*By courtesy of Benninger, S.A.*)

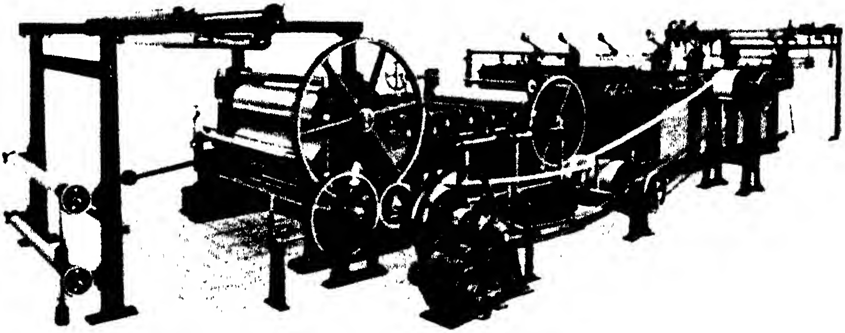

FIG. 116.—A Haubold chainless mercerising machine with recuperator and washing machine.

(*By courtesy of Messrs. Haubold, A.G.*)

[*To face page* 169.

measuring the warp tension and conditions which give low readings are recommended. For medium-weight cloths the machine is run at a moderate speed and adjusted to give a medium tension. All the rollers are utilised, but the washing does not take place until near the end of the machine. If the fabric construction is such that little shrinkage takes place in the alkali, it is advisable to miss some of the rollers at the entering end of the machine. In general the cloth should reach its original dimensions on the eighth or tenth roller. It is possible to over-stretch the cloth to about 5 % without damage, as the over-stretching takes place on the last of the rollers which are completely submerged; this over-stretching is occasionally required for the maximum lustre.

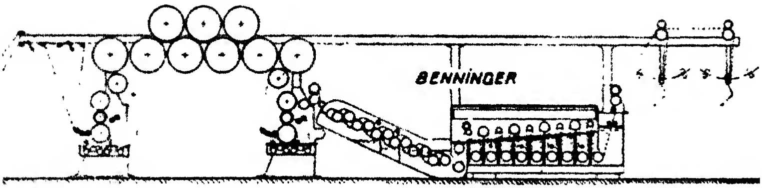

FIG. 109.—Descriptive drawing of Benninger chainless mercerising machine, type O.M.

Where the required width is not obtained, the trouble usually lies in excessive warp tension and not in the stretching apparatus itself, assuming efficient impregnation and washing.

The pairs of curved rollers are inclined, which enables the washing to take place on the counter-current system; there is no washing on the first six stretching rollers. Washing with hot dilute alkali should be such that there is no tendency to shrink when the cloth passes to the recuperator. This means a concentration of not more than 9 to 10° Tw. (6 to 7° Bé.) NaOH in the cloth and corresponding to 4·5 to 6° Tw. (3 to 4 Bé.) NaOH in the external solution. Owing to the counter-current system of washing, the concentration of alkali in the wash-water in the first of the three compartments gives a solution of 12 to 15° Tw. (8 to 10° Bé.) NaOH. This is usually worth recovering, but where the alkaline liquor is used for other purposes in the works and not recovered, the counter-current system may be operated more vigorously, but very dilute liquors are not advisable, particularly with hard water, where the smooth running of the machine would suffer.

The counter-current system is usually operated in conjunction with the recuperator, so that the only supply of fresh water is where the cloth leaves the recuperator.

In general, the wash liquors are heated to about 80 to 90° C. and the recuperator, of course, contains steam, but in the case of some coloured-woven materials the dyestuffs may not withstand the action of hot alkali and the temperature must be reduced to about 30 to 50° C. It is possible to open the top of the recuperator, shut off the steam and use this part of the range as a washing machine. It is also possible to replace the recuperator with a short washing machine which operates on the stenter principle previously described.

The Farmer Norton machine has several points of interest. In some cases the warp tension has been adjusted by means of cone pulley drives between the mangle and the stretching devices (stenter or expanders), but in the new system the longitudinal tension is controlled by a hydraulic compensator arrangement. The tension regulator consists of three guide-rollers, the middle one being moved hydraulically ; the length extension can be adjusted according to the cloth, by turning a hand-wheel which actuates the hydraulic mechanism. A uniform tension is thus given to the fabric and this benefits the lustre produced ; it is an essential feature of chainless mercerising which depends on the warp tension for its efficient weft extension. The optimum tension may be established for each quality and repeated when required without further special observations.

The expanders are so constructed that the bobbins on the extremities have a larger diameter than those in the middle. Consequently the cloth is moved forward at the same speed over the whole width, so that no distortion of the weft can take place. Some curved expanders have a tendency to distort the weft threads if the surface speed of the central bobbins is greater than that of the end bobbins. The first set of expanders is situated in front of the washing compartment and each expander has a covering of rubber which holds the cloth more firmly and gives a better stretch. The expanders in the washing compartment are made of cast iron and fitted with special bearings which require no oiling. The friction of the bearings under the liquid is very small, so that the wear is negligible.

The complete arrangement of the expanders is six or eight dry expanders covered with rubber, and followed by nine iron expanders running under water.

The washing compartment is divided into five different parts arranged for the counter-current system. The nip or squeezing rollers at the outgoing end is sprayed with water which flows forward, so that the most concentrated liquor is at the point where the cloth enters the washing compartment.

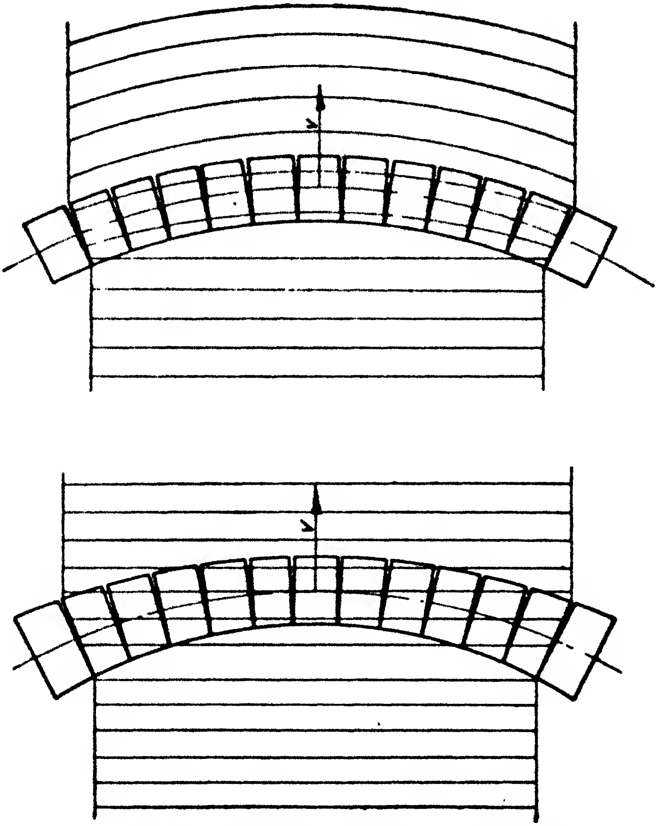

FIG. 117.—Effect of expander design on cloth distortion.

The fabric must pass over the expanders with a definite tension in order to stretch the weft. If it is too slack there will be no extension of the weft from its shrunken width. The hydraulic compensator previously mentioned determines the tension and consequently the amount of "bind" on the expanders which produces the weft extension. In this manner it is possible to arrive at the optimum condition for the production of lustre, removal of the alkali when the cloth has the dimensions of its grey state. The expander section is driven from the preceding portion of the machine by a variable speed device.

After leaving the washing compartment the cloth follows the usual processes; it may have the remaining alkali removed in a recuperator, in which case the lye which collects may be led back to the washing tank under the expanders, or the cloth, if grey, may go forward to the kiers where the residual alkali can be utilised.

The possibility of weft-distortion previously mentioned in connection with curved expanders received some comment in the technical literature. The general design of curved expanders allowed the elements to increase in diameter as they approached the ends, but in the Benninger system successive rollers have a decreasing amount of curvature. Obviously much depends on the true and accurate running of the cloth over the expanders and the extent of warp tension.

In the Zittau machine, type VC, the first stretching device comprised a set of five curved expanders of the Mycock design, but of larger diameter, followed by six or twelve cylindrical rollers, which also stretched the cloth in the weft direction.

The Haubold machine may be fitted with either a heavy hydraulic padding mangle capable of exercising pressures up to 22 tons or alternatively four sets of squeezing rollers arranged one behind the other and with a trough below.

The stretching and washing arrangement consists of 9 or 12 screw-shaped expanders placed in two horizontal rows, with a number of spurt-pipes above and below. These expanders are driven partly from the squeezing device at the end of the compartment and partly from the impregnating section; it is thus possible to regulate the longitudinal stretch as the cloth runs through the machine. Removal of the alkali from the impregnated cloth takes place on the counter-current principle, utilising spurt-pipes. Fresh water is applied at the end of the compartment and the cloth is then squeezed before going forward to the next stage; the supply of wash-water is adequate to ensure no shrinkage on further washing. Any surplus alkali may be removed by a recuperator running in tandem with the range or in an open souring and washing machine, which may also run in tandem.

A number of variations are possible with the various parts of the mercerising range, depending on the requirements of the works; in some cases, as previously indicated, the cloth

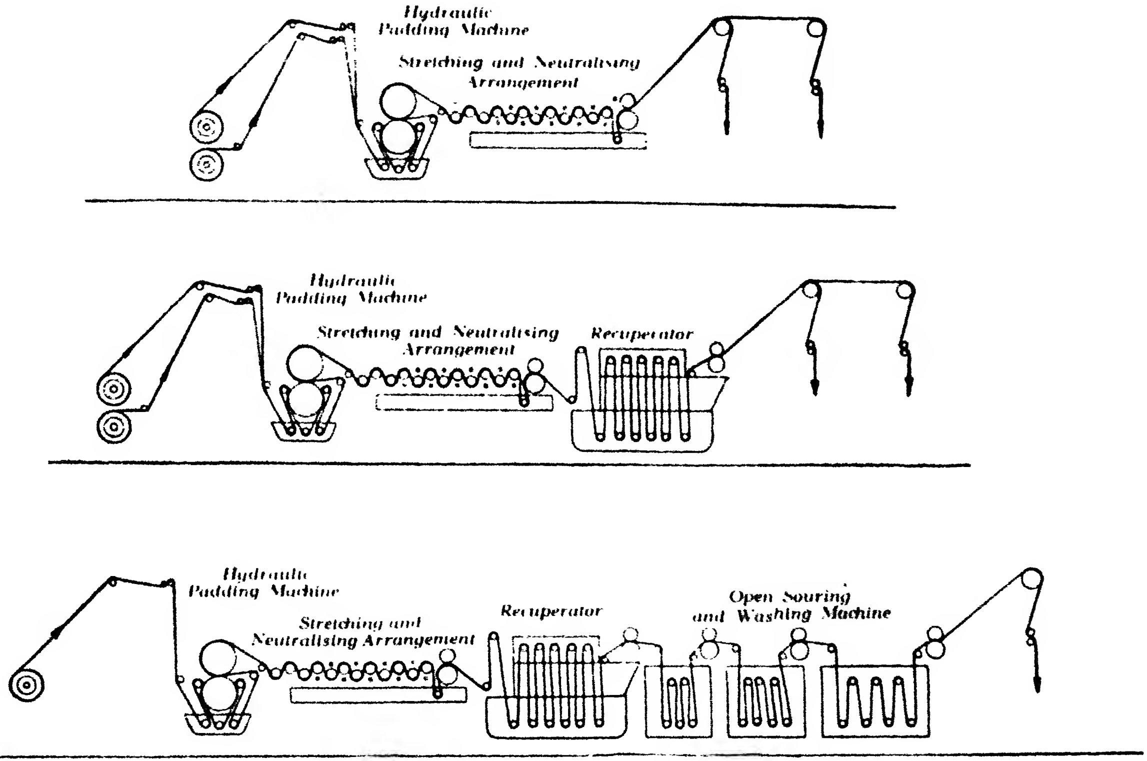

FIG. 118.—Descriptive drawings of chainless mercerising machines.

containing the residual alkali may go to the kiers for scouring, in other cases it may be " soured " or neutralised with dilute acid and then washed.

The Chainless Padless Machine

The type of machine for the mercerising of piece goods and working without either impregnating mangle or a stenter frame for washing under tension represents the most recent development in mercerising cloth. Machines of this type are made by Benninger of Switzerland, by Haubold and also Zittau of Germany. A French model is constructed by Deck of Mulhouse, but this method of mercerising does not appear to be popular in England, or U.S.A.

All models are capable of treating two pieces of cloth at a time, one on top of the other, and in this way a considerable output is assured. It is generally advisable to run two pieces of the same width and texture, and operate the machine rather more slowly than when running single thicknesses in order to ensure regular and even treatment. It is absolutely essential in working with these machines that the cloth should be quite straight at the moment of entry, all creases should be removed and the selvedges carefully controlled to avoid turning or rolling. This is accomplished in the Benninger machine by taking the cloth round an expanding roller driven by the cloth itself, and then over four curved rubber-covered expanding rollers, two of which may be raised or lowered in order to smooth the material, stretch it and apply the initial tension at the moment of entry. In the Zittau machine, the same effect is realised by a guide roller, followed by three curved expanders and a roller which presses the cloth or cloths on to the first of the rollers of the mercerising machine proper. A system of curved expander rollers is also employed in the Haubold machine.

The principle of the chainless and padless machine is that of mercerising under tension, whereas the other methods may be described as mercerising with shrinkage and stretching. The new departure, or more accurately, the return to an old idea, depends on the cloth entering the mercerising machine under tension and being held to its dimensions by passing over a series of rollers during the impregnating and washing processes ; the goods are not allowed to shrink.

Instead of the mercerising liquor being forced into the cotton by a heavy mangle, as in the other systems of cloth mercerising, it must be absorbed from the trough by the cloth which is held at tension by a series of rollers which make contact with each other. The use of wetting agents is almost essential, or alternatively the goods must be in a very absorbent state. Because the cloth is not allowed to shrink, it is important to pay attention to the type of cotton which is being mercerised ; in general in these new machines it is usual to give a longer period of immersion for long staple cottons, as their greater tendency to shrink is prevented, with consequent effect on the rate of penetration.

In the impregnating section of the Benninger machine there are two rows of strong bowls, one above the other, and the cloth runs alternately around a top and a bottom roller. The bowls of the top row are covered with rubber and are carried by the bottom row of bowls, which run on ball bearings. The cloth is, therefore, running under tension on the surface of these rollers. The drive allows regulation of the warp tension to suit individual fabrics.

This is done by means of a system of cone pulleys, controlled by a hand wheel which operates in conjunction with the scale of a device for measuring the tension. On this scale, the tension for light cloths is about 45 to 65 lbs., and may reach a figure of 250 lbs. for heavy cloths or material whose construction necessitates the maximum warp tension in order to develop the best lustre.

The first two lower rollers carry the cloth through the bath of caustic soda solution, but the efficiency of the impregnation is assisted by circulating the liquor from a supply tank through two pipes immediately above and in front of the first two top rollers from which positions it flows continuously over the cloth and into the bath or trough. Some three to four yards makes up the run of impregnation, after which a passage round the remainder of the rollers for a further six yards or so gives time for the alkali to penetrate the cloth. The material then passes through a mangle, which is capable of exerting a pressure of from five to eight tons, according to the type of cloth being mercerised. A further run of about eight yards gives a total period of 40 to 60 secs. contact with alkali from the first moment of immersion, before the washing starts.

The cloth is still carried forward by the same system of contacting rollers into the washing compartment of the machine and is washed under tension with hot water from spurt-pipes, or as the washing machine is arranged on the counter-current system, it is more correct to say that the washing is first effected with hot dilute alkali. A further mangling takes place after the series of sprays and troughs, and the cloth then passes to a recuperator with five compartments arranged also on the counter-current system, where the usual steaming reduces the amount of alkali in the cloth to very small proportions. In the final compartment of the machine, the cloth is sprayed with fresh water and then heavily mangled ready for plaiting on to wagons.

The standard Benninger machine (type N.M. III) has an output of from 9 to 26 yards per minute, according to the type of cloth ; the efficiency may be raised by superimposing cloths or running them side by side. The heavy cloths must be run at the lower speeds, as they require a longer time for removal of the alkali after mercerising. Where a "caustic prepare" or semi-mercerising is all that is required, the speed of the machine can be increased to give an output of 14 to 40 yards per minute, but for thorough mercerising with this output a special high production machine is advisable.

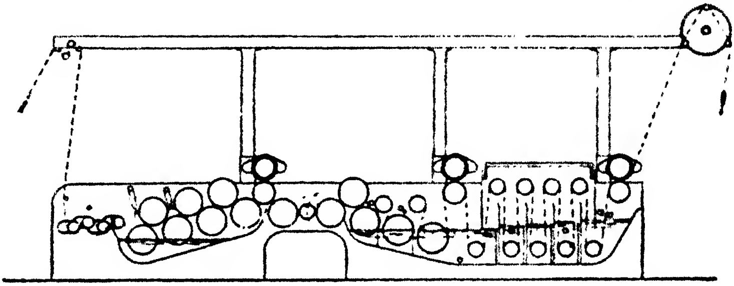

Fig. 119.—Descriptive drawing of Benninger chainless-padless machine, N.M. 111.

The Haubold machine differs mainly from that of Benninger by operating at one level, whereas the latter has the rollers of the impregnating section on an inclined plane and those of the washing section on a declined plane with a view to assisting the counter-current system. The essential parts of the Haubold machine consist of the immersion section and the spraying section separated by a mangle, which under hydraulic operation, exerts a pressure of from 10 to 20 tons. The impregnating section is made up of 18 or 20 rollers, according to the model, of light, but strong construction, in order to require the minimum of power, and to this end the lower rollers are mounted in ball-bearings. The lower rollers rotate in the alkaline liquor,

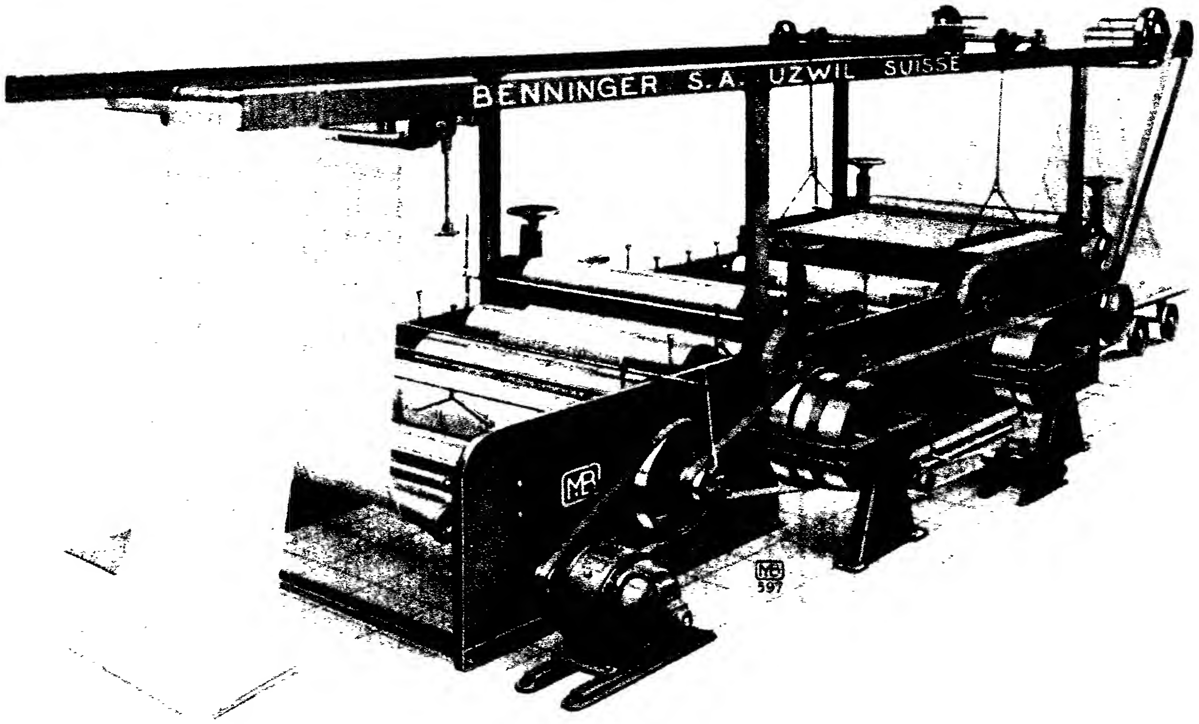

FIG. 120. The Benninger chainless padless machine, type N.M. 111.
(By courtesy of Benninger, S.A.)

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PLATE XLII.

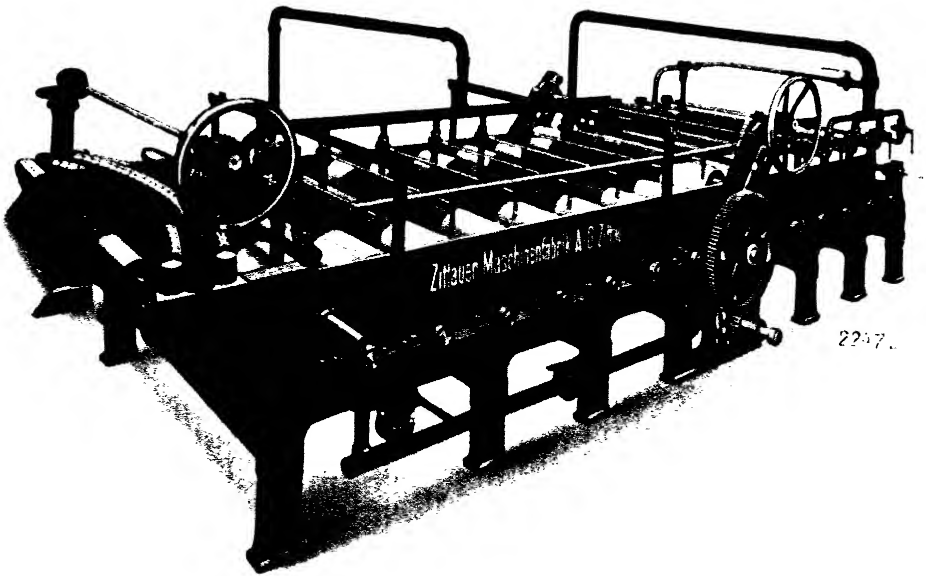


FIG. 121 – The Zittau chainless padless machine

(*By courtesy of Zittau Maschinenfabrik.*)

PLATE XLIII.

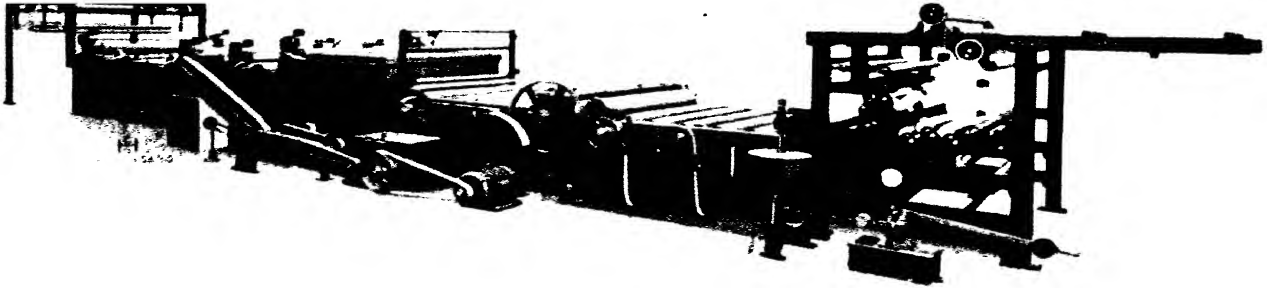


FIG. 122.—The Haubold chainless padless mercerising range.
(*By courtesy of Messrs. Haubold, A.G.*)

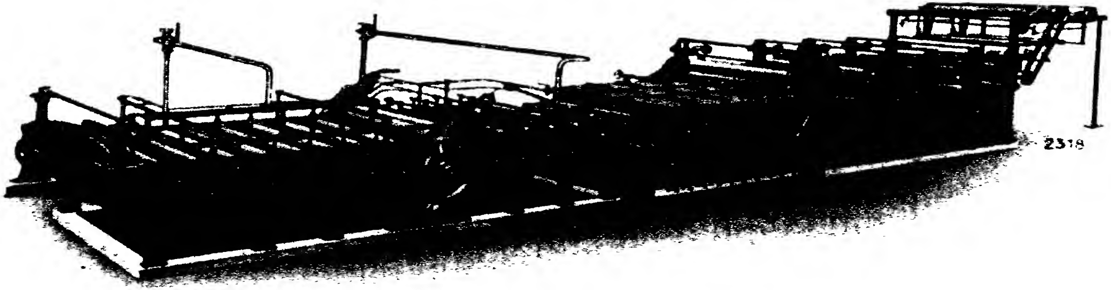


FIG. 123.—The Zittau chainless padless mercerising range.
(*By courtesy of Zittau Maschinenfabrik.*)

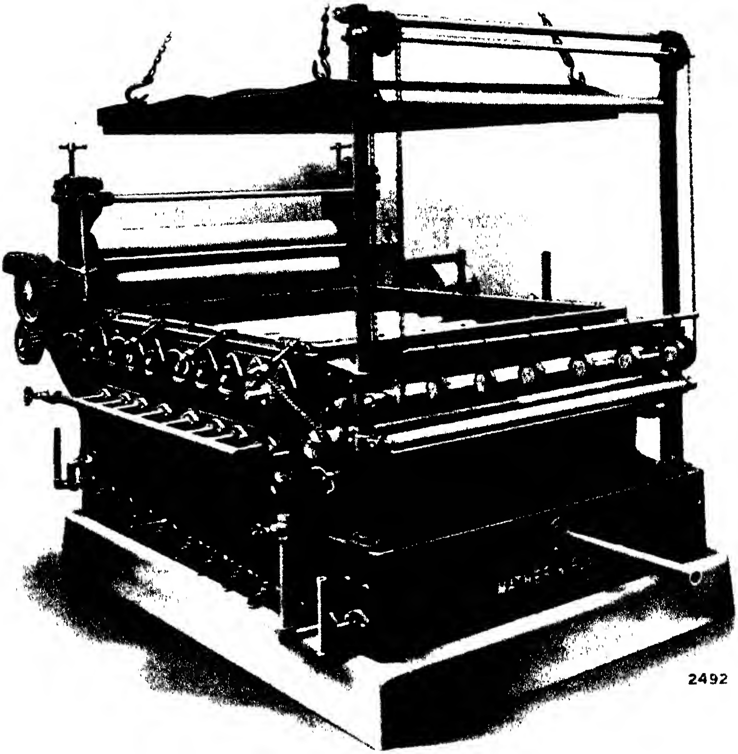


FIG. 124.—Recuperator for NaOH

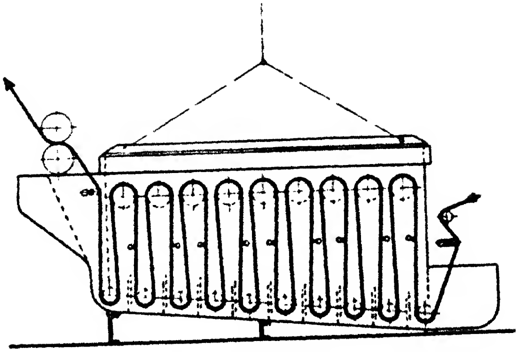


FIG. 125.—Descriptive drawing of recuperator.
(By courtesy of Messrs. Mather & Platt.)

[*To face page* 1

but the upper rollers are only partly submerged. The impregnation is thus as thorough as possible. The upper rollers are not driven.

The hydraulic mangle between the two compartments is a three-bowl mangle arranged in triangular manner, so that the cloth is squeezed twice under a pressure of ten tons each time.

This high pressure naturally assists the washing operation, which is also carried out with the cloth on two rows of rollers, twelve in all ; the washing process operates on the counter-current system and the hot solutions are applied by spurt-pipes. Another mangle removes excess of liquid, and the cloth is then taken over an expander into the recuperator, where the residual alkali is removed by steaming.

The Zittau padless and chainless mercerising machine is constructed in four sizes for daily outputs of 6,000 to 20,000 yards, running on single cloths. This output may be increased, however, by running two cloths either superimposed or side by side. The squeezing of the cloth as it passes from the impregnating section to the washing compartment may be effected by either spring or hydraulic pressure. It is also possible in the Zittau machine to have additional squeezing rollers fitted in the impregnating section and so impregnate the fibres as quickly as possible ; similarly their addition to the washing section may be an advantage in certain circumstances.

The washing compartment is operated on the counter-current system, the liquids being supplied by spurt pipes, after which it is recommended to pass the cloth through a recuperator in the usual manner.

One of the chief advantages of these machines is the possibility of running different cloths in respect of weight and width without being obliged to alter the machine ; there is also less risk of damage, particularly to light cloths.

The Recuperator

This apparatus ensures the strictest economy in the consumption of sodium hydroxide and removes the residual alkali from the cloth after it leaves the stenter, expanders or the mercerising machine proper. The machine consists of a cast iron chamber containing two rows of rollers, the top row being driven. The wash-water is fed into the chamber at the delivery end and forms a water seal ; another seal is at the entrance, and in this manner it is possible to exclude all air from the chamber by the admission of low pressure steam, which plays on to the cloth, condenses and removes the alkali in a remarkably efficient manner. The condensed liquor is removed from the cloth by the counter-current wash-water flowing through the bottom of the chamber. As no air is admitted, the formation of oxycellulose cannot occur. The liquor from the last trough of the recuperator generally forms the supply for the washing apparatus on the previous section of the mercerising range. The recuperator is seen in Figs. 124 and 125.

An efficient counter-current system of washing and a recuperator enable a high percentage of caustic soda to be used again ; by suitable handling it is possible to recover and use about 90 to 95 % of the original caustic soda carried over from the impregnation part of the mercerising process.

All steaming chambers or recuperators have a nip or pair of squeezing rollers at the delivery end.

Souring and Washing Machine

This machine is not essentially different from any open-width washing machine. It consists of a series of compartments each of which is fitted with a squeezing device and a series of guide rollers. If a recuperator is not used in mercerising, then extra or larger compartments are used to remove the alkali. After the washing compartments, the cloth passes to the acid bath or souring cistern, where the final trace of alkali is neutralised. Obviously with an efficient recuperator, only a dilute solution of acid will be required, and it is important to avoid too high a concentration of acid, which has only to be removed from the " neutralised " cloth. The final compartments give washes with hot and with cold water and spurt-pipes are generally fitted to the nips or squeeze-rollers. In passing through these washing cisterns a large number of immersions are given to the cloth, and at the same time the wash-water is arranged to flow in a counter-current fashion.

The souring and washing machine is omitted if the goods are mercerised in the grey state and then go forward to the kiers where the residual alkali entrained by the cloth is utilised in the scouring operation.

CHAPTER TWELVE

THE MERCERISING OF RAYON

Sodium Hydroxide

It would appear, on first thoughts, that there is no advantage in mercerising rayon, for it already possesses a high degree of lustre and a greater affinity for dyestuffs than even mercerised cotton ; these two properties are the chief reasons for the mercerisation of cotton goods.

There are many textile materials, however, which consist of mixtures of cotton and rayon, either in stripes or the common cotton warp and rayon weft. Staple fibre or spun rayon is frequently encountered mixed with the cotton hair in yarns for various reasons, one of which is to impart a certain improvement in tensile strength, particularly in the wet state. Such goods are frequently mercerised to bring the lustre of the cotton nearer to that of the rayon and also to reduce as far as possible the disparity in affinity for dyestuffs. For this reason, even though it may appear wrong to talk of mercerising rayon, yet it is necessary that the regenerated cellulose should withstand the mercerising process.

The usual strength of sodium hydroxide solution for mercerising cotton is from 50 to 60° Tw. where an improvement in lustre is required, but it is not infrequent, according to Continental practice, to mercerise cotton solely for the improvement in dyeing, in which case a solution of 25 to 35° Tw. is adequate. When rayon is subjected to these mercerising processes in the ordinary manner it becomes harsh and brittle ; there is also a loss of lustre.

Rayon is much less resistant than cotton to the action of caustic soda, and the ordinary mercerising process is apt to bring about a certain loss in weight due to solution of the material. Further, the most serious point in connection with the actual mercerising process is the greater swelling which takes place when the rayon is washed—actually it is possible to deal with the material while it is still saturated with alkali but in washing it becomes very highly swollen and loses nearly all its strength, with the result that the cloth is apt to split, to have its selvedges cut and suffer other forms of mechanical damage.

At room temperature, rayon swells to a very high degree in 9% NaOH solution—the maximum swelling concentration—as compared with about 14% in the case of cotton.

Weltzein (Textilber., 1926, 7, 338) has recorded his observations on the swelling curves for both viscose and cuprammonium rayons as shown in Fig. 126, from which it will be seen that the swelling reaches a maximum at 9 to 10% NaOH.

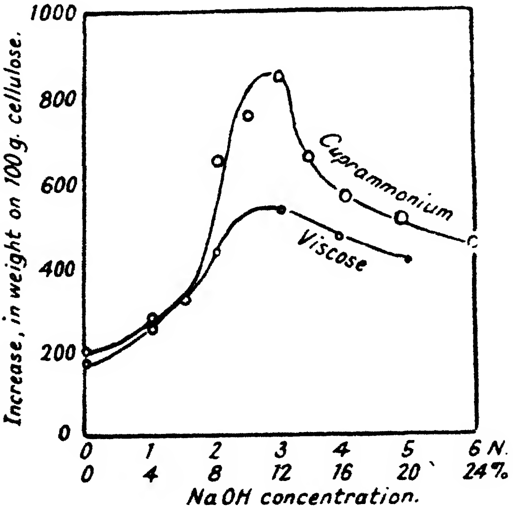


FIG. 126.
Swelling of viscose and cuprammonium rayons in NaOH solution.

The changes in length were also examined, and it was found that with increasing concentration of NaOH solution, viscose filament yarns contracted until they reached the region of maximum swelling, and then began to increase in length again.

The fact that the maximum swelling takes place in about 9% NaOH solution at room temperatures has been confirmed by numerous workers, including Hall (J.S.D.C., 1929, *45*, 98). Christoph (Kunstseide, 1937, *19*, 295) examined the solubility curves in NaOH of six typical German staple-fibre products at a temperature of 20° C. In all cases the curves showed a maximum swelling and a maximum solubility at 9% NaOH, but the amount dissolved varied from 5% to 45%, probably depending on the extent of the ageing of the alkali-cellulose.

The method of washing and weighing after immersion in the alkaline liquor gives higher results with concentrations above 20° Tw. NaOH, as the effect of washing is added to that of actual solubility, which is better determined by oxidation of the dissolved cellulose according to the method of Birtwell and Ridge (J.T.I., 1928, *19*, 341). With higher concentrations of NaOH, the washing process dilutes the alkali to the region of maximum solubility, approximately 20° Tw.

The solubility of viscose in the form of regenerated cellulose was investigated by Davidson (J.T.I., 1936, *27*, 112) as part of a larger examination of the effect of alkali on modified cotton cellulose. From Fig. 127 it appears that at each temperature there is a maximum solubility at a certain alkali concentration, and that this maximum solubility increases as the temperature is lowered. Neale (J.T.I., 1929, *20*, 373)—see page 305—measured the swelling of regenerated sheet cellulose in NaOH solutions at 25° C. and found that the maximum swelling occurred at about 3·2 *N*, compared with maximum solubility at the same temperature in 2·75 *N* NaOH.

Davidson's work on the solubility of modified cotton in solutions of sodium hydroxide showed that the principal factors involved were the degree of swelling produced by the alkaline solution and the average length of the chain-molecules composing the modified cotton. The manufacture of rayon from linters or wood pulp involves a reduction in chain-length of the cellulose (see page 214), and this reduction takes place mainly during the ageing of alkali-cellulose in the case of viscose manufacture (see page 245). The rayons formed from regenerated cellulose are, therefore, not only composed of dispersed cellulose, but also material of shorter chain-length than the starting product (see page 222). These shorter chain-molecules are less able to withstand the swelling action of alkali than are the longer chain-molecules of the native cellulose, so that their dissolution is more readily brought about. The behaviour of modified cotton towards solutions of NaOH should, therefore, offer certain resemblances to that of regenerated cellulose, and within certain limits this has been shown to be correct. At each temperature there is a maximum solubility at a certain concentration of alkali, and this maximum solubility increases as the temperature falls. With regenerated cellulose the concentration of alkali giving maximum solubility is lower than in the case of modified cotton, and the effect of temperature is less pronounced.

The chain-length of the cellulose is not the sole criterion for solubility in alkali. Staudinger and Jurisch (Kunstseide, 1939, *21*, 6) have shown that regenerated celluloses with degrees of polymerisation up to 1,500 are soluble in alkaline solutions in which cotton cellulose degraded to a degree of polymerisation of 400 to 500 is insoluble, namely, 11 % NaOH at —10 to —15° C., and 7 % LiOH solution. The differences in alkali solubility of native cellulose and regenerated cellulose are only observed where the degree of polymerisation is 400 or over, and persist in the fully dried materials and also in the solubility of the tri-acetates in organic solvents. The explanation of this difference is not yet clear.

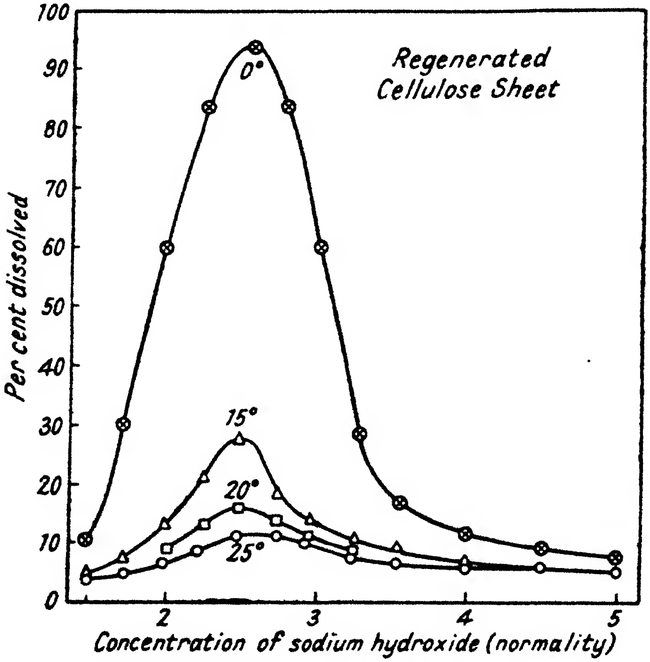


FIG. 127.—Solution of viscose in NaOH.

There is a general parallelism between the swelling and solubility of regenerated cellulose in alkali. Solutions of NaOH have a greater swelling action than those of KOH—a fact which is dealt with later in discussing the action of KOH on rayon (see page 190).

Hall (J.S.D.C., 1929, *45*, 98) observed that during treatment with solutions of NaOH not exceeding 7 %, the viscose rayon became very plastic and highly extensible ; it readily retained a permanent impression, and to a much greater degree even than cotton swollen with greater concentrations of alkali.

The shrinkage of rayon yarns in alkali naturally depends to a large extent on the nature of the yarn, but in the case of one particular yarn Hall obtained the following results:

SHRINKAGE OF RAYON IN NaOH

Concn.	Appearance.	Contraction. In alkali.	Contraction. After washing.	Contraction. After drying.
0%	Normal	+2·0	+2·0	−1·8
1%		+2·0	+2·0	−3·0
2%		+0·4	+1·6	−3·6
3%	Slightly pulpy	−0·4	−0·2	−6·0
4%	Pulpy	−1·0	−1·6	−8·4
5%		−3·4	−3·4	−10·8
6%		−4·6	−5·4	−17·0
7%		−6·4	−9·2	−20·4
8%	Pulpy and warm	−7·6	−11·6	−24·4

The yarn treated with 8% NaOH solution was so soft and swollen that it could only be handled with great difficulty; after washing and drying, those yarns which had been treated with 6 to 8% NaOH solutions assumed a harsh handle. In the case of treatments with 5% NaOH for six hours at ordinary temperatures there was no alteration in the tensile strength of the material, but higher concentrations are apt to cause brittleness.

An interesting observation by Hall was that although the moisture content of the viscose yarn did not increase as the result of treatment with solutions of NaOH up to 8%, yet the material became more absorbent in respect of water and dyestuffs. This increased absorptive capacity is reduced by high-temperature drying in a manner similar to mercerised cotton.

As far as the mercerising process is concerned it would appear to be safe to use concentrations on either side of the maximum swelling concentration of 9% NaOH; swelling commences at about 3% NaOH, and there is evidence to show that there is very little swelling in 70° Tw. In mercerising cotton-rayon mixtures, the lower concentrations would be useless, but it occasionally happens that there are certain advantages in the treatment of 100% rayon goods with these dilute concentrations of alkali which exert only a slight swelling action. Some types of filament rayon do not dye evenly, and it is possible to remedy this by a careful swelling treatment with sodium hydroxide. The improvement may be due to relaxing strains which may be in the material from winding or other mechanical processes or to the disorientation of the orientated skin which is present in many forms of rayon. In the case of spun rayon it is possible to impart a slight curl and so improve the spinning properties. It is also possible to improve the cover and handle of cloths made from spun rayon by an alkaline treatment. B.P. 253,853 discloses this " mercerising " effect of dilute sodium hydroxide solutions of less than 5% strength.

Removal of Alkali

In the case of cotton-rayon mixtures it is possible to treat the material with the higher concentrations of alkali as commonly used in mercerising, for the viscose does not swell unduly. The difficulty arises in the removal of the alkali when the concentration of the liquor on the cloth or yarn must pass through the dangerous maximum swelling concentration of 9% NaOH. B.P. 295,062 covers the use of hot water during the washing, with a view to the rapid removal of the alkali; temperatures above 50° C. are recommended. The lustre of the cotton is not affected by washing with hot or even boiling water. The success of washing with hot water is due to two factors: first, rayon is less soluble in hot alkali than in the cold solution, and secondly, the alkali is rapidly removed at the higher temperature. The danger of 20° Tw. NaOH at room temperatures is, therefore, avoided.

It would appear possible to treat cotton-rayon mixtures saturated with mercerising liquor with copious amounts of cold water in order quickly to pass through the dangerous swelling concentration of 20° Tw. NaOH, but experience has shown that this is hardly practicable.

The swelling of cotton and rayon is almost the same in the higher concentrations of alkali, and as both fibres swell less in hot alkali than in cold, it has been suggested that the goods could be successfully mercerised in hot alkaline liquor, provided that rapid removal of the alkali could be achieved. Experience has shown that this is possible within certain limits; concentrations of alkali of more than 40 to 45° Tw. have been employed at 30 to 40° C., but it is safer to use hot water for removal of the alkali than to rely even on large amounts of cold water. One difficulty of this method lies in

EFFECT OF MERCERISING ON STRENGTH AND EXTENSION.

Cotton-spun Fibre Mixtures.

Count.	Mixture.	Concn. of NaOH.	Breaking load (grey).	Mercerised.			Scoured.		
				Breaking load.	Effect on strength.	Effect on extension.	Breaking load.	Effect on strength.	Effect on extension.
I. 2/30s	Vistra 50% Cotton 50%	48° Tw.	455 g.	463 g.	−1·75%	− 9·5%	535 g.	+17·5%	−10·8%
II. 2/30s	Vistra 50% Cotton 50%	64° Tw	455 g.	443 g.	−2·65%	−13·5%	507 g.	+11·4%	− 8·1%
III. 2/30s	Snia 50% Cotton 50%	48° Tw.	432 g.	445 g.	+ 3 %	−18·4%	470 g.	+ 8·8%	−16·1%
IV. 2/30s	Snia 50% Cotton 50%	64° Tw.	432 g.	428 g.	− 0·9%	−21·8%	462 g.	+ 6·9%	−19·5%
V. 2/30s	Vistra 33% Cotton 67%	64° Tw.	672 g.	716 g.	+ 6·7%	−19·5%	758 g.	+12·8%	− 9·2%
VI. 12s	Vistra 30% Cotton 70%	48° Tw.	596 g.	682 g.	+14·4%	−16·7%	770 g.	+29·2%	−15·4%
VII. 36s	Vistra 16% Cotton 84%	48° Tw.	162 g.	201 g.	+24 %	−29·3%	207 g.	+27·7%	−34·5%
VIII. 36s	Vistra 16% Cotton 84%	64° Tw.	162 g.	183 g.	+13 %	−34·5%	203 g.	+25·3%	−36·2%

Snia refers to Sniafiocco, which is spun from ripened viscose, whilst Vistra refers to Vistra HB from unripened viscose.

the fact that the lustre of cotton is not improved to the same extent by mercerising in hot alkaline lye as in cold liquor, as the degree of swelling is less.

Intimate mixtures of cotton and staple fibre are quite common, and although in many cases the cotton is added to give a higher "wet strength" than that of the staple fibre alone it must not be assumed that such mixtures are capable of withstanding the ordinary mercerising process. Hees (Textilber., 1937, *18*, 367) has carried out a series of experiments on various yarns, mercerised with 28° Bé. and 35° Bé. (48 and 64° Tw) NaOH solutions containing 10 cc. of Leophen B per litre. The yarns were mercerised in the dry state for one minute at 30° C. and given about 10% stretch in the alkali. They were then washed with water at 75° C., soured with H_2SO_4 (5 cc. per litre at 45° C.), washed and dried.

The data given in the table on page 185, indicate that Vistra is superior to Sniafiocco in mercerised yarns, and that the increase in strength consequent upon mercerising falls as the amount of spun rayon in the yarn increases, until at 50% there is hardly any strengthening effect.

Use of Salts, etc.

The swelling of cotton in solutions of sodium hydroxide containing common salt is less than in solutions without salt, and the same principle has been utilised in the case of rayon. The addition of common salt to sodium hydroxide solutions of 20° Tw. or 12 Bé. to the extent of 40 g. per litre results in about 30% less swelling of the rayon. Potassium chloride is stated to be better than common salt in this connection. The lustre of the cotton is adversely affected by this addition to the mercerising liquor; the method is somewhat unreliable.

There are a number of other processes which aim at the mercerising of the rayon by the addition of various substances to the mercerising liquor. For instance, U.S.P. 1,316,958 covers the addition of 57 lbs. of denatured alcohol to 943 lbs. of 27% caustic soda solution; less alcohol is stated to give insufficient protection, whereas more than the stated amount reduces the effect of the alkali on cotton. U.S.P. 1,343,138 describes the use of a similar quantity of formaldehyde in the sodium hydroxide solution, and U.S.P. 1,343,139 the addition of 50 lbs. of phenol to 950 lbs. of 27% sodium hydroxide solution. The addition of 135 parts of glycerin to 865 parts of 29% NaOH solution is referred to in U.S.P. 1,346,802, whilst esters of glycerol are protected in U.S.P. 1,346,803 (181 parts of mono-acetin to 819 parts of 32% caustic soda solution).

Some of the patent specifications disclose early methods intended to protect the rayon during the process of merçerising by making use of protective colloids. Austrian Patent 458 describes the use of solutions of starch or glue. B.P. 230,187 reveals a treatment of the rayon with a 3% solution of gelatin before mercerising the dried material with NaOH of 65° Tw. containing 5% of glycerin. Where the rayon is later to be woven into a cotton warp or weft to make a mixed fabric, the rayon may be treated in hank form with a solution containing 1·5% of gelatin and 2% of 8° Tw. aluminium acetate solution—the latter rendering the gelatin insoluble in water, and so enabling the viscose rayon to withstand the mercerising process.

B.P. 274,266 discloses the interesting observation that non-desulphurised viscose rayon may be mercerised without ill effects and then desulphurised.

A process which has attracted considerable attention is that described in B.P. 323,307, where protective agents are used in the wash water. The substances mentioned are the chlorides, sulphates, nitrates, and chlorates, of sodium or potassium, sodium thiosulphate and certain organic compounds such as sucrose, glycerin and glucose. Common salt is naturally the material which has aroused most interest and it is recommended that a solution of at least 8% should be used at a temperature of 45° C. or upwards. The handle and lustre of the rayon is not adversely affected and the improved lustre and dyeing affinity of the mercerised cotton remains. B.P. 363,883 covers the use of sodium, potassium and ammonium carbonates and bicarbonates in a similar manner—the use of sodium or potassium carbonate enables the recovery of the caustic alkali to be effected more simply than when sodium chloride is employed. The simplest method seems to be the use of a 5 to 10% solution of soda-ash, according to the specification.

Rath (Z. ges. Textilind., 1936, *39*, 357) states that potash alum in the wash water gives still better results than common salt.

These processes make use of the osmotic theory of swelling. The viscose in the alkali absorbs a small amount of a concentrated solution of NaOH, which during washing, attracts water by osmosis—the tendency to dilution. This is obviated by washing with a salt solution which would become concentrated if water passed into the cellulose, and as this is in opposition to the natural tendency to dilution, the swelling is avoided.

A writer under the pseudonym of " Ajax " (Silk and Rayon, 1936, *10*, 518) has described the results of washing with water as opposed to washing with brine after the mercerising process. Hanks of yarn composed of 20 % cotton and 80 % staple fibre were treated for five minutes in solutions of caustic soda of various concentrations at room temperature. They were then washed with cold water or with a 20 % solution of common salt, soured with dilute hydrochloric acid solution, washed with water and measured in the wet state. The hanks were then dried at 50° C., conditioned and measured again. The shrinkage of the dry yarn was slightly more than the wet material.

COMPARISON OF WATER AND BRINE

Concn. of NaOH. Tw.	Shrinkage of dry yarn (brine wash). %	Shrinkage of dry yarn (water wash). %
5°	4·0	4
10	10	13
20	26	32
30	32	54
40	24·5	68
50	19	56
88	12	56

In the case of washing with brine, the length shrinkage reaches a definite maximum with NaOH of about 26° Tw., but this maximum is higher and less definite where water is used. The yarns washed with water were harsh and weak after drying, whereas those washed with brine were soft and strong. The lustre of the latter was also unimpaired. Concentrations of NaOH of 20° to 35° Tw. appear to be most harmful in respect of lustre when the mercerised rayon is washed with water after the alkali treatment.

Some interesting data have also been given concerning the extent of shrinkage of a 100 % spun viscose yarn of 40s count treated with NaOH solutions of various concentrations.

SHRINKAGE OF SPUN-VISCOSE YARN

Concn. of NaOH.	Shrinkage in alkali. %	Shrinkage on washing with brine. %	Shrinkage dry. %
water	0	2	2
5° Tw.	8	4	5
10	12	11	15
20	15	18	26
30	23	24	31
40	27	17	24
50	25	15	19
60	4	8	10
88	4	5	5

The maximum shrinkage when the yarn was in contact with the mercerising liquor occurred at 42° Tw. NaOH, but after washing with brine and also after drying the maximum shrinkage was observed for yarns mercerised with 30° Tw. NaOH.

In view of the additional shrinkage which takes place on drying, it would appear advisable to stretch this type of material to a greater extent during the mercerising process than would be usual with a similar construction in cotton.

Hall (J.S.D.C., 1929, *45*, 171) has carried out a series of experiments on the removal of alkali from viscose rayon saturated with sodium hydroxide. The yarn was previously immersed on 56° Tw. NaOH solution for 15 mins. at room temperature; the effect of various substances utilised to remove the alkali is tabulated below.

EFFECT OF VARIOUS METHODS OF ALKALI-REMOVAL.

Washing medium.	Effect on viscose rayon.
Acetone	Loss of lustre; brittleness.
Methylated spirit . . .	Retention of lustre and handle.
5 to 25% glucose solution . .	Higher concentrations give retention of lustre and handle.
10 to 30% glycerin soln. . .	As with glucose.
10% sucrose	Loss of lustre and handle.
2% phenol	Loss of lustre and softness.
Sodium chloride (10% and saturated)	Retention of lustre and softness.
Sodium carbonate (10%) . .	As above.
Sodium bicarbonate (10%) .	As above.
Sodium sulphate (10%) . .	Loss of lustre and softness.
Potassium chloride (saturated) .	Retention of lustre and handle.

Potassium Hydroxide

The difference in behaviour of viscose rayon to solutions of sodium hydroxide and potassium hydroxide is mentioned by Clement and Rivière in " Soies Artificielles," Paris, 1924, page 503, where in dealing with the difference between real and artificial silks the authors state that the latter are resistant to concentrated solutions of potassium hydroxide.

The use of solutions of potassium hydroxide for the mercerising of rayon has been protected in B.P. 295,488, and is a process of considerable importance in mercerising and one which has aroused considerable interest. Rayon may be treated in KOH solutions varying in concentration from 55 to 60° Tw. without becoming harsh or being deleteriously affected. In general, however, it is preferable not to use low temperatures, for then the material does show signs of harshness; the range of 15 to 50° C. is considered safer. The concentration of potassium hydroxide does not appear to be critical, for 30 to 90° Tw. is mentioned in the provisional specification, and although the maximum deleterious effect is stated to occur at 70° Tw., the influence of concentration is small. A point of greater importance is the time of treatment, which should be as short as possible; mercerising, stretching and washing should take about 80 seconds. The cotton in the mixture is then well mercerised and the rayon has its original strength, lustre and softness.

The solubility curve of rayon in solutions of KOH shows a flat maximum at about 43° Tw. in contrast to the sharp maximum at 20° Tw. NaOH. The amount dissolved in the optimum concentration of NaOH is about twenty times that in the optimum concentration of KOH.

Hall (J.S.D.C., 1929, *45*, 171) found that viscose rayon swells and contracts in length to a much greater extent in caustic soda than in caustic potash and is practically unaffected by treatment with the latter. Viscose rayon is also much less soluble in caustic potash than in caustic soda, and it was found practically impossible to dissolve the rayon in 10 % KOH solution at 0 to —9° C., whereas under similar circumstances viscose readily dissolved in 8 % NaOH solution. A comparison of the loss in weights of viscose filament rayon in NaOH and KOH solutions is shown in Fig. 128.

On account of the low swelling produced with KOH solutions the rayon material is less extensible and is also less subject to damage by shearing forces during the actual processing of the goods.

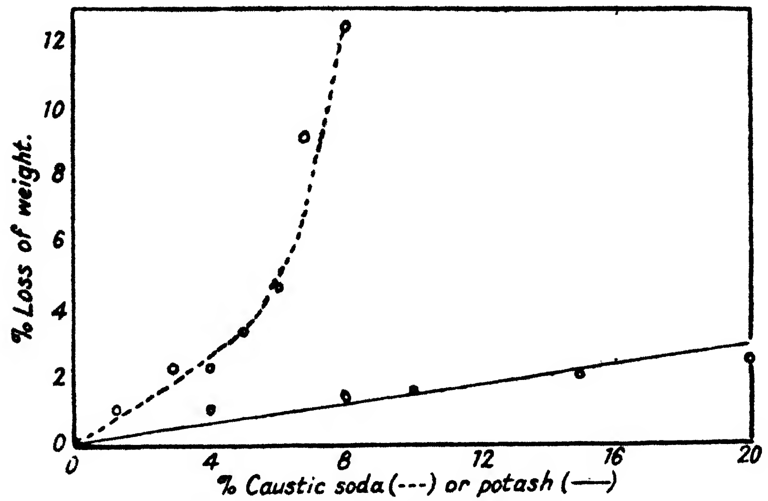


FIG. 128.—Solution of viscose rayon in NaOH and in KOH.

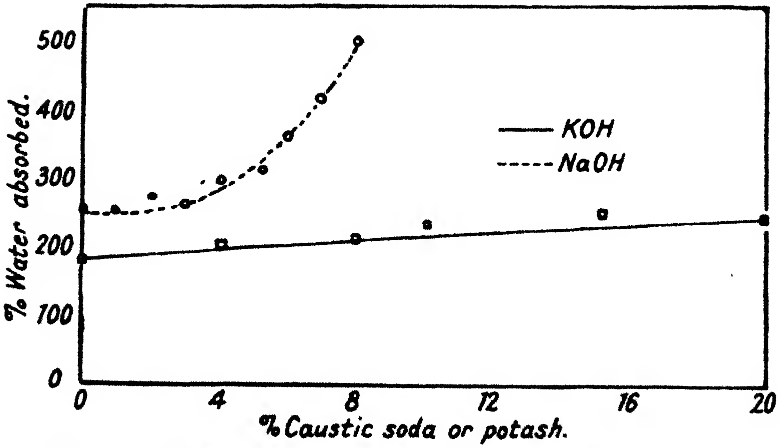


FIG. 129.—Swelling of viscose rayon in NaOH and in KOH.

Comparison of the water-retaining power of viscose yarns mercerised with solutions of potassium hydroxide and sodium hydroxide showed that the effect is much less in the case of the former. The results are shown in Fig. 129.

The curves of Davidson (page 264), as given in Fig. 169, are also of interest in showing the swelling and the solubility of sheet regenerated cellulose in solutions of potassium hydroxide. There is good correlation between swelling and solubility.

Hall (loc. cit.) has provided the following data concerning the shrinkage in length of viscose filament rayon on treatment with various solutions of potassium hydroxide:

SHRINKAGE OF VISCOSE YARN IN POTASSIUM HYDROXIDE.

		Contraction.		
Concn.	Appearance.	In alkali.	After washing.	After drying.
0%	Normal	+3·0	+3·0	0·0
4		+1·0	+2·0	−0·5
8	Severe swelling	−1·0	0·0	−3·4
10		−1·0	−0·0	−4·1
15	Slight swelling	−3·0	−2·0	−5·7
20		−3·0	−2·5	−7·0

It will be noticed that here again only part of the shrinkage takes place while the viscose is in the wet state and the remainder occurs on drying.

Mecheels (Textilber., 1936, *17*, 725), in describing the mercerising action of potassium hydroxide solutions, points out that, whereas there is a large difference between the maximum swelling concentrations of sodium hydroxide in the case of rayon and cotton, the maximum swelling concentration of potassium hydroxide occurs at a strength which is suitable for the mercerising of cotton, i.e. 30° Bé. or 50° Tw. The swelling and shrinkage curves of cotton and rayon in potassium hydroxide solutions are broadly similar; as far as lustre of the cotton is concerned, the use of 28° Bé. NaOH gave the same result as 30° Bé. KOH.

The treatment suggested for mercerising with KOH is to use a solution of 27 to 30° Bé. (46 to 52° Tw.) at temperatures up to 18° C. for one minute, or longer in the case of grey goods. Potassium hydroxide is more expensive than sodium hydroxide, but the technical advantages are the decreased solubility of viscose in the alkali, shorter immersion, easier removal of the alkali and the absence of common salt. The lustre of the rayon is not impaired by the use of KOH solutions and there is a slight increase in wet strength.

Schneider (Klepzig's Textil. Z., 1938, *41*, 182) has produced the following test for mercerised rayon:

The material is wetted with water, squeezed and treated for 2 mins. with zinc chloride-iodine solution. The excess is removed and the sample again squeezed and transferred to 250 cc. of water, to which is added 3 to 5 cc. of N $Na_2S_2O_3$. After the blue colour disappears, concentrated chlorine water is added with stirring until an iodine-brown colour appears. Mercerised staple fibre becomes green and the untreated material remains white or yellow.

Mixed Solutions

Russina (Monat. Seide u. Kunstseide, 1938, *43*, 136) has carried out experiments on staple fibre yarns using solutions of sodium hydroxide, equal parts of sodium and potassium hydroxides and of potassium hydroxide of 22° Bé. (36° Tw.).

None of the treatments produced any improvement in tensile strength in the dry state, but there was a slight improvement in wet strength on treatment with caustic potash, according to the following figures :

BREAKING LOAD OF STAPLE FIBRE YARN.

	Dry.	Wet.
Untreated yarn	273 g.	126 g.
Mercerised NaOH . . .	229	87
Mercerised NaOH/KOH . .	259	125
Mercerised KOH . . .	263	134

Load-extension diagrams showed practically no difference between the behaviour of the untreated yarn and yarn mercerised with sodium hydroxide solutions, with or without the addition of common salt. In the case of yarns treated with potassium hydroxide solutions or mixtures of sodium and potassium hydroxide solutions, there is a perceptible improvement in elasticity.

Heide (Kunstseide, 1937, *19*, 314) has made a study of three methods of mercerising spun rayon materials and mixtures.

(I) Sodium hydroxide solutions of 28 to 32° Bé. containing a suitable wetting agent (Floranit HF) and also 40 to 50 g. of common salt per litre ; this solution should be used at 30° C.

(II) Mixtures of sodium and potassium hydroxides to give 30° Bé. when mixed.

(III) 10° Bé. sodium hydroxide.

The best method depends on the constitution of the mixture of cotton and rayon which composes the yarn.

METHODS FOR MERCERISING COTTON AND STAPLE FIBRE.

Composition.	Best method.	Possible method.
100–80% cotton 0–20% spun viscose	I	
80–40% cotton 20–60% spun viscose	I	II
40–10% cotton 60–90% spun viscose	I, II	
10–0% cotton 90–100% spun viscose	II	I, III
100% spun viscose	II	III
100–40% cotton 0–60% spun cuprammonium	I	II
40–10% cotton 60–90% spun cuprammonium	II	III
100% spun cuprammonium	III	

Data obtained from the treatment of various types of spun rayon, in various proportions and in different yarns, are of some interest.

EFFECT OF MERCERISING PROCESSES.

% Rayon.	Origin.	Yarn.	Method.	Breaking load. Grey.	Breaking load. Merc.	Extension. Grey.	Extension. Merc.
16	Viscose	2/40	I	289g.	356g.	4%	15%
16	,, flox	2/30	I	512	658	15·5	15
30	,, ,,	2/60	I	181	201	14	13
30	,, vistra	2/28	I	524	670	17·5	17·5
30	,, ,,	2/40	I	304	359	11	12·6
30	Cuprama	2/40	II	292	329	11·3	13·1
36	Viscose	4 × 2/18	I	718	898	19·3	18·6
50	,, flox	2/40	I	239	289	15	13·5
50	Cuprama	2/40	I	291	304	11·7	18·5
56	Viscose	2/60	I	162	173	15	16
70	,, flox	2/60	II	139	151	15	22
100	,, vistra	2/40	II	265	245	15	26
100	Cuprama	2/40	III	226	258	12·3	27·3

Taking broad averages, the effect of the mercerising process in respect of tensile strength is seen to vary with the proportion of cotton in the mixed yarn.

EFFECT OF MERCERISING ON BREAKING LOAD.

Proportion of spun rayon.	Improvement in strength.
16%	25%
30%	20–22%
50–70%	10%
100%	nil

In the case of a yarn composed of 100% spun viscose (vistra) the effects of mercerising processes have been given in more detail, particularly in respect of the relation between the physical properties in the dry and wet states.

MERCERISATION OF SPUN-FIBRE.

	Strength.		Extension.		Effect of wetting.	
	Dry.	Wet.	Dry.	Wet.	Strength.	Extension.
	g.	g.	%	%	%	%
Unmercerised .	266	117	15	23	−66	+56
Mercerised (I) .	245	130	25	32	−47	+26
Mercerised (II).	287	140	19	19	−51	nil

The mercerising process brings about definite improvement in the relation between the physical properties in the wet and dry states.

For mixtures of cotton and spun rayon it is practically essential to make use of a mercerising liquor which will bring about an improvement in lustre and dyeing properties in the case of the cotton, without any adverse effect on the rayon as regards handle and lustre. The use of potassium hydroxide alone is expensive so that mixtures of sodium and potassium hydroxides have received most attention. (Heide's Method II).

The composition of these mixtures requires a little care, and Heide suggests that the proportions of the two alkalis should vary with the proportions of the two fibres, e.g. in the case of a mixed yarn containing 70% cotton and 30% spun rayon a suitable mercerising liquor may be made from 70 parts by volume of NaOH of 30° Bé. and 30 parts by volume of KOH of 30° Bé.

It is important to use solutions which have the equivalent mercerising effect of 30° Bé. NaOH in order to ensure a full mercerising of the cotton ; working with 30° Bé. liquors, it is possible to do this with mixtures of within the range of 70–80 parts by volume of NaOH and 30–20 parts by volume of KOH solutions, but with other proportions this does not hold.

VOLUME MIXTURES OF NaOH AND KOH.

Parts of 30° Bé. liquors.		Mercerising equivalent in NaOH.
70 NaOH :	30 KOH	27–28° Bé.
60	40	25° Bé.
50	50	23° Bé.
40	60	21–22° Bé.
30	70	19–20° Bé.

Quantitative Comparisons

Schramek (Leipz. Monat. Text. Ind., 1938, *53*, 106) has compiled a series of tables showing the effect of various mercerising processes on a 2/20s yarn spun from a 44/56 mixture of cotton and staple fibre. Even if the yarn as a whole shows no decrease in strength, yet the staple fibre from it always appears to suffer ; in many cases there is an increase in extensibility. The data confirm the superiority of caustic potash as a mercerising agent. The effect of repeated washes on the various yarns is very interesting.

MERCERISING OF MIXED YARN.

Treatment.			Tensile strength g/100 den.	Extension. %	Lustre.
Grey			118	8·2	1·2
5% NaOH no tension			114	7·6	1·5
,, ,, tension			115	7·2	1·5
25% ,, no tension			114	5·1	2·5
,, ,, tension			116	5·8	2·3
,, ,, ,, (works' product)			122	5·8	2·4
25% NaOH no tension, washed with brine			111	5·4	2·4
	NaOH	KOH			
25% alkali,	75%	25%	118	5·4	2·4
,, ,,	50%	50%	124	5·2	2·5
,, ,,	25%	75%	118	5·2	2·5
25% KOH			121	5·3	2·5

The four last experiments refer to mercerising under tension. The yarn was a 44/56 mixture spun to 2/20s.

TESTS ON SINGLE FIBRES.

Treatment.	Spun rayon.				Cotton.			
	Strength. dry.	Strength. wet.	Extension. dry.	Extension. wet.	Strength. dry.	Strength. wet.	Extension. dry.	Extension. wet.
	g.	g	%	%	g.	g.	%	%
Grey	2·55	1·61	15·5	14·3	3·0	3·73	8·5	11·1
5% NaOH ; tension .	2·18	1·19	14·5	9·2	3·4	3·44	8·1	8·1
25% ,, no tension	1·77	0·82	11·5	7·9	4·9	4·5	7·6	9·5
,, ,, tension .	1·89	0·84	10·7	7·3	4·6	4·25	7·5	9·5
,, ,, ,, (works)	2·18	1·35	11·7	10·8	3·03	3·36	8·5	9·7
25% NaOH, no tension, wash with brine .	2·01	1·11	13·4	11·9	4·04	4·11	7·0	8·7
25% alkali ; 50 NaOH, 50 KOH, tension .	2·10	1·35	12·6	12·5	3·56	4·0	8·0	10·3
25% KOH . . .	2·20	1·40	10·6	13·6	3·52	3·48	6·9	10·6

EFFECT OF WASHING.

Treatment.	Yarn breaking load. Dry.			Wet.		
	No. of washes.					
	0	10	50	0	10	50
Grey . . .	290 g	280 g.	251 g.	279 g.	270 g.	216 g.
Hot water . .	310	310	285	295	287	234
5% NaOH no tension	293	293	277	272	267	241
,, ,, tension .	293	291	288	276	280	248
25% ,, no tension	287	282	270	257	256	244
,, ,, tension .	287	281	294	260	274	258
20% alkali, 50% KOH, 50% NaOH, no tension . . .	208	300	303	276	277	262
25% KOH, no tension	293	290	295	276	292	255
	Yarn extension.					
Grey . . .	8·0%	9·5%	10·3%	9·8%	13·2%	12·7%
Hot water . .	7·8	8·6	10·1	9·6	12·2	12·6
5% NaOH no tension	7·9	10·1	10·8	8·4	10·6	11·9
,, ,, tension .	7·0	8·9	10·7	6·6	10·9	11·5
25% ,, no tension	5·4	8·2	9·0	5·6	7·7	9·4
,, ,, tension .	4·9	8·1	10·8	5·8	7·6	9·1
20% alkali, 50% KOH, 50% NaOH, no tension . . .	5·0	7·0	9·9	5·6	7·2	9·3
25% KOH, no tension	4·6	7·0	8·0	5·9	7·9	9·0

Cellulose Acetate

Artificial silk made from cellulose acetate is a compound of cellulose and acetic acid, the former being substituted to the extent of 2·5 of the available three positions. It is not a regenerated cellulose, but an ester and, therefore, is liable to hydrolysis with alkali. This fact had to be taken into consideration in dealing with the mercerisation of cotton-acetate mixtures, and one of the first attempts to deal with this is seen in B.P. 259,394, where the mercerising alkali contained certain protective salts such as those of the alkali metals and of aluminium; substances specifically mentioned being the chloride, chlorate, sulphate, thiosulphate, nitrate, nitrite, borate, acetate, chloracetate, and glycolate, of sodium or potassium; zinc or aluminium oxide, chloride, sulphate, citrate, acetate; sodium zincate; sodium aluminate. Polyhydric alcohols, carbohydrates, and phenols such as glycerol, sucrose, phenol, resorcinol, and acetin, are also mentioned.

In another specification, B.P. 273,830, a process is described in which artificial silk is impregnated with an oil or with a water-resisting substance such as benzene in order to prevent wetting by the alkaline liquor.

These processes are rarely employed because it was found, that whereas cellulose acetate is readily hydrolysed by dilute solutions of sodium hydroxide, yet this was not the case with the more concentrated solutions normally used in mercerising practice. This was disclosed in B.P. 210,484, and there is reason to believe that substantial quantities of mixed goods have been and are being treated in this manner. It is recommended that the temperature of the caustic soda solution should not exceed 15° C. Although the ordinary mercerising liquor is utilised, it is essential to conduct the mercerising process as quickly as possible and also rapidly to remove the alkali by means of cold water instead of the hot water which is frequently used in ordinary practice. Another precaution is that the goods should be mercerised in the dry state in order to avoid any dilution of the alkali with consequent risk of hydrolysis of the cellulose acetate.

The specification covering this successful process was the subject of legal dispute (see J.S.D.C., 1929, *45*, 350), and the patent was declared invalid on the grounds that there was no novelty in the process. The application of an old and well-known process to a new textile material without the necessity of definite restricted conditions was not patentable.

It would appear that the reason for the resistance of cellulose acetate fibres to the mercerising liquor is connected with the high viscosity of that liquor, it being known, in any case, that cellulose acetate is not easily wetted, even by aqueous liquors of low viscosity; the high viscosity probably enables the artificial silk to withstand penetration for the few moments necessary for the mercerising of the associated cotton material. It must be noted that if the cellulose acetate is allowed to stand in contact with the mercerising liquor for more than a few minutes, then hydrolysis does take place.

Rolland (R.G.M.C., 1934, *38*, 41) recommends immersion in caustic soda of 52° Tw. for two minutes at 10° C., followed by washing with copious supplies of water at 10° C., and souring with 1 % sulphuric acid at 18° C.

CHAPTER THIRTEEN

THE MERCERISING OF LINEN

Flax is an annual plant which grows to two or three feet in height. After reaching full growth it is gathered and the leaves and seeds are removed by a series of upright forks in a process called rippling.

The straw, or flax stalk, is then tied in bundles for the retting process, which decomposes the woody matter, releasing the cellulose fibres. Retting is a fermentation process and must not be carried too far, as over-retted flax is weak and brittle on account of the removal of the pectic matter which holds the fibres together. The retted flax when dried is passed through several pairs of fluted rollers to break up the woody matter (a process of scutching), and this woody matter is then removed by hackling in a machine with a rotating cylinder on which is fixed a number of wooden blades.

Flax straw contains some 27% of flax in the inner bark.

The flax fibre is multi-cellular and each cell has tapering pointed ends and a very narrow lumen. The fibre shows longitudinal striations and peculiar cross-like dislocations called nodes, both of which are much less apparent in mercerised flax. The cross section of flax is polygonal and the thickness of the cell wall is uniform.

There is great variation in the length of flax fibres, from a few inches to three feet, good flax having an average length of about twenty inches; the individual cell, however, varies from 2·5 to 0·25 inches in length and from 0·005 to 0·001 inches in diameter.

Flax is much stronger than cotton, but has a lower extension at break.

Mercerised Linen

Linen possesses quite a high degree of natural lustre which renders it unnecessary to mercerise the material for the reasons which apply to cotton. A certain amount of linen is mercerised to improve the affinity for dyestuffs, but the

FIG. 130.

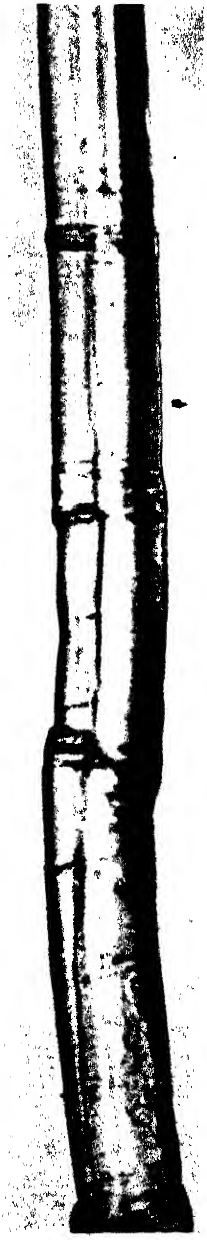


FIG. 131.

FIG. 132.

FLAX.

[*To face page* 200.

PLATE XLVI.

FIG. 133.—Photomicrograph of cross-section of flax stalk.

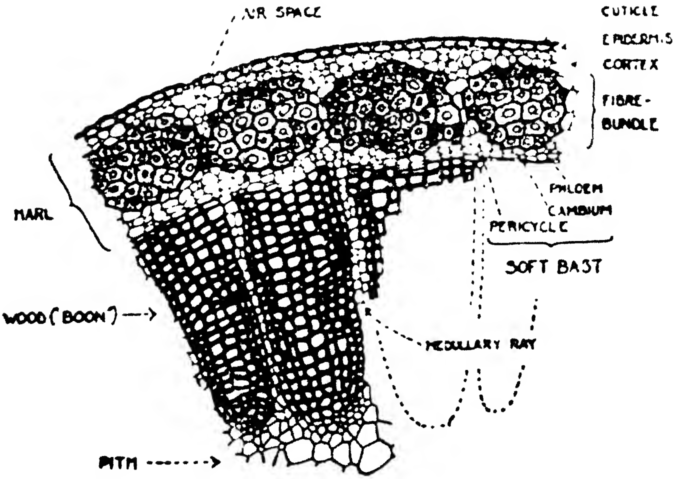


FIG. 134.—Diagram of the cross-section of flax stalk.

(*By courtesy of L.I.R.A.*)

[*To face page* 201.

general stiffness of the cloths when impregnated with alkali, coupled with their great slipperiness, make the process rather a difficult one, particularly where the stenter type of mercerising machine is used, as the clips do not grip so well as in the case of cotton.

The general procedure is to mercerise in 50-60° Tw. NaOH solution at a speed of about 60 yards per minute. The pressure of the impregnating mangles is generally not so high as in the impregnation of cotton goods. The washing of the goods takes a longer time than in the case of cotton.

There is reason to believe that the mercerising of linen is undertaken more in connection with the crease-resisting process than for any other purpose. Linen creases more than cotton, possibly on account of the more regular arrangement of the fibres and the better orientation of the micelles making up the cellulosic structure ; the extensibility and elasticity of flax is less than that of cotton, Application of the well-known methods described in B.P. 291,473 and 4 ; 304,900 and 449,243 showed that although the resistance to creasing of treated linen cloths was very considerably improved, yet the goods were brittle and showed a definite decrease in tensile strength and resistance to wear. This has been successfully overcome by a mercerising process on the anti-crease material as described in B.P. 437, 361 and on page 205.

The work of Nodder (J.T.I., 1923, *14*, 142) has been discussed on page 64.

Otherwise references to the technical mercerising of linen are very scarce. For instance, Beltzer and other early authorities merely state that similar methods apply to linen as in the case of cotton, and many patent specifications for mercerising methods include linen, but give detailed examples for the treatment of cotton only. Hertzog's paper (Textilber., 1920, *1*, 136) shows that mercerising of linen is carried on, but most of the papers in the literature refer to the work of the X-ray and other scientific investigators on the question of fine structure. Fort (J.S.D.C., 1921, *37*, 161) has commented on the difficulty of mercerising linen goods which often results in actual injury to them, owing to roughening and deterioration. This may be due to separation into the ultimate fibres and a partial " cottonisation " of the flax. Fine linen goods, however, appear to present less difficulty.

Victoroff (Textilber., 1925, *6*, 169) has supplied practically all the measurements of strength, extension and affinity for dyes. His first experiments relate to the treatment of yarns when he observed that a "woolly" appearance and handle resulted when the yarn was mercerised in 30° Bé. NaOH solution; this was most marked when the yarn was allowed to shrink during the mercerising process and may be associated with the cottonisation of flax. The bundles of fibres which make up the flax yarn are dissociated into the separate fibres when given a severe treatment with alkali. There was an improvement in lustre in both cases, but the yarn mercerised under tension was superior in this respect.

Victoroff's data were mainly obtained from the use of linen cloth made of 54 threads per cm. of 38s in the weft and 59 threads per cm. of 31s in the warp. The fabric was soaked in water overnight and then boiled for one hour in 1·5 % soda solution. The dried sample was then cut into strips, which were impregnated in 30° Bé. (52° Tw.) NaOH solution at room temperature—a double impregnation lasting three minutes was given in all cases, after which the strips were hung on glass rods and covered with muslin cloth impregnated with the same concentration of alkali and allowed to remain for various lengths of time. The strips were then washed with hot and cold water and finally dried.

A second series of experiments was on very similar lines, except that the cloth remained in contact with the impregnating liquor for the stated time instead of being hung on a glass rod with a possibility of partial drying.

The results of these two series of experiments are shown in the following tables where (A) indicates the method of hanging on glass rods and (B) that of immersion in the liquor for the stated times.

TENSILE STRENGTH AND TIME OF CONTACT (A).

Time.	Breaking load, Kg./40 mm.	Breaking load, calculated on 100 threads.
Untreated cloth	61·5	67
3 mins.	67·8	66·7
5 ,,	65·9	64
10 ,,	68·0	66
15 ,,	71·3	69·2
30 ,,	63·4	61·5
1 hour	69·8	67·1
3 hours	66·5	63·9
5 ,,	67·6	65·6
7 ,,	65·0	63·7

TENSILE STRENGTH AND TIME OF CONTACT (B).

Time.	Shrinkage. %	Breaking load, Kg./40 mm.	Breaking load, 100 threads.
Untreated	—	61·5	67
15 mins.	11·4	65·2	63·3
1 hour	13·2	66·5	62·7
3 hours	13·2	69·9	66
5 ,,	13·2	69·7	65·7
7 ,,	13·2	70	66
9 ,,	13·2	71	67
24 ,,	14	68·8	64·4
15 mins. (soured)	11·6	63·5	63·5

From these data it is evident that although the apparent strength of the fabric was increased by treatment with mercerising liquor, the results were obscured by the shrinkage of the material, and when this was taken into consideration a decrease in tensile strength averaging 6 % (maximum 8 %) is the real result. The shrinkage of the material amounted to 12 13 %, which was the same as that of a cotton muslin material similarly treated, but which gave an average increase in strength of 25 %.

Although these samples were mercerised without tension, yet Victoroff observed an increase in lustre, and in some samples which were mercerised under tension the lustre was still better. In no case was there any indication of the woolly effect noted on yarns.

The extension at break was also measured on material mercerised without tension and immersed in the alkali for the stated times.

EXTENSION AT BREAK.

Time of treatment.	Extension. %	Extension as percentage of original.
Untreated	9·2	100
15 mins.	19·1	208
1 hour	20·7	225
3 hours	22·3	243
5 ,,	21	228
7 ,,	21·1	230
9 ,,	20·7	225
24 ,,	22·9	249

The extension at break appears to be about 2·5 times that of the untreated material; in the case of the cotton muslin material referred to above and used for comparative experiments, the extension at break was increased four times as the result of mercerising without tension.

Experiments on the effect of the temperature of the sodium hydroxide solution of 30° Bé. (52° Tw.) were also carried out, but in this case, after a double impregnation, the samples were allowed to lie in the alkali for a period of one hour at various temperatures before washing.

EFFECT OF TEMPERATURE.

Temperature of alkali.	Breaking load, Kg./40 mm	Breaking load per 100 threads.	Shrinkage. %
Untreated	60·4	61·7	—
0° C.	64·7	56·4	14·8
20	65	57	14·65
50	65·8	57·2	14·8
80	63·3	55	14·8

From these figures it appears that the effect of temperature within the above limits is negligible.

The effect of various concentrations of alkali was also investigated; the temperature of the liquor was 20° C. and the samples were allowed to lie in the alkali for one hour without tension.

EFFECT OF ALKALI CONCENTRATION.

Concentration of NaOH.	Breaking load, Kg./40 m.m.	Breaking load per 100 threads.	Shrinkage. %
Untreated	58·9	60·1	—
20° Bé.	65	58·6	11·9
30	62	54·4	14·7
40	59·3	51·1	15·4

It will be noted that the concentration of 40° Bé. (76° Tw.) causes the greatest shrinkage and the biggest reduction in strength—about 15 %.

Summarising the data obtained for mercerising linen under free shrinkage it would appear that the extension at break is increased about 2·5 times as compared with four times in the case of cotton. The tensile strength falls about 6 to 8 % compared with a rise of 25 % in the case of cotton.

The above experiments were all laboratory trials and the data refer to mercerising without tension.

Owing to the smooth nature of linen saturated with caustic soda, Victoroff found difficulty in mercerising the cloth under tension on a mercerising machine as the goods tended to slip out of the stenter clips. A superior lustre was observed to that which was found on goods mercerised without tension.

LINEN MERCERISED UNDER TENSION.

	Breaking load, Kg./100 threads.	Shrinkage on mercerising.
Warp unmercerised .	61·3	
Warp mercerised . .	93·1	22% extension.
Weft unmercerised .	74·4	
Weft mercerised . .	66·9	3·2% shrinkage.

There was an increase of 52% in the strength of the warp accompanied by 22% increase in length, whereas the 3% weft shrinkage brought about a 10% reduction in strength. Victoroff assumed that under properly controlled conditions of works' practice it should be possible to mercerise linen without any decrease in strength, provided the original dimensions could be maintained.

The increase in affinity for dyestuffs of mercerised linen was also examined by Victoroff, who found that in mercerising without tension some 40% increase occurred in the case of Benzopurpurin 4B and about 23% in the case of indigo.

Crease-resisting Linen

The first step in the application of the crease-resisting process to linen is the preparation of the impregnating bath by dissolving 50 parts by weight of urea in 100 parts by weight of 40% formaldehyde solution which has been carefully neutralised with sodium hydroxide solution. To this solution is added 3% of ammonium hydroxide solution (sp. gr. 0·88), calculated on the total weight, and the whole is boiled for three minutes under a reflux condenser and then rapidly cooled. The refluxed mixture is then diluted to about 60% by volume with water according to the goods to be treated and the expression of the mangles used for impregnation. About 1% by weight of tartaric acid (estimated on the dilute solution) is then added and the goods are impregnated. The cloth should be in a dyed or printed state, if necessary, for the crease-resisting process is a final process, and should be so constructed as to permit of shrinkage. For example, a cloth of 36–38 ins. wide, when impregnated, should be dried at a temperature below 100° C., and stretched to, say, 38-40 ins. It is then heated for two to three mins. at 170° C. (or a lower temperature if the methods of B.P. 449,243 are followed). It is important at this stage that the material should not contain more than 20 to 25 % of resin, or the subsequent processes are rendered more difficult. The fabric is well wet in an aqueous solution containing 0·25 % sodium carbonate and 0·25 % of the alkali salt of a sulphonated fatty alcohol at 80° C., and mangled. The wet cloth is then mercerised by treatment with 50 to 63° Tw. NaOH solution and, whilst still containing the alkali, is allowed to shrink both in warp and weft directions; a second impregnation is followed by washing and stretching, souring with acetic acid, washing and drying to a finished width of 34 to 36 inches.

In so far as machinery is concerned, it is quite easy to use the common two-mangle mercerising range and arrange to allow the necessary shrinkage and the interval of time for its accomplishment.

It will be realised that this is one of the few processes of mercerising for swelling and shrinkage as against the common mercerising for lustre. The shrinkage treatment is essential if strong and durable goods are to be obtained; this fact is all the more remarkable in view of the behaviour of untreated linen, which suffers a decrease in tensile strength when mercerised without tension. Victoroff (page 203) gives some 6 to 8 % decrease, but according to B.P. 437,361 the tensile strength of a crease-resisting linen cloth was increased from 17·3 lbs. to over 30 lbs. as a result of the "after-mercerising" process, involving about 12 % shrinkage. There was also a manifold increase in the resistance to wear.

The reason for this is not yet clear, but there are some interesting speculations which may be advanced.

PART FOUR

NATIVE CELLULOSE AND HYDRATE CELLULOSE

CHAPTER FOURTEEN

CONSTITUTION AND STRUCTURE

Constitution

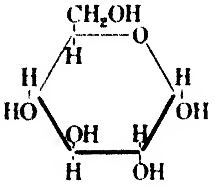
ANALYSIS of cellulose gives the following composition: C 44·4%; H 6·2% and O 49·4%, corresponding to the empirical formula $C_6H_{10}O_5$. Consideration of the structure of native cellulose, its colloid properties and inertness in the chemical sense led to its being regarded as $(C_6H_{10}O_5)_n$; the formation of derivatives such as the tri-nitrate and tri-acetate point to the presence of three hydroxyl groups.

The relationship between cotton cellulose and *glucose* has been known for very many years and yields of some 95 to 98% were obtained by Fleschig in 1883, by Ost and Wilkening in 1910, and by Willstätter and Zechmeister in 1913; the glucose was estimated by reducing power and optical rotation, and obtained by hydrolysis of cotton with dilute H_2SO_4 or dilute HCl.

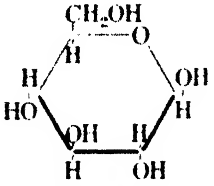
The actual isolation of glucose from cotton was accomplished by Monier-Williams (J.C.S., 1921, *119*, 803) and confirmatory evidence was produced by Irvine and Hirst (J.S.C., 1922, *121*, 1,585). The position of the three hydroxyl groups was established in a series of papers by Denham and Woodhouse (J.C.S., 1913, *103*, 1,735; 1914, *105*, 2,357 and 1917, *111*, 244) on methylation. Similar investigations by Irvine and Hirst (J.C.S., 1923, *121*, 1,585) confirmed the presence of hydroxyl groups in the *2* : *3* : *6* positions.

Combined hydrolysis and acetylation of cotton gives considerable yields of the octa-acetate of a disaccharide known as *cellobiose*; this was isolated by Franchimont in 1879 and examined by Maquenne and Goodwin in 1904. Haworth and Hirst (J.C.S., 1921, *119*, 193) showed that this sugar consisted of two glucose residues united by a *1* : *5* or *1* : *4* β-glucosidic linkage and suggested that a similar linkage was represented in cellulose. Hydrolysis of the methylated product gave equal amounts of tetramethyl and trimethyl glucose and the latter was identical with the *2* : *3* : *6* trimethyl glucose of Denham and Woodhouse.

A very important advance in our understanding of the chemistry of the sugars was made by Haworth (Nature, 1925, *116*, 430 ; J.C.S., 1926, p. 89) when he formulated the structure of glucose as a six-membered ring, instead of the previously accepted five-membered structure. The use of atomic models is really essential to the full understanding of the position, for the problems are mainly stereo-chemical. Representation of the formulæ on flat paper is difficult, but differences of configuration may be shown by distribution of hydroxyl groups above and below the plane of the paper. For example, the α and β forms of glucose differ only in stereo-chemical arrangement.

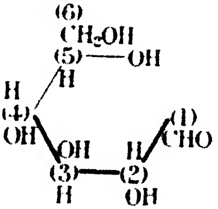


α-glucose.

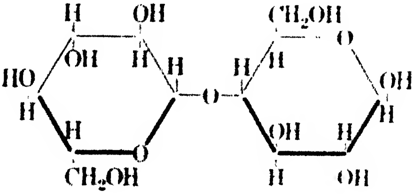


β-glucose

The aldose form of glucose may be represented by

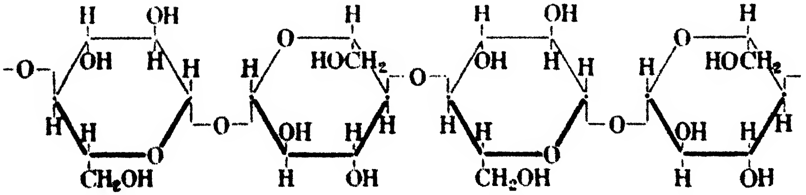


The most symmetrical method of linking the glucose units is between the carbon atoms in the *1* and *4* positions ; this linkage also occurs in maltose and hence in starch, but in this case α-glucose is involved. Comparison of atomic models shows that in maltose the hydroxyl group in the *4* position is below the plane of the ring and in a position to combine with the hydroxyl of the other glucose residue and the two rings are then in alignment. This condition can only be realised in the case of cellobiose by turning one of the β-glucose units through 180° so as to bring the hydroxyl in the *1* position of one unit below the plane in order to unite with the hydroxyl in the *4* position of the other glucose unit. This new conception of cellobiose was confirmed by Haworth, Long and Plant (J.C.S., 1927, p. 2809).



Prior to this time there had been tentative suggestions by Tollens and by Freudenberg that cellulose was a long chain structure, but the general opinion of a small structural unit was strengthened by the early X-ray evidence. Cellulose was, of course, recognised as a highly polymerised material and it was assumed that some of its characteristic properties were due to the formation of large aggregates produced by forces of association.

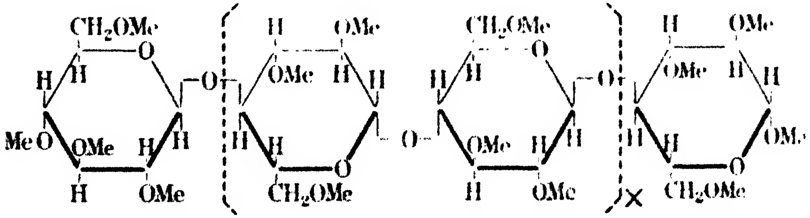
The general advance in the technique of X-ray analysis due to the work of W. H. and W. L. Bragg produced data which enabled models to be constructed of compounds whose properties were obscure unless a three-dimensional picture was available. Sponsler and Dore had been collecting data on the structure of cellulose for some years and were of the opinion that the cellulose units were long chains of glucose residues lying along the length of the fibre. When models were constructed and compared with the X-ray diagrams for ramie fibre it was found that Haworth's ring-structure for β-glucose agreed with the lattice spacings, but instead of the *1* : *4* linkage throughout Sponsler and Dore (Colloid Symposium Monograph, 1926, *4*, 174) adopted alternate *1* : *1* and *4* : *4* linkages.



The idea of alternate glucosidic and ether linkages presented difficulties to chemists and the general scheme of interpretation was re-examined, at Haworth's suggestion, by Meyer and

Mark, who found that the structural arrangement would allow for the cellobiose or *1 : 4* linkage throughout. *Sponsler and Dore recognised that the constituent units are arranged in continuous chains which lie parallel to the fibre axis and through the unit cell of the X-ray determinations.* The glucose units are bound longitudinally by primary valencies and laterally by secondary valencies. The primary valencies account for the chemical and mechanical stability of the fibre ; the secondary valencies are easier to rupture, which explains the relatively low tranverse strength. Further, this idea covers the swelling of cellulose by liquids, which do not attack it chemically, but may enter between the chains and widen the space between them. Esterification and etherification are possible without loss of fibre form on the assumption that the new groups will accommodate themselves in the spaces between the chains.

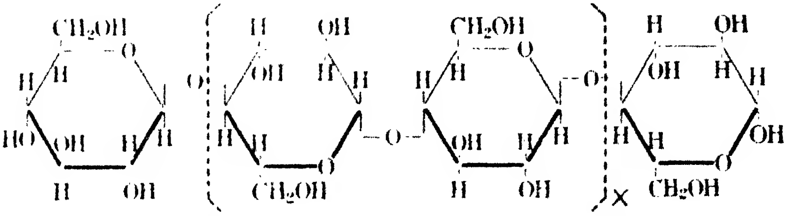
If the hypothesis of the molecular chain is correct, then in each terminal glucose residue there should be one more group open to methylation than in the other residues forming the chain. At one end of the chain it is the reducing group which should be open to methylation and the methoxyl group would be split off again on hydrolysis, but the non-reducing terminal hydroxyl group when methylated should withstand hydrolysis. This means that hydrolysis should yield a certain proportion of tetramethyl glucose which had not been found previously ; indeed, its absence has been regarded as evidence for some of the early alternative structures of cellulose. Haworth and Machemer (J.C.S., 1932, *134*, 2372), however, were able to supply the final piece of chemical evidence for the molecular chain theory by the isolation of tetramethyl glucose from the hydrolysis of trimethyl glucose. This is illustrated from the following formula :



Hydrolysis gives tetramethyl glucose.

Hydrolysis gives 2 : 3 : 6 trimethyl glucose and methyl alcohol.

The modern view of the constitution of cellulose is represented by



(The free reducing group is that on the right.)

Molecular Weight

The following data, taken from a discussion at the Faraday Society Symposium (Trans. Farad. Soc., 1933, *29*) show a wide range of values.

COMPARISON OF MOLECULAR WEIGHTS.

Material.	Mol. wt.	Method.
Cellulose from linters .	20,000-40,000 (minimum)	Chemical — tetramethyl glucose ; Haworth and Machemer.
Cellulose acetate .	120,000	Viscosity ; Staudinger.
Cellulose acetate .	35,000 (average)	Osmotic pressure ; Buchner and Samvel.
Cellulose linters .	40,000	Ultra-centrifuge ; Stamm.
Cellulose . .	16,000	Chemical ; Schmidt.
Ramie . . .	24,000-32,000	X-ray ; Mark.

Various methods have been applied to different products so that no comparison is really satisfactory. Staudinger's recent work, however, gives higher results than those previously obtained, and his contribution to the problem is based on a property of substances of high molecular weight, the high viscosity of their solutions in relatively low concentrations. Most of his publications refer to the " degree of polymerisation " from which the molecular weight may be obtained by multiplying by 162 in the case of cellulose and a corresponding figure for the derivatives. The degree of polymerisation is the number of glucose residues in the molecule, and for native cellulose this is about 2,000 (Ann., 1936, *526*, 72). An interesting table which follows the degree of polymerisation through the manufacturing processes for artificial silk shows the following figures :

DEGREE OF POLYMERISATION.

	Cuprammonium rayon.	Viscose rayon.	Nitrate rayon.	Cellulose acetate.
Raw linters	1,400	—	—	1400–700
Bleached linters	700	—	—	700
Wood pulp	—	700–900	—	—
Spinning solution	400–500	—	~500	250–350
Rayon	400–500	300–450	~200	250–350

Staudinger (Papier Fabrikant, 1938, *36*, 381) has given a list of the constants to be used in viscosity calculations for the various solvents for cellulose and its derivatives. Good agreement has also been shown for the degree of polymerisation according to the osmotic pressure, viscosity and ultra-centrifuge methods of determining molecular weight.

Molecular Arrangement

The anisotropic character of cellulose, the directional nature of its physical properties, was known from its optical behaviour for some time before the definite theory of structure was proposed by Nageli (Die Starkekorner ; Schultub, Zurich, 1858), who postulated that all cellulose fibres were built up of submicroscopic *crystalline* particles termed " micelles." Many properties were explained by Nageli on this basis, but the theory was not generally accepted at the time. The investigation of the double refraction of textile fibres by Ambronn (Ber. Saechs. Ges. Wiss., Leipzig, 1911, *63*, 249) revived interest in the micelle theory.

The work of von Laue (Interferenz-Erscheinungen bei Rontgenstrahlen ; Ber. de l'Acad. des Sc. Bavaroise—June, 1912) established recognition of the fact that a crystal behaves as a three-dimensional grating to X-radiation, and this indicated a regularity of interatomic distances and hence of internal structure. The X-ray technique was utilised by Herzog and Jancke (Z. Phys., 1920, *3*, 196) to show that cellulose has a definite crystalline structure which is the same whatever the source of material. Polanyi (Naturwiss., 1921, *9*, 288) made the first observations on the size of the unit cell—the smallest unit which still possesses the geometrical properties of the whole crystal lattice—assuming the arrangement to be of the rhombic-quadratic type. The dimensions were calculated as follows :

PLATE XLVII

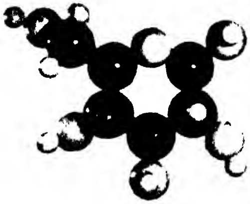


FIG. 135.
γ—glucose
(Strainless model).

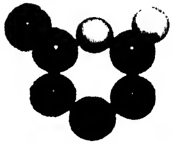


FIG. 136.
γ—glucose
(Skeleton model).

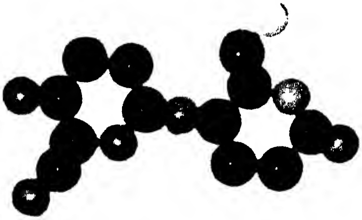


FIG. 137.
Cellobiose
(Skeleton model).

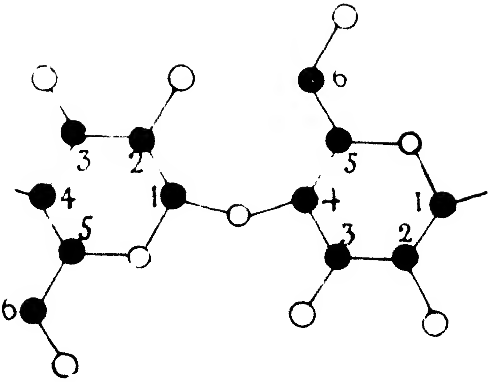


FIG. 138.—Diagram of cellobiose residue.

From "The Constitution of Sugars," by W. N. Haworth.
(London: Edward Arnold & Co.)

[*To face page* 214.

PLATE LXVIII

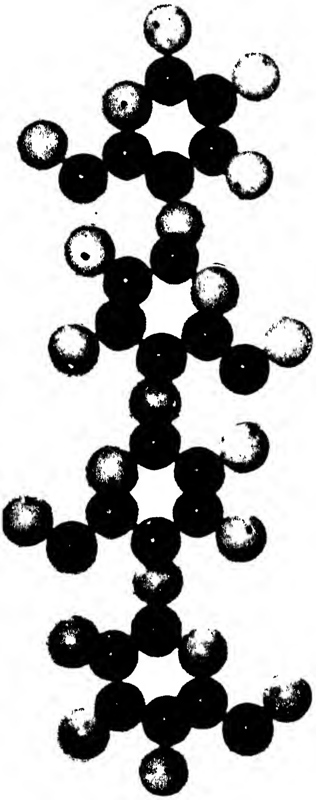


FIG. 139.—Haworth's model for cellulose showing four units.

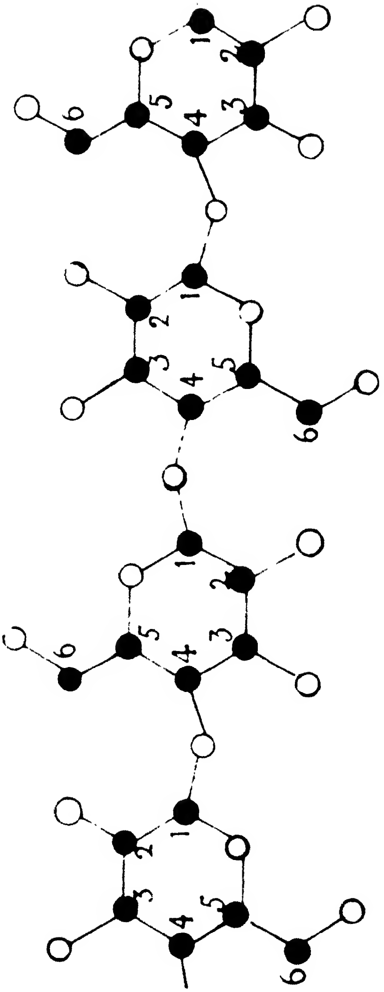


FIG. 140.—Diagram corresponding to Fig. 94.

From "The Constitution of Sugars," by W. N. Haworth.
(London: Edward Arnold & Co.)

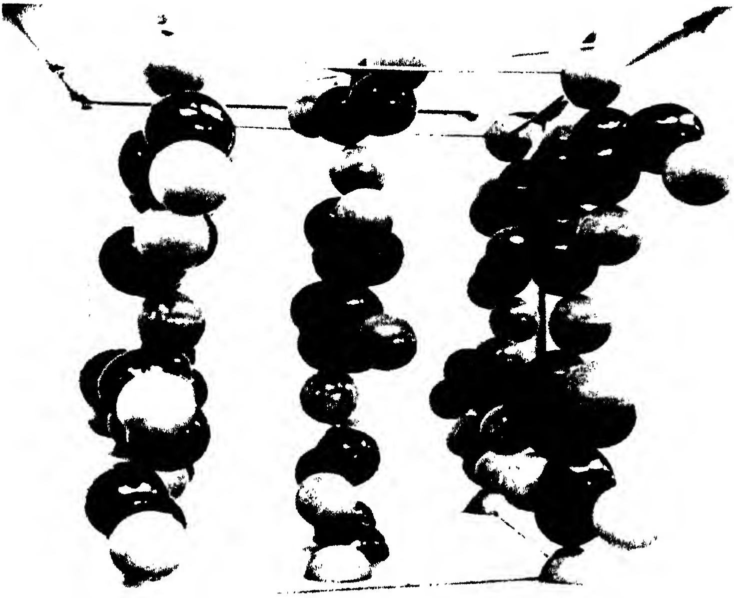


FIG. 141.

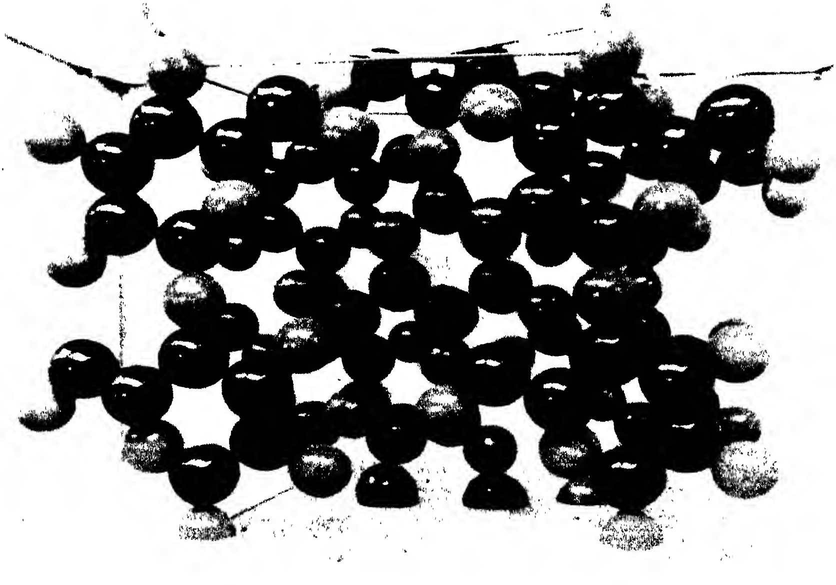


FIG. 142.

PLATE L.

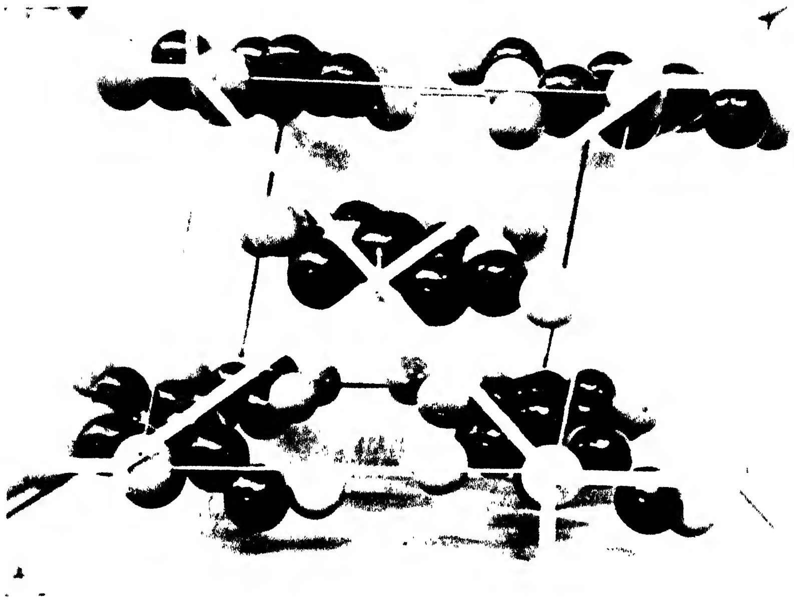


FIG. 143.

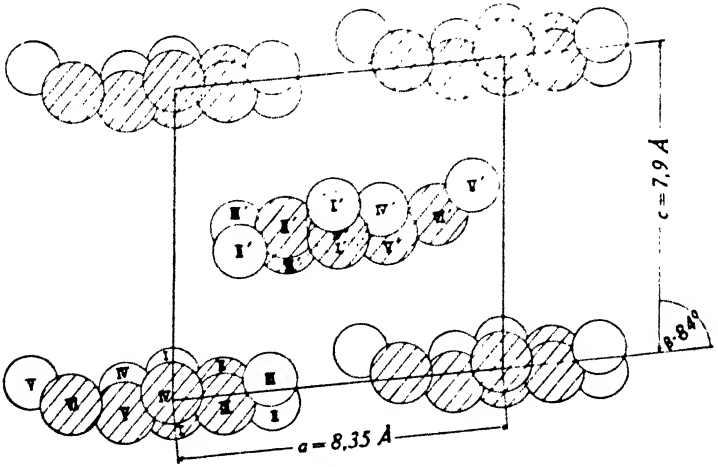


FIG. 144.

Meyer's Model of Cellulose.

Model by courtesy of Kurt Meyer. *Diagram from Helv. Chim. Acta.*

[*To face page* 215.

Unit Cell of Cellulose.

a	8·65 to 8·75 Å	Horizontal.
b	10·25 to 10·35 Å	Vertical period along the fibre axis.
c	7·8 to 7·9 Å	Forming an angle with "*a*."

It must be remembered that at this time it was thought that cellulose was an association of glucose or celloboise anhydrides, so that when calculations showed that the unit cell could accommodate four glucose residues, it was assumed that the cellulose molecule was identical with the unit cell of the X-ray work.

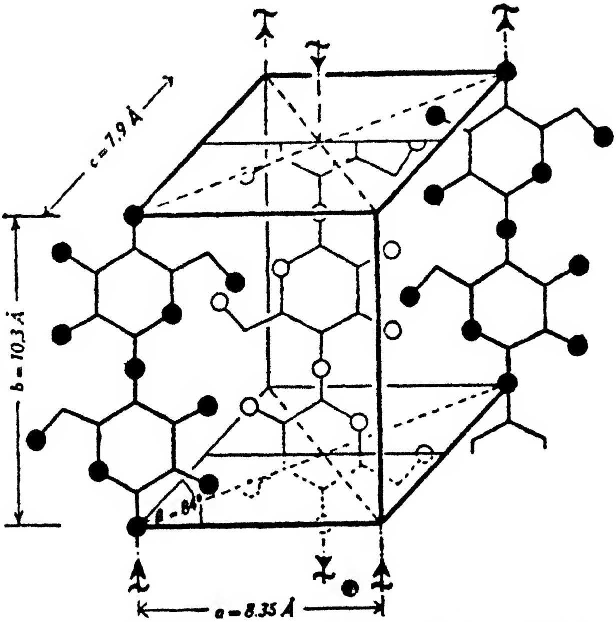


Fig. 145.—The revised crystal unit of cellulose. (Meyer.)

The work of Sponsler and Dore (see page 211) in 1926 was an important departure from the prevalent idea, even if their chemical considerations had to be revised. This was done by Meyer and Mark (Ber., 1928, *61B*, 593), who showed that a model could be produced which agreed with the chemical requirements of Haworth and the X-ray data of Polanyi.

The crystal unit is the pattern which repeats itself in all directions and the long chains run through it along the "*b*" axis ; it must not be confused with the cellulose molecule or with the micelle.

New X-ray data by Meyer and Misch (Ber., 1937, *70*, 266) entailed some revision of the old model, mainly on the lines of alternating orientation in each network of chains, and the calculated intensities required by the new model showed good agreement with the observations.

Sponsler (Trans. Farad. Soc., 1930, *26*, 813) has expressed the view, based on the probable structure of the cellulose in the cell wall of the native material, that the plane of the glucose residues lies at an angle of about 45° to the wall surface, which is, therefore, studded with hydroxyl groups ; this results in a highly reactive surface.

Mercerised Cotton

The difference between mercerised and unmercerised native fibres was observed by many of the X-ray investigators comparatively early in the history of this aspect of the work. It will be remembered that the term cellulose hydrate was applied to mercerised cotton and to regenerated cellulose a generation ago in the belief that a true hydrate was formed, but this theory was soon shown to be incorrect (see page 358) ; nevertheless, the term hydrate cellulose or hydrate modification is used to describe mercerised cotton, mercerised ramie and the various regenerated celluloses.

Katz and Vieweg (Z. Electrochem., 1925, *31*, 157) observed that in the case of ramie treated with 8% NaOH there was no change in the spectrum, but with a 12% solution of NaOH a new spectrum appeared. The view was expressed that in the case of mercerised cotton, mercerised ramie, and regenerated cellulose, there is a considerable change from the unmercerised state, the lattice being bigger in the hydrate modification. Katz and Mark (ibid., 1925, *31*, 105) had previously recorded that in the case of cotton and ramie mercerised without tension the interference points became spread into indistinct arcs and the spectrograms merged into Debye-Scherrer rings. A considerable increase in parallel orientation was observed in material mercerised under tension compared with material mercerised without tension (see page 432). Herzog (Phys. Rev., 1926, *27*, 457) also noted the difference in X-ray diagram between unmercerised cellulose and similar material mercerised with and without tension, the differences being more pronounced the greater the extent of mercerisation.

Andress (*Z. phys. Chem.*, 1929, *B4*, 190) showed the effect of mercerising on the unit cell; it appears that the long chains of β-glucose residues, or rather the planes of these chains, have been moved apart.

CHANGES ON MERCERISING.

	Unmercerised cotton.	Mercerised cotton.
a	8·35 Å	8·1 Å
b	10·3 Å	10·3 Å
c	7·9 Å	9·1 Å
β	84°	62°

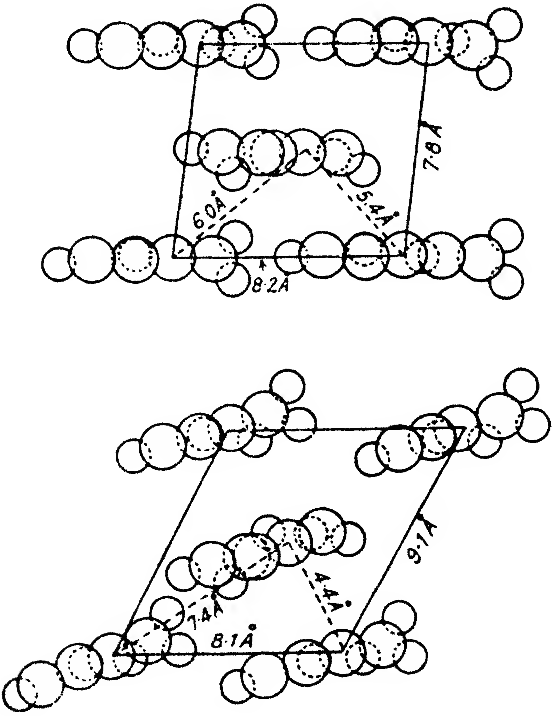


FIG. 146.—Comparison of native and mercerised cellulose.

The longitudinal period (*b*) is unchanged and the first transverse period (*a*) is practically unchanged, but the other transverse period (*c*) is much larger. This means that the long chains of glucose residues remain unaffected in respect of length, but that the planes of the molecular chains have moved apart. This conception is in accordance with the modern view of dispersed cellulose and the observed properties of dispersed cellulose, namely, the increase in absorptive capacity as shown by the increase in moisture absorption and the affinity for dyestuffs. A slight twist of the chains of glucose residues renders the hydroxyl groups more accessible and is in agreement with the observed increased reactivity to chemical reagents. Sisson (J. Phys. Chem., 1936, *40*, 343) has pointed out in this connection that some of the planes of the lattice of mercerised cellulose have about 25 % more available hydroxyl groups per unit of surface than in the lattice of unmercerised cellulose.

The volume of the unit cell is hardly affected by the mercerising process—a fact which is of interest with reference to the determinations of specific volume by Davidson (J.T.I., 1927, *18*, 175).

SPECIFIC VOLUME.
(cc. per gram.)

	Helium.	Water.	Toluene.
Scoured cotton .	0·638	0·621	0·645
Mercerised cotton .	0·645	0·622	0·651
Viscose rayon .	0·646	0·622	0·652
Cuprammonium rayon	0·653	0·625	0·657

The slight increase of about 1 % in the case of the dispersed cellulose appears to be quite definite.

The increase in absorptive capacity of mercerised cotton is discussed on pages 357 and 378, and one of the characteristic features is that this absorption depends to a large extent on the treatment of the cotton after mercerising, particularly on the drying. The partially irreversible contraction of the swollen fibre on drying is less striking than the observation of Coward and Spencer (see page 374) that *boiling in water* also causes contraction. This observation has received support from the X-ray data of Sakurada and Hutino (Kolloid Z., 1936, *77*, 346), who showed that when soda-cellulose was washed with cold water until free from alkali and then examined in the wet state it revealed a new and fairly sharp X-ray diagram of a lattice still more extended than that of mercerised cellulose, indicating that water had penetrated into the crystal lattice. This super-swollen type of dispersion was termed "*water-cellulose*," and the following measurements show its relation to unmercerised and mercerised cotton :

X-RAY DATA.

	Unmercerised cellulose.	Mercerised cellulose.	"Water" cellulose.
a	8·35 Å	8·1 Å	10·03 Å
b	10·3 Å	10·3 Å	10·3 Å
c	7·9 Å	9·1 Å	9·98 Å
β	84°	62°	52°
Vol. in cubic Å	678	688	810

When the soda-cellulose is washed with water at 100° C., the usual mercerised lattice is observed instead of the more extended form. Drying of the "water-cellulose" even at 25° C. caused a change to the ordinary mercerised lattice, but the change is slow at the lower temperatures. Water-cellulose was observed to swell more in water than did mercerised cellulose.

Some data on this effect are given by Sakurada and Okamura (J.S.C.I., Japan, 1938, *41*, 70B), similar results being obtained from ramie, cotton wool and cotton paper mercerised by steeping in 18% NaOH solution at 20° C. and washed free from alkali. "Water-cellulose" was kept in the wet state and part of the material transformed into hydrate cellulose by drying at room temperature. The samples were then soaked in water for four to eight hours and pressed between sheets of filter paper. When the moisture absorption was measured, the three forms of initial product gave very similar results. "Water-cellulose" took up about 1·53 times as much water as the mercerised cellulose which had been dried (0·45 g. more per gram of dry cellulose), corresponding to about four mols. per $C_6H_{10}O_5$. The "super-swollen" type of mercerised cellulose may also be obtained from lithium-cellulose and potassium-cellulose.

Conversion to Native Cellulose

Until quite recently the process of mercerisation was regarded as irreversible for there was no evidence to show that it was possible to convert the hydrate form into the native type of cellulose. On this account many scientific workers regarded the hydrate form of cellulose as the stable variety. The first observations on the recovery of native cellulose from the dispersed form were made by Barry, Peterson and King (J.A.C.S., 1936, *58*, 333).

When ramie fibre was immersed in anhydrous liquid ammonia a swelling took place which, according to X-ray examination, increased the interval along the *a* axis from 8·3 to 9·83 Å and the *c* axis from 7·9 to 10·05 Å. The angle between *a* and *c* (β) decreased from 84° to 53·5°. When the "ammonia-cellulose" was heated at 105° for several hours, it lost its ammonia and gave a diffraction pattern very similar to that of hydrate cellulose, but when the ammonia cellulose was decomposed by weak acid, water or aqueous ammonia, then the pattern of the recovered cellulose was found to be the same as that of the untreated ramie. This regeneration of native cellulose from a highly dispersed form had not previously been encountered.

Hess and Gundermann (Ber., 1937, *70*, 525) found that when alkali-cellulose is washed with water at 100° C. it gives the diagrams of both native and hydrate cellulose together.

Meyer and Bodenhuizen (Nature, 1937, *140*, 281) have shown that it is possible to convert hydrate cellulose to the native form directly. Lilienfeld rayon, i.e. highly stretched hydrate cellulose, when heated for 30 minutes, in water at 200° C., gave an X-ray diagram which showed the interferences of native as well as hydrate cellulose. Heating for eight days in water at 200° C. gave very little more native cellulose than heating for 30 minutes.

The reconversion may also be effected by heating at 140 to 250° C. in formamide or glycerol.

As native cellulose, in the form of ramie, was unchanged after five days in water at 150° C., Meyer concluded that native cellulose is the stable form and hydrate cellulose the unstable modification—the opposite state of affairs had previously been accepted by most investigators.

Hess and Gundermann (supra) obtained native cellulose interferences when alkali cellulose was washed at 100° C., but Meyer has detected native cellulose in preparations washed at 60° C. If the preparation is washed with water at 20° C. and then heated, no native cellulose appears even at 100° C. Fibres of alkali cellulose gave native cellulose almost entirely when dipped into formamide at 100° C. In all these cases it was observed that the temperature required for the formation of native cellulose from alkali cellulose was considerably lower than that necessary for the transformation of hydrate cellulose as such, into the native form.

A further study of this effect has been made by Kubo and

Kanamaru (J.S.C.I., Japan, 1938, *41*, 303). Mercerised ramie and cuprammonium and viscose rayons were heated with ethylene glycol, pyridine, aniline, mono-acetin and various indifferent solvents; with the most polar liquids there was a reconversion into native cellulose, but it was necessary to heat the material to at least 200° C. for at least 30 minutes—the lower temperatures or shorter times brought about only a partial conversion. Ethylene- and di-ethylene glycols were found to be the most suitable liquids, but the conversion was more nearly complete if the sample contained a little water or was swollen, but some conversion was observed in the case of samples which had first been dried in vacuo. Excessive heating caused disintegration of the fibre and some weakening was also observed when water was present in the fibre or in the liquid.

Kubo (Kolloid Z., 1939, *88*, 62) has shown that the conversion of hydrate cellulose to native cellulose is more easily and completely effected by way of the alkali-celluloses I and II as intermediate products. These are heated with glycerol for two to three minutes at 250° C.; mixed products are obtained at lower temperatures.

According to Meyer and Mark (Der Aufbau der hochpolymeren organischen Naturstoff; Leipsig; 1930, page 143), it had been observed, apparently by Hess and Trogus, that the denitrification of Cellulose Trinitrate I gave native cellulose whereas Trinitrate II gave hydrate cellulose. Similarly the saponification of two forms of cellulose triacetate gave native and hydrate cellulose respectively.

Micelle and Chain Molecule

Among the views expressed by Mark and Meyer (Ber., 1928, *61B*, 593) was the theory that cellulose is not composed of molecules in the usual sense but of micelles (*cf.* Nagelli, page 214) made up of cellobiose chains in parallel arrangement, held together by intermicellar forces which are similar to Van der Waal's forces. The chains are not necessarily all of the same length, but from the breadth of the X-ray interference lines and diffusion co-efficients it was estimated that there must be about 1,500–2,000 glucose residues per micelle.

Hengstenberg and Mark (Z. Kryst., 1928, *69*, 271) showed that in the ramie fibre the micelle is present as a rhombus measuring 500 to 600 Å along the fibre axis and 50 by 55 Å across the axis. The estimate of micelle size was in good agreement with that previously advanced by Herzog (J. Phys. Chem., 1926, *30*, 457) and was verified by Clark (Ind. Eng. Chem., 1930, *22*, 474) by the use of relatively long X-ray wave lengths.

A comparison between the micellar size of native cellulose and viscose rayon by Hengstenberg and Mark (Z. Krist., 1928, *69*, 271) gave the following results :

SIZE OF MICELLE.

	Perpendicular to fibre axis.	Parallel to fibre axis.
Ramie . .	55 Å	600 Å
Viscose rayon .	41 Å	305 Å

This decrease in micellar size supports the view that the cellulose chains have been broken in the processes of manufacturing rayon. It is also in agreement with the lower tensile strength of rayon, particularly in the wet state.

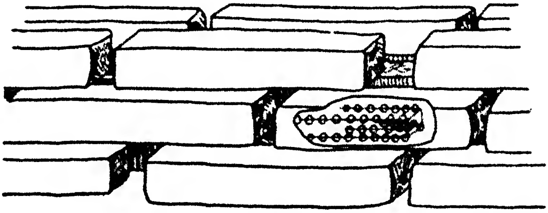


FIG. 147.—Diagram of the arrangement of micelles and the chain-molecule in the micelle.

The active hydroxyl groups with which the surface of the micelles is studded provide the forces which hold the micelles together ; if the micelles are reduced in size, then the tensile strength must fall, particularly in the case of random orientation. With smaller micelles there is also a better and more rapid penetration by water, which is adsorbed on the hydroxyl-studded surface and so covers those groups which normally hold the structure together. The cellulose swells, and as the forces are operative to a lower degree and on a smaller area than for native cellulose, the tensile strength in the wet state is very poor.

In the simplest hypothesis the micelles may be likened to bricks in a wall, overlapping each other in much the same way. These discrete brick-like submicroscopic crystalline particles are orientated with respect to the axis of the fibre and account for the estimate of 75 % of cellulose existing in the crystalline state, the remaining 25 % being amorphous matter separating the micelles and allowing them to move as units during intermicellar swelling and to be dispersed during dissolution. In this structure the mechanical properties were supposedly due to the cohesive forces between the individual crystallites, in which the length of the cellulose chain molecule was some 600 Å ; this may be a minimum value, for more recently Meyer (Ber., 1937, *70*, 266) has estimated 1,000 to 1,500 Å for the length of the micelle.

The theory of continuous structure, according to the school of Staudinger, envisages much longer chain-molecules, 10,000 to 15,000 Å, which have come together in such a manner that the crystalline regularity is interrupted by regions which behave as amorphous matter to X-rays and also to swelling and dispersing agents.

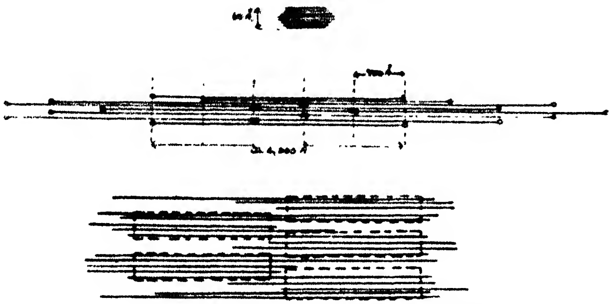
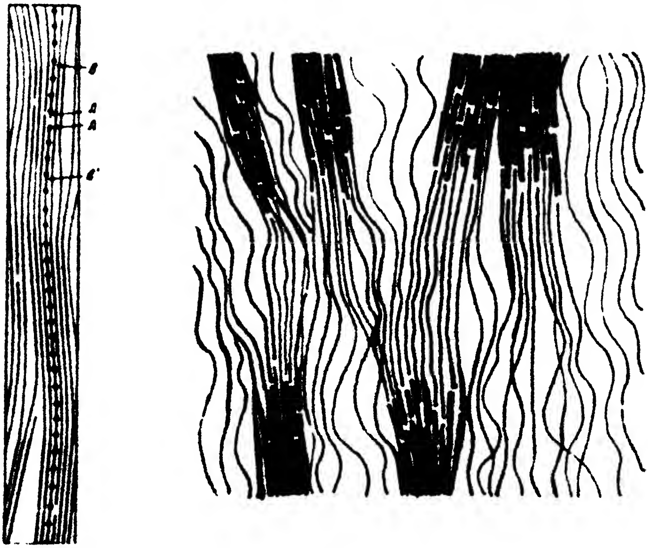


FIG. 148.—Micelle and chain-molecule.

The simple micellar hypothesis is no longer rigidly upheld, for it is now clear that the molecular order only approximates to crystalline perfection, and further, it is difficult to account for the high tensile strength and other mechanical properties of native cellulose by postulating a simple brick-like structure. More recent views developed by Astbury, Gerngross, Hermann, Frey-Wyssling, Krakty, Mark and others embrace the possibility of some of the chain-molecules persisting through the micelles, or the distribution of chain-endings giving the effect of regularly arranged units. Some of these speculations have been represented diagrammatically by Frey-Wyssling (Die Stoffausscheidung der hoheren Pflanzen ; Springer ; Berlin).—Fig. 148. The possibility of individual chain-molecules persisting through the micelles reconciles the conflicting deductions derived from X-ray and viscosity data, and is in agreement with the mechanical properties of cellulose fibres.

Further developments are illustrated in Fig. 149, the chain molecules being shown as lines which are not always parallel but occasionally come together in orderly manner (as indicated by the darker lines) to give the effect of discrete crystalline particles. Nevertheless these aggregates or chain bundles are linked together by chains which extend from one region of regular arrangement to another, protruding from the ends of the crystallites as amorphous fringes. In the diagram, chain endings are shown by *A* and *A′*, which come within the crystalline region, which extends from *B* to *B′*.



Figs. 149–150.—Micelle and chain molecule.

More recent developments in the structure of cellulose have come from consideration of regenerated cellulose. The chain molecules of cellulose are not necessarily straight ; indeed, since free rotation is possible at every glucosidic linkage, there is a tendency to agglomeration where the chains are sufficiently free. On the other hand, the secondary valency forces of the hydroxyl groups tend to bring about an alignment of adjacent chain molecules, producing an orderly arrangement ; the secondary valencies cause a crystalline arrangement.

The agglomerated state predominates when the cellulose exists in dilute solution, and the crystalline state predominates in the solid form, but even here there are some agglomerated molecules whose presence becomes more prominent on swelling. Individual micelles are no longer held to exist as fundamental structural elements but, as in other aspects of cellulose chemistry, the old term is still employed with a different meaning. Micelles are regions where the crystalline tendency predominates but they have fringes of chain molecules in which the disorderly array accounts for the presence of "amorphous" material. (See Fig. 150.) The persistence of some of the chain molecules through the micelles explains the high tensile strength of a system of small units and reconciles the requirements of X-ray and viscosity measurements.

One of the difficulties of the older conceptions of the structure of cellulose was to explain the cohesion of highly swollen regenerated cellulose on the basis of non-swelling crystallites, for the X-ray pictures of dry and wet cellulose show no difference. The modern view assumes that water penetrates between the micelles and into the fringes or clusters of molecular chains which open and close, umbrella fashion, on wetting and drying.

Boulton, Delph, Fothergill and Morton (J.T.I., 1933, *24*, 113P) pictured cellulose as a three-dimensional network of more or less parallel chain molecules which occasionally produce regions of crystalline regularity. Between the crystallites, the molecular chains form, in the swollen condition, an open network through which small molecules easily pass. The network basis has been extended further in recent years, and the micellar system of cellulose is now pictured as a porous structure in which regions of crystalline arrangement are suspended by fringes or regions predominated by the tendency to agglomeration.

Further developments are being made by Hermans and Krakty (Kolloid Z., 1939, *86*, 245), who are attempting to bring the mechanical properties of viscose filaments with different amounts of orientation into some sort of scientific system. Krakty's publications (ibid., 1938, *84*, 149; 1939, *88*, 78) envisage a network of long chains of micelles held together by cross-linkages of micelles. This is represented in Fig. 151, where micelles are shown as lines and the amorphous intermediate areas as ellipses. Two types of structure were postulated (*a*) the ideal loose network which on deformation behaves as separate chains, and (*b*) the ideal close network; a number of equations were developed on this basis. In the loose network, the micelles are suspended in the swelling medium without any mutual interaction, but in the close network, the swelling is such that owing to the expansion of the pores a considerable extensibility is established, but there is always some interlocking of the whole porous system which prevents a slipping of the chain bundles over one another.

Deformation of the close network produces a volume contraction due to a tightening up of the net.

Highly extensible, swollen, isotropic filaments of regenerated cellulose have been examined by Hermans and Krakty, and during extension it was found that increase in orientation accompanied extension up to 80 %, but in the further extension from 80 to 120 % no further orientation took place. The cluster of chain molecules protruding from the micelles and acting as hinges must, therefore, be regarded as elastic and not as inextensible. During extension, when the point is reached where the transverse connections of the micelles offer appreciable resistance to stretching, then an extension of the molecular fringe takes place without any improvement in micellar orientation.

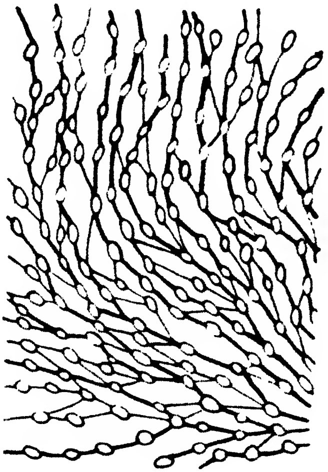


FIG. 151.—The network basis of the micellar system of cellulose.

The stretching of swollen isotropic filaments produced orientation with the crystallites in the direction of extension, but there was much less orientation with air-dry filaments of equal extensibility.

Measurements have been made of length, diameter, breaking load, extension, degree of swelling, refractive index and orientation according to X-ray diagrams, in the case of isotropic filaments and films in which orientation is progressively produced by stretching. The form of the load-extension curves varied with the degree of orientation and the fully isotropic viscose filaments gave curves closely resembling those for wool and rubber; they were equally strong in both dry and wet states. These measurements were compared with the calculated values based on the two limiting cases of the ideal loose network and the ideal close network, and the results for swollen filaments showed good agreement with the theory; the greatest deviations occurred with the least swollen filaments, which represent a state between that of free micelles and a rigid network. The researches are continuing.

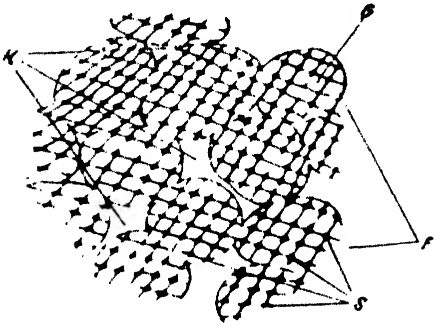


FIG. 152.
The intermicellar system.

The *intermicellar system* of cellulose has been examined by Frey-Wyssling (Protoplasma, 1937, *27*, 372). Cellulose was impregnated with solutions of gold and silver salts and crystals of the metals precipitated by reduction; these produce both dichroic and X-ray effects. It was estimated that the particles of gold and silver deposited in the cellulose fibres have diameters of about 100 Å, which is about twice the width of the micelles. Hence the fibres must contain coarse capillaries, which accommodate the colloidal dyestuffs, but fine capillaries of the order of 10 Å are also postulated, water and molecular solutions being presumed to penetrate into these. The two capillary systems possess branching habits (anastomosis) and merge into one another forming a hetero-capillary system.

The cross section of the intermicellar system is shown diagrammatically in Fig. 152. The micelles (small white areas *G*) are grouped together to form "micro-fibrils" shown as indefinite ellipses *F*— between which runs the coarse capillary system (*K*) of diameter from 50 to 130 Å. The fine hetero-capillary system between the micelles is indicated in black (*S*).

The data of Frey-Wyssling are perhaps open to criticism on account of the swelling process during impregnation with the salt solutions ; 100 Å must be regarded as a maximum value. The theory of dyeing has also contributed to our knowledge of pore size and the present position has been reviewed by Boulton and Morton (J.S.D.C., 1940, *56*, 145). Dry viscose sheet is impermeable to alcohol, benzene and picric acid, which pass easily through the swollen material. Hence the capillary canals may be estimated to be about 5 Å or less in the dry material and 20 to 30 Å in the water-swollen state. In the swollen state all fibres take up dyestuffs, but in the unswollen condition viscose rayon and cotton mercerised under tension are almost unstained, whereas cuprammonium rayon and the native fibres absorb dyes almost as easily as in the swollen state. Presumably the capillary system of the latter class contains comparatively large canals.

It is frequently stated that the amount of pore space in cotton is some 30 to 40 % of the structure, but a recent publication by Peirce and Lord (J.T.I., 1939, *30*, 173) indicates that the volume of the minute crevices in dry cotton is less than 1 % and increases to about 3·5 % at a moisture content of 6 %.

The micro-fibrils of Frey-Wyssling, mentioned above, must not be confused with the fibrils seen in native cellulose under the microscope, for the micro-fibrils are submicroscopic and consist of chains of micelles. Fibrils, on the other hand, may actually be obtained from native cellulose by a combination of chemical and mechanical treatment and may even be dissected further to smaller particles known as fusiform bodies, dermatasomes, etc. (See page 36.)

The dimensions of some of the components which go to make up cotton cellulose have been tabulated by Frey-Wyssling, as shown on page 229.

Orientation

In discussing the orientation of the micelles in cellulose, Herzog (Naturwiss., 1921, *9*, 320) pointed out that in ramie and other bast fibres the micelles are orientated parallel to the fibre axis, in cotton they are turned spirally round the axis, whereas in rayon this orientation may be missing, but it can be produced by stretching.

When X-ray photographs of cellulose are examined, interference spots seem to be more sharply defined where the fibres have a high degree of orientation, but where the orientation is

From Frey-Wyssling (Die Stoffausscheidung der höheren Pflanzen : Springer ; Berlin).

The figures refer to the number of times the smaller structure is contained in the larger ; the value for the chain molecule is arbitrary.

The Angström unit, Å, is 10^{-8} cm.

	Hair. (0·01)^2 π × 50 mm.	Section. (0·01)^2 π × 50 mm.	Lamella. 0·4 × 10π × 5 × 10^{4}μ	Fibril. 0·4 × 0·4 × 100 μ	Dermatasome. 0·4 × 0·4 × 0·5 μ	Micelle. 60 × 60 × 750 Å	Chain molecule. 7·5 × 750 Å	Cellobiose residue 7·5 × 10·3 Å	Glucose residue. 7·5 × 5·2 Å
AMICROSCOPIC. Glucose residue. 7·5 × 5·2 Å									
Cellobiose residue 7·5 × 10·3 Å									2
SUBMICROSCOPIC. Chain molecule. 7·5 × 750 Å								about 75	about 150
Micelle. 60 × 60 × 750 Å							about 100	7·5 × 10^3	1·5 × 10^4
MICROSCOPIC. Dermatasome. 0·4 × 0·4 × 0·5 μ						3 × 10^4	3 × 10^6	2·2 × 10^8	4·5 × 10^8
Fibril. 0·4 × 0·4 × 100 μ					200	6 × 10^6	6 × 10^8	4·4 × 10^{10}	9 × 10^{10}
MACROSCOPIC. Lamella. 0·4 × 10π × 5 × 10^{4}μ				4 × 10^4	8 × 10^6	2·4 × 10^{11}	2·4 × 10^{13}	1·8 × 10^{15}	3·6 × 10^{15}
Section. (0·01)^2 π × 50 mm.			25	1 × 10^6	2 × 10^8	6 × 10^{12}	6 × 10^{14}	4·5 × 10^{16}	9 × 10^{16}
Hair. (0·01)^2 π × 50 mm.		1	25	about 1 million	about 1/10 milliard	order of 1 billion	order of 1 billiard	order of 1/20 trillion	order of 1/10 trillion

less perfect, the spots tend to spread into arcs of circles. These features may be noticed in Figs. 260 and 261.

The high degree of orientation in the ramie fibre was the reason for its almost exclusive use in most of the X-ray examinations of cellulose, particularly in the early days.

Morey (Text. Res., 1934, *4*, 491) made important contributions to the knowledge of micellar orientation and spiral structure of fibres, by measurements of the polarisation of the fluorescence from fibres dyed with strongly fluorescent dyes; quantitatively, the method is perhaps open to criticism. He found that the highest orientation occurred in flax, whereas it was hitherto thought that ramie was the best orientated cellulose fibre. The method also showed the degree of spiral arrangement in the native fibres to be higher in flax than in ramie. The following results were obtained when a 5% dyeing was used from Thioflavine S (Du Pont).

Flax was the most highly orientated of the fibres examined, giving an orientation of 73%, with 5 to 10% of unorientated structure. The highest value observed was 85%. In view of the preference for ramie in X-ray work, this high value is surprising, but the angle of spiral is greater, 5·5°, which means a greater spreading of each X-ray spot into an arc is obtained than with ramie.

Ramie fibre gave a mean orientation of 69%, but the spiral which runs in the same direction as in flax was 3·5° only and showed much less variation. (Average deviation of ± 1°, compared with ± 3°.)

Hemp had a mean orientation of 59% with an average spiral of 0°.

Cotton was chiefly characterised by the absence of well-defined values for orientation or spiral. The mean orientation was only 39% with a deviation of ± 15%, compared with ± 7% for flax and ± 6% for ramie, but in spite of this great variation it is possible to assign an average orientation value. For the angle of spiral, however, the values ranged from 45° in one direction to 50° in the other, though it is usually accepted as lying between about 25° and 30°. Where some sort of average value is desired, the X-ray method is to be preferred, for this gives an integrated value over a considerable volume of fibres at once.

It is well known that cellulose fibres are very strong in the longitudinal direction; this is another example of their anisotropic character. The fact that well-orientated viscose fibres have a tensile strength of 80 Kg./sq. mm. as compared with 100 Kg./sq. mm. for flax shows the importance of the position of the micelles. Orientated viscose has a strength not much below that of flax, whilst the strength of cotton varies from a quarter to three-quarters of this strength although cotton cellulose has a longer molecular chain-length than viscose.

The extensibility of cellulose fibres also depends on the arrangement of the component micelles. When perfectly orientated, the micelles of a fibre under tension will slip on each other with a consequent diminution in cross-sectional area until the fibre breaks with an extension of about 2%. Owing to the parallel arrangement of the micelles, considerable force is required to overcome the friction, which may be assumed to be proportional to the area of contact, so that the tensile strength is relatively high. If, on the other hand, the degree of orientation is low, the effect of tension is to bring about extension and orientation—the extension at break is relatively high and the breaking load low.

Double Refraction

Stained fibres, in general, do not absorb light in the same way in every direction, and if they are observed under the polarising microscope the colour varies with the arrangement of the fibres parallel, or at right angles, to the plane of vibration of the light. This double absorption or dichroism is another example of anisotropic optical behaviour.

The double refraction of fibres depends on the liquid in which they are immersed, as shown by Ambronn, and as the fibres are porous they tend to form a " mixed system " with the penetrating liquid. When there is no difference between the refractive indices of the two components, the double refraction disappears, the system being optically homogeneous.

With cellulose fibres, the complication of intrinsic double refraction (as in crystals) of the " micelle " did not receive great attention and its full value as affecting the fine structure of cellulose fibres was not appreciated until the prediction of anisotropic crystalline structure was confirmed by X-ray diffraction measurements (see page 214).

The double refraction of cellulosic material was first intensively studied by Ambronn (Kolloid Z., 1911, *9*, 147) and in a series of papers in the same journal during 1916 and 1917. The experimental measurement of refractive index is not carried out by measuring the velocity of light in a substance, but by measuring the effect of relative velocities in that substance and a reference substance whose refractive index is known. The measurement depends on the fact that light is refracted when it crosses the boundary of substances which transmit light with different velocities, i.e. substances of different refractive indices. This is used in Becke's method, sometimes termed the immersion method, and is fully described by Preston (Modern Textile Microscopy, Emmot, 1933).

A simple means of measuring the extent of anisotropy is by the double refraction, i.e. the difference between the two refractive indices. This is positive for most fibres, although certain cellulose nitrates, cellulose acetates and some fibres from wool show negative double refraction.

The immersion method was used by Herzog (Untersuchung der naturlichen und kunstlichen Seiden ; Dresden ; 1910) and gave the following results :

Refractive Indices (Herzog).

Fibre.	n_α	n_γ	$n_\gamma - n_\alpha$
Flax . . .	1·528	1·595	0·067
Cotton . . .	1·533	1·580	0·047
Silk . . .	1·538	1·595	0·057
Nitrate rayon . .	1·515	1·549	0·034
Cuprammonium .	1·527	1·548	0·021
Viscose . . .	1·524	1·548	0·024

n_γ is the axial refractive index and n_α the transverse refractive index.

Frey-Wyssling (Kolloidchem. Beih., 1926, *23*, 40) in applying the immersion method pointed out that the indices of the whole fibre (n_o and n_a) are obtained and not the required indices (n_α and n_γ) ; n_o and n_a, however, are functions of the refractive powers of the imbibition fluids (n_i and n_{ii}), so that by a skilled choice of immersion liquids and a long period of imbibition the condition may be established where the fluid on the fibre possesses the same composition as the immersion fluid itself. In this case, $n_i = n_a$ and $n_{ii} = n_\gamma$, in which case also n_o and n_a coincide with n_α and n_γ.

The recorded values for some cellulosic fibres are as follows :

Refractive Indices.

	n_α	n_γ	$n_\gamma - n_\alpha$
Ramie . . .	1·534	1·595	0·061
Flax . . .	1·532	1·594	0·062
Cotton . . .	1·534	1·580	0·045

The double refraction is higher the more nearly the micelles are orientated in the fibre direction. Making the assumption that the fibril structure is wrapped about the fibre axis of cotton at an angle of 30°, Frey-Wyssling calculated by means of an ellipse equation that the axial refraction for perfect axial alignment should be 1·596, which is in agreement with the observed value for ramie.

Preston (Trans. Farad. Soc., 1933, *29*, 65) adopted the opposite course of procedure and by substituting the values for ramie of $n\alpha$ and $n\gamma$ in the ellipse formula obtained an angle of 30° for cotton—this shows fair agreement with the observation of 24° by Balls (Proc. Roy. Soc., 1923, *B95*, 72).

REFRACTIVE INDICES. (Preston.)

	$n\gamma$	$n\alpha$	$n\gamma - n\alpha$	Calculated angle.
Ramie and flax .	1·596	1·528	0·068	—
Cotton . .	1·578	1·532	0·046	30

These figures show good agreement with those of Frey-Wyssling.

Mercerising

When native fibres are mercerised with or without tension, Preston (loc. cit.) found that there is a fall in both the higher and lower refractive indices. The greater change of both refractive indices when the fibres were free to shrink shows that contraction produces disorientation.

Where tension was required, the individual fibres were fastened under a load of 2 g. across a glass frame that permitted no contraction; otherwise the individual fibres were free to contract for "no tension." The experiments were carried out in 18 % NaOH solution at a temperature of 21° C. and after 10 minutes immersion the fibres were washed in very dilute acetic acid and then in several changes of distilled water. They were finally allowed to dry in the air at room temperature.

The values are set out in the following table, and for comparison the refractive indices are given for a Lilienfeld viscose rayon mercerised without tension.

It will be noticed that the effect of full shrinkage, compared with the effect of mercerising, under tension, is to produce a lowering of $n\gamma$ and an increase of $n\alpha$. Preston argued that if this was due to an increased inclination of the cellulose micelles in the fibre relative to the fibre axis, then the fall in $n\gamma$ should

EFFECT OF MERCERISING ON REFRACTIVE INDICES (PRESTON).

Fibre.	Condition.	$n\gamma$	$n\alpha$	$n\gamma - n\alpha$
Ramie or flax .	Native . .	1·596	1·528	0·068
,, ,, .	Mercerised with tension . .	1·571	1·517	0·054
Ramie or flax .	Mercerised without tension .	$n\gamma'$ 1·556	$n\alpha'$ 1·518	$n\gamma' - n\alpha'$ 0·038
Cotton . .	Native . .	1·578	1·532	0·046
,, . .	Mercerised with tension . .	1·566	1·522	0·044
,, . .	Mercerised without tension .	1·554	1·524	0·030
Lilienfeld viscose rayon .	As manufactured	1·559	1·515	0·044
,, ,, .	Mercerised without tension . .	1·550	1·515	0·035

be a measure of the contraction of the fibre on mercerising without tension. The average angle of inclination of the micelles was calculated for the fibres mercerised with and without tension, and from the fact that the length of the fibre after contraction will be proportional to the cosine of the angle of inclination, it is possible to obtain the contraction. The observed and calculated values are shown in the following table from which it will be seen that there is reasonably good agreement.

MERCERISATION AND REFRACTIVE INDICES.

Fibre.	Mercerised with tension.		Mercerised without tension.		Calculated contraction	Observed contraction.
	$n\gamma$	θ_0	$n\gamma$	θ_1	$100\ (\mathrm{Cos}\theta_0 - \mathrm{Cos}\theta_1)$	
Ramie or flax .	1·571	0°	1·556	34·1°	17·2%	21%
Cotton . .	1·566	20·5	1·554	35·6	12·4	14
Lilienfeld viscose rayon .	1·559	28·8	1·550	37·8	9·8	10

Frey-Wyssling (Helv. Chim. Acta, 1936, *19*, 900) has provided the following data on the mercerising of ramie :

EFFECT OF MERCERISING ON REFRACTIVE INDICES.

Ramie.	$n\gamma$	$n\alpha$	$n\gamma-n\alpha$
Native fibre . . .	1·599	1·531	0·068
Mercerised with tension	1·574	1·525	0·049
Mercerised without tension . . .	1·571	1·525	0·046

The method employed was to vary the wave length of the light instead of the nature of the mounting medium. The results show good qualitative agreement with those of Preston.

Preston (loc. cit.) has also pointed out that the change in refractive indices, particularly of $n\gamma$, may be used as a test for the identification of mercerised fibres. In the case of ramie or flax, the fibres may be mounted in aniline (n_D = 1·587) or in isosafrol (n_D = 1·580), whilst cotton fibres may be examined in benzyl benzoate (n_D = 1·570) or methyl isoeugenol (n_D = 1·570); it is a simple matter to determine whether the fibres have a higher or lower value of $n\gamma$ than that of the liquid. If the value is higher then the fibres are unmercerised, if lower then they have been mercerised. As an exact determination of refractive index is not required, the examination may be quickly undertaken, but the observations should be made by sodium light or by some other source of monochromatic yellow light.

Fluorescence

Reference has been made on page 230 to Morey's use of the polarisation of fluorescence from fibres dyed with fluorescent dyes as a means of examining orientation; fluorescence has also been used to determine whether cotton has been mercerised or not, but the method is limited to undyed material. Mecheels (Textilber., 1923, *13*, 146) described a method in which a suspension was prepared of 30 g. of Naphthol AS–RL in 500 cc. of water and 500 cc. of alcohol; the material was impregnated in this suspension, centrifuged and dried—mercerised goods showed a fairly strong naphtholate fluorescence under ultraviolet light, and this is not exhibited in the case of unmercerised cotton. Grunsteidl (Chem. Zentr., 1932, 2261, and Rayon and Melliand Textile Monthly, 1934, *15*, 88) pointed out that, whereas the characteristic dull grey-violet fluorescence of mercerised cotton had been observed in 1928 by numerous workers—Nopitsch (Textilber., 1928, *9*, 136) and Sommer (ibid., 753)—the macroscopic test was somewhat unreliable, especially in the case of fabrics. By means of the fluorescence microscope, however, a greater degree of reliability could be obtained. Raw cotton appears a bright bluish-white, whilst the raw mercerised yarn is dull grey with a tinge of yellow. Bleached mercerised cotton shows a distinct bluish-grey which is quite distinct from the raw material. It is not particularly easy to distinguish between bleached yarn and bleached mercerised yarn, but the fluorescence of the former has a duller character with a tinge of yellow. Comparison with known samples is frequently an advantage.

If, however, the samples under examination are dyed with Eosine Extra Yellow, this fluorescent dyestuff shows the difference between mercerised and unmercerised material very distinctly. The cotton is immersed in a dilute solution of eosine for two or three minutes, well rinsed in running water and quickly dried with filter paper. On examination the mercerised cotton shows an intense yellow fluorescence whilst on the unmercerised material there is no perceptible change; this method is not suitable for bleached cotton.

CHAPTER FIFTEEN

THE CHEMICAL REACTIONS OF CELLULOSE

General

In the organic chemistry of cellulose the chief feature is the presence of three functional groups which are alcoholic in nature ; those hydroxyls in the *2* and *3* positions belong to secondary alcohol, and that in the *6* position to primary alcohol classifications.

The general formation of cellulose derivatives is a matter of the substitution of these groups, and it is now becoming common to show this more clearly by using the formula $C_6H_7O_2(OH)_3$ in place of $C_6H_{10}O_5$. Thus cellulose trinitrate becomes $C_6H_7O_2(ONO_2)_3$; cellulose triacetate $C_6H_7O_2(OCOCH_3)_2$ and the trimethyl ether of cellulose $C_6H_7O_2(OCH_3)_3$.

The formation of soda-cellulose is sometimes an intermediate step in the production of cellulose esters and ethers.

The chemical reactions of cellulose are complicated by several factors, one of which is the degree of orientation of the material, and this also exerts a great influence on the physical properties, as shown on page 231. The extent of orientation controls the rate of penetration of the reactant into the interior of the fibre and so influences not only the simpler process of dyeing, but also the mechanism of chemical reaction ; for instance, Elöd and Schmid-Bielenberg (Z. phys. Chem., 1934, *B25*, 27) found that the velocity of acetylation of cellulose increased in the order of decreasing orientation of the structural units in flax, ramie and cotton.

The early views on the nature of the lower derivatives of cellulose supposed these to be mixtures of cellulose and the tri-substitution product, but this idea has given way to the more complex conception of heterogeneous micellar reactions.

In the case of purified fibres, it was assumed that the reagent penetrates the fibre, and first attacks the surface of the micelle, which is transformed into the tri-derivative. The reagent then penetrates into the micelle and produces a partially reacted area in which only some of the hydroxyl groups are substituted and which lies between the fully-substituted surface and the untreated interior. It has been estimated that the molecules which make up the surfaces of cellulose comprise 70% of the fibre, so that in the case of cellulose acetate, for example, 70% acetylation is required to produce a monomolecular layer of tri-acetate on the micellar surfaces. This layer is not detected by X-ray analysis, according to Hess and Trogus (Z. phys. Chem., 1932, *B15*, 157), whereas the unreacted residue in the centre of the micelle is sufficient to give the characteristic pattern of native cellulose. This has been suggested as an explanation of the fact that cellulose tri-acetate is not detected by these methods until 50% of the cellulose has reacted (Textilber., 1934, *15*, 29). For a purely surface reaction of the fibre there should be X-ray evidence at about 6% transformation. This explanation, however, does not allow for a sufficient residue of unchanged cellulose to give a diffraction pattern. It would appear that in many cases the heterogeneous nature of reactions with cellulose is due to both micellar structure and fibre structure. The less organised parts of the structure tend to react before the crystalline regions, and this may produce a random arrangement of substituted groups along the cellulose chains. The outer sections of the fibre and the external chains of the crystallites probably tend to be more highly substituted than the interior. Recent work on the cellulose acetates by Sakurada (J.S.C.I., Japan, 1938, *41*, 381) indicates that chemical reaction first takes place in the non-crystalline fringes which unite the micelles and then spreads along the chain molecules to the micelles.

Modified Cellulose

The chemical modifications of cellulose do not include the typical organic derivatives such as esters and ethers, but refer to the early products of degradation—the water-insoluble modifications produced by the action of acid or oxidising agents. The former are still referred to as " hydrocelluloses " and the latter as " oxycelluloses," probably on account of the belief of early investigators that these were chemical compounds which could be recovered from the portion of the material which, unlike native cellulose, was soluble in cold alkali of moderate concentration as used in mercerising, for instance.

The early literature on hydrocellulose has been well reviewed by Clifford (J.T.I., 1923, *14*, 169) ; Clifford and Fargher (J.T.I., 1922, *13*, 189) have given a good summary of the work on oxycellulose.

At one time there was a little confusion between hydrocellulose, the result of acid hydrolysis of cellulose—and hydrate cellulose, the result of swelling with sodium hydroxide solutions. No such confusion exists to-day, but it is perhaps interesting to point out that the modified celluloses have new chemical properties, whereas the mercerised cellulose has the old chemical properties to an enhanced degree. This has been shown very clearly by Neale (Trans. Farad, Soc., 1933, *29*, 228) in tabular form, which is reproduced in the following pages.

The chief methods used for the evaluation of the modified celluloses are copper number, solubility number and fluidity. The experimental details have been described in " The Methods of Cellulose Chemistry," by Dorée (Chapman and Hall; London; 1933), and " An Introduction to Cellulose Chemistry," by Marsh and Wood (Chapman and Hall; London; 1938).

Copper numbers are usually determined by the method of Clibbens and Geake (J.T.I., 1924, *15*, 27), and are measures of the reducing properties of cellulose on account of the terminal reducing group in the molecular chain. Any scission of chain will result in the production of a larger number of shorter chain molecules each with terminal reducing groups, so that the copper number may be regarded as a measure of the average chain length of the cellulosic material. There are certain drawbacks to this hypothesis, as will appear later, for if the oxidation of cellulose proceeds as described by Davidson (J.T.I., 1938, *29*, 195) it is possible for the glucose ring to be attacked, so that copper number may be a measure of oxidative attack without reflecting the chain length. The experimental method is based on the reduction of copper sulphate to cuprous oxide. A micro-test for copper number has been described by Heyes (J.S.C.I., 1928, *47*, 90).

Clibbens and his associates found that the average copper number for raw cotton and grey cloth was 0·9 and bleached cotton gave a value of 0·2. The copper number of bleached material should not exceed 0·3, except in the case of the regenerated celluloses, where values of 0·8 to 1·2 are recorded for viscose rayon.

Solubility number according to the methods of Birtwell, Clibbens and Geake (J.T.I., 1928, *19*, 349) and the micro-method of Nodder (ibid., 1931, *22*, 416) may be regarded as a measure of chain length in that the method is a type of frac-

PROPERTIES WHICH CHANGE WITH "DEGRADATION" OF CELLULOSE.

		Tensile strength dynes/cm^2	Fluidity in 0·5% Solution	Copper No. (Braidy) Gms. Cu. reduced by 100 g. of Cellulose	Absorption of Methylene Blue (Basic dye)
Natural cotton cellulose scoured with 1–2% NaOH under 10–40 lb./sq. in. pressure		$4{\cdot}0 \times 10^{9}$	1·5	0·02	0·3 to 0·8
"Degraded" cotton cellulose.	Treated HCl 200 g./l for 24 hrs. at 20° C.	$1{\cdot}5 \times 10^{9}$	34·5	2·44	,,
	Oxidised by alkaline hypobromite 0·32 g.	...	...	...	...
	O_2 consumed by 100 g. cellulose	$2{\cdot}4 \times 10^{9}$	31	0·5	3·0
	Oxidised by hypochlorous acid 0·32% O_2 consumed	...	29	3·4	1·1
"Activated" cotton cellulose.	Treated 25% NaOH without restraint on swelling or shrinkage, washed, air dried	These properties are unaffected by swelling or activation of cellulose.			
	As above, but without allowing shrinkage	...	...	...	...
	Treated without shrinkage, but dried at 110° C.	...	...	...	...
	Swollen in 65–70% H_2SO_4 without restraint (Time of action—5 mins.)	...	...	...	...
		See refs. (20, 6, 12, 7, 8, 3.)			
Cellulose both "degraded" and "activated"	Viscose rayon	About 4×10^{9}	40	1·1	...
	Cupra rayon (Bemberg)		28	0·5	...
REF. Nos.		19, 12, 6	9, 4, 12, 21	4, 6, 21	3, 4

References.

2. Birtwell, Clibbens, Geake and Ridge . J.T.I., 1920, ***21***, 285.
3. Birtwell, Clibbens and Ridge . . . J.T.I., 1923, ***14***, 297.
4. Birtwell, Clibbens and Ridge . . . J.T.I., 1925, ***16***, 13.
6. Clibbens . . . . J.T.I., 1923, ***14***, 217.
9. Clibbens and Geake . . . . J.T.I., 1928, ***19***, 77.
12. Farrow and Neale . . . . . J.T.I., 1924, ***15***, 157.
17. Neale . . . . J.T.I., 1931, ***22***, 320.
18. Neale . . . . J.T.I., 1931, ***22***, 349.

PROPERTIES WHICH INCREASE WITH SWELLING OR "ACTIVATION" OF CELLULOSE.

Absn. of water gms./gm. at 50% Relative Humidity.	Absn. of NaOH from N/2 soln.	Absn. Ba(OH)$_2$ from N/5 soln.	Rise in Cu. No. (Schwalbe) after 15 mins in boiling 5% H_2SO_4	Cu. No. (Braidy) after 2 hrs. in N/10 KOH, N/10 KBrO at 18° C.	Absn. Sky Blue FF (Direct dye) at 100° C.
	Milli Equivalents per Glucose Unit.				
0·055 Ratios.	42·5	71	2·2	1·5	0·15%
0·07	Unaffected by hydrolysis or oxidation of the cellulose. (See refs. 17 and 18)		Tests obviously invalidated by great degradation of cellulose, but unaffected by mild degradation. (See ref. 2)		
0·07	...	...	...	...	...
	Expressed as Ratios Relative to Scoured Cotton.				
1·50	2·35	2·70	1·7	1·6	1·8
1·35	1·96	2·05	...	1·45	1·6
1·2	1·80	1·90	...	1·45	...
1·83 (max.)	3·20	3·20	...	2·54 (max.)	...
2·0	3·6	4·0	5	...	0·9
1·84	3·4	3·8	5	...	2·9
27,25,2,26,28	17	18	22	2	29

19. Peirce . . . . J.T.I., 1923, *14*, 170.
21. Ridge, Parsons and Corner . . . J.T.I., 1931, *22*, 118.
22. Schwalbe . *Z. angew. Chemie.*, 1908, *21*, 1321; 1909, *22*, 197.
25. Urquhart and Williams . . . . J.T.I., 1924, *15*, 138, 433. 1926, *17*, 38.
26. Urquhart and Williams . . . . J.T.I., 1927, *18*, 55.
27. Urquhart, Bostock and Echersall . . J.T.I., 1932, *23*, 135.
28. Urquhart and Eckersall . . . . J.T.I., 1932, *23*, 163.
29. Neale.

tionation into longer and shorter chain molecules—the solubility number is a measure of that proportion of the material whose chain-length is below a certain limit, and is therefore dependent on chain-length distribution. The experimental method is to treat the material with 10 N and 2 N.NaOH solutions.

Fluidity determinations are described by Clibbens and Little (J.T.I., 1936, *27*, 285) in some detail. The previous viscosity determinations of Farrow and Neale (ibid., 1924, *15*, 157) and Clibbens and Geake (ibid., 1928, *19*, 77) dealt with solutions of cotton in cuprammonium hydroxide solution, and it was established that neither viscosity nor its logarithm were very suitable for correlation with tensile strength, but when the fluidity, i.e. the reciprocal of the viscosity, is plotted against " tendering " the resulting curve approximates to a straight line. Increased chemical attack is accompanied by increased fluidity. With solutions of 0·5 % concentration, the fluidity scale extends from 2 to 70, but when 40 is reached there is almost complete disintegration of the hair; for practical purposes, therefore, the useful range is from 2 to 40. In the case of regenerated cellulose in 0·5 % solutions the range extends from 40 to 60, at which point the filaments are too weak to handle. The fluidity of rayons is usually measured in 2 % solution, when the range becomes about 7·5 to 35, and is then calculated to 0·5 % solution. The most careful preparations of cotton have fluidities (0·5 % solution) between 1 and 5, and normally bleached material gives figures of 5 to 10. Fluidities of 20 to 30 indicate chemical attack. Most rayons give fluidities of 40 in 0·5 % solutions.

The viscosity (and fluidity) of the cellulosic solution is a measure of the average chain length of the material.

Considerable work has been published on the relation between these various properties, and it is not always realised that mercerised cotton behaves somewhat differently in certain respects from unmercerised material, and these differences are important in considering the results of the above tests.

Oxycelluloses

Systematic investigation of the *oxycelluloses* by Birtwell, Clibbens and Ridge (J.T.I., 1925, *16*, 13) showed that the products fall between two extreme types, one characterised by great affinity for Methylene Blue and abnormal retentive power for alkali, the other by high reducing power as shown by

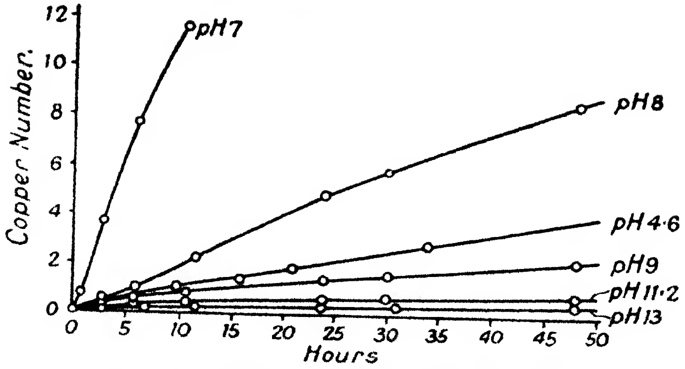


FIG. 153.—Rate of increase of copper number.

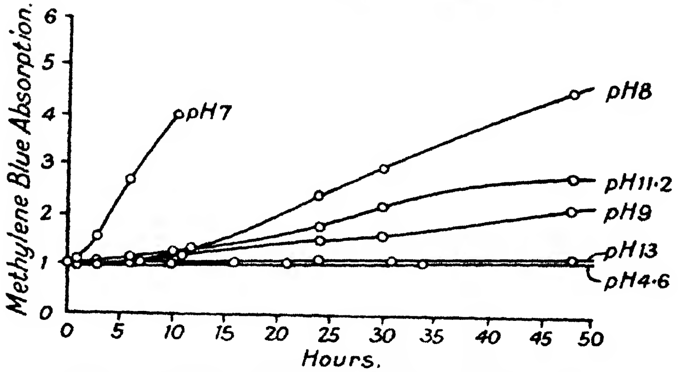


FIG. 154.—Rate of rise in methylene blue absorption.

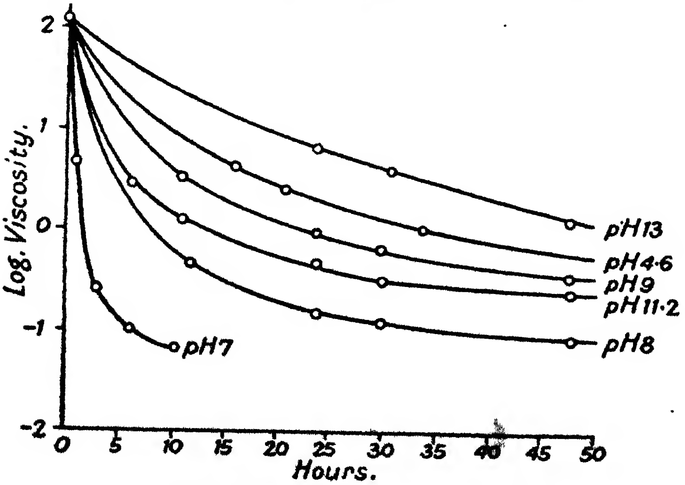


FIG. 155.—Rate of fall in viscosity.

copper number, and excessive loss in weight on boiling in alkali. Both types show a decreased tensile strength.

The type of oxycellulose which is produced in the case of hypochlorite depends chiefly on the alkalinity or acidity of the solution, non-alkaline solutions giving high copper number.

When oxycelluloses of the reducing type are boiled with dilute alkali under suitable conditions they become indistinguishable by chemical means from normal unmodified cotton. The viscosity measurement of such material reveals the change, no matter what the subsequent treatment may have been. Oxycelluloses with increased affinity for basic dyes are not greatly altered in this respect by boiling in alkali.

Clibbens and Ridge (J.T.I., 1927, *18*, 135) pointed out that the rate of oxycellulose formation is a term which cannot possess a precise significance, as the word "oxycellulose" denotes the product of a group of reactions rather than a unique chemical individual. Examinations were made of the rate of consumption of oxygen by cotton cellulose and also the rate of change of properties which vary with oxidation, i.e. copper number, methylene blue absorption and viscosity. No general correlation can be expected between the various properties, as a rapid loss in strength may be accompanied by either a slow or rapid change in solubility in alkali.

In the case of cotton treated with hypochlorite solution of varying acidity or alkalinity the results are shown in Figs. 153–155. The rate of increase of copper number is slow with alkaline liquors and at pH 13 the cotton is scarcely affected. With neutral hypochlorite the rate of increase of copper number is very high, but falls again with hypochlorous acid. The maximum effect of the neutral solution is again seen in relation to the rate of rise in methylene blue absorption and the rate of fall in viscosity.

Hypobromite oxidation, when examined under conditions of relatively high alkalinity, showed a much greater rate of oxidation than hypochlorite. Alkaline hypobromite, however, under certain conditions acts as a sort of automatic copper number regulator—a fact which is utilised in the measurement of the reactivity of mercerised cotton (see page 272).

Oxidation of Alkali-cellulose

In the first stage of viscose manufacture the oxidation of the alkali-cellulose is an essential feature. This "ageing" process shows that appreciable oxidation occurs even at room temperatures. This phenomenon has been investigated by Davidson (J.T.I., 1932, *23,* 95), who examined the effect of concentrations of NaOH solutions varying from 2·5 *N* to 15·2 *N* at 40° C., as the attack by oxygen is rather slow at room temperatures. The maximum absorption of oxygen considered was 3·5 cc. per gramme of cellulose, which roughly represents the limit of interest for textile technology.

The rate of oxidation, measured as the absorption of oxygen, increases for some time and then becomes practically constant, which indicates that the oxidation process consists of several consecutive reactions. Birtwell, Clibbens, Geake and Ridge (J.T.I., 1930, *21,* 85) suggested a somewhat similar hypothesis.

Comparison of the rates of oxidation at different temperatures is complicated by the fact that the rate of absorption is not constant for any concentration of NaOH, but some idea of the relative rates of oxidation at 20, 40 and 60° C. can be obtained. When 10·3 *N*.NaOH solution is employed for the preparation of the soda-cellulose, the volume of oxygen absorbed in 48 hours at 20° C. is absorbed in about six hours at 40° C., and in about 1·2 hours at 60° C. The rate of oxidation of soda cellulose increases rapidly when the concentration of the alkali is increased from 2·5 *N* to 5 *N* ; it then increases less rapidly as the concentration rises to about 10 *N*, where a well-defined maximum rate of oxidation is observed (see Fig. 156).

As the concentrations of NaOH is further increased, the rate of oxidation falls.

The presence of iron in the soda-cellulose has a very important catalytic effect in the rate of oxidation ; nickel and copper also accelerate the reaction, but to a less degree.

The rate of oxidation of soda-cellulose, according to Davidson, is due to the combined effects of four separate factors, (*a*) the increased reactivity of the swollen cellulose, (*b*) the concentration of NaOH in the cellulose phase, (*c*) the solubility of oxygen in soda-cellulose, and (*d*) the rate of diffusion of oxygen in soda-cellulose. These factors might be expected to lead to curves of the shape found when the rate of oxidation is plotted against the concentration of NaOH, the increase in rate of oxidation up to a concentration of 10 *N*.NaOH being explained as increased reactivity due to swelling, and to the progressive increase in the concentration of NaOH in the soda-cellulose.

Cotton which has been treated with solutions of sodium hydroxide more concentrated than about 3 *N*, washed and dried (i.e. mercerised), acquires an increased reactivity in respect of absorption of moisture, dyestuffs, etc., increased rate of hydrolysis by acids, increased rate of oxidation by hypobromite, preferential absorption of sodium and barium hydroxides and of copper from dilute solutions of cuprammonium hydrate. In agreement with these observations Davidson (loc. cit.) showed increased rate of oxidation by oxygen in presence of sodium hydroxide solution not sufficiently concentrated to cause swelling. Samples of cotton were treated with 5 *N*.NaOH solution and washed with 15 % NaCl solution to prevent the transient swelling effect, followed by a treatment with sulphuric acid to remove traces of iron, and then washed with distilled water. The air-dried material was then impregnated with 2·5 *N*.NaOH solution and oxidised at 60° C. in the usual manner.

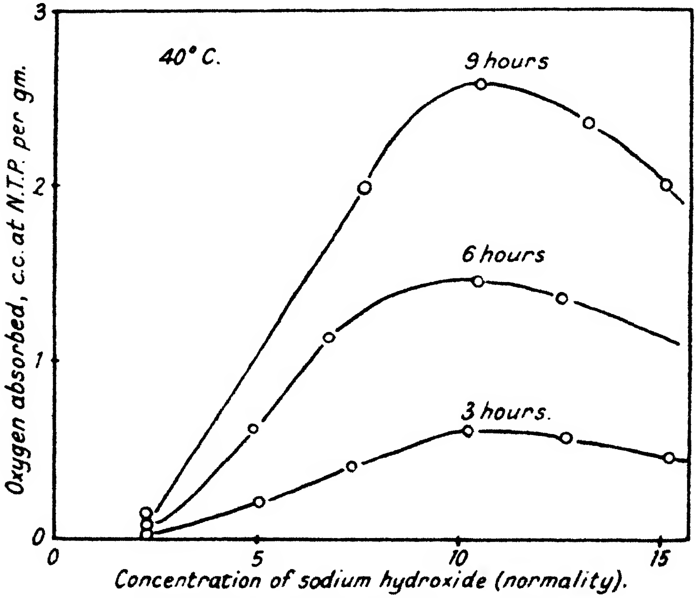


FIG. 156.—Rate of oxidation of alkali-cellulose.

The following figures show the results expressed as a ratio of the volume of oxygen absorbed in five hours by the previously swollen cotton, to the corresponding absorption by cotton not previously swollen. The rate of oxidation by oxygen in presence of 2·5 *N*.NaOH solution is a measure of the reactivity of previously swollen cotton.

OXIDATION OF PRE-SWOLLEN COTTON.

Normality of NaOH in swelling solution . .		5·00	7·37	10·33	12·72	15·20
Relative rate of oxidation in 2·5 *N*.NaOH . .	1·00	2·09	2·20	2·42	2·56	2·51

It is, of course, a well known fact that if, during the mercerising process, the impregnated goods are allowed to remain in the air for any length of time, then oxycellulose is formed, particularly in presence of light—this is shown by difficulties in dyeing later. The presence of air in the kier during the alkali boil or scouring process also produces oxycellulose ; it is essential that the goods be completely submerged.

Hydrocellulose

Hydrocellulose formation is a relatively simple matter, merely involving scission of the molecular chain of cellulose. The term hydrocellulose was originally applied to the powdery material which resulted from the action of acids on cellulose but the modern definition is confined to products which still retain their fibrous form. In technical practice, damage by the action of acids is generally confined to a partial loss of tensile strength and the powdery hydrocelluloses have received little attention for the past twenty years.

One of the best and most systematic surveys of the preparation and properties of hydrocellulose was made by Birtwell, Clibbens and Geake (J.T.I., 1926, *17*, 145). The fall in tensile strength of cotton caused by the action of acids is accompanied by a fall in the viscosity of the material when dissolved in cuprammonium hydroxide solution, and by a rise in the reducing value or copper number. Both of these properties reflect the average chain length of the cellulose material, so that one might reasonably expect to find some inter-correlation between these properties and the tensile strength. An acid attack which causes the viscosity (log. η) to fall to the value 1 produces a loss in strength of 10 %, whilst a loss of 80 % in tensile strength corresponds to a viscosity (log. η) of —1.

There is also a definite relation between the strength and the copper number of the hydrocelluloses, a diminution of 10 %

in breaking load corresponding to a rise of 0·25 in copper number, and a decrease of 80 % in tensile strength to a rise of 3·5. The copper number is, however, of relatively little general value as a measure of the extent of acid tendering, owing to the fact that it is greatly reduced by alkali boiling under conditions which have little effect on the viscosity. The copper number of carefully purified material should not be significantly different from zero; it is never zero because of the terminal reducing group of the cellulose chain. At a copper number value of 5 the fibres disintegrate into powder, but the copper number or reducing value of glucose is 300.

Birtwell, Clibbens and Geake (loc. cit.) also made a quantitative examination of the increased affinity for basic dyes as the result of the action of sulphuric and phosphoric acid of high concentration on cotton, compared with the decreased affinity in the general case of acid attack. The initial fall in absorption is followed by a rapid rise when the concentration passes a certain value. This is due to retention of the acid.

Some preliminary experiments were also done on the effect of boiling with dilute alkali; the percentage loss in weight was found to be roughly six times the copper number. This relationship is almost the same as that observed for oxy-celluloses of the same copper number (J.T.I., 1925, *16*, 13). The copper number in all cases is greatly diminished by boiling in alkali, but the viscosity is only slightly affected. The effect on the single thread strength is not considerable until the loss in weight becomes great.

Solubility of Modified Cellulose

Oxycelluloses suffer a considerable fall in viscosity as the result of an alkaline boil, and differ in this respect from the hydrocelluloses. The extent of the viscosity change varies according to the manner in which the oxycellulose is formed, but is greater for neutral hypochlorite oxycelluloses. The effect of the alkali boil on the other properties does not show such a sharp distinction according to Clibbens, Geake, and Ridge (J.T.I., 1927, *18*, 277). The increased copper numbers are reduced to about one-fifth of their value after six hours' treatment with 1 % NaOH solution at the boil under atmospheric pressure and to one-tenth by a similar treatment at 20 lbs. excess pressure. As a general rule, the methylene blue absorption of modified celluloses increases as the result of an alkaline boil.

The percentage loss in weight on boiling for four hours with 1 % NaOH solution at ordinary pressure is about six times the copper number when the latter does not exceed 2·5 ; for modification which results in a copper number greater than 2·5, hydrocelluloses experience a greater loss, and oxycelluloses a smaller loss of weight than corresponds with this relation, and the divergence becomes wider with increasing modification of the cellulose. This relation is shown in Fig. 157.

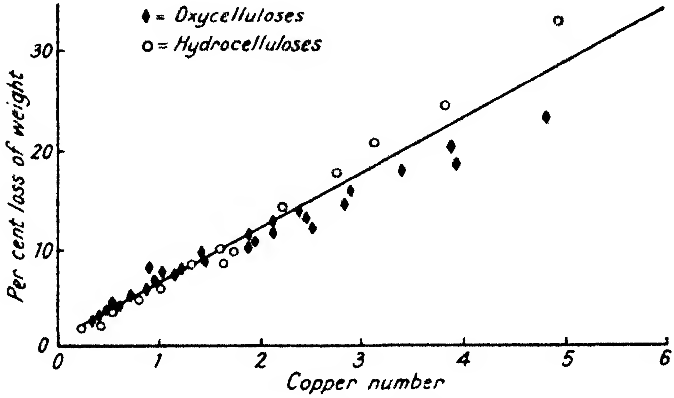


FIG. 157.—Relation between copper number and loss in weight.

As neither the viscosity of cellulose in cuprammonium hydroxide solution nor its logarithm was found to be a very suitable mode of expressing the results, as the same change of viscosity corresponds to very different strength changes at different parts of the viscosity scale, a change was made to the fluidity or reciprocal of the viscosity. When the fluidity is plotted against the extent of chemical damage, the resultant curve often approximates to a straight line. Increased tendering means increased fluidity (i.e. decreased viscosity).

The early results (prior to 1928) were expressed as rates of flow in 2 % solutions, but in the case of fluidity 0·5 % solutions are measured, as discussed on page 242.

Further work confirmed the point that copper number measurements were of very little value as a general guide to the loss in strength of chemically modified cellulose. A rise of one unit may be accompanied by almost complete loss of strength, as in the case of the action of alkaline hypochlorite solution, by 50 % decrease in strength, as in acid tendering, or by a very small decrease in strength, as in the action of dichromate on cotton. Further, the copper number reveals no clue as to the source of the damage, and even ceases to be a characteristic of chemically modified cotton which has been subsequently treated with a hot alkaline solution. Fluidity measurements, on the other hand, according to Clibbens and Ridge (J.T.I., 1928, *19*, 389), are a valuable control of the extent of tendering.

The two graphs (Figs. 158 and 159) show the relation between fluidity and percentage strength. The curve for acid tendering is very similar to that for hypochlorite and hypobromite, but it rises less steeply, i.e. a given rise in fluidity corresponds to a somewhat greater loss of strength than in the case of oxidised yarn.

The effect of boiling in alkali as influencing the tensile strength is shown in Fig. 160. There is little further loss in the case of cotton modified with acid or with alkaline hypochlorite (curves *1* and *2*), but there are large additional losses after boiling where modification has been due to neutral hypochlorite, or dichromate in presence of sulphuric acid and of oxalic acid (curves *3*, *4* and *5*).

It was also shown that the fluidity of acid-tendered material was not altered by kier-boiling, nor was there any alteration in the fluidity of cotton oxidised with alkaline hypochlorite. With other oxidising agents, both tendering and fluidity are increased by the alkaline boil. Now the most marked rise in fluidity on boiling is shown by the neutral hypochlorite oxycelluloses, but the rise is comparatively slight with the materials oxidised by dichromate, which latter, however, show the greatest additional loss of strength on boiling with alkali.

In this connection, it is interesting to recall the observation of Jeanmaire (Bull. Soc. Ind. Mulhouse, 1873, *43*, 334) some ten years before the invention of the word "oxycellulose," to the effect that cotton could remain in contact with dichromate for some time without suffering any obvious change, but that subsequent treatment even with mild alkali (soap) at temperatures of 50° to 60° C. produced great tendering. These observations were extended by Witz (Bull. Soc. Ind. Rouen, 1883, *11*, 169) in his work on oxycellulose, as a means of distinguishing between the attack of acids and of oxidising agents on cotton. It was only in the latter case that he observed a further loss in strength on boiling in alkaline solutions.

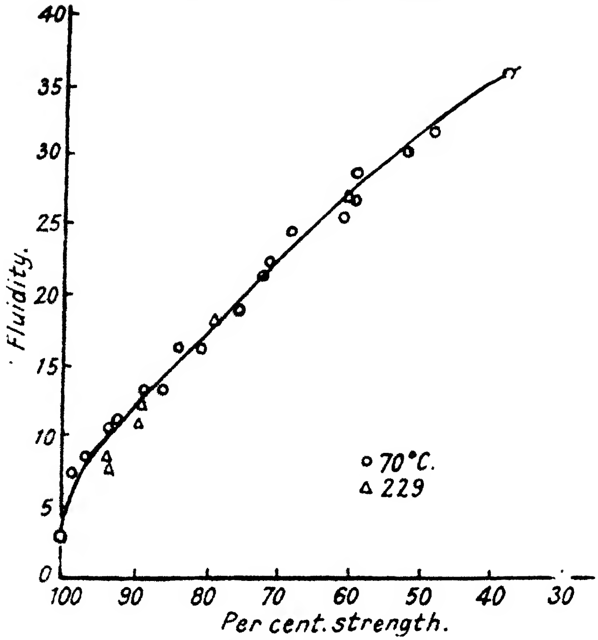


Fig. 158.—Relation between tensile strength and fluidity for attack by neutral or alkaline hypochlorite.

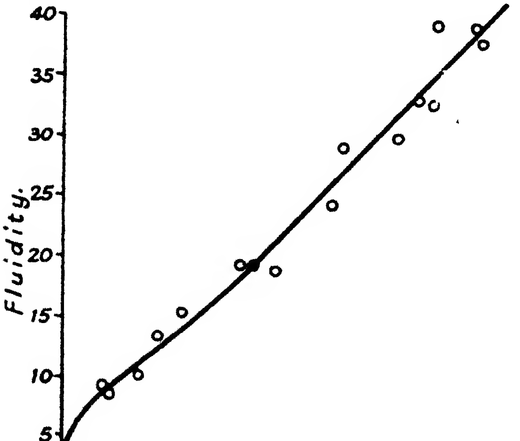


Fig. 159.—Relation between tensile strength and fluidity for acid attack.

The action of dichromate on cotton yarn, according to Clibbens and Ridge (J.T.I., 1928, *19*, 389) produces a much smaller loss in strength for a given rise in fluidity than is the case with other oxycelluloses ; a fluidity of nearly 40 is only accompanied by 20% decrease in tensile strength after the action of dichromate-oxalic acid mixture. [This point is discussed later on page 267.]

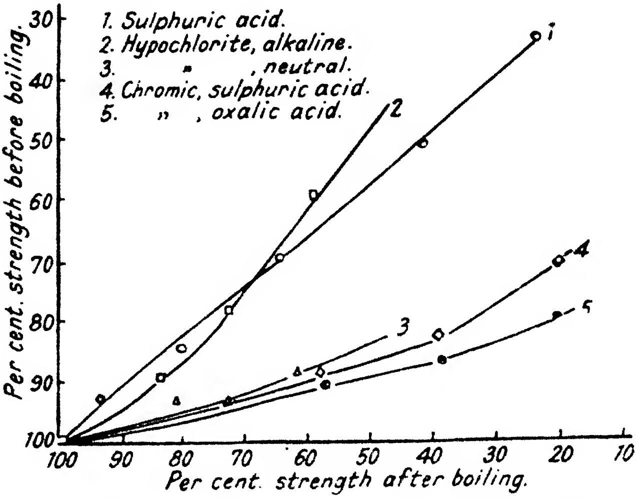


FIG. 160.—Effect of alkaline boil on the tensile strength of modified cellulose.

Clibbens and Ridge (J.T.I., 1928, *19*, 389) in a paper on the tensile strength and fluidity of cotton have given some data on *the effect of mercerisation* on the strength of modified cotton yarn. The yarn was 40s ring spun warp of combed Sakel, which was mercerised without shrinkage in 7·5 *N*.NaOH (53° Tw.) for periods of five minutes and one hour, followed by washing on the frame and drying at room temperature.

The mean of 100 single thread tests on the yarn mercerised for 5 mins. was 103, and for one hour 100, the strength of the unmercerised yarn being expressed as 100. Unlike soft twisted single or double yarns, this warp yarn did not experience a significant increase in strength on mercerising.

Samples of the boiled yarn were then modified by treatment with neutral hypochlorite and dichromate-oxalic acid, in both cases to an extent which produced approximately 10 % decrease in strength, and the modified materials were then mercerised as described above. The means of 100 tests were 76·2 for the hypochlorite samples and 72·5 for the dichromate samples, the strength of the modified but unmercerised yarn being expressed as 100.

The normal mercerisation process, therefore, produces a similar effect to an alkaline boil when applied to yarn already slightly tendered by neutral hypochlorite or dichromate, i.e. an additional loss of tensile strength.

Sisson (private communication) has found that if cotton is first slightly degraded by acid then the mercerisation process is more complete as shown by X-rays. Attempts have been made to use alkaline solutions of hydrocellulose for rayon, and some mild acid treatment is frequently a preliminary to the production of cellulose derivatives.

Some of the earlier experiences with the combined effects of mercerising and oxidation are worthy of attention.

Prudhomme (Moniteur Scientifique, 1891, *38*, 595) was one of the first to show that mercerised cotton is more susceptible to the action of oxidising agents than is ordinary bleached cotton yarn. He also found that the copper number of mercerised yarn was invariably higher after oxidation than that of ordinary cotton similarly treated. Micheli (Z. Farb. Text. Chem., 1903, *2*, 437) stated that cotton yarns which had been tendered by excessive treatment could have their strength restored by mercerisation, but his statement was not accompanied by any numerical results.

Knecht and Muller (J.S.D.C., 1926, *42*, 46) examined these phenomena and confirmed that mercerised cotton is more susceptible to oxidation than unmercerised cotton. The extent of oxidation was effected by controlling the rate of oxygen consumption on the broad lines described by Knecht and Thompson (J.S.D.C., 1920, *36*, 252).

The effect of the mercerising process on oxycellulose was examined in some detail, and it was found that in the very early stages of oxidation, corresponding to the consumption below 0·0064 atoms of oxygen per molecule, mercerisation increased the tensile strength and raised the copper number of the yarn, but where the degree of oxidation exceeded the above-mentioned limit, mercerising reduced the tensile strength and decreased the copper number.

Ridge and Bowden (J.T.I., 1932, *23*, 319) emphasised the experience of many textile chemists in their statement that quantitative description of modified cellulose by purely chemical methods (copper, silver and permanganate numbers, methylene blue absorption, etc.) is only possible as a measure of tensile deterioration in special circumstances, and is completely unreliable if the material has received an alkaline treatment after attack. For example, a low copper number may be accompanied by little or by considerable loss of strength, according to the precise conditions of oxidation and subsequent treatment. On the other hand, chemical modification is always reflected by an increase in fluidity, which bears a general relation to the percentage loss in strength of fibres and yarns. Their paper is mainly concerned with the fluidity of rayons, and they suggest that this should never greatly exceed the figure 11 (2% solution). They also show that when the initial stages of oxidation are exceeded, a rise of fluidity of five units corresponds fairly well with a further loss of 10% in the strength of yarns. This applies to unmercerised cotton and rayon materials which have not been submitted to boiling in alkaline liquor and also to unmercerised cotton yarns bleached in neutral or alkaline hypochlorite solutions and then subjected to an alkaline boil. Over-bleached viscose yarns show a much greater loss, amounting to 16 to 17% per five units rise in fluidity when they are given an alkaline boil.

The behaviour of mercerised cotton differs from that of cotton. The fluidity-percentage strength relationship is quite different from that which holds for either ordinary cotton or for the regenerated cellulose type of rayon. The rise of fluidity on oxidation with hypochlorite is greater than would be expected from the comparatively small decrease in tensile strength. The fluidity of unmodified mercerised cotton is no higher than that of unmodified unmercerised material, but with oxidised cotton the fluidity corresponding with a given percentage loss of strength is much higher for the mercerised material. When mercerised yarns are given an alkali-boil after chemical modification, the relation between strength and fluidity of the boiled material is found to be much closer to that for plain unmercerised cotton yarns, although the curves are not coincident.

When mercerisation follows oxidation, the reduction in strength is apt to be greater than that produced by boiling with alkali (see page 253). When mercerisation precedes oxidation, the relations shown in Fig. 161 are observed. Curve *1* shows the fluidity-strength relation for cotton and viscose yarns, and curve *2* the relation for mercerised cotton, from which it appears that fluidities of 14 to 16 scarcely indicate over-bleaching, whilst a value as high as 29 corresponds to a loss in strength of only 20 %. The same figure for rayon or for unmercerised cotton would correspond to a loss in strength of over 40 %.

When the mercerised and oxidised yarns are given an alkali-boil the strength is much reduced and the fluidity-strength relationship becomes much nearer that for ordinary cotton yarns, as shown by curve *3* in Fig. 161, and also by the following results :

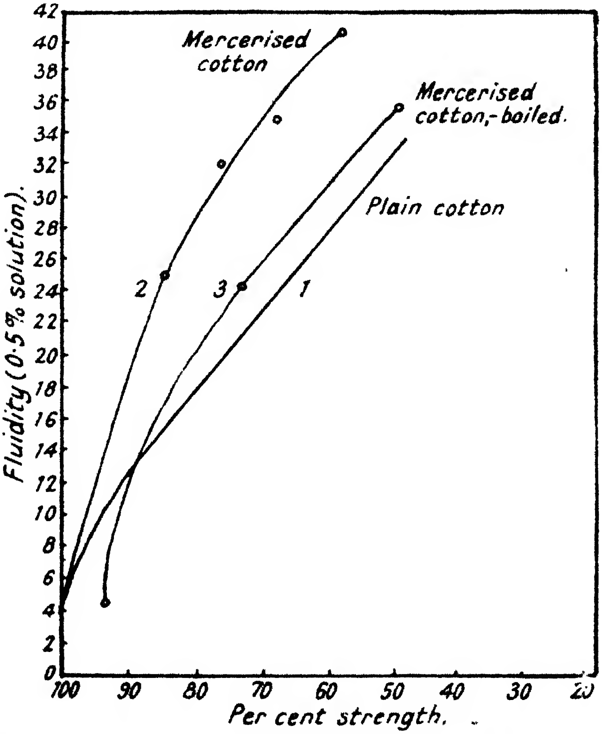


FIG. 161.—Relation between fluidity and tensile strength.

MERCERISED COTTON OXIDISED WITH HYPOCHLORITE.
FLUIDITY-STRENGTH RELATION.

Before alkali-boil.

Fluidity . .	3·5	13·8	25·1	32·1	35·3	40·5	40·1
% strength . .	100	90·0	84·3	75·6	67·3	57·0	48·0

After alkali-boil.

Fluidity . .	4·6	24·4	35·8
% strength .	93·4	72·3	48·7

Solubility at Room Temperature

It has been known almost since the chemically modified cotton celluloses were first described that they possess the property of dissolving to some extent in sodium hydroxide solutions at room temperature and could be precipitated without much change. It was probably this property which led the early investigators to attempt to isolate an individual product to which the name "oxycellulose" or "hydrocellulose" might properly apply.

Birtwell, Clibbens and Geake (J.T.I., 1928, *19*, 349) have made a fundamental study of the solubility of modified cellulose in caustic soda solutions at room temperature—the term "solubility" means the percentage weight of the material which dissolves under stated conditions. The maximum solubility of modified cotton on treatment with any single solution at 15° C. is produced by 3 *N*.NaOH (12%) and falls off rapidly with either increase or decrease in alkali concentration. (It is interesting to note that this concentration for maximum solubility of modified cotton is close to the maximum swelling concentration for "rubbed" hairs—see page 92). If, however, the cotton is first treated with a more concentrated solution (6 to 10 *N*) and the alkali then diluted by the addition of water, a much larger percentage weight of the material may be brought into solution. The conditions which make for maximum solubility at 15° C. are first to steep the material in 10 *N*.NaOH, which is then diluted with water to 2 *N* whilst still in contact with the cotton. The solubility number is determined by volumetric analysis of the solution (J.T.I., 1928, *19*, 341).

The dilution of the sodium hydrate to ensure greater solubility of the modified cellulose presents an obvious parallel to the transient swelling during mercerising (see page 350). Birtwell, Clibbens and Geake (loc. cit.) established that in the case of the hydrocelluloses formed from bleached cotton the solubility is completely defined if the copper number is known, irrespective of the mode of acid attack. In the case of the oxycelluloses, however, different relations obtain, for although in any one series of oxidised cottons formed by the action of the same oxidising agent under the same conditions for varying times the copper number defines the solubility, yet for different oxidising agents or the same agent under different conditions, there is no general relationship between solubility and copper number. There appears to be a general correlation between the solubility of modified cotton in $10\,N - 2\,N$ NaOH and its fluidity in cuprammonium solution, which is independent of the manner of modification.

Relations of this type do not apply to the case of mercerised cotton. A hydrocellulose of given copper number, formed from mercerised cotton, dissolves to a much smaller extent than a hydrocellulose of the same copper number formed

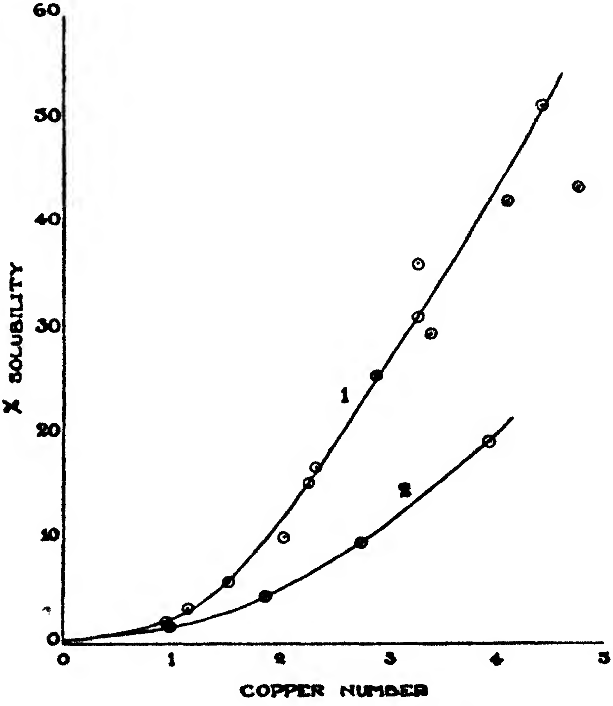


Fig. 162.—Relation between copper number and solubility.

(Curve 1 relates to bleached cotton attacked by acid; curve 2 to mercerised bleached cotton attacked by acid.)

from unmercerised cotton; the same is true for oxycelluloses. Diminution in solubility due to mercerisation is also accompanied by an increase in the reducing value of the dissolved material. The different solubilities of hydrocelluloses of the same copper number from mercerised and unmercerised cotton may be allied to a change in the relative rates of hydrolysis and dispersion caused by mercerisation.

The mercerisation process itself is at a maximum with caustic soda solutions near 3 *N* at ordinary temperatures and is affected by successive treatments with solutions of different strengths as well as by temperature.

Fig. 162 shows the relationship between copper number and solubility in 10 *N* — 2 *N* NaOH. Curve *1* relates to bleached loose cotton and cloth attacked by 20% HCl for different times at 20° C. and also to loose cotton boiled with *N*/10 H_2SO_4 for different times. Curve *2* shows the relation between solubility and copper number for hydrocelluloses formed by the action of 20% HCl on loose bleached cotton subsequent to mercerisation. These possess a much lower solubility for the same copper number than hydrocelluloses formed in the same manner from unmercerised cotton.

Solubility at Low Temperatures

Davidson (J.T.I., 1934, *25*, 174), in his examination of the solubility of modified cellulose in alkali, established the point that the solubility is at a maximum at a certain alkali concentration for any temperature, and that as the temperature is lowered from the normal, the maximum solubility is greatly increased and occurs at a lower alkali concentration. This is shown in Fig. 163, which refers to hydrocellulose ; oxycelluloses gave qualitatively similar results.

In the case of modified cottons prepared from mercerised material, however, the maximum solubility at —5° C. occurs at a rather higher alkali concentration. This is shown in Fig. 164, where curve *1* refers to hydrocellulose from unmercerised cotton and curves *2* and *3* to hydrocellulose and oxycellulose from mercerised cottons.

Davidson also established that when modified cottons are boiled under pressure with dilute alkali, the residual material is more soluble in NaOH solution at —5° C. than the original modified cotton, in spite of the loss in weight. The increase in solubility is slight in the case of hydrocelluloses from unmercerised cotton, but is considerable in the case of hydrocellulose from mercerised cotton and also with oxycelluloses of the hypochlorite series.

The solubility of any modified cotton, measured under optimum conditions at —5° C. was found to increase with increasing fluidity—samples with very high fluidities being completely soluble. Hydrocelluloses from unmercerised cotton, whether boiled after modification or not, have approximately

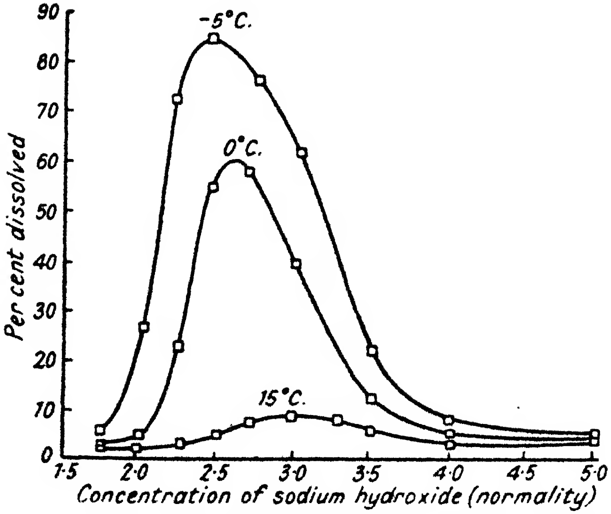


FIG. 163.—Effect of temperature on the solubility of hydrocellulose from unmercerised cotton.

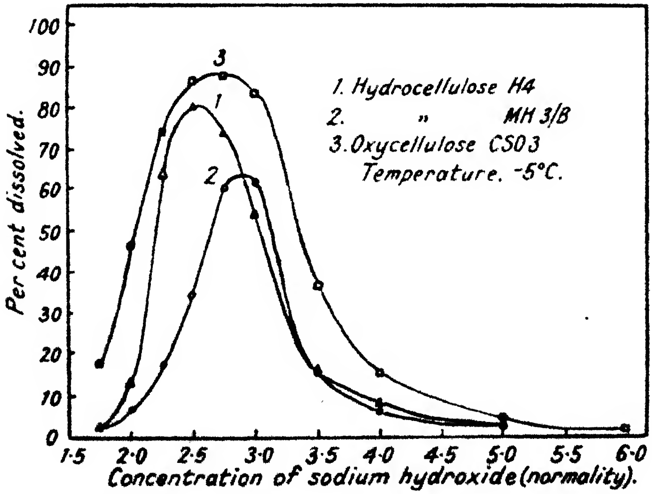


FIG. 164.—Solubility of modified cellulose—curves 2 and 3 refer to mercerised material.

the same fluidity-solubility relation, but hydrocelluloses from mercerised cotton are much less soluble than material of equal fluidity similarly prepared from unmercerised cotton. This is shown in Fig. 165.

The commonly accepted view of mercerisation is that hydroxyl groups are liberated whose residual affinity was satisfied in the unmercerised state. There is also considerable evidence to show that the cellulose chains move apart during mercerisation, so that on either view the proportion of the chain molecules accessible to chemical reagents is greater in mercerised than in unmercerised cotton. This is supported by considerable experimental evidence. Davidson argued on this basis that the chain length frequency distribution of the resulting hydrocelluloses should differ in the sense that a hydrocellulose from mercerised cotton should be more nearly uniform as regards chain length than a hydrocellulose from unmercerised cotton.

For a given fluidity, therefore, a hydrocellulose from unmercerised cotton should contain a relatively large proportion of short chain-molecules and should be more soluble in NaOH solution than a hydrocellulose from mercerised cotton. This agrees with the experimental evidence. Mercerised cotton yarn modified by acid attack suffers less decrease in tensile strength for a given increase in fluidity than unmercerised yarn. Ridge and Bowden (see page 254) obtained similar results, which can be explained in the same manner, for mercerised yarn modified by oxidation with hypochlorite.

Oxycelluloses of the hypochlorite series are more soluble than hydrocelluloses of the same fluidity, but after an alkali-boil these oxycelluloses show a fluidity-solubility relation nearly the same as that found for hydrocelluloses from unmercerised cotton. On the other hand, oxycelluloses from swollen cotton have a relatively low solubility for a given fluidity. These points are shown very clearly in Fig. 166.

In the case of the hydrocelluloses (see Fig. 167) a somewhat similar observation had been made by Birtwell, Clibbens and Geake (see page 256).

If the dissolution of modified cotton in sodium hydroxide is caused by the same forces that produce swelling, then there should be some similarity between the solubility relations of modified cottons and the swelling relations of cellulose in these solutions. Davidson has pointed out that the observations of Birtwell, Clibbens, Geake and Ridge on the shrinkage of

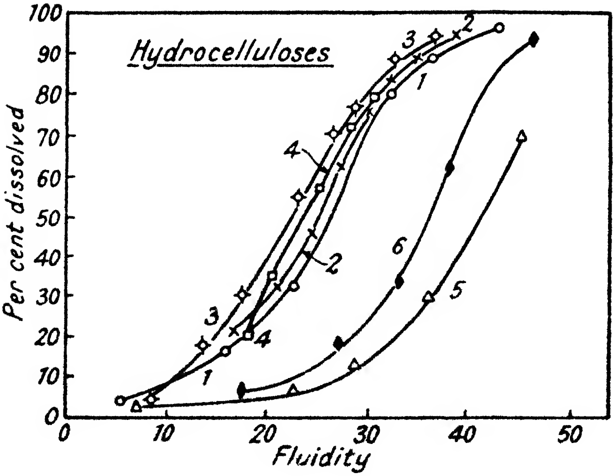


FIG. 165.—Effect of alkali-boil.

Curves 2 and 4 represent alkali-boiled cottons corresponding to those of curves 1 and 2; curve 5 represents mercerised cotton, and curve 6 the same material after an alkali-boil.

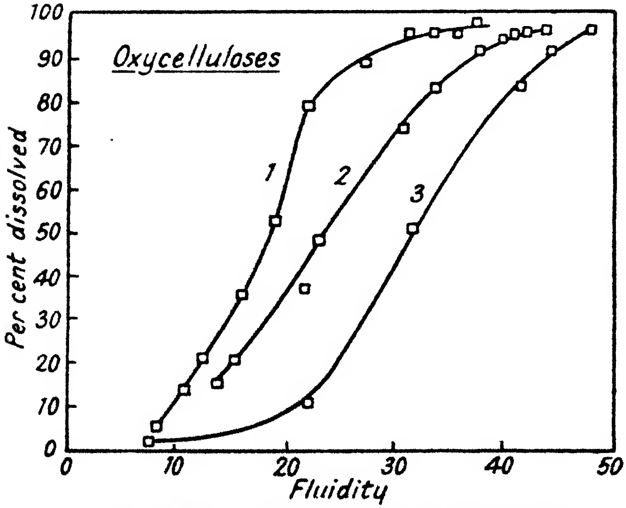


FIG. 166.—Relation between solubility and fluidity.

Curve 1 relates to the hypochlorite series; curve 2 to similar material after alkali-boil, and curve 3 to material from the oxidation of alkali cellulose.

cotton yarn in NaOH solutions show that as the temperature is reduced, the maximum swelling is greater and occurs at a lower alkali concentration (see page 279). This has its counterpart in the solubility results of Fig. 167. Similarly interesting comparisons may be made with the data of Beadle and Stevens (see page 304) on the water absorption of rayon from solutions of NaOH at various temperatures.

Davidson also demonstrated that a preliminary treatment of a modified cotton with 5 *N* NaOH, which causes swelling but not dissolution, has the effect of depressing the solubility under the optimum conditions for dissolution at low temperatures (see Fig. 167). As shown by the work of Birtwell, Clibbens and Geake (see page 256), treatment with 5 *N* NaOH at 15° C. followed by dilution to lower concentrations produces the dissolution of a larger fraction of oxycellulose than can be dissolved by extraction with any single solution at the same temperature. Maximum solubility occurs when the final concentration is between 2·0 and 2·25 *N*. If, after a similar treatment, the mixture of modified cotton and NaOH is cooled to —5° C. the initial solubility is increased, but except at low concentrations where the dilution has already produced greater dissolution than occurs on extraction at —5° C. without pre-treatment, this solubility is much less than that obtained without pre-treatment. Hence a treatment causing swelling but not dissolution applied after modification has an effect on the concentration for maximum solubility similar to swelling before modification (see Fig. 167 and compare Fig. 163).

A comparison has been made by Davidson (J.T.I., 1936, *27*, 112) of the solvent action of solutions of various hydroxides on modified cellulose. The action of lithium and tetramethylammonium hydroxides on modified cottons is qualitatively similar to that of sodium hydroxide ; the maximum solubilities found with these three bases differ according to temperature. The order of increasing solvent action on modified cotton being $LiOH < NaOH < N(CH_3)_4OH$ at 15° C. and $N(CH_3)_4OH < LiOH < NaOH$ at —5° C. The solvent action of KOH solutions is much less than that of the other bases, and is also less affected by temperatures.

The solubility curves of modified cellulose prepared from unmercerised cotton possess two maxima, which become more pronounced at temperatures below the normal (see Fig. 168), but examination of the solubility curves of regenerated sheet

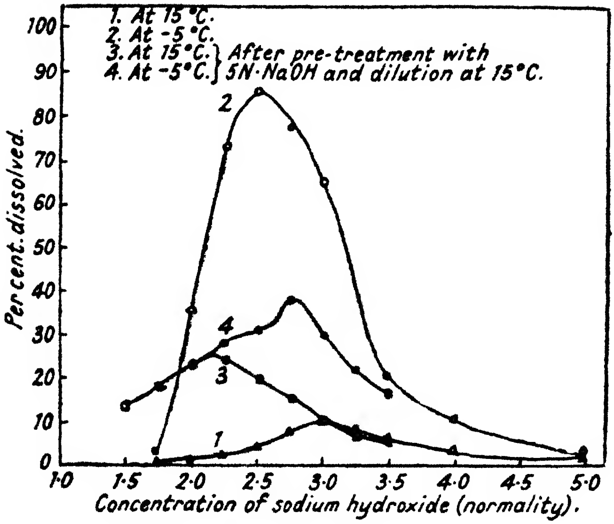


FIG. 167.—Solubility of modified cellulose in NaOH solutions.

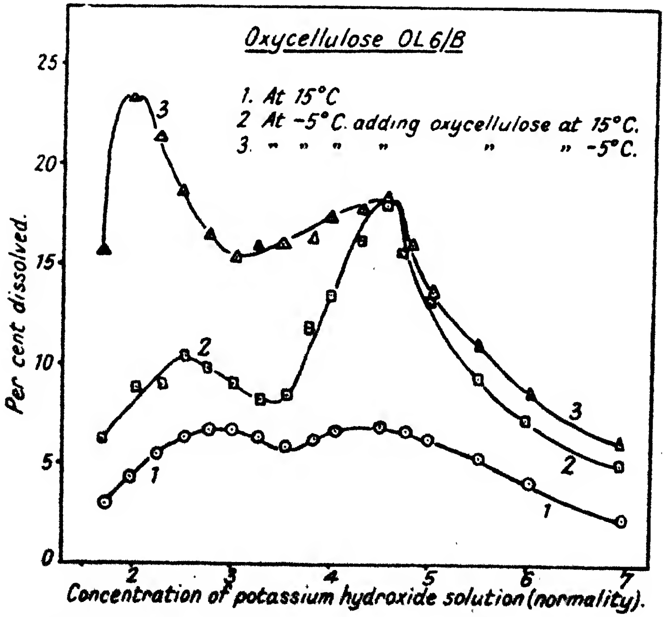


FIG. 168.—Solubility of oxycellulose in KOH solutions.

cellulose under similar conditions revealed only one maximum (see Fig. 169). In order to establish whether the two maxima are a characteristic feature of the solubility of modified celluloses a series of estimations was undertaken on (*1*) oxycellulose from unmercerised cotton, (*2*) oxycellulose prepared by the oxidation of alkali-cellulose, (*3*) hydrocellulose from unmercerised cotton, (*4*) similar material subjected to an alkali-boil and (*5*) hydrocellulose from mercerised cotton.

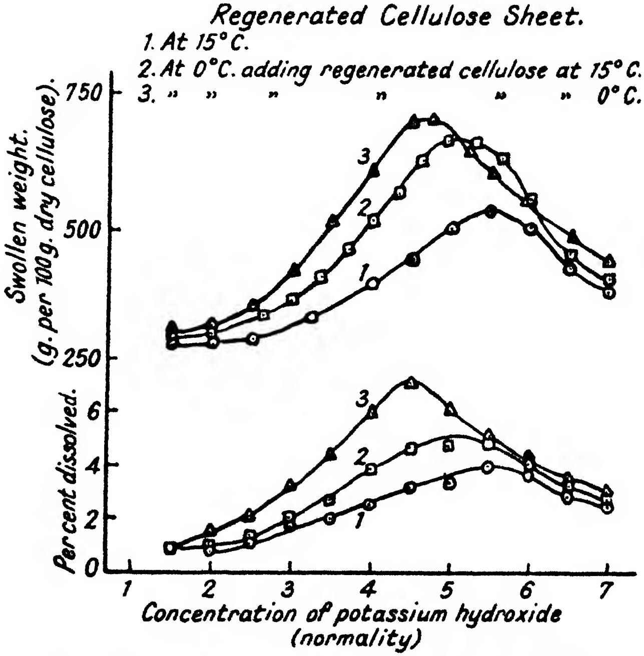


FIG. 169.—Swelling and solution of viscose in KOH.

The results are shown in Fig. 170, from which it will be seen that with the exception of curves *2* and *5* two maxima appear, but that the effect of a previous swelling treatment is apparent in the solubility of modified cellulose, making it similar to that of the regenerated cellulose in showing one maximum.

In view of the general correlation of the swelling of cellulose and the solubility of modified cellulose in alkaline solutions of the same concentration and composition it is remarkable to find that there are two maxima in the solubility curves for KOH where modified cellulose from unmercerised cotton is concerned. The swelling of cotton yarn in KOH solutions (see page 279) gives no indication of this; swelling of regenerated cellulose is a more satisfactory measure, but unfortunately it is almost impossible to measure this at low temperatures with any accuracy.

Mercer's observation that the swelling action of NaOH on cotton could be increased by solution of zinc oxide in the alkali has also been utilised by Davidson (J.T.I., 1937, *28*, 27) in his study of the solubility of modified cellulose in alkali.

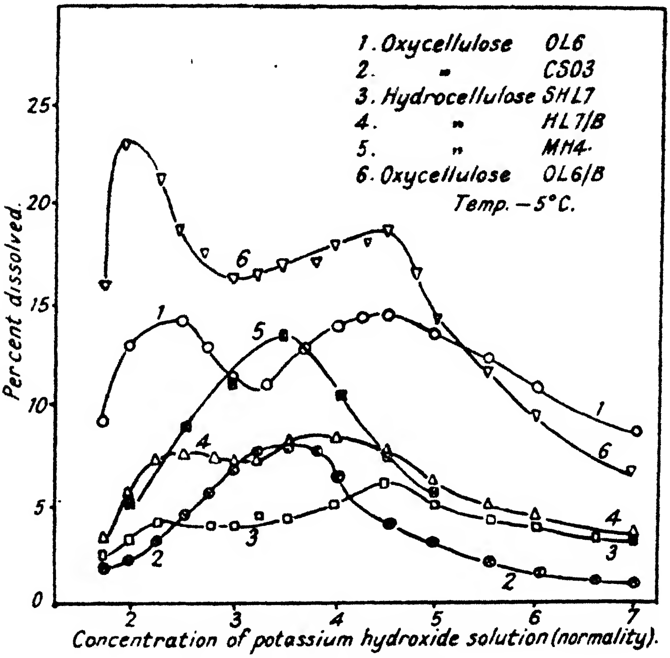


FIG. 170.—Solubility in KOH.
(Curves 2 and 5 relate to mercerised cotton.)

The presence of dissolved zinc oxide in KOH solutions increases the maximum swelling of regenerated cellulose sheet and the solubility of modified cotton. The curves are similar to those for KOH alone, and again the material from mercerised cotton shows a single maximum compared with the two maxima for modified unmercerised cellulose.

Modified cotton cellulose dissolves to a greater or less extent in cold concentrated solutions of sodium hydroxide and the dissolved fraction may be recovered by acidification without great change. In technical mercerising, this affects the handle of the goods.

Both modified and unmodified cotton celluloses swell considerably in cold concentrated solutions of sodium hydroxide, and there is a direct connection between the swelling and solubility, as the greater the swelling, the greater is the amount of the material which dissolves. For a certain degree of swelling it is assumed that the chain molecules below a particular length are able to overcome the cohesive forces of the swollen material and escape into the solution. Solubility, therefore, becomes a fractionation into longer and shorter chains and measures the proportion of the material below a certain chain length. The relationship between the solubility of modified and dispersed or regenerated cellulose is thus explained. As the solubility is dependent on chain length distribution, it can be correlated with tensile strength, reducing power and fluidity. The fact that the reducing power of the soluble portion of a hydrocellulose is greater than that of the whole material confirms the idea that the shorter chain molecules are more easily dissolved.

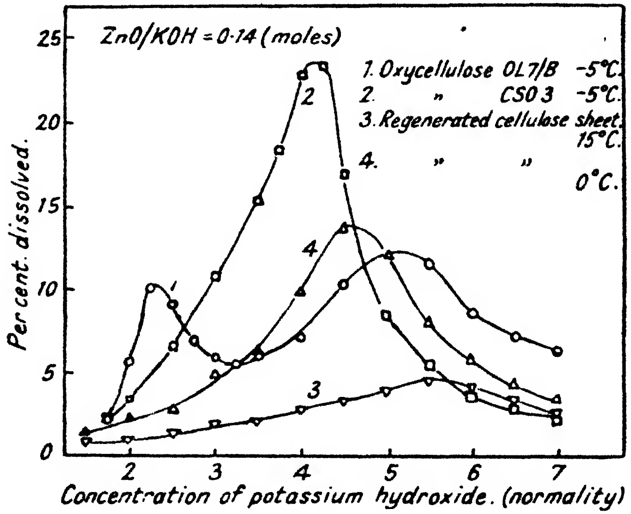


FIG. 171.—Solubility in alkali.
(Curve 1 refers to unswollen material.)

General

Although the properties of the various oxycelluloses vary according to the method of formation, there is always a fall in tensile strength and a rise in fluidity; the relation between these two properties has shown that the loss in strength for a given rise in fluidity is greatest for the hydrocelluloses and least for the oxycelluloses prepared by the action of dichromate in oxalic acid solution. If the modified celluloses are subjected to an alkali boil, the tensile strength is diminished and the fluidity increased to an extent which also depends on the manner of modification—the dichromate oxycelluloses suffering the greatest additional loss in strength. The changes of fluidity and strength produced by boiling are such that the fluidity-strength relation for the boiled material is approximately the same whatever the method of modification (see page 250). The behaviour of the dichromate oxycelluloses and those prepared by oxidation in non-alkaline solutions is difficult to interpret on the theory of cellulose as a chain molecule, but Davidson (J.T.I., 1934, *25*, 174 ; 1938, *29*, 195) suggested that oxidation does not necessarily result in the scission of the chain molecule, but that the alcohol groups in the glucose residue are first oxidised to an aldehyde or that the ring structure may be broken, causing a weakening of the glucosidic linkage. This weak linkage may then be broken by boiling the oxycellulose with weak alkali or even with water and also by treatment with an alkaline solvent such as cuprammonium hydrate—processes which are without much action on hydrocellulose and have comparatively little effect on the oxycelluloses prepared in alkaline solutions. The effect of the alkali-boil is shown by the following figures, which also refer to Fig. 160 on page 252.

EFFECT OF ALKALI-BOIL.

% Loss of strength (single thread breaking load).

Boiled yarn after modification.	Boiled yarn after modification and re-boiling.				
	Modified with acid.	Modified with alkaline hypo-chlorite.	Modified with neutral hypo-chlorite.	Modified with dichromate and sulphuric acid.	Modified with dichromate and oxalic acid.
5	5	8	16	20	25
10	12	16	35	40	50
15	17	21	48	55	67
20	24	26	61	67	81

Even boiling water has a great effect on the tensile strength of the dichromate oxycelluloses, causing a reduction to 45% of the strength of the original yarn and to almost 50% of the strength of the oxidised yarn without any substantial difference in copper number or loss in weight. The earlier observations of Clibbens and Ridge (J.T.I., 1928, *19*, 389) on the fluidity of the dichromate oxycelluloses showed two important differences from the neutral-hypochlorite oxycelluloses—a definite rise in fluidity on modification corresponds with a smaller loss in strength, while alkali-boiling is accompanied by a large additional loss in strength with a comparatively small rise in fluidity. (See page 252.)

The sensitivity to alkali of this type of oxycellulose was obscured by the fact that the medium in which the fluidity measurements were made—cuprammonium hydrate—is itself a strong alkali. The possession of alkali-sensitive linkages is, therefore, only a potential tendering (see page 250), but Davidson put forward certain data which helped to reconcile the general observations on modified cellulose and the molecular chain of cellulose, by making use of a non-alkaline medium for fluidity measurements. This obviates the difficulty of the alkali-sensitive linkage and enables a true measure of chain length to be made. The method adopted was to observe the fluidity of the cellulose nitrates in acetone solution, Berl and Rueff (Cellulosechem., 1933, *14*, 115) having shown that an anhydrous mixture of nitric and phosphoric acids was capable of producing cellulose nitrates of very high viscosity. Apparently the high concentration may prevent dissociation of the acids and degradation of the cellulose (cf. Staudinger, Cellulosechem., 1934, *15*, 66). The work of Davidson (J.T.I., 1938, *29*, 195) showed that within each series of modified cottons there is a definite relation between cellulose fluidity and cellulose nitrate fluidity, and this relation differs widely for the various methods of modification, but that boiling the modified celluloses with 1% NaOH solution under pressure brings about a change whereby the relation between cellulose fluidity and cellulose nitrate fluidity is expressed by a single curve, irrespective of the method of modification, and corresponding to that for hydrocelluloses before alkali-boiling. (See Fig. 172.)

Boiling with alkali under pressure also demonstrates the presence or absence of alkali-sensitive linkages in modified cellulose whose average chain length may be measured in the non-alkaline medium. The alkali-sensitive material shows an increase in cellulose nitrate fluidity as the result of rupture of the chain. The results of Fig. 174 illustrate the point clearly. The hydrocelluloses are little affected, but the oxycelluloses from neutral or acid-oxidising solutions show a great increase in cellulose nitrate fluidity as the result of the alkali-boil. Relatively small increases of cellulose nitrate fluidity are shown in the case of the oxycelluloses prepared by the action of alkaline oxidising agents.

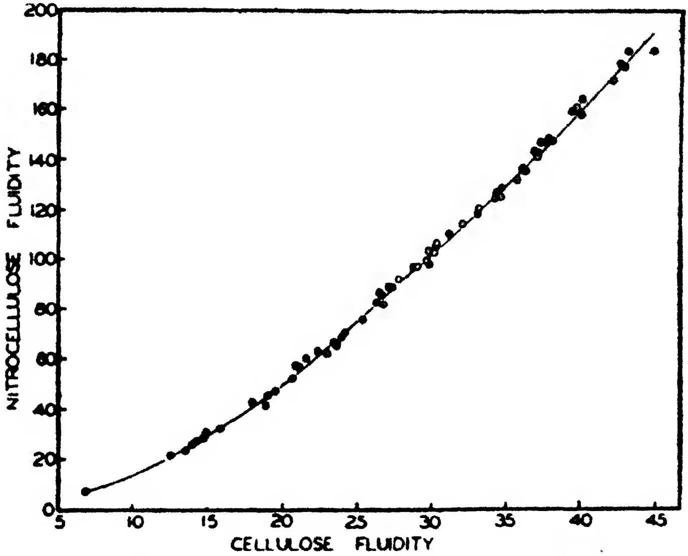


FIG. 172.—Relation between cellulose fluidity and cellulose nitrate fluidity for modified cellulose after boiling with NaOH solution.

Where milder conditions of boiling were employed, those oxycelluloses which show a large increase in cellulose nitrate fluidity when boiled under pressure with NaOH showed a smaller but, nevertheless, considerable increase when boiled with water. Intermediate increases were shown on boiling with soap or sodium carbonate solutions. The acid and neutral-hypochlorite oxycelluloses which show the greatest rise in cellulose fluidity on boiling with NaOH solution under pressure, show almost the same effect after boiling with soap or sodium carbonate solutions; hydrocelluloses and oxycelluloses of the alkaline hypobromite and alkaline hypochlorite types show small increases in fluidity, both for cellu-

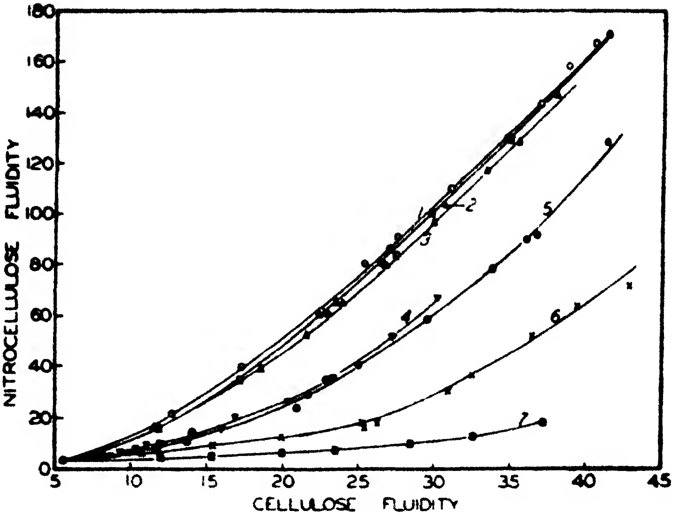


FIG. 173.—Relation between cellulose fluidity and nitrocellulose fluidity.
1-hydrochloric acid; 2-alkaline hypobromite; 3-alkaline hypochlorite, 4-acid hypochlorite, 5-neutral hypochlorite, 6-dichromate and sulphuric; 7-dichromate and oxalic.

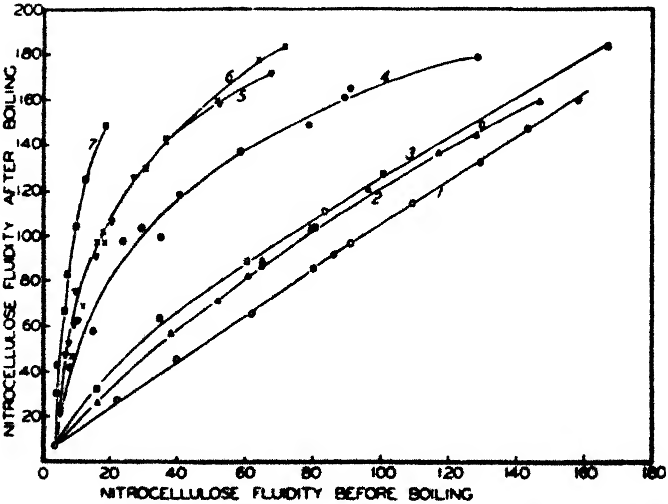


FIG. 174.—Cellulose nitrate fluidities of modified celluloses before and after an alkaline boil.
1-hydrochloric acid; 2-alkaline hypochlorite; 3-alkaline hypobromite; 4-neutral hypochlorite; 5-acid hypochlorite; 6-dichromate and sulphuric; 7-dichromate and oxalic.

loses and nitrocellulose, when boiled in water, soap or sodium carbonate solution.

The effect of cold dilute solutions of alkali (NaOH or Na_2CO_3) is to increase both the cellulose fluidity and cellulose nitrate fluidity of alkaline hypochlorite oxycelluloses, but there is little increase in the case of hydrocelluloses. The effect on neutral hypochlorite, acid hypochlorite and dichromate oxycelluloses is similar to that produced by the boiling alkali, in that there is a great increase in cellulose nitrate fluidity, though somewhat less for the cold treatment.

Hydrocelluloses prepared from mercerised cotton show the same relation between cellulose fluidity and cellulose nitrate fluidity as hydrocelluloses from unmercerised cotton.

As a result of the fluidity measurements on cellulose nitrates derived from oxycelluloses, Davidson was able to divide these into two classes :

(*a*) Those prepared from alkaline oxidising solutions which give almost the same relation between cellulose nitrate fluidity and cellulose fluidity as hydrocelluloses ; the cellulose nitrate fluidity of these is little affected by alkaline treatment of the original oxycellulose.

(*b*) Those prepared with neutral or acid oxidising solutions, which give considerably lower cellulose nitrate fluidities than hydrocelluloses of equal cellulose fluidities ; the cellulose nitrate fluidity of these may be greatly increased even by cold treatments of the original oxycellulose with feebly alkaline solutions.

There is very strong evidence that the oxycelluloses prepared by the action of acid or neutral oxidising agents contain alkali-sensitive linkages in the molecular chain. This type of attack probably oxidises the secondary alcohol groups in the *2* and *3* positions, and so produces high copper numbers. Instead of a scission of the chain-molecule, there may be a rupture of the pryanose ring between the carbon atoms in the *2* and *3* positions which would not affect the tensile strength, but which would produce oxidation products easily capable of alkaline hydrolysis. (See J.T.I., 1938, *29*, 195 ; 1940, *31*, 81.)

CHAPTER SIXTEEN

THE REACTIVITY OF MERCERISED COTTON

THE greater reactivity of mercerised cotton, compared with the unmercerised product, is best demonstrated by the increased rate of reaction on hydrolysis or oxidation, and to a minor degree by the yields in the production of cellulose derivatives.

Native celluloses which have been purified in the usual manner are characterised by a more or less uniform level of reactivity which is increased by treatment with a swelling agent such as sodium hydroxide in concentration exceeding 3 *N*. These swelling agents do not produce any of the changes associated with " Modified Cellulose," i.e. cellulose whose chemical properties have been modified by treatment with acids or oxidising agents, involving some chemical degradation of the cellulose. The properties usually associated with this degradation are loss of hair strength, increase of fluidity in cuprammonium hydrate solution, increase in copper number and increased absorption of methylene blue. The modified celluloses—the old hydrocellulose and oxycellulose—often acquire new chemical properties, such as strong reducing power, but the mercerised cotton has the old properties in an enhanced degree, or to a greater extent.

It is important to emphasise the difference between the two types of change, for one of the tests for increased reactivity of " activated cellulose " is the *rate of formation* of modified cellulose.

The effect of mercerisation on the chemical properties of scoured cottons has been examined by Ridge, Parsons and Corner (J.T.I., 1931, *22*, 140), and the results are shown in the following table. This evidence is in support of that previously supplied by the work of Clibbens and Geake (J.T.I., 1924, *15*, 27 ; 1926, *17*, 127), and of Farrow and Neale (J.T.I., 1924, *15*, 157). The results show that there is no significant increase in any of the values as the result of mercerising. Slightly higher values for loss of weight on boiling in alkali are shown for some samples, but a high degree of accuracy can

EFFECT OF MERCERISATION ON THE CHEMICAL PROPERTIES OF SCOURED COTTONS.

Variety.	Unmercerised.				Mercerised.			
	Fluidity.	Copper number.	Methylene blue absorption.	Loss of wt. in alkali boil %.	Fluidity.	Copper number.	Methylene blue absorption.	Loss of wt. in alkali boil %.
Egyptian Sakel . .	3·68	0·01	1·17	1·32	3·70	0·01	0·96	1·23
Egyptian Uppers .	3·38	0·01	1·10	1·20	3·34	0·01	0·95	1·31
Tanguis . . .	3·47	0·015	1·24	0·84	3·42	0·01	1·09	1·28
Arizona . . .	3·87	0·01	1·35	1·37	3·67	0·01	0·98	1·30
Peru Mitafifi . .	3·52	0·01	1·03	0·88	3·21	0·01	0·88	1·0

hardly be expected owing to difficulties in manipulation, and the fact that the loss is determined by finding a small difference between two relatively large weights.

Hydrolysis Number

A quantitative measure of the increased reactivity of mercerised cotton was first suggested by Schwalbe (Z. angew. Chem., 1908, *21*, 1321) on the basis of the increase in copper number after treatment with 5% sulphuric acid at the boil for 15 minutes. The increase in copper number was termed the "hydrolysis number."

The copper number method of estimating the reducing power of cellulose was originally due to Schwalbe (Ber., 1907, *40*, 1347) and utilised Fehling's solution. The weight of reduced copper when referred to 100 g. of dry cotton was termed the "copper number."

Later work showed that this procedure was open to several errors, but the following figures and the hydrolysis numbers relate to the original Schwalbe method.

HYDROLYSIS NUMBER AND COPPER NUMBER.

Material.	Schwalbe hydrolysis number.	Schwalbe copper number.	Difference.
Surgical cotton wool . . .	3·3	1·1	2·2
,, ,, treated 8% NaOH	3·2	0·9	2·3
,, ,, ,, 16% NaOH	5·0	1·3	3·7
,, ,, ,, 24% NaOH	6·1	1·2	4·9
,, ,, ,, 40% NaOH	6·6	1·9	4·7

Bernardy (Z. angew. Chem., 1926, *39*, 259) pointed out many errors and variations in this process and described slight modifications of the test, nevertheless, the hydrolysis number continued to be of limited value as a measure of mercerising efficiency.

Birtwell, Clibbens, Geake and Ridge (J.T.I., 1930, *21*, 85) extended Schwalbe's idea to the measurement of the copper number after oxidation with alkaline hypobromite solution, a method which has certain advantages over that originally put forward by Schwalbe. Slight variations in the time or temperature of the treatment of cotton with 5% H_2SO_4 solution have a considerable effect on the copper number, but owing to the peculiar nature of oxidation with hypobromite, the resulting copper number, within certain limits, is almost independent of the time and temperature of treatment. Further, all bleached cottons, irrespective of origin, mechanical form or bleaching process yield the same copper number when oxidised with hypobromite and the reactivity is unaffected even by very slight over-bleaching or acid attack. On the other hand, the preparation of the reagent requires much more time than that of 5% H_2SO_4 and it must be freshly prepared for each series of measurements; these disadvantages are compensated by the greater significance of the measurement.

The figure obtained by analysis is expressed as a ratio to that given by plain bleached cotton and is referred to as the *Reactivity Ratio.*

Clibbens and Ridge (J.T.I., 1927, *18*, 135) had previously established that when plain bleached cotton is brought into alkaline hypobromite solution, its copper number increases rapidly at first, but quickly attains a value which remains almost constant for some time, a fact which makes the test of reactivity ratio possible, for similar constant copper numbers, but of higher value, are obtained with mercerised cotton.

THE MEASUREMENT OF THE REACTIVITY RATIO

1. Simplified Procedure

For many purposes sufficiently accurate results are obtained by the following procedure:

(*a*) *Preparation of the Hypobromite Solution.*—The hypobromite solution is conveniently prepared from a stock standard solution of potassium bromate containing an excess of potassium bromide. By acidification of this solution free bromine is liberated in quantity equivalent to the bromate, and the correct volume of standard caustic soda solution is then added to neutralise the excess acid, to react with the free bromine yielding an equivalent quantity of hypobromite, and to furnish the necessary concentration of excess alkali when the mixture is diluted to a convenient total bulk.

The stock bromate-bromide solution contains 14·4 grams (weighed accurately to 0·1 gram) of pure potassium bromate and 60 grams (weighed to the nearest gram) of potassium bromide per litre. In order to prepare one litre of hypobromite solution, 200 cc. of the bromate solution are pipetted into a 1,000 cc. measuring flask and 200 cc. of the $2N$ sulphuric acid added quickly from a measuring cylinder. The flask is stoppered immediately after the addition of the acid in order to prevent the escape of bromine, and the stopper is tied in position with string. The acid solution is allowed to stand for at least half an hour; it is sometimes convenient to carry out these operations on the day previous to that on which the measurements are to be made, and to allow the acidified solution to stand overnight, but in this case care must be taken to use a flask with a well-fitting stopper to avoid loss of bromine. The stoppered flask and its contents are cooled in running water, 250 cc. of $2N$ sodium hydroxide solution are added rapidly from a measuring cylinder, the stopper replaced and the flask gently shaken, the cooling being continued for a short time to avoid decomposition of hypobromite by the heat generated in the neutralisation of the acid. Finally, the total bulk is made up to 1,000 cc. and the resulting solution should then be very near to $N/10$ in oxidising value and $N/10$ in free caustic soda. It should not be allowed to stand more than 24 hours before use, and its composition should be checked by titration as described later. The concentration of oxidising agent should lie between $0{\cdot}95 \times N/10$ and $1{\cdot}05 \times N/10$ and that of free alkali between $0{\cdot}9 \times N/10$ and $1{\cdot}1 \times N/10$.

The equations are :

1. $KBrO_3 + 5KBr + 3H_2SO_4 \longrightarrow 6Br + 3K_2SO_4 + 3H_2O$
2. $6Br + 6NaOH \longrightarrow 3NaOBr + 3NaBr + 3H_2O$

The stock bromate-bromide solution slightly exceeds $N/2$ in oxidising value. Since it is finally diluted five-fold (200 cc. to 1,000 cc.) the final solution is approximately $N/10$ in oxidising value. The amount of acid consumed in reaction 1 is exactly equivalent to the amount of alkali consumed in reaction 2. Since 200 cc. of $2N$ acid are used to liberate the bromine (a great excess), the subsequent addition of 200 cc. of $2N$ alkali would, therefore, produce an exactly "neutral" hypobromite solution in the stoichiometric sense. The actual addition of sodium hydroxide is 250 cc. of $2N$—an excess of 50 cc.—and this, diluted to 1,000 cc., corresponds to $N/10$ excess alkali.

(*b*) *Oxidation of the Cotton and Determination of the Copper Number.*—One hundred cc. of the hypobromite solution are poured from a measuring cylinder into a 200 cc. stoppered bottle and 2·50 grams of the air-dry cotton under examination are introduced into the solution. The mixture is allowed to stand with occasional gentle shaking for 1½ hours, if the temperature of the room is between 20° C. and 25° C., or for two hours if it is between 15° C. and 20° C. At the end of this time the cotton is filtered through a perforated plate, and washed in the funnel, (1) with water, (2) a dilute solution of hydrogen peroxide to ensure complete removal of hypobromite, (3) again with water, (4) with dilute ($N/10$) sulphuric acid, and finally with water to a neutral reaction. The cotton is pressed as dry as possible on the funnel, and transferred to a conical flask, in which its copper number is determined by the usual Schwalbe-Braidy method without further drying or weighing. The copper number, referred as usual to 100 grams of oven-dry material, is calculated on the basis of the 2·5 grams of air-dry material originally taken for the oxidation, a correction being made for its moisture content. The value so obtained divided by 1·5 is called the reactivity ratio.

2. ACCURATE PROCEDURE

The success of the method described above in yielding a solution which is exactly $N/10$ in oxidising value is affected by impurities in the bromate, by loss of free bromine from the acid solution, and by decomposition of hypobromite in the alkaline solution. Slight variations occur owing to these causes, and though they may be ignored for many purposes, as, for example, if it is merely required to know whether material has or has not been mercerised, the following more exact procedure for preparing hypobromite solutions of the correct concentration has been used to obtain most of the results recorded. In this method the hypobromite solution, slightly more concentrated than $N/10$, is prepared in a special measuring flask. This has a bulb sealed into its neck, and is provided with two graduation marks, one at 1,000 cc. below the bulb and one at 1,100 cc. above the bulb. The 100 cc. of solution between the two marks is available for analytical determinations of its precise oxidising value and alkalinity. Liquid can then be withdrawn from the flask until its contents measure exactly 1,000 cc., and the necessary additions of water and standard alkali, calculated from the analyses, can be made to secure a solution exactly $N/10$ both in oxidising value and excess alkalinity. Two hundred and twenty cc. of the bromate-bromide solution prescribed above are run into this flask from a measuring cylinder, followed by 200 cc. of $2N$ sulphuric acid, also from a cylinder. The solutions are mixed by gentle shaking after the stopper has been replaced, and flask and contents are allowed to stand for at least half an hour. To the cooled acid solution 275 cc. of $2N$ sodium hydroxide solution are added from a cylinder, and the bulk finally made up to 1,100 cc., all the precautions mentioned under the simplified procedure being observed at each stage. The actual composition of the solution is next determined. For measurement of its oxidising value, 20 cc. are titrated against an accurate $N/10$ solution of sodium arsenite after the addition of 1 to 2 grams of sodium bicarbonate, starch-iodide paper being used as external indicator. For measurement of excess alkalinity, 20 cc. are treated with excess of dilute and carefully neutralised hydrogen peroxide solution in order to destroy the hypobromite, Methyl Red is added as indicator, and the solution titrated against $N/10$ acid. Two cc. of 10 volume hydrogen peroxide (roughly $2N$) are sufficient to destroy the hypobromite, and an unnecessarily large excess should be avoided or bleaching of the indicator will occur. The solution should prove to be slightly more concentrated than $1{\cdot}000 \times N/10$ in hypobromite—usually the factor lies between 1·02 and 1·03—and it is adjusted so that the factor lies within the limits 0·995 and 1·005. In order to do this, solution is pipetted from the flask until the meniscus falls to the 1,000 cc. mark, and a previously calculated addition made to its volume. The alkalinity of the solution must be kept between $0{\cdot}9 \times N/10$ and $1{\cdot}1 \times N/10$, and if the calculated addition of water necessary for the adjustment of the hypobromite concentration fails to bring, or to maintain, the akalinity within these limits, the addition must include a suitable volume of $2N$ sodium hydroxide or sulphuric acid. The solution is kept out of direct sunlight and stored in the dark as far as possible; it is used within 24 hours of the adjustment to the correct concentration.

The oxidation of the cotton and determination of its copper number are carried out as already described, except that the oxidation is continued for one hour only, and at a temperature of 25° C., the bottle and its contents being immersed in a thermostat at that temperature. In order to obtain the maximum accuracy, careful control of hypobromite concentration is the most important factor.

(J.T.I., 1930, *21*, 93.)

In Fig. 175 the copper number is plotted against the time of oxidation, and it will be seen that all the curves are of the same form and that the maximum value is practically independent of temperature.

A collection of some 36 white mercerised cotton materials—fabrics and yarns of all kinds representing the normal production of a number of different works—gave a mean reactivity ratio of 1·45 with a range of 1·22 to 1·63. Although the range may be regarded as a wide one, yet no sample of plain bleached material has ever been observed with a reactivity ratio within this range.

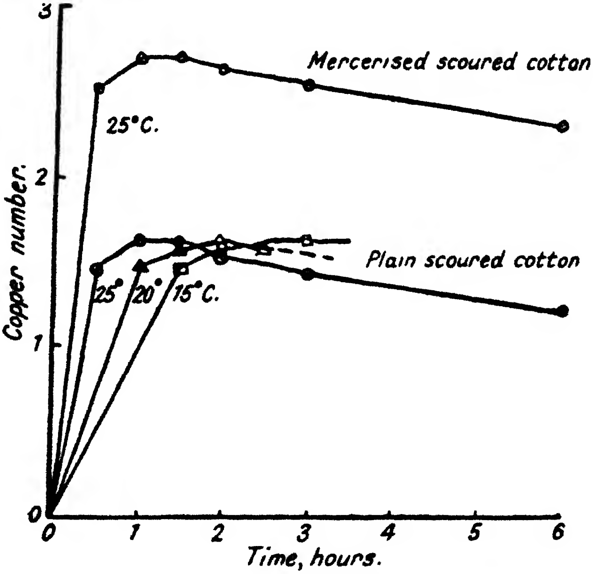


Fig. 175.—Reactivity ratio to hypobromite solution.

In the case of plain bleached cotton materials, no reactivity ratios have been observed outside the limits of 0·95 to 1·12.

Figs. 249–251 show photomicrographs of sections through the warp of white mercerised cloths of the same construction—the swelling of the individual hairs in the samples of low reactivity ratio is much inferior to that of the hairs in the average sample.

The effect on the reactivity ratio of mercerising under different conditions has been examined in the case of yarn. Fig. 176 shows the reactivity ratio of yarn treated with NaOH

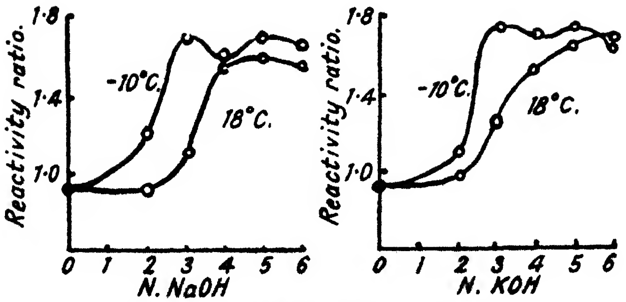


FIG. 176.—Reactivity ratios for NaOH and KOH solutions.

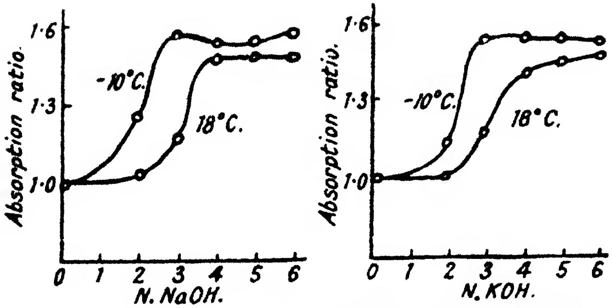


FIG. 177.—Absorption ratios for NaOH and KOH solutions.

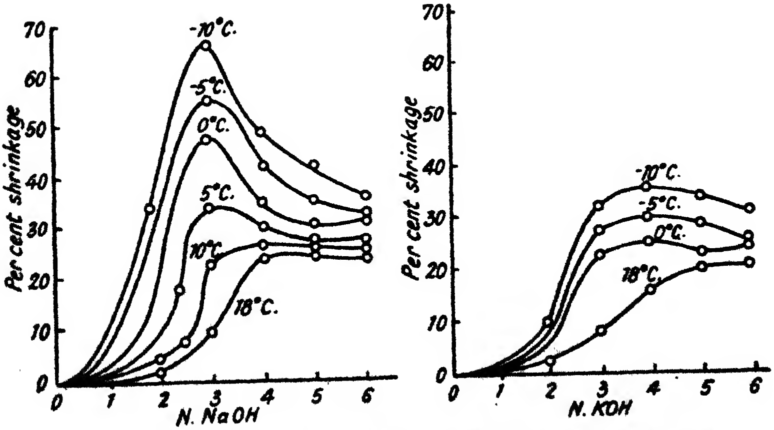


FIG. 178.—Shrinkage of cotton yarn in NaOH and KOH solutions.

of various concentrations from 0 to 6 *N* (0° to 45° Tw.) and subsequently washed with water and air-dried, plotted against the concentration of alkali for two different temperatures of treatment. The maximum effect of the alkali on the reactivity is produced in lower concentrations at lower temperatures, in agreement with well-established observations on general mercerising.

Fig. 176 shows similar curves with potassium hydroxide as the swelling agent—the effect of temperature, too, is similar. Fig. 177 shows the moisture absorption ratios of the same material used for the reactivity ratios; the forms of the curves are almost identical and there is close correlation between the two measurements. In the case of yarn shrinkage (see Fig. 178, page 279) the maximum effect with NaOH occurs at lower concentrations with decrease in temperature; this is the only similarity. The great shrinkage at low temperatures is not reflected in the reactivity or absorption ratio curves. Curves for yarn treated with KOH do not exhibit the very prominent shrinkage at low temperatures as for NaOH, and are more similar in form to the reactivity and absorption curves.

The effect of tension during the mercerising process is slightly to reduce the reactivity ratio—as with the absorption ratio. Skeins of 2/40s Egyptian cotton were reeled to 54 ins. girth and immersed in 5 *N* NaOH solution. After complete shrinkage, different skeins were stretched back to different girths and washed under tension. All the skeins were then scoured and the following reactivity ratios obtained.

Effect of Tension on Reactivity Ratio.

Unmercerised 1·02.

	Shrunk.	52 ins.	53 ins.	54 ins.	55 ins.
Reactivity ratio .	1·59	1·51	1·47	1·46	1·47

The reactivity ratio of cotton which has been mercerised after scouring (boiling with dilute NaOH) is slightly greater than that of the same cotton mercerised under the same conditions in the grey state, 1·68 compared with 1·59.

The reactivity of mercerised cotton is not appreciably affected by boiling with dilute caustic soda, indeed neither dry nor wet conditions of heating appear to have much effect—a point of difference from the absorption ratios.

EFFECT OF HEATING ON REACTIVITY RATIO.

	Reactivity ratio.
Mercerised, washed and air-dried . . .	1·71
do. dried 4 hours at 110° C., and conditioned 2 days	1·68
do. boiling water for 4 hours, air-dried .	1·70
do. boiling 1% NaOH for 4 hours, washed and air-dried	1·68

Rhomberg (Diss., Stuttgart, 1930) has also worked out a hydrolysis method which depends on the fact that with increasing extent of mercerisation cotton is more susceptible to attack by acid. The method is as follows:

One gram of the cotton material is placed in a stoppered bottle (200 cc.) and this is filled with 15% H_2SO_4 solution previously warmed to 40° C. The whole is well mixed and kept in a thermostat for seven hours, after which the acid is poured off, and the cloth washed with distilled water. The Kauffman "boil-off" number is then determined; this is the number of cc. of $N/10$ $KMnO_4$ solution required to oxidise the organic matter dissolved from 1 g. of cotton by boiling with 3% NaOH solution. The Kauffman number obtained in this special case is termed the *hydrolysis number* and is suggested as a measure of mercerising value.

PART FIVE

THE THEORETICAL ASPECT OF THE ACTION OF ALKALI

CHAPTER SEVENTEEN

THE PREFERENTIAL ABSORPTION OF ALKALI

When cotton is placed in a solution of sodium hydroxide, there is a preferential absorption of the alkali from the solution ; no other aspect of the mercerising phenomenon has aroused as much interest or been the cause of as many publications in the scientific and technical literature.

This preferential absorption is associated with the question of compound formation—is the association of sodium hydroxide and cellulose merely a matter of absorption or does a definite chemical compound " soda-cellulose " exist ?

John Mercer was the first to observe the preferential absorption, for " in order to maintain at 45° Tw. a bath of caustic soda through which cloth was passed, it was found necessary to supply liquor of at least 60° Tw." Mercer was also of the opinion that cellulose combined chemically with sodium hydroxide, the resulting compound being so unstable that washing with water completely destroyed it.

Gladstone (J.C.S., 1852, *5*, 17) considered that any uncombined sodium hydroxide could be removed from the system cellulose-sodium hydroxide by washing with alcohol, thus enabling determinations to be made of the composition of soda cellulose by converting the alkali into the corresponding sulphate. Experiments led him to the conclusion that the compound $(C_6H_{10}O_5)_2 . NaOH$ was formed.

The method of treating " soda-cellulose " with alcohol appears to rely on the belief that the latter is merely an indifferent solvent, but actually its presence only serves to increase the difficulty of the problem.

It was assumed that a chemical compound was formed by the action of sodium hydroxide on cellulose as suggested by Mercer. Many different methods have been employed to investigate this point.

Change in Titre

The work of Vieweg (Ber., 1907, *40*, 3877) resulted in the production of his well-known absorption curve—the subject of much experiment and discussion by other investigators.

Vieweg's method was to place 3 g. of cotton wool—dried at 90° C.—in a flask containing 150 cc. of a solution of sodium hydroxide at room temperature, shake for one hour and allow to stand for two hours. The alkali-content of the liquor was determined before and after addition of the cotton, and from the change in titre Vieweg was able to calculate the alkali absorbed by the cotton from solutions of various concentrations.

The results are illustrated in Fig. 179. (The lower curve represents the amount of NaOH absorbed from dilute solutions—2 %—by cotton treated as in the upper curve ; see page 386).

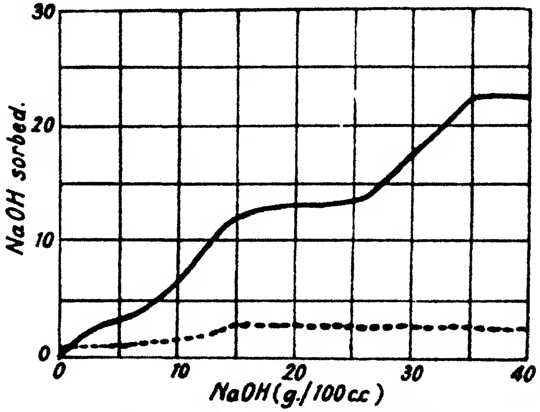


Fig 179.—Absorption of NaOH

With concentrations of sodium hydroxide between 0 and 16 g. per 100 cc. the absorption of alkali by cotton increases continuously with the concentration, but in the case of concentrations between 16 and 24 g. per 100 cc. the absorption remains substantially constant at about 12·5 g. of NaOH per 100 g. of cotton. With higher concentrations of NaOH in the solution, the absorption again increases until at concentrations of over 35 g. of NaOH per 100 cc. in the mercerising liquor, there is a second halt in the curve corresponding to an absorption of about 22·5 g. NaOH per 100 g. of cotton. These two definite inflexions in the curve correspond to the compounds $C_{12}H_{20}O_{10}$. NaOH and $C_6H_{10}O_5$. NaOH.

The trend of the various curves which may typify the action of NaOH on cellulose is seen in Fig. 180, from a further publication by Vieweg (Z. angew. Chem., 1924, *37*, 1009); the reaction may be one of absorption, the distribution of NaOH between cellulose and water, or the formation of a chemical compound. The flat portion of Vieweg's curves was held to point to compound formation.

In a further paper Vieweg (Ber., 1924, *57B*, 1917) reaffirmed that a definite compound was formed between cotton cellulose and sodium hydroxide $(C_6H_{10}O_5)_2NaOH$ when the alkali was used in concentrations of 17·5 to 33%, approximately 13·5 g. of NaOH being taken up by 100 g. of cellulose. Experiments on sulphite pulp and on viscose showed a break in the absorption curves and a flattening indicative of compound formation which occurred at different concentrations for different celluloses. The concentration of alkali (in g. per 100 cc.) was roughly 12% for ramie fibre and for viscose, 16% for native cotton (Mako) and for surgical "cotton wool," and between 16% and 21% for sulphite pulp. In the case of ramie fibres, the X-ray work of Katz and Mark (see page 319) revealed no change in the diagram of the alkali cellulose from 8% NaOH, but a complete change with 12% NaOH indicated a definite alkali cellulose at this concentration.

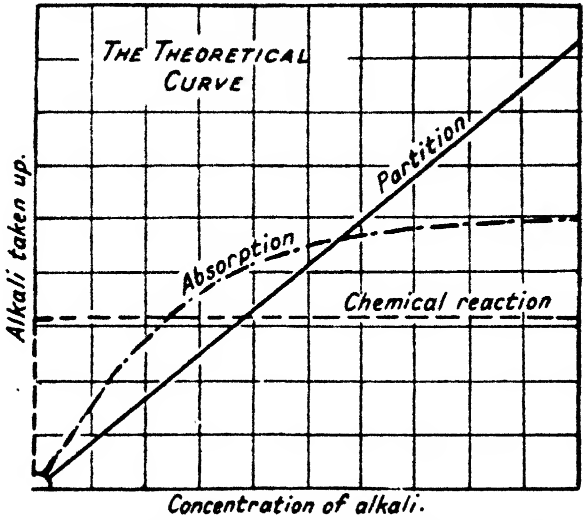


FIG. 180.—Theoretical curves for NaOH and cellulose.

Experiments with other alkalis were done by Dehnert and König (Cellulosechem., 1924, *5*, 107 ; 1925, *6*, 1) and by Heuser (Chem. Zeit., 1924, *37*, 742), from which it was concluded that the following compounds were formed :

$(C_6H_{10}O_5)_2 \cdot LiOH$	7·39% LiOH
$(C_6H_{10}O_5)_2 \cdot NaOH$	12·34% NaOH
$(C_6H_{10}O_5)_2 \cdot KOH$	17·31% KOH
$(C_6H_{10}O_5)_2 \cdot CsOH$	46·23% CsOH
$(C_6H_{10}O_5)_2 \cdot CsOH$	30·8% CsOH

A great many similar experiments were carried on by various investigators, sometimes with conflicting results, and although it was realised that the small ratio of the total mass of solid to liquid phase was a source of experimental error, it was not appreciated that the method itself depended on the wrong assumption that no water is taken up by the solid phase.

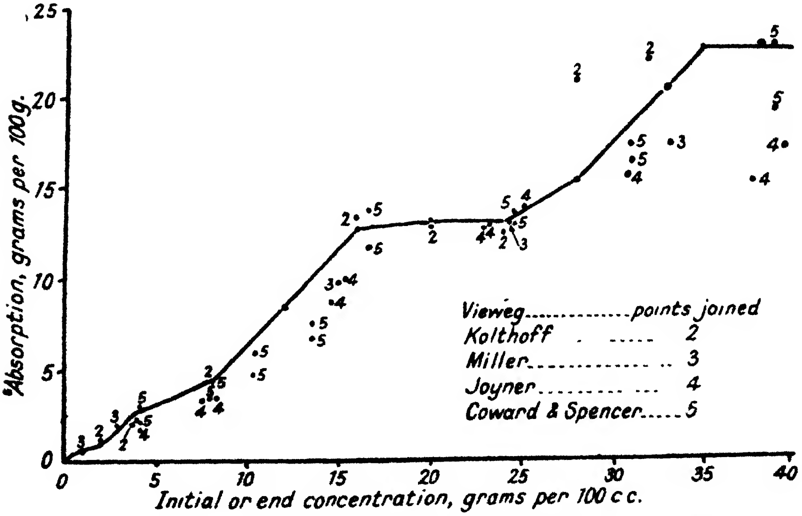


FIG. 181.—The absorption of NaOH (composite graph by Clibbens).

Some useful summaries of the work on the preferential absorption of alkali by cellulose have been published from time to time, Clibbens (J.T.I., 1923, *14*, 217), D'Ans and Jäger (Cellulosechem., 1925, *6*, 137), Blanco (Ind. Eng. Chem., 1928, *20*, 926) and Bancroft and Calkin (Text. Res., 1934, *4*, 119);

the two former references are of interest for the composite graphs they contain and these are reproduced in Figs. 181 and 182.

D'Ans and Jäger followed the plan of Clibbens and recalculated some of the data in order to have them all on the same basis of grams of NaOH per 100 cc. of solution.

Inspection of the graphs reveals some similarities and some striking divergences.

Any attempted explanation of the reaction between cellulose and sodium hydroxide is complicated by the fact that the composition of the mixture is not constant, but depends on the type of cellulose and on the temperature. D'Ans and Jäger showed that the absorption of NaOH was higher at 2° C. than at 23° C. Although the curves for the two temperatures were similar in shape they were not parallel and, further, the curve for 2° C. did not give a flat portion at 0·5 mols. NaOH per $C_6H_{10}O_5$. Bancroft and Calkin (Text. Res., 1934, *4*, 119), in their review, have pointed out that although a change in temperature might affect part of the curve, yet if there is compound formation at 23° C., there should be a similar compound at a different temperature.

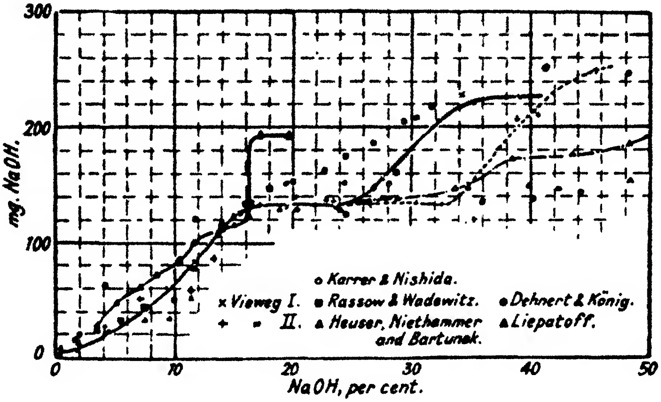


FIG. 182.—The absorption of NaOH.

In general, the literature is very definite on the fact that a decrease in temperature increases the amount of NaOH absorbed. Beadle and Stevens (see page 304) have shown that in the case of regenerated cellulose, a decrease in temperature results in increased absorption of NaOH. Conversely, Dehnert and König (Cellulosechem., 1924, *5*, 19) found that increasing the temperature decreased the absorption of NaOH, and

Heuser and Bartunek (ibid., 1925, *6*, 19) found that 17·4% NaOH was taken up at room temperature compared with 12·36% at 80° C. from solutions of the same concentration.

Addition of Various Compounds

There has been a number of attempts to prevent the shrinkage which takes place when cotton is immersed in caustic soda solutions, in order to obviate the use of power to counteract this tendency; the general method was to incorporate various compounds in the mercerising liquor, but there is no evidence that any attempt was successful in maintaining lustre or increased dyeing capacity. Soap, alcohol, dextrin, benzene, petrol, and sodium silicate have all been suggested.

The use of sodium zincate is in a different category. It was observed by Mercer that this had the effect of rendering efficacious solutions of NaOH which were too dilute for use in ordinary mercerising—say 8·5% NaOH. Lewis (J.T.I., 1933, *24*, 122) has utilised sodium zincate in NaOH for the swelling of cotton hairs as a means of testing for chemical or mechanical damage, but the zincate solution in this case was prepared by saturating hot 60° Tw. NaOH solution with $Zn(OH)_2$, cooling and filtering.

Use of Salts

The greatest interest appears to have centred on the use of common salt. Vieweg (Ber., 1908, *41*, 3269) found that the addition of sodium chloride to the mercerising lye considerably increased the amount of NaOH which was absorbed by the cotton. The effect is shown in Fig. 183.

This publication gave rise to the belief that it was possible not only to effect economies by the addition of salt, but also to obtain more efficient mercerising.

Hübner (J.S.C.I., 1909, *28*, 228) made a number of comparative experiments with cotton hanks on a hank mercerising machine. The material was immersed in caustic soda of 12% and 20% concentration respectively, with and without the addition of salt.

After immersion, the following results were observed:

EFFECT OF NaCl ON NaOH.

			Shrinkage %.
Soda lye,	12 per cent.	sodium hydroxide .	−11·5
„	„	saturated with salt .	− 6·8
„	20 „	sodium hydroxide .	−18·6
„	„	saturated with salt .	−15·7

It will be seen, therefore, that the effect of salt is considerably to reduce the shrinkage which takes place in the ordinary caustic soda.

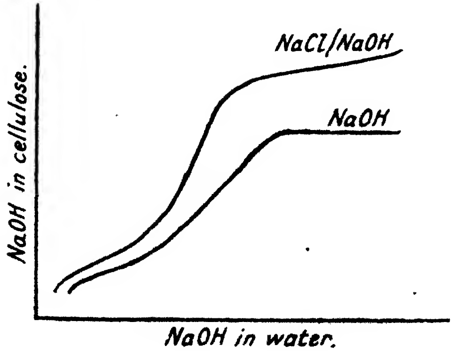


FIG. 183.—Effect of NaCl on absorption of NaOH.

Dyeing trials by Knecht showed that the affinity of the cotton for direct colours was considerably lower after caustic soda solution saturated with salt than after NaOH alone.

ABSORPTION OF DYESTUFFS.

	Untreated.	Treated with sodium hydroxide.	Treated with sodium hydroxide and salt.
Diamine sky blue .	1·06%	1·66%	1·25%
Chrysophenin .	0·74%	1·17%	1·01%
Benzopurpurin 4 B	1·02%	1·97%	1·67%

The lustre was also found to suffer when the caustic soda solution was saturated with sodium chloride before mercerising under tension, and a similar effect was found by Pope and Hübner (J.S.C.I., 1904, *23*, 404) in the case of additions of sodium silicate, which was stated to prevent shrinkage without affecting lustre (D.R.P., 98,601).

D'Ans and Jäger (Cellulosechem., 1925, *6*, 137) found that the absorption of NaOH is not affected by NaCl or Na_2CO_3 in the case of solutions of less than 12% NaOH.

Numa (Cell. Ind., Tokyo, 1925, *1*, 87) reported that the absorption of NaOH is increased by the addition of sodium salts, the carbonate having the most pronounced effect, and the sulphate least. Fischer and Moore (Z. Chem. Ind. Koll., 1909, *5*, 197) had previously found that equimolecular salt solutions do not exert equal effects in retarding the swelling of fibres in alkali solutions; the retarding action of any salt is roughly proportional to the sum of the constituent ions.

In order of retardation of swelling, the anions are Cl, Br, NO_3, SCN, I, SO_4, PO_4 and the cations K, Na, NH_4, Mg, Ca, Cu, Fe.

The effect of additions of NaCl to the caustic soda solution was examined for cuprammonium rayon by Beadle and Stevens (8th Inter. Cong. Appl. Chem., 1912, *13*, 25), whose work is referred to on page 303; in the case of the region of maximum hydration at 5° C., the extent of swelling was only one-tenth of that which occurs in absence of NaCl. As the concentration of NaOH in the caustic soda solution increased from 15 to 25% at 5° C., in presence of 20% NaCl, the hydration diminishes, the NaCl absorption also diminishes, but the absorption of NaOH increases.

The greater adsorption of NaOH by cotton and rayon which occurs when a neutral salt is added to the aqueous solution of sodium hydroxide appears to be a similar phenomenon to that which takes place in the case of solutions of the substantive dyes.

The Effect of Alcohol

The absorption of NaOH by cellulose is stronger from alcoholic solutions than from aqueous solutions at the same temperature. This was observed by Briggs (Chem. Zeit., 1910, *34*, 455) who worked with *N/2* NaOH solution in 95% ethyl alcohol. This was suggested as a test for the degree of "hydration" of various forms of cellulose (compare page 386). The range of concentrations did not cover those which comprise mercerising liquor.

The washing of "soda-cellulose" with alcohol, referred to on page 285, only gives the amount of alkali retained when the sample is washed under the prescribed conditions. Some further work on these lines has been done by Rassow and Wadewitz (J. pr. Chem., 1923, *106*, 266) and Rassow and Wolf (Ber., 1929, *62B*, 2949), who pointed out that the most important point was to determine where the break takes place between removal of the excess alkali and the practically constant amount of alkali resulting from the decomposition of the alkali-cellulose. Heuser and Niethammer (Cellulosechem., 1925, *6*, 13) maintain that slight traces of water in the alcohol are apt to give erroneous results, but in any case the break in the curve of alkali absorption is not so sharp as with Vieweg's method for aqueous solutions of NaOH, so that the evidence is not so clear. (Heuser and Niethammer extracted the NaOH in a Soxhlet apparatus.) The method was found to give very high results when absolute alcohol was used in place of 95% alcohol, and it was assumed that alcohol causes deposition of NaOH on the alkali cellulose. The more nearly anhydrous the alcohol, the firmer does the NaOH appear to be fixed on the cellulose.

The absorption of sodium hydroxide from aqueous-alcoholic solution has also been studied by Vieweg (Ber., 1924, *50*, 1917), who found that a greater amount of alkali was absorbed at a given concentration of NaOH solution as the alcohol content of the solution increased; there appeared to be about four times as much alkali taken up in presence of 50% alcohol as with 10%. The change in titre method (whether correct or not) gave no indication of the existence of a compound. D'Ans and Jäger (Cellulosechem., 1925, *6*, 137), on the other hand, in the case of 10% alcohol, found a flat portion in the absorption curve between 16 and 24% NaOH, and even where higher amounts of alcohol were used, the rate of absorption of alkali was decreased in this region. This conflict of evidence is typical of the results from the change in titre method. However, it was confirmed that at any concentration of sodium hydroxide solution, the amount of NaOH taken up by the cellulose increased with increasing amounts of added alcohol.

Bancroft and Calkin (Text. Res., 1934, *4*, 159) confirmed again that considerably more sodium hydroxide is taken up from 95% alcohol solution than from an aqueous solution of the same concentration. A higher absorption might be expected on account of the lower solubility in alcohol bringing about a precipitation of the alkali on to the cellulose.

Even if the change in titre method was fundamentally sound, the formation of any alkali cellulose may be masked by the increased absorption of NaOH caused by the addition of alcohol.

The swelling of cellulose in sodium hydroxide solutions is less when alcohol is present in the solution; this has been confirmed by many workers, including Hess (Z. angew. Chem., 1925, *38*, 230), Heuser and Bartunek (Cellulosechem., 1926, *38*, 169), Beadle and Stevens (8th Inter. Cong. Appl. Chem., 1912, *13*, 25) and Tanemura and Miyoshi (J.S.C.I., Japan, 1930, *33*, 431).

Although there is some difference of opinion amongst the published results on the effect of alcohol on caustic soda solutions, it appears that the swelling of cellulose is lower than in purely aqueous solutions, probably on account of the lower degree of ionisation in the alcoholic solvent, and that the absorption of NaOH is increased by reason of the lower solubility of NaOH in alcohol.

Critical Review

Bancroft and Calkin (Text. Res., 1933, *4*, 119) reviewed most of the work on the action of sodium hydroxide on cellulose, and emphasised the point that the Vieweg " change-in-titre " method had been used by many investigators to calculate the total amount of sodium hydroxide taken up by the cellulose, in spite of its inherent error, as pointed out by Leighton (J. Phys. Chem., 1916, *20*, 32), due to the fact that cellulose absorbs water in addition to the alkali. The phase rule was unknown at the time of Vieweg's original work, but Bancroft and Calkin pointed out that even on the data of those who follow the Vieweg method a proper " stepped " curve is not obtained, so that there is no evidence for the formation of a compound in the mass. Heuser and Niethammer (Cellulosechem., 1925, *6*, 13), Heuser and Bartunek (ibid., 1925, *6*, 19), Dehnert and König (ibid., 1924, *5*, 107 ; 1925, *6*, 1), and D'Ans and Jäger (ibid., 1925, *6*, 137) all worked in the same way as Vieweg and obtained similar results.

Leighton (supra), Miller (Ber., 1907, *40*, 4903) and Joyner (J.C.S., 1922, *121*, 2395), on the other hand, believed that the process is one of adsorption. The first total adsorption data were those of Coward and Spencer (J.T.I., 1923, *14*, 28), but more material being available since that date, Bancroft and Calkin have used an algebraic relation to calculate back the change-in-titre data. The method of calculation is based on the following arguments:

Those investigators who followed the Vieweg " change-in-titre " method assume that the water in the supernatant liquor is constant, whereas the centrifuge or blotting-paper methods are directed towards a measure of the absolute amount of NaOH taken up. The difference between the two may be explained on the following basis:

Let G = Grams of solvent in NaOH solution at start.
X_0 = Mols. NaOH per g. solvent in outside solution at start.
X = Mols. NaOH per g. solvent in outside solution at end.
A = Mols. NaOH taken up by the sample.
B = Grams of solvent taken up by the sample.

The total initial NaOH is composed of the NaOH taken up by the solid phase plus the NaOH in the liquid phase at the end.

Substituting the above symbols it appears:

$$\text{NaOH} = GX_0 = A + X(G - B)$$

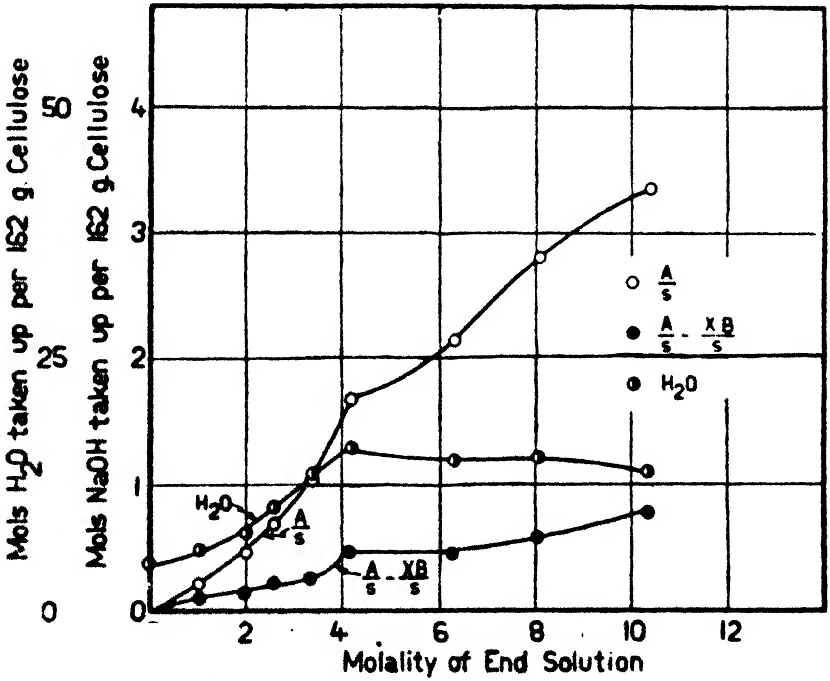
or $$GX_0 = A + XG - XB$$

which gives $$G(X_0 - X) + XB = A$$

If the symbol "s" denotes the mols. of cellulose in the sample, then

$$\frac{G(X_0 - X)}{s} + \frac{XB}{s} = \frac{A}{s}$$

The final values for the change-in-titre method (on the basis of 1 mol. cellulose = 162 g.) are given by $G(X_0 - X)/s$ and neglect the correction term XB/s, which is adsorbed solution. If no water were taken up, then B would be zero, and if, on the other hand, the solution was absorbed without change, then $G(X_0 - X)/s$ would be zero. The Vieweg method assumes that G is the weight of solvent at the end instead of the actual amount, G − B. The total amount of NaOH taken up is A/s.



Sodium Hydroxide and Water taken up by Cotton (Coward and Spencer's data).

FIG. 184.

NaOH AND H_2O TAKEN UP BY CELLOPHANE. BLOTTING METHOD.

(Data from Neale, J.T.I., *20*, 373 T (1929).)

Molality of end solution mols. NaOH/1000 g. H_2O	Total NaOH taken up $\left(\frac{A}{s}\right)$ mols. NaOH/162 g cellulose	Total water taken up mols. H_2O/162 g cellulose.	Change-in-titre. Amount taken up $\left(\frac{A}{s} - \frac{XB}{s}\right)$ mols. NaOH/162 g. cellulose
0·0	0·0	10·05	0·0
0·482	0·265	14·7	0·137
1·215	0·672	18·95	0·258
1·97	1·412	29·7	0·358
3·09	2·955	43·7	0·525
3·175	3·21	47·6	0·490
3·345	3·085	42·85	0·504
4·00	3·15	38·6	0·370
5·16	2·985	28·25	0·360
6·55	3·435	25·15	0·470
7·89	3·843	23·2	0·555
10·92	4·105	18·7	0·425
12·45	4·30	16·5	0·601
13·52	4·555	15·4	0·805
14·16	4·75	16·45	0·561
16·18	5·455	16·7	0·593
17·7	5·615	16·05	0·500
18·5	5·90	16·15	0·520
19·6	6·19	15·95	0·565
21·2	6·865	16·05	0·745
23·3	7·28	15·55	0·760

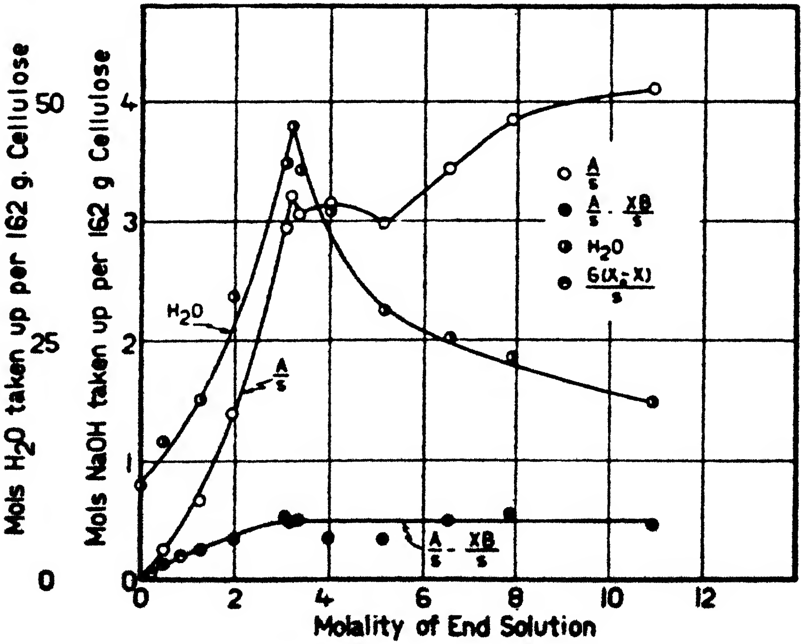
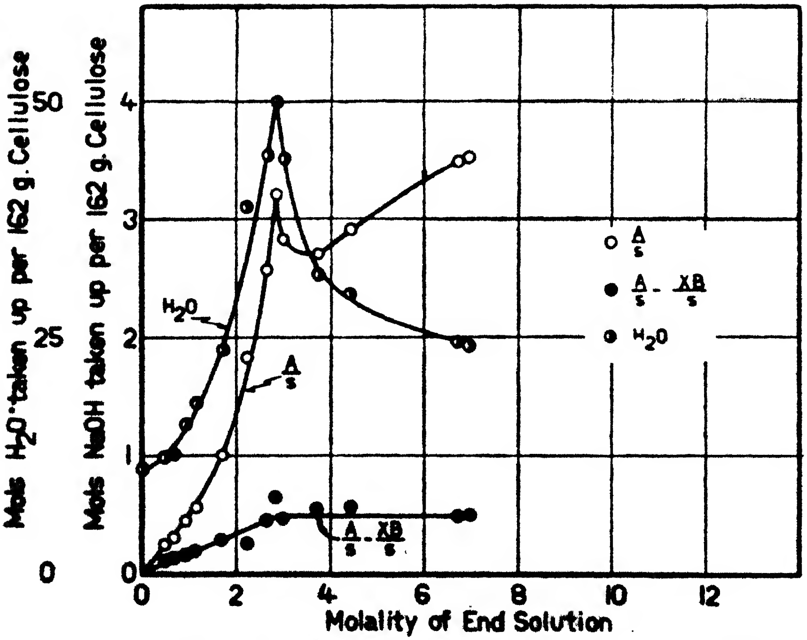


FIG. 185.—NaOH and H_2O sorption.

NaOH AND H_2O TAKEN UP BY CELLOPHANE.
BLOTTING METHOD.
(Data from Pfeffer, M.I.T., Thesis, 1932.)

Molality of end solution mols. NaOH/1000 g. H_2O	Total NaOH taken up $\left(\frac{A}{s}\right)$ mols. NaOH/162 g. cellulose.	Total water taken up mols. H_2O/162 g. cellulose.	Change-in-titre. Amount taken up $\left(\frac{A}{s} - \frac{XB}{s}\right)$ mols. NaOH/162 g. cellulose.
0·0	0·0	11·29	0·0
0·490	0·243	12·42	0·133
0·495	0·233	12·42	0·122
0·688	0·303	12·56	0·148
0·692	0·343	13·23	0·178
0·903	0·434	15·88	0·176
1·16	0·577	18·20	0·197
1·70	1·013	23·62	0·290
1·77	1·061	22·95	0·330
2·21	1·825	39·0	0·274
2·66	2·579	44·31	0·457
2·84	3·22	50·25	0·650
2·99	2·841	44·1	0·468
3·73	2·712	31·9	0·571
4·42	2·925	29·57	0·575
6·72	3·48	24·7	0·492
6·97	3·56	24·22	0·520

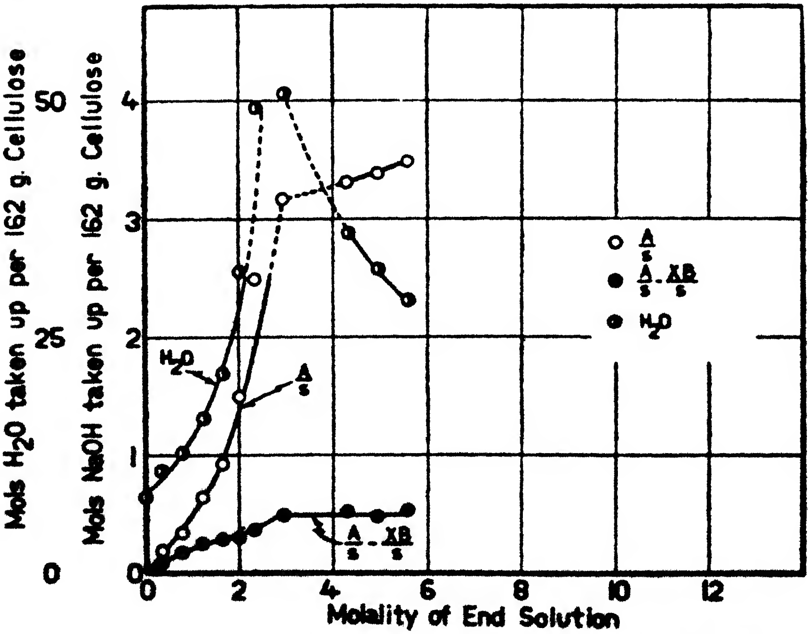


Sodium Hydroxide and Water taken up by Cellophane at 25° C. (Pfeffer's data).

FIG. 186.

NaOH AND H_2O TAKEN UP BY VISCOSE RAYON. CENTRIFUGE-BLOTTING METHOD.

Molality of end solution mols. NaOH/1000 g. H_2O	Total NaOH taken up $\left(\frac{A}{s}\right)$ mols. NaOH/162 g cellulose	Total water taken up mols. H_2O/162 g. cellulose.	Change in titre. Amount taken up $\left(\frac{A}{s} - \frac{XB}{s}\right)$ mols. NaOH/162 g cellulose
0·0	0·0	8·05	0·0
0·383	0·192	10·85	0·121
0·381	0·185	10·95	0·113
0·805	0·370	12·91	0·183
0·808	0·381	12·91	0·193
1·236	0·608	16·22	0·247
1·247	0·618	16·48	0·254
1·670	0·924	21·2	0·286
1·672	0·922	21·02	0·289
2·005	1·505	32·9	0·317
2·01	1·466	31·47	0·328
2·33	2·485	50·0	0·387
2·34	2·44	49·15	0·370
2·935	3·19	51·0	0·500
2·935	3·17	50·8	0·481
4·30	3·32	36·2	0·520
4·32	3·24	34·9	0·526
4·90	3·44	33·07	0·523
5·01	3·35	31·75	0·488
5·60	3·49	29·1	0·560
5·58	3·51	29·3	0·565



Sodium Hydroxide and Water taken up by Viscose Rayon 1 at 25° C.

FIG. 187.

The results of calculations made in the total adsorption data of various investigators are shown in Figs. 184–187. It will be noted that in every case the amount taken up by the change-in-titre is lower than the total amount, and also, that where sufficient data are available, a flat portion of the curve is apt to occur at 0·5 mol. of NaOH per mol. (162 g.) of cellulose. The amount of water taken up cannot be neglected—the fact that the water taken up with the sodium hydroxide passes through a maximum and then decreases has been noted by Beadle and Stevens (8th Inter. Cong, Appl. Chem., 1912, *13*, 25), Coward and Spencer (J.T.I., 1923, *14*, 28), Neale (J.T.I., 1929, *20*, 373) and Pfeffer (Massachussets Institute of Technology, Thesis, 1932).

This critical examination supports in large measure the previous work of Schwarzkopf (see page 301), which was not included in Bancroft and Calkin's considerations.

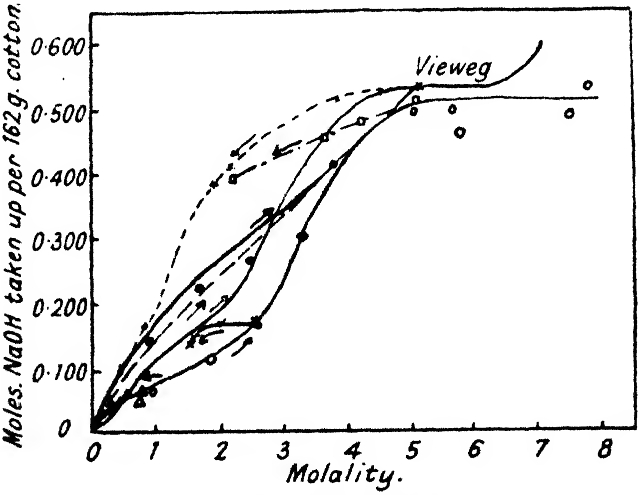


FIG. 188.—NaOH taken up by change in titre method.

From these considerations, Bancroft and Calkin concluded that the constant composition part of the curves obtained by the Vieweg method is the result of a balance between the increased sodium hydroxide and decreased water taken up.

Bancroft and Calkin (loc. cit.) also showed that when curves were drawn by plotting the amount of NaOH taken up against initial concentration, there was no passing back along the same curve when the sodium hydroxide was washed out, except in the case of very low concentrations ; the apparent adsorption of NaOH by cotton is a partially irreversible process. The curves for estimations with increasing concentrations of NaOH in the initial solution came together at 14% NaOH—the region of maximum swelling—where X-ray evidence shows the change from one lattice to another with consequent change in the degree of adsorption.

Neale (J.S.C.I., 1931, *50*, 177) has also expressed interesting opinions on the results which have led to the Vieweg hypothesis. Neale's view of the mercerising process (see page 325) is that cellulose behaves as a weak monobasic acid which forms a sodium salt according to the law of mass action in increasing amount with the alkali concentration. If the concentration of free alkali in the cellulose phase is not equal to that of the external solution, but is determined by the Donnan equation of membrane equilibrium, then it follows algebraically that the amount of salt formation is not equal to the preferential absorption of alkali from the solution, but at high concentrations is approximately twice that amount. On this account most of the " change-in-titre " evidence for the supposed formation of $C_{12}H_{19}O_{10}Na$ is rather to be interpreted as pointing to a substance in which one molecule of alkali reacts with each glucose residue.

CHAPTER EIGHTEEN

THE ABSORPTION OF WATER AND OF ALKALI

Pressure Methods

THE "pressure methods" are based broadly on the technique employed by Schreinemakers for the determinations of the composition of double salts in 1893 and by Sörensen in his investigations of egg albumen in 1917.

Van der Want (Chem. Weekblad., 1931, *28*, 507–510) has also applied this idea to the investigation of the system cellulose—caustic soda—water, in presence of a substance such as sodium chloride or iodide which is not absorbed by the solid phase.

A more detailed investigation along similar lines has been undertaken by Schwarzkopf (Z. Elektrochem., 1932, *38*, 353). The amount of common salt added to the system was 2 %, for it was established that proportions less than 5 % did not affect the amount of alkali taken up. The amounts of NaOH and NaCl retained by the cellulose, in this case ramie, after various amounts of pressure were plotted in a graph and the amount of NaCl extrapolated to zero. The NaOH line was also extrapolated and the following graph (Fig. 189), obtained from the result in 11·4 % NaOH solution.

A number of experiments with different concentrations of caustic soda covered the required range of values, but owing to the large errors involved in the direct estimation of the apparent absorption of water, this was calculated from the values obtained for the apparent and real absorption of alkali.

The apparent NaOH absorption is shown as NaOH/100 g. cellulose; the true NaOH absorption as $NaOH/C_6H_{10}O_5$, and the water held as $H_2O/C_6H_{10}O_5$. Temperature 20·5° C.

The true absorption of caustic soda is constant between 12 and 24 % NaOH corresponding to compound formation in molecular equivalents, i.e. twice the alkali of Vieweg, but the most interesting observation from these curves is the strongly marked maximum absorption of water from a solution of 13 % NaOH approximately, and this point corresponds to six molecules of water per $C_6H_{10}O_5$. There is a sharp fall in the water absorption after this point, in contrast to the behaviour of the alkali. (See Fig. 190.)

Schwarzkopf also established that alkali absorption is not a reversible reaction for in the case of mercerised ramie there

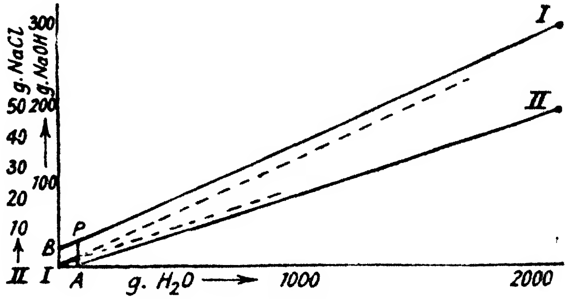


FIG. 189.—Absorption of NaOH.

OB is apparent NaOH absorbed, OA the water absorbed and AP the true alkali absorption. The dotted lines represent g. NaOH and NaCl in the solution.

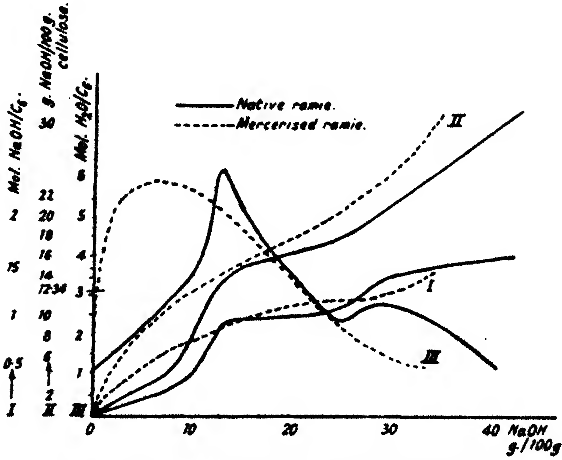


FIG. 190.—Absorption of NaOH and H_2O.

is no sign of the Vieweg " step " in the curve for true alkali-absorption. The curve for water absorption shows a broad maximum with mercerised ramie.

Another interesting fact observed by Schwarzkopf was that the horizontal part of the curve of true alkali-absorption for native ramie disappears if the experiments are done at 40° C.

These results of Schwarzkopf show that the deductions of many previous workers were wrong both from the qualitative and quantitative standpoints. Further work by Hess, Trogus and Schwarzkopf (Z. phys. Chem., 1932, *A162*, 187) emphasised the point that reversible reactions giving true equilibria are necessary for solving the question of the chemical nature of the cellulose-alkali complex, so that no work on native fibres by these methods is really pertinent and even the alkali absorption of mercerised cellulose cannot be considered a completely reversible reaction. Surface changes are also accompanied by changes in the interior of the micelles, which necessitate other methods of examination.

The most important part of this work is the realisation of the rôle and extent of water absorption which falls sharply after reaching its maximum, causing the alkali absorption to remain constant and give the " Vieweg effect." The compensation of the rise in absorbed NaOH by the fall in the absorbed water was first shown by Coward and Spencer (see page 310) ; Schwarzkopf's work emphasises the importance of the point, which is also supported by the later work of Bancroft and Calkin (see page 315).

Blotting Methods

The work of Beadle and Stevens (8th Inter. Cong. Appl. Chem., 1912, *13*, 25) appears to be the first attempt to investigate the absorption of alkali and the swelling phenomenon in the case of regenerated cellulose. The object of the research was primarily to determine the influence of temperature on the behaviour of regenerated cellulose towards caustic soda of different concentrations. The material employed was cuprammonium rayon of 360 denier ; small skeins weighing 0·2 g. were immersed in 20 cc. of the various solutions for periods of 30 minutes. The skeins were then removed and weighed after careful removal of any surface liquid. The total amount of alkali in each was determined by titration. The " hydration figure " was obtained by deducting the amount of NaOH found from the gain in weight. The " hydration " and the NaOH absorption figures were calculated to a percentage of the original weight of the cellulose.

The results are recorded in the table on page 304, and the NaOH absorption results are plotted in Fig. 191.

The results at 0° C. are of a different order and are influenced by the partial solution of the regenerated cellulose.

ABSORPTION OF WATER AND ALKALI.

NaOH in bath.	HYDRATION. Cellulose = 100.					NaOH ABSORPTION. Cellulose = 100.				
	at 5° C.	at 12° C.	at 20° C.	at 30° C.	at 40° C.	at 5° C.	at 12° C.	at 20° C.	at 30° C.	at 40° C.
1·0%	217	160	182	197	167	3	3	3	3	3
2·0	279	210	217	212	192	8	8	8	8	8
3·0	324	237	241	231	216	16	13	14	14	14
4·0	426	358	280	237	224	24	16	16	18	16
5·0	615	456	300	260	230	42	30	22	19	17
6·0	1380	600	310	278	238	83	44	25	23	20
7·0	1960	710	380	300	240	150	60	36	30	25
8·0	2576	1200	562	360	261	224	96	56	37	30
9·0	2699	1450	758	485	338	256	130	74	57	38
10·0	1800	1558	920	558	440	210	162	98	70	56
11·0	1483	1380	861	610	458	182	152	110	78	66
12·0	1310	1030	719	620	480	170	131	112	82	72
13·0	1200	885	620	519	412	161	120	102	82	76
14·0	1003	760	558	460	360	142	113	96	82	78
15·0	798	665	500	400	334	132	108	88	80	74
16·0	762	600	458	385	310	128	104	84	79	72
17·0	715	540	420	360	300	124	102	82	78	71
18·0	658	500	400	340	280	122	101	82	78	70
20·0	590	438	360	330	240	110	98	84	78	72
22·0	540	400	325	310	220	114	99	86	81	73
25·0	461	360	280	260	220	120	101	86	84	76

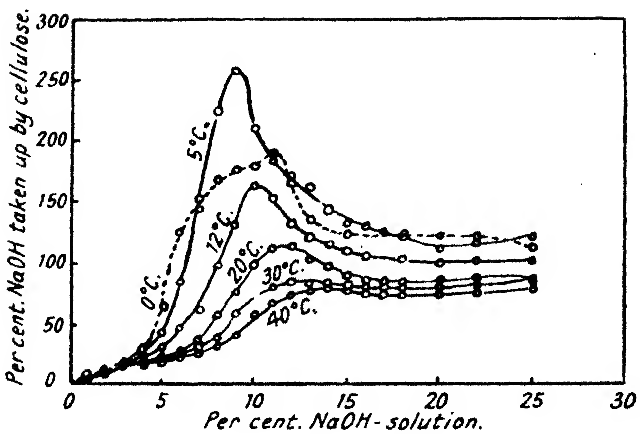


FIG. 191.—Alkali taken up by cuprammonium rayon.

It appears that for any given temperature between 5° and 40° C. a maximum absorption takes place, these maxima being greater the lower the temperature. Further, near each maximum the difference per degree of temperature is greater, the lower the temperature. In accordance with the older work on cotton, the maxima for absorption take place at lower concentrations as the temperature falls.

ABSORPTION MAXIMA.

Temperature.	Approximate Conc.
5° C.	9% NaOH
12	10% NaOH
20	11 to 12% NaOH
30	12 to 14% NaOH
40	14% NaOH

Neale (J.T.I., 1929, *20*, 373) considered that the difficulties of removing entrained liquor from any mass of fibres or filaments were so considerable that it was preferable to use sheet cellulose such as "Cellophane." The dried and weighed samples were transferred to NaOH solution and kept at 25° C. for two days. The swollen sheets were then removed from the solution, rapidly dried with filter paper and weighed in stoppered bottles to obtain the total swollen weight. The alkali absorbed was determined by titration with standard HCl, and the cellulose sheets were then washed for several days in distilled water to remove sodium chloride, dried and weighed as before. The experimental results are plotted in Fig. 192, and are given in the table on page 296, with certain additional calculations of Bancroft and Calkin, for convenience.

Other data obtained by the blotting method are given in the tables on pages 297 and 298 and shown in Figs. 186 and 187.

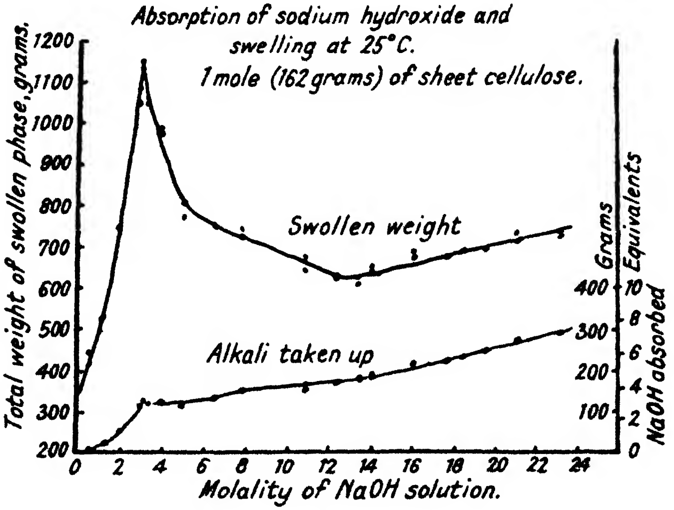


FIG. 192.—Swelling and absorption of NaOH by cellulose.

Removal of Excess Liquor

In connection with the possible formation of soda-cellulose, Champetier has proceeded along two lines of experiment which have yielded broadly similar results. The first publication (Compt. rend., 1931, *192*, 1593) described experiments of the following type: five grams of dry cotton linters were treated for 24 hours at a temperature of 18 to 20° C. with 200 cc. of an aqueous solution of sodium hydroxide of known concentration. The alkali cellulose was then subjected to progressive pressure, during which samples were withdrawn. For each sample the total weight, alkali, weight of cellulose after washing and drying at 100 to 105° C. were determined, from which data the amount of sodium hydroxide fixed by the cellulose was calculated for various initial concentrations. The number of molecules of NaOH fixed by each $C_6H_{10}O_5$ unit was plotted against the concentration of the initial sodium hydroxide solution, and the resulting curve showed four breaks, indicating that the fixation proceeds in a discontinuous series of definite molecular combinations:

$2C_6H_{10}O_5 . NaOH$; $3C_6H_{10}O_5 . 2NaOH$; $4C_6H_{10}O_5 . 3NaOH$ and $C_6H_{10}O_5 . NaOH$.

Similar conclusions were reached in a later publication (ibid., 1932, *195*, 499). Cellulose was immersed in a solution of the alkali and then pressed; when samples were taken at intervals during the pressing operation and analysed, the variation of the sodium hydroxide content of the samples, expressed as a function of the water content, gave a straight line. When these lines were drawn for different concentrations of the original solution, the composition of the addition compounds was determined by the points of intersection. (Compare page 375.) The same alkali celluloses described above were detected here, but the work is difficult to assess.

Centrifugal Methods

This method of attack was first adopted by Leighton (J. Phys. Chem., 1916, *20*, 32), whose criticisms of the change-in-titre methods have been referred to on page 294. Cotton was treated with aqueous solutions of sodium hydroxide and then centrifuged to remove the excess of solution. This method is only accurate if the centrifuged cotton may be considered as " dry." Leighton provided no experimental proof for his statement that it is possible to remove most, and possibly all, of the adhering liquid by centrifuging. Nevertheless, any error in the centrifugal method is smaller than the error from the Vieweg method.

The centrifuge employed by Leighton included a brass basket, 4·5 inches in diameter and designed to run at about 4,000 r.p.m. Experiments showed that in order to obtain equilibrium in the initial part of the experiment, three hours immersion, with constant shaking, in the alkaline liquor was adequate; the material was then centrifuged for one hour. The cotton was then treated with H_2SO_4 in a platinum crucible, ignited, and the NaOH weighed as Na_2SO_4. The results produce a smooth curve indicative of absorption and without evidence of compound formation. The Vieweg absorption curve was also checked—the difference between the titration curve and the gravimetric curve is most marked, as will be seen by reference to Fig. 193.

Coward and Spencer (J.T.I., 1923, *14*, 32) utilised a centrifuge whose acceleration was 2,900 times that of gravity as compared with 1,000 in the case of Leighton's centrifuge. Their results are of greater value on this account and also because they examined the performance of the machine. The greater part of the water associated with wet cotton was found to be removable in the first minute of centrifuging, the subsequent loss being very slow. The scoured fibres, which originally contained their own weight of water, gave the following results :

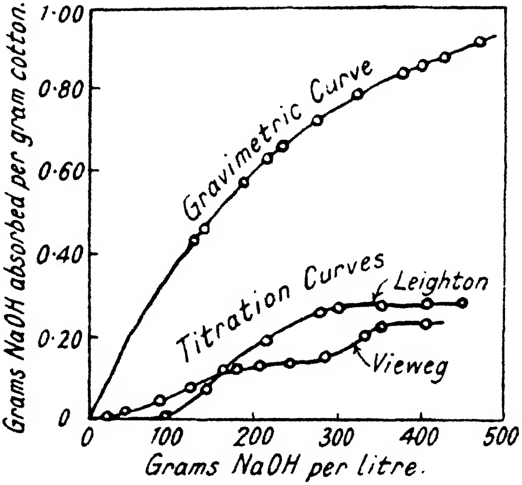


FIG. 193.—Comparison of gravimetric and titration curves.

RATE OF REMOVAL OF WATER.

Time (mins.)	0·25	0·5	1	2·5	5	6·5	10	15	25
Water retained (g./100 g.)	66·9	63·6	59·1	55·1	53	51·7	50·5	49·5	47·6

The weight of water retained is much higher than that absorbed from an atmosphere saturated with water vapour. It was deduced that most of the water retained after centrifuging is held in the substance of the cotton hairs as the results of experiments illustrated by Fig. 194. Curve *1* shows the water retention results, and curves *2* and *3* the results obtained when the cotton hairs had been well soaked in xylene and in alcohol respectively before centrifuging. Curve *4* shows the amount of water retained by glass wool of equal diameter under comparable circumstances ; hence the amount of entrained liquor must be very small after centrifuging.

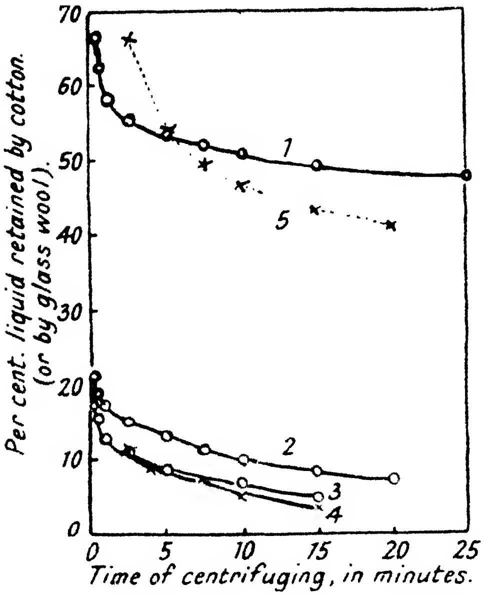


FIG. 194.—Water retention after centrifuging.

The observation that the amount of water discharged after one minute at 7,000 r.p.m. is comparatively small was confirmed for sodium hydroxide solutions also.

RATE OF REMOVAL OF LIQUOR.

Time (mins.).	Grams of solution retained by 100 g. of cotton.		
	Water.	20·1% NaOH.	48·8% NaOH
0·5	62	232	
1·0	58	226	
2·5	55	223	296
5·0	53	218	
7·5	52		288
10·0	50	216	
15·0	49	215	

As the viscosity of the strong NaOH solution is about 60 times that of water, experiments were made with castor oil, whose viscosity is about 1,000 times that of water ; the results are shown in curve *5* of Fig. 194. As no swelling of the fibre was observed, it follows that a high viscosity impedes the removal of liquor by the centrifuge.

However, the fact that a liquor which is 16 times as viscous as the strongest NaOH solution is only retained to the extent of one-sixth of the amount of the NaOH solution makes it evident that the greater part of the alkali solution retained has permeated the cotton hairs.

Scoured Egyptian sliver was immersed overnight in solutions of sodium hydroxide of the indicated weight-composition. The fibres were then centrifuged for 7·5 minutes at 7,000 r.p.m. The amounts of NaOH and water removed from the alkaline solutions of various composition were calculated from determinations of the weight of the cotton (dry), of the total centrifuged mass, and of the NaOH present in it as determined by titration. The results are shown in Fig. 195 and in the table.

ABSORPTION OF NaOH BY COTTON.

Initial composition of solution. Grs. NaOH/100 grs. solution.	Weight absorbed in grs./100 grs. cotton.			Composition of absorbed solution. Grs. NaOH/100 grs. solution.	Calculated volume of absorbed solution. Ccs./100 grs. cotton.
	Total.	NaOH	Water.		
0·0	52·3	0·0	52·3	0	52·3
4·0	73·5	5·6	67·9	7·6	67·4
7·4	99·8	11·1	88·7	11·1	88·6
9·4	133·3	17·3	116·0	13·0	116
11·9	177	26·2	150·8	14·8	151
14·3	222	41·6	180·4	18·7	183
20·1	220	53·2	166·8	24·2	173
24·4	239	69·5	169·5	29·1	180
29·3	236	82·9	153·1	35·1	171
39·0	251	112·9	138·1	45·0	169
48·8	288	155	133·0	53·8	(184)

There are two parts to each curve, the first representing a rapidly increasing rate of absorption of the solution, with increasing concentration. This ends at about 14% NaOH, which corresponds to the minimum concentration which gives well-defined commercial mercerisation. Beyond this point, the weight of solution increases more slowly and the rapidly increasing amount of absorbed NaOH is compensated for by the fall in the quantity of absorbed water. The volumes which would be occupied by the absorbed solutions have been calculated from the weight and composition of each of the sodium

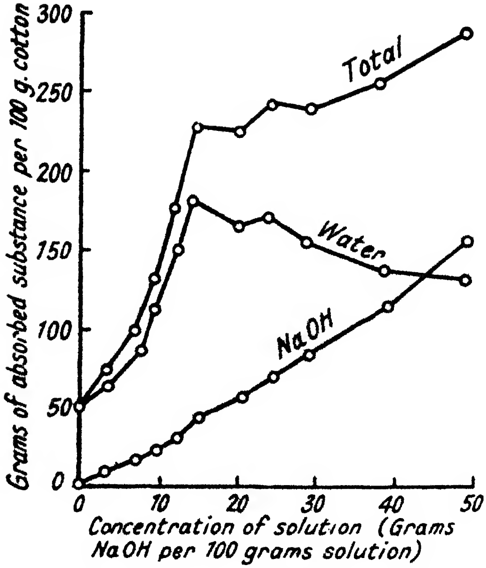


FIG. 195.—Absorption of sodium hydroxide by cotton.

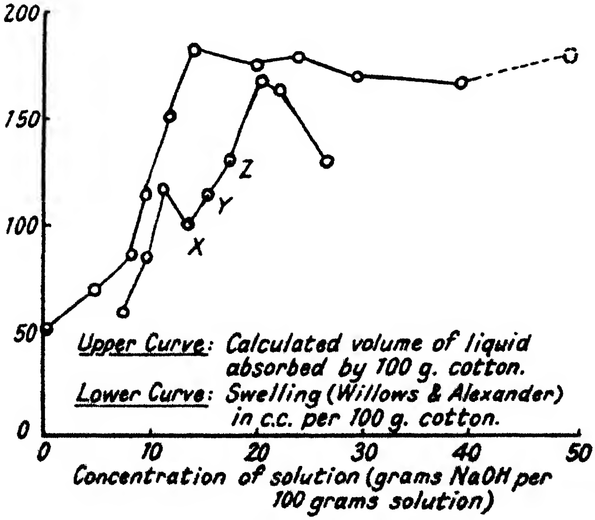


FIG. 196.—Volume of NaOH solution absorbed by cotton hairs.

hydroxide solutions absorbed by the fibre ; the results are shown in the last column of the table and in the upper curve of Fig. 196, where the lower curve is taken from the data of Willows and Alexander (J.T.I., 1922, *13*, 237—see page 56), and represents the swelling of cotton hairs in similar solutions. The two sets of results are of the same order of magnitude, but the agreement is not close ; however, in view of other results, the swelling may be represented approximately by the calculated volume of the absorbed solution.

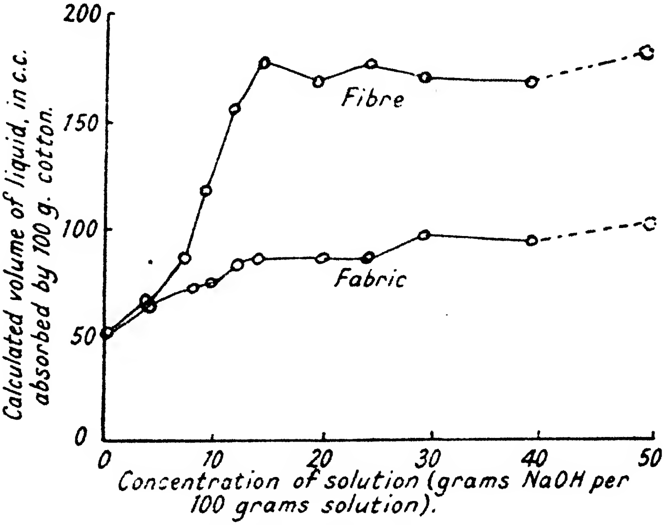


FIG. 197.—Volume of liquid taken up by fibre and fabric.

Coward and Spencer also carried out similar experiments with strips of fabric prepared from Egyptian cotton, and found that they were qualitatively affected like loose fibres ; the quantitative difference is due to the restrictions imposed on the swelling of the hair by the fabric structure. This point is emphasised by a comparison of the calculated volumes of fibre and fabric as shown in Fig. 197.

The fact that the volume of mercerising liquor absorbed by the loose fibres is twice that absorbed by the cloth (although they both take up equal amounts of water) has an important bearing on the question of the superiority of yarn mercerising over the treatment of piece goods. The difficulties of mercerising hard-spun yarn must, therefore, be associated with the impossibility of obtaining the highest degree of swelling, in addition to the more obvious difficulties of wetting and penetration.

Calculation of the preferential absorption of NaOH for both loose fibres and cloth gave the following results:

PREFERENTIAL ABSORPTION.

Original solution. G./100 g.	Grams NaOH per 100 g. of cotton. Fibre.	Fabric.
0·0		
4·0	2·9	2·1
7·4	4·3	3·4
9·4	5·9	4·7
11·9	6·7	7·5
14·3	13·6	11·6
20·1	12·9	13·5
24·4	17·3	16·4
29·3	22·6	19·2
39·0	28·6	25·5
48·8	33·0	34·8

The amount of preferentially absorbed sodium hydroxide was calculated from the following formula:

$$S - W \frac{pvd - gS}{(100 - p)\ vd - gW} \text{ grams per 100 grams cotton.}$$

in which S = Total NaOH absorbed by 100 grams cotton.
W = Total H_2O absorbed by 100 grams cotton.
p = Weight percentage of NaOH in the original solution.
p' = Weight percentage of NaOH in the residual solution.
v = Volume of original solution used (100 cc.).
d = Density of original solution used.
g = Weight of cotton used, in grams.
utilising the data previously obtained.

Approximately the same amount of preferential absorption of NaOH is obtained with fabric as with fibre in spite of the great difference in absorption of solution. The amount of preferential absorption appears to be roughly proportional to the concentration of the solution with which the cotton is in contact. (See Fig. 221, page 373.)

The conclusions drawn by Coward and Spencer are that the curves for the total sodium hydroxide absorbed (Figs. 195 and 198) give no indication of the formation of definite chemical compounds, nor are they of the form commonly found for simple absorption.

The number of grams of sodium hydroxide preferentially absorbed by 100 grams of cotton is given by the formula:

$$100\,\frac{vd}{g}\cdot\frac{p-p'}{100-p'}$$

This formula is essentially the same as one developed by A. M. Williams (Proc. Roy. Soc. Edin., 1919, *39*, 50). The data from this formula are shown by small crosses in Fig. 221, and are independent of the centrifuge method.

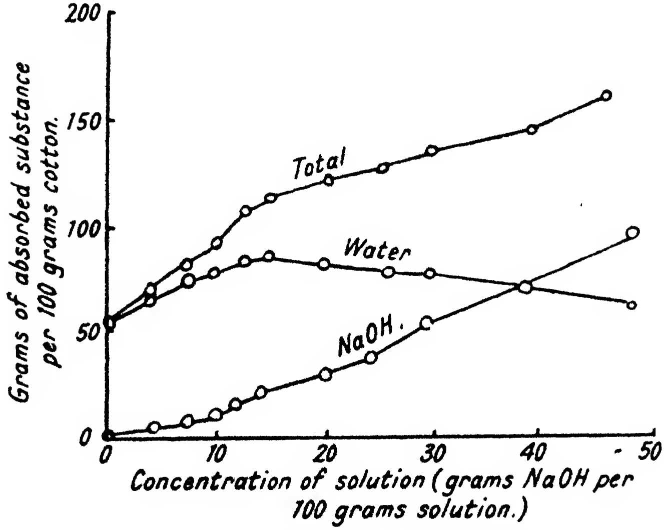


FIG. 198.—NaOH and H_2O taken up by cotton fabric.

As previously stated, Leighton assumed that he had removed most, and possibly all, of the adhering liquid by centrifuging, nevertheless he reported that the cotton he worked with retained about 400 % of water after centrifuging at 4,000 r.p.m. Coward and Spencer, by means of a more efficient centrifuge, were able to reduce the amount of water to something of the order of 50 %, whilst Bancroft and Calkin were able to obtain a figure of 42 % by a combination of the centrifuge and blotting-paper. The use of a high speed centrifuge was described by these investigators (Text. Res., 1934, *4*, 371), and when speeds of 15,000 r.p.m. were obtained with a cup radius of 2·5 cm. (a force of 6,300 times that of gravity) it was possible to reduce the amount of water in cotton to 17·1 %, by centrifuging for 15 minutes material which had previously been immersed in water for seven hours. It was also shown that the water absorbed by cotton from a saturated atmosphere of water vapour can be partially removed by centrifuging.

REMOVAL OF WATER FROM COTTON.

(After 138 hours exposure to saturated water vapour at 25° C.)

Time of centrifuging mins.	Water retained per cent.
0	23·8
1	19·1
3	15·4
5	12·9
7	12·4

Experiments with a machine which can remove water to an extent where the originally wet material contains less moisture than it can absorb from a saturated atmosphere are obviously of great importance in considering the sodium hydroxide taken up from aqueous solutions.

When this machine was applied to the study of the system water—NaOH—cotton, the results given in the table on page 316 were obtained. The values for "centrifuged liquid by difference" in the fourth and fifth columns were obtained by subtracting the values for "centrifuged cotton" in the second and third columns from the corresponding concentrations given under "initial concentration" and "assumed initial concentration." The value given under "solution in equilibrium with cotton" is a direct determination. The break comes at about the half-minute observation, showing that truly adsorbed liquor is being thrown off from the solid. This break may be made sharper (quarter-minute interval) by centrifuging a system containing much less supernatant liquor, as shown in the lower part of the table. From analyses of this type it is possible to determine the exact point where all the supernatant liquor is removed. The table on page 316 shows the calculated values for the true adsorptions obtained from centrifuge determinations with various initial concentrations of NaOH. The results are also shown in Fig. 199, from which it appears that the curve for adsorbed NaOH is smooth and shows no sign of the occurrence in mass of any definite chemical compound in stoichiometric proportions between sodium hydroxide and cellulose. It will also be noticed that, as Coward and Spencer found, the amount of water taken up by the cotton first increases with increasing sodium hydroxide and then passes through a maximum.

DETERMINATION OF TRUE ADSORPTION BY COTTON.

Time of centrifuging.	Centrifuged cotton.		Centrifuged liquid by difference.		Centrifuged liquid NaOH per gram H_2O
	NaOH per gram cotton.	H_2O per gram cotton.	NaOH	H_2O	
Initial concentration : 3,5971 g. NaOH per gram cotton, 18,379 g. H_2O per gram cotton.					
Mins.	Grams.	Grams.	Grams.	Grams.	Grams.
0	Solution in equilibrium with cotton.				0·18832
¼	0·5435	2,169	3·0536	16·210	0·18838
½	0·5315	2·099	3·0656	16·280	0·1883
1	0·5172	2·013	3·0799	16·366	0·18819
3	0·5108	1·983	3·0863	16·416	0·1880
Assumed initial concentration : 0·7008 g. NaOH per gram cotton, 3,000 g. H_2O per gram of cotton.					
Mins.	Grams.	Grams.	Grams.	Grams.	Grams.
0	Solution in equilibrium with cotton.				0·18832
¼	0·5435	2·169	0·1573	0·831	0·1893
½	0·5315	2·099	0·1693	0·901	0·1879
1	0·5172	2·013	0·1836	0·987	0·1860
3	0·5108	1·963	0·1900	1·037	0·1833

The calculated values for the true absorption are shown in the following table and also in Fig. 317.

TRUE ADSORPTION OF SODIUM HYDROXIDE AND WATER BY COTTON.

Molality of end solution.	Adsorption per gram of cotton.	
	NaOH	H_2O
M.	Grams.	Grams.
1·741	0·0767	0·701
3·421	0·3573	1·914
4·040	0·4938*	2·290*
4·708	0·5315	2·099
5·923	0·5923	1·894

* The quarter-minute centrifuging was too long, so these points have been obtained by extrapolation.

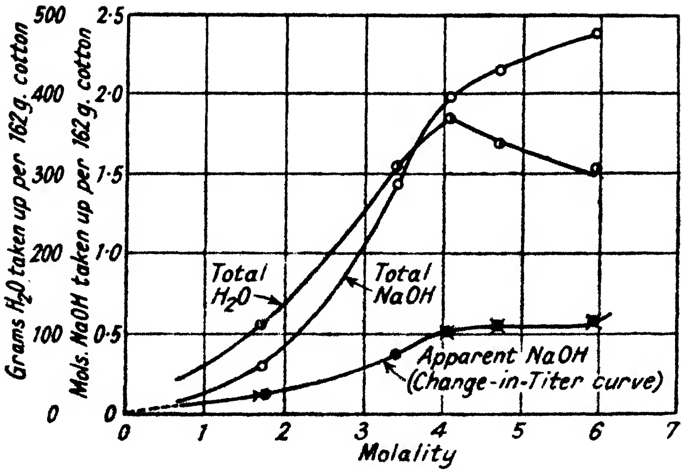


FIG. 199.—Absorption of NaOH.

The important feature of the results of Bancroft and Calkin is the high centrifugal action to which the system was subjected, circumstances under which the ratio NaOH/water in the solid centrifuged liquor is actually found to fall. This point was emphasised by Neale (J. Phys. Chem., 1935, *39*, 1245)—the steady fall in the concentration of adsorbed solution removed by powerful centrifuging is explicable if the concentration of free hydroxyl ion in the adsorbed solution is determined by the Donnan equation.

The data obtained by the change-in-titre technique has thus been severely criticised by later workers, and the flat portion of the Vieweg curve cannot be regarded as proof of compound formation. The main qualitative error lies in the assumption that no additional water is taken up during the swelling process. The alternative methods of investigation, where the liquor is removed by pressure or by the centrifuge, clearly show the inter-relation of decreasing water-absorption and increasing alkali-absorption at the point of maximum swelling, but these methods do not negative the idea of compound formation, they only demonstrate the absence of proof.

There are other methods of attack on the problem, including those of the X-ray investigators where any deep-seated effect as distinct from surface reaction, may be observed. Pure organic chemistry contributes the evidence of the action of sodio-ammonia to this most complex effect.

CHAPTER NINETEEN

DIRECT EVIDENCE FOR ALKALI-CELLULOSE

Sodio-ammonia

Kraus and White (J.A.C.S., 1923, *45*, 768) made use of the fact that metallic sodium is soluble in liquid ammonia to investigate the action on alcohols; they found that a sodium alcoholate was formed with the liberation of an atom of hydrogen according to the equation

$$R.OH + Na = R.ONa + \tfrac{1}{2}H_2.$$

This type of reaction was utilised by Scherer and Hussey (ibid., 1931, *53*, 2344) for application to cellulose. Careful determination of the amount of hydrogen liberated from definite amounts of sodium and cellulose showed that the latter, too, reacted in the above general manner.

One atom of sodium appears to combine with the cellulose quite rapidly, but the second and third atoms of sodium react more slowly. The evolved hydrogen can only come from the reaction; there is an absence of any appreciable amount of sodium amide. The maximum number of sodium atoms which combines with the cellulose was found to be three per glucose residue, and examination of the final product showed that it possessed in full the characteristic property of ordinary soda-cellulose, reaction with carbon disulphide to form xanthates.

Schorigin and Makarowa-Semljanskaja (Ber., 1936, *69*, 1713) studied this reaction more closely, but used the same methods. Since commercial liquid ammonia always contains some water-insoluble gases, the liquid was vapourised and re-condensed and all precautions taken to ensure a pure product. It was found that the reaction between cellulose and sodio-ammonia proceeded much more slowly than indicated by Scherer and Hussey and that there was no special reactivity of any one hydroxyl group. The reaction became sluggish towards the end.

The blue solution of sodium was completely decolourised by cuprammonium rayon in seven to eight hours, by sulphite cellulose in 24 hours and by cotton linters in 24 to 48 hours. The end of the reaction corresponds with the evolution of three atoms of hydrogen per $C_6H_{10}O_5$ residue and this amount was not increased by the use of an excess of sodium. It was established that when the tri-sodium cellulosate was treated with alcohol, considerable amounts of sodium were removed, leaving a product containing between one and two atoms of sodium per $C_{12}H_{20}O_{10}$, so that apparently the three sodium atoms are combined with different degrees of strength, but this may be due to the heterogeneous micellar nature of cellulose rather than to a difference in the chemical linkages. The tri-sodium cellulose showed less activity towards carbon disulphide than ordinary soda-cellulose ; the product of xanthation was not homogeneous and was insoluble in 4% NaOH solution. The number of molecules of CS_2 in ester union with 100 glucose residues was not more than 34, whereas in ordinary viscose it is 40 to 50, and in the case of tri-sodium cellulose might be expected to reach 300.

In addition to this direct evidence there is the point made by Karrer (Celluloschem., 1921, *2*, 124) that the evidence of chemical analogy is very strong. There is a large range of complex compounds formed by glycerol with the alkaline hydroxides, the alkaline earths and the heavy metals. The same power of complex-formation is shown by the sugars and the crystalline amyloses ; investigation of the system sugar/lime-water has shown that several complex compounds probably occur and the equilibria are attained so slowly that even partial elucidation of the relations is a highly involved problem. The case of cellulose is further complicated by factors, such as the morphology of the fibres, the colloid properties and the characteristic absorption effects. It is very difficult to account for some of the reactions of cellulose—the viscose reaction in particular—without assuming formation of a chemical compound between cellulose and the alkali.

The X-ray Evidence

Katz and Mark (Z. Electrochem., 1925, *31*, 105, 157) and Katz and Vieweg (ibid., 157) found that the spectrogram of cellulose which had been treated with concentrations of NaOH solution up to 8% was in no way different from that of native cellulose. In the case of a 12% solution of NaOH, the original picture had given place to a new one, whilst intermediate concentrations gave rise to a diagram in which the two spectra co-existed. In the case of ramie, the cellulose spectrum disappeared when concentrations of NaOH between 12·1 and 13·2% were used, whereas for cotton the change took place with concentrations between 15·4 and 16·5% NaOH; the breaks in Vieweg's curves occur at 12 and 16% for ramie and cotton respectively. The new bands which appeared were assumed to be those of a soda-cellulose compound. Similar effects were recorded for potassium and lithium hydroxides and the cellulose spectrum was found to disappear at approximately equimolecular quantities of absorbed alkali. Investigations of this kind were amplified by Susich and Wolff (Z. phys. Chem., 1930, *8*, 221); Hess and Trogus have published a series of papers on the action of alkalis on cellulose as shown by X-ray spectroscopy.

Na-cellulose I is formed when cotton is treated with 12·5% aqueous NaOH solution, according to Hess and Trogus (Z. phys. Chem., 1931, *B12*, 381); if the concentration of alkali is increased to about 19% NaOH there is no further change, but above this concentration the interferences of *Na-cellulose II* appear. Further increase in alkali concentration gives increasing amounts of Na-cellulose II, and the interferences of I tend to disappear when 22% NaOH is reached, although Hess and Trogus (Z. Elektrochem., 1936, *42*, 704) state that homogeneous Na-cellulose II is only produced by treating native cellulose with 30 to 45% NaOH solution at 60° C.

It is only Na-cellulose I and II which are produced by the direct action of alkali on native cellulose and they are of most importance in considering the question of compound formation. When either Na-cellulose I or II is washed with water until the alkali is removed, the X-ray diagram changes to the mercerised or "hydrate" modification.

According to X-ray evidence, only about 75% of native cellulose exists in the crystalline form, so that the amorphous or less organised parts of the structure may react with alkali without any perceptible change in the diagram. It is also known that in the case of other chemical reactions such as esterification, it is possible for from 45 to 70% of the native cellulose to be transformed without any change in the X-ray diagram, due to the fact that surface effects do not cause distinctive diffraction diagrams which necessitate multimolecular layers. Owing to the smallness of the crystallites, the extent of surface is such that about half of the cellulose may be changed before the interior starts to react. These two factors probably account for the fact that the swelling of cellulose and the absorption of 0·5 mols. of NaOH per $C_6H_{10}O_5$ in 8 to 9% NaOH solution, according to Schwarzkopf and to Bancroft and Calkin, is not accompanied by any change in the X-ray diagram. This region of concentrations marks reaction with the non-crystalline parts and with the surface of the crystallites.

The concentration of about 13% NaOH, however, marks the maximum shrinkage in length of the native fibres, the maximum swelling, and an absorption of NaOH at a ratio of 1 mol. per $C_6H_{10}O_5$ which presumably represents the composition of Na-cellulose I. The composition of Na-cellulose II is less certain and may possibly only differ from Na-cellulose I in that the amount of hydrate water is less. When Na-cellulose II is dried there is no change in the fibre diagram, but drying Na-cellulose I produces a new diagram, that of the so-called *Na-cellulose III*. This may also be formed by treating Na-cellulose I with absolute ethyl or methyl alcohol, but mixed products are obtained, as when "hydrate cellulose" is treated directly with 26 to 28% NaOH solution.

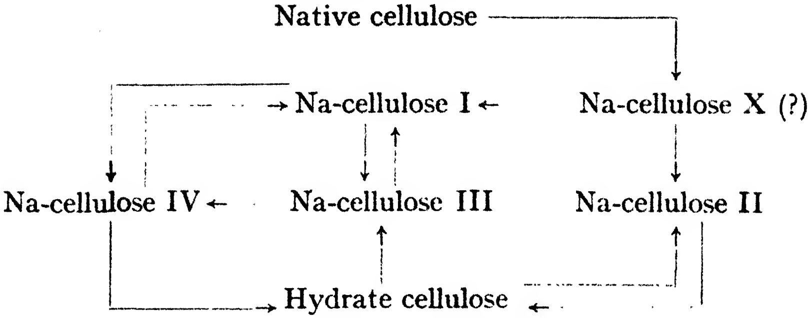
Na-cellulose II may be formed from hydrate cellulose by treatment with NaOH of more than 28% concentration at 20° C.

When Na-cellulose I is washed with alkali of diminishing concentration, the interferences are still apparent down to 10% NaOH solution; similarly Na-cellulose II is stable in solutions of NaOH from 21 to 6·6%, below which it gradually vanishes.

Hess and Trogus originally termed *Na-cellulose III* the product obtained by treating hydrate cellulose with dilute solutions of NaOH, 2·5 to 9·8%, but later altered this to *Na-cellulose IV*, which may also be formed by washing Na-cellulose I with NaOH solutions between 0·4 and 4·2% concentration.

These authorities regard Na-cellulose II as a derivative of native cellulose and Na-cellulose III as essentially a derivative of hydrate cellulose. Na-cellulose IV is formed by the gradual dilution of the system produced by the direct action of alkali on native cellulose, i.e. from Na-cellulose I or II.

In considering the mercerising process, Hess and Trogus postulate a labile hypothetical *Na-cellulose X*, which is included in the following scheme:



The process of technical mercerising follows the course—native cellulose, Na-cellulose X, Na-cellulose I, Na-cellulose IV to hydrate cellulose. The transformations Na-cellulose I to III and I to IV are regarded as reversible.

A so-called *Na-cellulose* V has been shown to be identical with Na-cellulose III by Schramek and Succolowsky (Kolloid Z., 1937, *80*, 129), who consider it to be an unstable intermediate modification produced by gradual dilution of the system produced by treating hydrate cellulose with concentrations of NaOH between 17 and 27%.

An important feature of the X-ray evidence is the absence of true equilibrium at any time, which renders phase rule considerations inapplicable to the question of compound formation. Further, the phase rule only applies to reversible equilibria, and Calkin (J. Phys. Chem., 1936, *40*, 27), for instance, has shown that mercerised cotton changes to Na-cellulose I in concentrations of NaOH between 10·8 and 11·85%, compared with 12·8 and 14·4% for unmercerised cotton. The formation of Na-cellulose I in both cases occurs in the region of maximum swelling, a point previously emphasised by Hess and Trogus (Z. phys. Chem., 1931, *B11*, 381). Before the evidence from X-ray work, the assumption of chemical combination between cellulose and alkali was based on hypothesis, but the appearance of a new X-ray picture indicates the existence of a chemical compound, for the effect is not that of sodium hydroxide superimposed on cellulose. The fact that the new picture gradually appears is in agreement with the idea that it is only when all the internal surface is available that true combination can occur.

The decrease in water absorption after the 13% concentration of NaOH, as shown by various investigators (see page 302), is accompanied by the change of Na-cellulose I to II, the latter being practically free from water of crystallisation according to Hess, Trogus and Schwarzkopf (Z. phys. Chem., 1932, *A 162*, 187). Na-cellulose II, unlike I, does not change on drying. However, it must not be assumed that all the water which swells the cellulose must be hydrate water associated with the salt formed by chemical combination between cellulose and alkali, for the greater part is probably in the intermicellar regions in much the same manner as is assumed for cellulose which has been swollen in pure water.

Bancroft (J. Phys. Chem., 1936, *40*, 43) pointed out that phase rule and X-ray methods are complementary and not contradictory. The use of mercerised cotton as a starting product eliminated the change from " native " to " hydrate " modification and gives a smooth absorption curve with no sign of two solid phases, but the X-ray results point to the existence of definite chemical compounds. It appears that mercerised cotton adsorbs NaOH as such from dilute solutions, a definite sodium cellulosate from stronger solutions and another definite sodium cellulosate from still stronger solutions.

According to the modern idea of the structure of cellulose, the lower concentrations of alkali do not enter into combination with the cellulose as the interior of the micelles is not available. The structure expands with increasing concentration of alkali and the interior of the micelles becomes more and more available; only under conditions of optimum swelling, when all the internal surface is available, can the taking up of alkali be considered a true chemical reaction.

CHAPTER TWENTY

THE SWELLING OF CELLULOSE

Two broad explanations are possible for the swelling of cellulose in alkaline solutions ; first, that swelling is due to molecular attraction with associated hydration in this instance, and secondly, that it is due to purely osmotic phenomena. Thermodynamical analysis is limited as the heat of swelling is masked by the heat of reaction.

For the first hypothesis it must be assumed, with some reason, that the alkali cellulose is more hydrated than the native cellulose. Maximum swelling concentration is the result of the attraction of the alkali cellulose on the one hand and the remaining free alkali on the other ; the hydration of the cellulose increases with the increased fixation of alkali in solutions of rising concentration. up to a certain limit, after which the free alkali exerts a dehydrating effect on the alkali cellulose to a greater extent.

Dissociation of the alkali ions from the alkali cellulose compound corresponds to an absorption of OH ions, and in this manner a negative charge results. The cellulose particles repel each other and absorb water, this absorption being greater the greater the charge. If, however, the dissociation of the alkali cellulose salt is forced back, then there is a reduction of the charge. Further, if the concentration of free electrolyte in the swelling liquor becomes high, then the charge of the cellulose particles is shielded by the free ions and the force of repulsion is diminished.

The swelling of cellulose in alkali solution as an osmotic phenomenon was put forward by Ristenpart (Färb. Zeit., 1912, *23*, 48), who argued that the fibre was surrounded by a hardened cuticle which acted as a dialysing membrane to induce osmotic action. When the fibre is steeped in NaOH solution the water tends to diffuse faster from the fibre to the liquid and the NaOH diffuses into the fibre. This osmotic condition demands an increased pressure which causes the fibre to swell.

This simple explanation has been subject to considerable modification later, but the osmotic basis still persists as the reason for the swelling of cellulose in alkali solutions; the modern view is due to the work of Neale.

In their examination of the swelling of cotton cellulose in solutions of sodium hydroxide, Collins and Williams (J.T.I., 1923, *14*, 287) drew attention to the analogy with the solubility of a heavy metallic hydroxide of pronounced acidic character. The point of maximum swelling (14·5% NaOH) corresponds to the point of maximum solubility, the reduction in swelling in more concentrated alkali to reduced solubility on account of repression of ionisation of the salt, the absence of swelling in acid to insolubility of the solid acid in the mineral acid solution, and the minimum swelling in approximately 10% HCl corresponding finally to an isoelectric point. From this aspect, the mercerised cellulose may be regarded as possessing preponderatingly acid functions, in agreement with its other properties, such as electrical charge in water and various aqueous solutions, heats of reaction with alkali and acid, and dyeing affinities.

Neale's theory of the swelling of cellulose in solutions of sodium hydroxide (J.T.I., 1929, *20*, 373) is based on the assumption that cellulose behaves as a very weak monobasic acid, and forms a sodium salt to an extent increasing with the concentration of the alkali. Excess alkali diffuses into the mechanically separable cellulose phase in amount determined by Donnan's thermo-dynamic equation of membrane equilibrium. The resulting unequal distribution of ions brings about an osmosis or movement of water which distends the cellulose until the osmotic pressure is balanced by the forces arising from the cohesion of the gel. When the alkali solution is replaced by a large excess of water, the sodium cellulosate is hydrolysed, the osmotic pressure falls, and the cellulose is recovered chemically unchanged, but permanently distorted if the osmotic pressure has been sufficiently high.

Owing to the unequal rates of diffusion of water and alkali, there are some curious complications, such as abnormal transient swelling and shrinkage of the material.

[The fundamental ideas of salt formation and of the distribution of diffusible ions according to Donnan's equation had previously been applied to the swelling of gelatin in dilute acid by Proctor and Wilson (J.C.S., 1916, *109*, 307)].

Now, as is well known, the Donnan theory refers to the distribution of diffusible ions in a system containing a non-diffusible ion. Briefly, where some restriction on the movement of one species of ion results in its uneven distribution, then all the other species of ions present in the system will also be distributed unevenly. Further, the theory leads to equations from which the exact distribution of the ions may be calculated.

Neale's Theory

Starting from the premise that cellulose is a very weak acid, it is possible to calculate the amount of acid converted into salt by making two assumptions. The first is that all the reactive points of the molecular network which constitutes cellulose are accessible to water and to alkali. The considerations of probability which are utilised as a kinetic basis for the law of mass action may be applied as in the usual case where both reactants are diffusible. The rate of re-association of hydrogen ion and cellulose ion will be proportional to the product of the concentration of hydrogen ions in the cellulose phase and to the number of acid points which have lost a hydrogen ion. These points would correspond to the anions in an ordinary electrolyte, but in cellulose they are joined together and to the undissociated units to form a network which has some mechanical rigidity. Hence if A is the negatively charged radicle corresponding to each acid hydrogen atom, it is possible to represent cellulose in dilute sodium hydroxide solution as follows :

$$\begin{array}{ccccccccccc} & & \mathrm{Na}^+ & & & & \mathrm{Na}^+ & & \mathrm{H}^+ & & \\ \mathrm{H} & & & & \mathrm{H} & & & & & & \\ -\mathrm{A} & — & \mathrm{A}^- & — & \mathrm{A} & — & \mathrm{A}^- & — & \mathrm{A}^- & — & \mathrm{A}- \end{array}$$

The cations may be imagined as moving continually along the network from point to point, replacing and being replaced by others, so that under given conditions a state of dynamic equilibrium is reached with the same total amounts of either sodium ions, hydrogen ions or undissociated acid points in existence at any instant. Each acid point will have a definite ionisation constant—defined as a function of time—when surrounded by water at a given temperature, and the degree of ionisation of the solid acid as a whole will be a function of the respective ionisation constants of the individual acid units.

The second assumption is that each glucose residue contains one acid hydrogen atom as indicated from consideration of the solutions of cellulose in cuprammonium hydrate. It is also assumed that the various ionisation constants of the acid groups are so nearly identical that they may be represented by a single mean ionisation constant, which is similar to that of a soluble weak electrolyte whose ions and molecules are considered to be separate and identical.

Some experimental data on sheet cellulose (cellophane) showed that one gram-molecule takes up about 181 g. of water at 25° C., so that the concentration of cellulose hexose units is 5·5 molal in the mechanically separable solid or gel phase.

The acid ionisation constant of cellulose K_A is given by

$$\left[H^+\right]\left[A^-\right] / \left[HA\right] = K_A$$

If the very small ionised fraction compared with the undissociated acid be neglected, for the particular form of cellulose used,

$\left[HA\right] = 5{\cdot}5$ (since 5·5 moles of cellulose take up 1,000 g. H_2O). Some preliminary measurements of the variation in concentration of the aqueous phase when the system cellulose-sodium hydroxide was diluted over the range 0·9 to 0·05 molal led to the conclusion that the ionisation constant of the sheet cellulose was $2{\cdot}0 \times 10^{-14}$ at 25° C. Later work (J.T.I., 1930, *21*, 225) gave a more reliable figure of $1{\cdot}84 \times 10^{-14}$, but the calculations which follow are not seriously affected by this accurate determination.

DISTRIBUTION OF SODIUM HYDROXIDE BETWEEN CELLULOSE AND WATER, AND THE MAXIMUM SWELLING FORCE DUE TO ITS REACTION WITH CELLULOSE ACID

A system consisting of cotton or other mass of cellulose immersed in a solution of caustic soda may be divided into " gel " and liquid phases containing the following molecular species:

Cellulose or Gel Phase. (1)	*Liquid Phase.* (2)
Undissociated acid HA	
Ionised sodium salt $Na^+ A^-$	
Ionised sodium hydroxide $Na^+ OH^-$	$Na^+ OH^-$
Hydrogen ion H^+	
Water H_2O	H_2O

where $A = C_6H_9O_5$

and for equilibrium we may write the following very approximate relations (more exact equations in terms of activity may be employed, but present knowledge does not suffice for their complete solution):

$$\left.\begin{array}{l}[\mathrm{Na}^+]_2 = [\mathrm{OH}^-]_2 \\ [\mathrm{Na}^+]_1 = [\mathrm{A}^-] + [\mathrm{OH}^-]_1\end{array}\right\}\begin{array}{l}\text{for electric neutrality,} \quad \ldots\ldots\ldots (1) \\ \text{neglecting } [\mathrm{H}]^+ \quad \ldots\ldots\ldots\ldots (2)\end{array}$$

$$[\mathrm{H}^+]_1[\mathrm{A}^-]/[\mathrm{HA}] = K_A \left(\begin{array}{l}\text{ionisation constant of cellu-} \\ \text{lose} = 2{\cdot}0 \times 10^{-14} \text{ approx.}\end{array}\right) \ldots (3)$$

$$[\mathrm{H}^+]_1[\mathrm{OH}^-]_1 = K_w \text{ (ionic product of water} = 10^{-14} \text{ approx.)} \quad (4)$$

Donnan's equation of membrane equilibrium, which determines the distribution of diffusible ions in the presence of a non-diffusible ion (A^-) gives in the present instance

$$[\mathrm{Na}^+]_1 \times [\mathrm{OH}^-]_1 = [\mathrm{Na}^+]_2 \times [\mathrm{OH}^-]_2 \ldots\ldots\ldots\ldots\ldots (5)$$

If it be assumed that the cellulose is prevented from swelling, so that its total concentration is unchanged when the gel is plunged into a solution of alkali, while the alkali diffuses into the gel until equilibrium is attained, we may write

$$[\mathrm{HA}] + [\mathrm{A}^-] = \text{constant} = C \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Owing to the unequal distribution of ions there will exist between the two phases an osmotic pressure, or a pressure tending to drive water from one phase to the other. In the present instance this is not calculable with precision, but may be written as very roughly proportional to the difference in total concentration of diffusible ions in the two phases.

P (tending to force water into gel phase)

$$= RT\left([\mathrm{Na}^+]_1 + [\mathrm{OH}^-]_1 - [\mathrm{Na}^+]_2 - [\mathrm{OH}^-]_2\right) \ldots\ldots\ldots (7)$$

Since $[\mathrm{Na}^+]_2$ and $[\mathrm{OH}^-]_2$ are equal, and $[\mathrm{Na}^+]_1$ and $[\mathrm{OH}^-]_1$ are unequal, whereas their respective products are equal (equation 5), the analogy used by Procter and Wilson, that the sum of two unequal sides of a rectangle is greater than the sum of two sides of a square of equal area, shows clearly that P is always positive. That is to say, in alkali of any concentration the gel tends to swell beyond the volume it occupied in water.

The solution of equations (1) to (7) gives relations between $[\mathrm{A}^-]$, $[\mathrm{Na}^+]_1$, P, and $[\mathrm{Na}^+]_2$, the known concentration of sodion in the outside alkali, involving the constants K_A and K_w. Thus

$$P = \left(\frac{C\beta\left[OH^-\right]_1}{1+\beta\left[OH^-\right]_1} + 2\left[OH^-\right]_1 - 2\left[Na^+\right]_2 \right) RT \quad \ldots\ldots (8)$$

$$\text{where } \left[OH^-\right]_1^2 \left(\frac{C\beta}{1+\beta\left[OH^-\right]_1} + 1 \right) = \left[Na^+\right]_2^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

and $\beta = K_A / K_W$ (the reciprocal of the hydrolytic constant).

C is the concentration of cellulose plus cellulose ion, and on the assumption that swelling is prevented is the same as the concentration of cellulose in the gel swollen in water.

The elimination of $\left[OH^-\right]_1$ from equations (8) and (9) would lead to such a complex relation between P and $\left[Na^+\right]_2$ that an indirect method was employed in order to arrive at a graphical solution.

Various values of $\left[OH^-\right]_1$ were assumed and the corresponding values of $\left[Na^+\right]_2$ and P calculated from these assumed values. If the value 2 is given to β (since $K_A = 2 \times 10^{-14}$), and 5·5 to C (i.e. the value in pure water), the curve shown in Fig. 200 was obtained as the theoretical expression for the

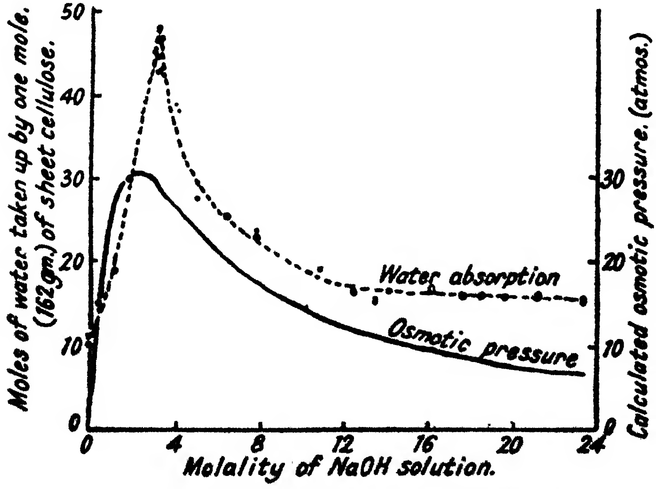


FIG. 200.—Swelling of cellulose in NaOH solution.

variation of osmotic pressure with alkali concentration, when swelling is prevented.

In actual fact the concentration of cellulose C decreases as the gel swells, and on this account the pressure never reaches the maximum value given by equation (7). A new set of concentration relations comes into operation when the swelling pressure is finally balanced by the cohesion of the cellulose. However, the assumption that C is constant simplifies the mathematical treatment and avoids the introduction of a complex relation between pressure and distention.

In effect, these assumptions mean that the calculated swelling pressure may be regarded only as a qualitative index of the tendency for water to enter the cellulose phase, and as such may be compared with the curve of actual water absorption, also plotted in Fig. 200, and taken from the data in the table on page 296. The points of similarity are such that the theory may be held to depict with fair accuracy the variation in the effect of alkali with change in concentration. There are certain points of disagreement which show that the simple theory is inadequate from a quantitative standpoint ; the swelling curve rises more sharply to its maximum than does the curve for calculated swelling pressure, but this is the usual relation between strain and stress in solids, the strain increasing more rapidly than the stress when the yield point is passed. On account of the approximations which the theoretical treatment involved and the uncertainty regarding the value of K_A, the discrepancy between the predicted maximum swelling in 2·7 M alkali, and the experimental peak lying between 3·1 and 3·3 M may have been expected. In the most concentrated solutions the swelling curve ceases to fall in accord with the simple theory.

As stated above, beyond a certain value of the osmotic stress, the swelling increases at a disproportionate rate, but in most solid systems, when the stress is low, the strain is proportional to the stress, so that in this region the swelling curve should have the same shape as the predicted osmotic pressure curve. The osmotic stress is low in dilute alkali solutions and the swelling curve at low concentrations has been followed by Neale (J.T.I., 1930, *21*, 225), in this case, by observing the increase in length of strips of sheet cellulose when immersed in alkali solutions of increasing concentration ; the strips were cut so that the length lay in the direction of maximum extension. In Fig. 201 the dotted line is the curve of calculated osmotic pressure and is displaced upwards to facilitate comparison. The rapid early rise of the swelling curve is probably due to a small osmotic pressure, not part of the simple theory, and due to the complete reaction with very dilute alkali of a small proportion of groups more acid than hydroxyl—perhaps carboxylic acid groups formed in the viscose process during oxidation of the alkali cellulose.

The swelling curve and the calculated curve agree as far as 2 % extension, i.e. in the region where the strain is low and is proportional to the osmotic stress. Beyond 2 % extension, the swelling increases more rapidly than the pressure.

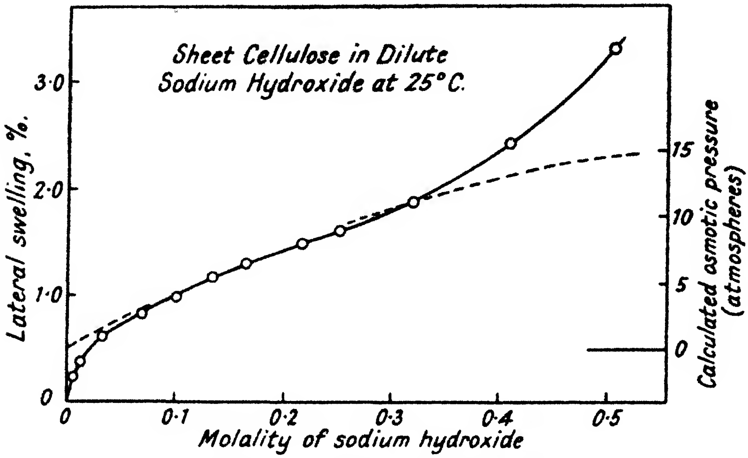


FIG. 201.—Comparison of observed swelling with calculated osmotic pressure.

Returning to the main treatment of more concentrated solutions of alkali as discussed by Neale in the former paper (J.T.I., 1929, *20*, 373), it has been shown that with the introduction of one arbitrary constant, and proceeding from first principles, the theory accounts in an approximate manner for the shape of the curve of water absorption for sheet cellulose. If the experimental values of water absorption are taken into account, however, the theory of Neale should permit of a less approximate calculation of the absorption of sodium from a solution of any concentration, and this calculation is susceptible to numerical check in a manner which is not possible in the case of osmotic pressure.

Thus considering one gram formula weight of cellulose, and, for more convenient use of the data of page 296, expressing concentrations as mole ratios (gram molecules per gram molecule of water = molality × $\frac{18}{1{,}000}$), the condition of electric neutrality is

$$\left[\mathrm{Na}^+\right]_1 - \left[\mathrm{OH}^-\right]_1 = \left[\mathrm{A}^-\right] \qquad \text{(10)}$$

and if W = number of moles of water per mole of cellulose in the gel phase

$$\left[\mathrm{HA}\right] + \left[\mathrm{A}^-\right] = 1/W \qquad \text{(11)}$$

Considering the ionisation of cellulose and of water (making the usual assumption and applying the law of mass action to the weak acid and its ion)

$$\left[\mathrm{A}^-\right] \Big/ \left[\mathrm{HA}\right] = \beta \cdot \gamma_{\mathrm{OH}} \left[\mathrm{OH}^-\right]_1 \times 55{\cdot}5 \qquad \text{(12)}$$

where γ_{OH} is the activity coefficient of the hydroxyl ion, $\beta = K_A / K_W$, and the factor 55·5 is introduced to allow for the conversion of molalities to mole ratios. ($\gamma_{\mathrm{OH}} \left[\mathrm{OH}^-\right]$ = activity of hydroxyl ion, i.e. that function of concentration for which the law of mass action should hold). The Donnan equation gives strictly

$$\alpha_{\mathrm{Na}_1} \times \alpha_{\mathrm{OH}_1} = \alpha_{\mathrm{Na}_2} \times \alpha_{\mathrm{OH}_2}$$

where α = the activity of the ion, or

$$\gamma_{\mathrm{Na}_1}\left[\mathrm{Na}^+\right]_1 \times \gamma_{\mathrm{OH}_1}\left[\mathrm{OH}^-\right]_1 = \gamma_{\mathrm{Na}_2}\left[\mathrm{Na}^+\right]_2 \times \gamma_{\mathrm{OH}_2}\left[\mathrm{OH}^-\right]_2 \ldots \quad \text{(13)}$$

where γ = activity coefficient of the ion.

Now since, in the two phases, the total ionic strengths are of the same order, it is probable that

$$\gamma_{\mathrm{Na}_1} \times \gamma_{\mathrm{OH}_1} = \gamma_{\mathrm{Na}_2} \times \gamma_{\mathrm{OH}_2} \qquad \text{(14)}$$

is a fair approximation, if we may extend to concentrated solutions the generalisation due to Lewis and Randall (J.A.C.S., 1921, *43*, 1112), that in dilute solutions the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength. We then obtain

$$\left[\mathrm{Na}^+\right]_1 \times \left[\mathrm{OH}^-\right]_1 = \left[\mathrm{Na}^+\right]_2 \times \left[\mathrm{OH}^-\right]_2 = \left[\mathrm{Na}^+\right]_2^2$$

and by elimination

$$\left[\mathrm{OH}^-\right]_1^3 + \left(\frac{1}{55{\cdot}5\,\beta \cdot \gamma_{\mathrm{OH}}} + \frac{1}{W}\right)\left[\mathrm{OH}^-\right]_1^2 - \left[\mathrm{Na}^+\right]_2^2\left[\mathrm{OH}^-\right]_1 - \frac{\left[\mathrm{Na}\right]_2^2}{55{\cdot}5\beta \cdot \gamma_{\mathrm{OH}}} = 0 \qquad \text{(15)}$$

and for the fraction of a mole of cellulose present as ionised salt

$$\mathrm{A}^- = \frac{55{\cdot}5\beta \cdot \gamma_{\mathrm{OH}}\left[\mathrm{OH}^-\right]_1}{1 - 55{\cdot}5\beta \cdot \gamma_{\mathrm{OH}}\left[\mathrm{OH}^-\right]_1} \qquad \text{(16)}$$

Inserting the value $\beta = 2$, the experimental values of the water absorption as an approximation to W, and the values of γ_{OH} corresponding to the alkali concentration (*see* p. 334), we may calculate $\left[OH^-\right]_1$ from equation (15) for any value of $\left[Na^+\right]_2$, and from this by equations (16) and (10) a first approximation to the total sorption of sodium from a solution of any concentration. The true value of W, however, is greater than the water absorption of the table on page 296, since the new water is formed by the reaction postulated, or more precisely the amount of water (W) present in the cellulose phase is defined by equations (10), the Donnan equation, and the stoichiometric relation :—

Total swollen weight =

$$\left\{18 + 162\left[HA\right] + 161\left[A^-\right] + 23\left[Na^+\right]_1 + 17\left[OH^-\right]_1\right\}W$$

The exact theoretical values obtained are given in the table on page 334.

The calculated values of sodium in the cellulose phase agree with those determined experimentally within 2 to 3%, except at the two lowest concentrations of alkali. In these two solutions there is comparatively little swelling of the cellulose and it is possible that some of the acid groups are not accessible to alkali ; as the gel swells with increasing alkali concentration the whole of it becomes accessible and obeys the law of mass action more precisely. The question of accessibility is of great importance in considering the behaviour of cotton hairs, but the agreement of the above data for sheet cellulose confirms the theory that the amount of sodium reacting chemically with cellulose is determined by the law of mass action, and that an amount of excess alkali determined by the water absorption and Donnan's equation is also present at equilibrium. Estimated on a constant weight of cellulose, the combined sodium increases steadily with the alkali concentration, whilst superimposed on the steadily rising concentration of the excess or uncombined sodium are the fluctuations of water absorption or gel phase volume, which are qualitatively explained by the more general form of the theory.

Cotton

Theoretical or precise experimental treatment is easier with sheet cellulose than with the cotton hair, where complications of structure restrict the scope, particularly because the form of the cotton hair precludes many kinds of accurate measurements. Neale has shown, however, that the behaviour

CELLULOSE AND SODIUM HYDROXIDE AT 25° C. CALCULATED AND OBSERVED ABSORPTION OF SODIUM.

Solution.	Solid or gel phase (per 162 g. cellulose).							Calculated.
Experimental.	Experimental mean values.		Calculated values.					
Mole ratio NaOH $[\mathrm{Na}+]_s = [\mathrm{OH}-]_s$	Total swollen weight g.	Moles of Na $[\mathrm{Na}+]_1$ W.	Moles of H_2O W.	Moles of $\mathrm{OH}-$ $[\mathrm{OH}-]_1$ W.	Moles of cellulose $A-$	Moles of $\mathrm{Na}+$ $[\mathrm{Na}+]_1$ W.	Activity coeff. assumed for $\mathrm{OH}-$, γ_{OH}	Mole ratio $\mathrm{OH}-$ in gel $[\mathrm{OH}-]_1$
0·0	343	0·0	10·0	6×10^{-9}	6×10^{-8}	0·0	—	6×10^{-10}
0·00868	432	0·265	14·7	0·057	0·229	0·286	0·70	0·00388
0·0219	530	0·672	19·3	0·243	0·495	0·738	0·70	0·0126
0·0354	751	1·412	30·2	0·785	0·67	1·455	0·75	0·0260
0·0556	1067	2·96	44·6	2·11	0·80	2·91	0·84	0·0474
0·0571	1148	3·21	48·4	2·38	0·82	3·20	0·85	0·0493
0·0615	1058	3·08	43·6	2·31	0·83	3·14	0·86	0·0528
0·0720	982	3·15	39·2	2·42	0·86	3·28	0·91	0·0619
0·0928	790	2·99	28·8	2·25	0·90	3·15	1·0	0·0782
0·1179	752	3·44	25·8	2·61	0·92	3·53	1·0	0·101
0·1420	734	3·84	24·1	2·99	0·93	3·92	1·0	0·124
0·1965	663	4·12	19·2	3·32	0·95	4·27	1·0	0·173
0·224	630	4·30	17·1	3·41	0·96	4·37	1·0	0·198
0·243	622	4·56	16·4	3·55	0·96	4·51	1·0	0·216
0·255	646	4·75	17·1	3·88	0·96	4·84	1·0	0·227
0·292	681	5·46	17·4	4·61	0·97	5·58	1·0	0·265
0·319	675	5·62	16·6	4·82	0·97	5·79	1·0	0·291
0·333	689	5·90	16·7	5·09	0·97	6·06	1·0	0·305
0·353	696	6·19	16·5	5·35	0·98	6·33	1·0	0·325
0·382	727	6·86	16·8	5·98	0·98	6·96	1·0	0·354
0·419	734	7·28	16·3	6·36	0·98	7·34	1·0	0·390

of the cotton hair, too, is at least in qualitative agreement with the theory (J.T.I., 1929, *20*, 373).

The exact shape of the swelling curve depends on a number of factors which are difficult to understand, but in agreement with the theory, it is well established that the swelling is at a maximum in solutions of moderate concentration.

The fact that the maximum occurs at a higher concentration of alkali than in the case of sheet cellulose may be explained in terms of the greater concentration of the cellulose phase as a whole, since less water is taken up with the alkali. The departure from predicted values in the swelling curves for cotton showing lower swelling at low concentrations of alkali may be due to the failure of the cotton hair to show visible increase in width in the early stages of swelling. The cellulose swells inwards, filling up the space occupied by the lumen and changing the shape of the cross-section from bean-shape to elliptical. Theoretical considerations require a single peak to the swelling curve and this is shown in the work of Calvert and Summers (J.T.I., 1925, *16*, 233), although other investigators,

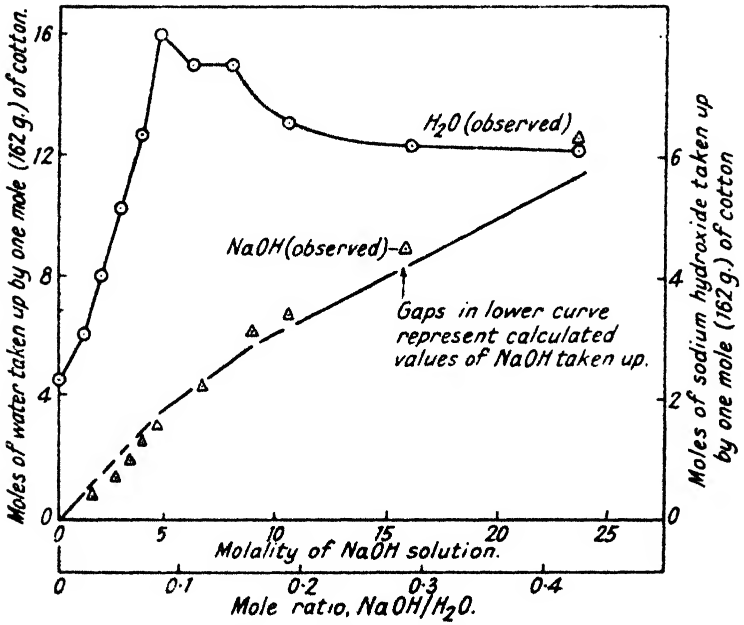


FIG. 202.—Absorption of water and of NaOH by cotton.

notably Willows and his co-workers (see pages 80 and 53), have found a double peak ; the theoretical interpretation of swelling by Neale does not take into account the botanical structure of the cotton hair or its complex response to various applied forces.

The amount of sodium hydroxide taken up by the cotton hair from aqueous solution is the sum of two factors, the sodium corresponding to the partial conversion of the cellulose into the ionised sodium salt, and the excess alkali which is determined by Donnan's equation of membrane equilibrium. Both the amount of sodium salt and the concentration of excess alkali in the cellulose phase increase steadily with the rising alkali concentration, but the actual amount of excess alkali is dependent on the water absorption or on the volume of the swollen cellulose phase. This means that the inflexions of the swelling curve indicated by theoretical considerations are impressed to a certain extent on the curve for alkali absorption. Equation (15) is the quantitative expression of these considerations and has been employed to calculate the absorption of sodium hydroxide from the absorption of water by cotton as determined by Coward and Spencer (J.T.I., 1923, *14*, 32—see page 310). The results of the calculations are compared with the observed values for alkali absorption in Fig. 202 and again a fair agreement is seen ; the discrepancies are no greater than one might expect from the assumptions made and from experimental error.

In the case of low concentrations of alkali, the theory requires greater alkali absorption than is actually observed, but this may be explained by incomplete accessibility of the unswollen cellulose, which is supported by the lessening and final disappearance of the discrepancy as the concentration of alkali approaches that of maximum swelling. It must also be granted that the more swollen mercerised cotton absorbs more alkali than unmercerised cotton (see page 386). For Neale's hypothesis, the total absorption of water and of alkali are the significant factors, and the preferential absorption is an arithmetical resultant. Now this can be determined by measuring the change in alkali concentration and has often been used to investigate the system alkali-cellulose (see page 285). The presence of a flat portion of the curve of preferential absorption has been regarded as evidence of definite compound formation. However, since the curve showing the amount of water taken up from the alkali solution (Fig. 195) is, on Neale's hypothesis, determined by a balance between the distending osmotic force and the resistance offered by the cotton hair, and as this curve shows inflexions corresponding to dimensional changes, these changes may cause slight inflexions in the curve of preferential alkali absorption, whilst the amount of combined sodium increases steadily. The calculation of the alkali sorption of cellulose according to equation (15) demonstrates that in this case the flat portion of the curve for total alkali sorption may be attributed to a fortuitous balance between the rising concentration of alkali and the decreasing swelling of the cellulose, rather than to discontinuous compound formation.

CHAPTER TWENTY-ONE

THE HEAT OF REACTION

THE fact that heat is developed when cotton is treated with moderately concentrated solutions of sodium hydroxide was one of the many general observations arising from the technical process of mercerising. The heat effect is not sufficiently pronounced in scoured or bleached material to warrant special cooling devices, but in the case of grey material the rise in temperature may become considerable in view of the additional heat produced by the action of the alkali upon the size in the goods. It is, therefore, general practice to adopt some cooling system, as opposed to actual refrigeration, in order to maintain the alkali at room temperature. The effect of low temperatures is described on page 104.

Smetkin (Nachrichten d. Ges. f. Ford. d. Manufaktur. Ind., Moskau, 1914, page 206) examined the mercerising process under works' conditions and found that the heat of reaction increases with increasing concentration of alkali and that there was little difference in this respect between ordinary and mercerised material.

Scientific examination of the heat of reaction was first attempted by Vignon (Compt. rend., 1890, *110*, 909) using an ordinary calorimetric method. 6·5 calories were evolved when 1 g. of unbleached cotton thread with full moisture content was added to *N*. NaOH solution. Rosenbohm (Kolloid Beihefte, 1914, *6*, 177) used an ice-calorimeter and obtained a result of 9·6 calories per gram for cellulose in the form of completely dried filter paper and 20·8 calories per gram for dried cotton waste. Various other solids were examined.

The first systematic examination of the effect of solutions of NaOH of various concentrations on the one solid, cellulose, in the form of cotton hairs were made by Barratt and Lewis (J.T.I., 1922, *13*, 113). A special apparatus was designed for these measurements, because the amount of heat to be measured is small and is only slowly evolved, and the corrections to be applied to any thermometric measurement become increasingly important and difficult to determine with any degree of accuracy. An electrometric method was, therefore, utilised. The cotton used was Egyptian sliver which had been " kiered " for five hours under a pressure of 20 lbs. per square inch in 1 % solution of NaOH, well washed and allowed to dry. Great care was taken in the maintenance and measurement of the moisture-content, which was 5·1 % of the weight of the cotton. The main conclusion of the investigation was that the heat of mercerisation of cotton by NaOH solutions increases with the strength of the solution but is not proportional to it. This is shown in Fig. 203, which contains two inflexions between 10 and 15 % NaOH and at about 30 % NaOH, i.e. between 22 and 34° Tw. and at 55° Tw.

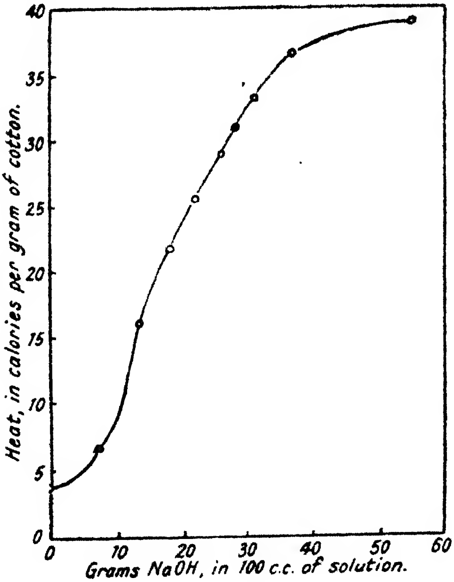


FIG. 203.
Heat of reaction of cotton and NaOH.

The lower point is that at which true mercerisation begins, as demonstrated by swelling in section or contraction in length of the hair. The higher point is near the upper limit of solutions ordinarily employed in mercerising.

Barratt and Lewis (supra) also examined the rate at which heat is evolved on the addition of cotton to NaOH solutions of various concentrations. With solutions of density below 1·20 and above 1·125 all the heat is given up in the first two minutes, but outside these limits the time required is much greater. For example, in the case of a solution of 55% strength some 20 minutes is required. (The concentrations of NaOH in the above paper are given as grams of NaOH in 100 cc. of solution.)

D'Ans and Jäger (Kunstseide, 1925, *7*, 252) in the course of work on the action of NaOH on the various forms of cellulose, found that in the case of cellulose with a moisture content of 6%, the heat of wetting in water was 2·6 cals. per gramme, and in 17% NaOH solution (volume %) it was 24 cals. per gramme.

The method of Barratt and Lewis was improved by Neale (J.T.I., 1929, *20*, 373), whose adiabatic apparatus appears more suitable for determination of the slow heat effects typical of the region of high concentration. In this case the cellulosic material employed was conditioned by standing for several weeks over alkali of the concentration with which it was to react, as this method probably reduces to a minimum heat effects which might arise in the case of dry cotton from hydration of the hydroxyl groups, i.e. heat of wetting, and in the case of over-moist cotton from dilution of the alkali by excess of water. The three types of cellulose examined were (*a*) American Upland sliver which had been boiled for 10 hours at 40 lbs. pressure in 2% NaOH solution, (*b*) the same material after treating with 4·4 *M* (15%) NaOH solution at 25° C., washing and drying at room temperature, and (*c*) 300 denier viscose rayon. The approximate time for complete reaction with the alkali was less than five minutes for concentrations up to 10 moles per 1,000 g. of water. Above these concentrations the time varied according to the material treated as shown on page 341.

Neale's determinations are also shown in Fig. 204.

In order to compare the results of Barratt and Lewis (loc. cit.) with those of Neale (supra) it is necessary to make a small correction to allow for the fact that the former worked with cotton at 5·1% regain. If this allowance is calculated from the absorption data of Urquhart and Williams (J.T.I., 1924, *15*, 559), agreement is found in the case of soda-boiled cotton up to an alkali concentration of 10 molal. Above this concentration, the curve of Barratt and Lewis indicates little increase in the evolution of heat, whilst that of Neale shows a steady rise towards the highest concentrations. (The data of Barratt and Lewis include only a single measurement beyond 10 molal alkali.)

HEAT OF MERCERISATION.

Concentration of NaOH moles per 1,000 gm. H_2O.	Final Temperature °C.	Actual gram calories observed.	Kg. calories per mole (162 g.) cellulose.	Mean.	Approximate time for complete reaction (minutes).
VISCOSE ARTIFICIAL SILK.					
1·66	24·5	19·1	1·88	1·86	< 5
	24·8	38·2	1·84		
2·49	24·7	51·5	2·43	2·41	< 5
	25·1	50·8	2·38		
4·13	25·2	20·1	3·25	3·17	< 5
	25·2	19·1	3·10		
6·40	25·2	50·9	4·20	4·19	< 5
	25·4	53·4	4·18		
8·53	24·8	63·5	6·12	6·00	< 5
	25·0	70·4	5·88		
11·35	24·7	65·6	7·30	7·38	< 5
	25·0	89·8	7·45		
12·33	24·8	83·1	8·31	8·23	< 10
	25·2	106·9	8·15		
13·7	26·1	157·8	11·50	11·61	100
	25·0	182·0	11·72		
20·3		Too slow to measure.			>500
SODA BOILED COTTON SLIVER.					
0	24·9	0·5	0·04		
	24·9	0	0		
2·195	24·0	10·4	0·558	0·562	< 5
	24·05	7·82	0·565		
2·99	24·6	16·25	1·30	1·24	< 5
	24·7	14·3	1·18		
4·02	24·5	54·6	2·78	2·73	< 5
	24·7	50·5	2·68		
4·48	24·8	55·5	3·13	3·10	< 5
	25·2	47·0	3·06		
9·26	25·5	86·1	5·88	5·78	< 5
	25·5	73·0	5·68		
13·26	25·1	129·9	8·10	8·00	10
	25·4	95·8	7·90		
22·14	26·4	168·9	12·3	12·45	100
	26·3	180·0	12·6		
SODA BOILED COTTON SLIVER "MERCERISED" IN 15% NaOH AT 25° C.					
2·20	25·2	13·6	0·720	0·72	< 5
2·40	24·9	17·1	0·95	0·99	< 5
	25·0	26·7	1·03		
4·13	24·8	56·2	2·75	2·76	< 5
	25·0	47·7	2·77		
20·3	24·6	137·0	13·54	13·55	150
	24·8	179·0	13·56		

These determinations of Neale formed only part of a larger work on mercerising, in which he regards cellulose as a very weak monobasic acid which forms a sodium salt to an extent increasing with the concentration of the alkali. On this hypothesis it is possible to calculate the heat effect per mole of cellulose ($C_6H_{10}O_5$), making allowance for the heat of dilution of the alkali by water formed during the neutralisation. The heat of dilution of sodium hydroxide is known. The heat of formation of water from its ions is 13·65 cals. and the negative heat of dissociation of the very weak cellulose acid was taken by analogy with a simple sugar, to be approximately 10·4 cals. The total heat effect per mole of cellulose converted into salt, plotted against the concentration of the alkali present in large excess, is shown in Fig. 205.

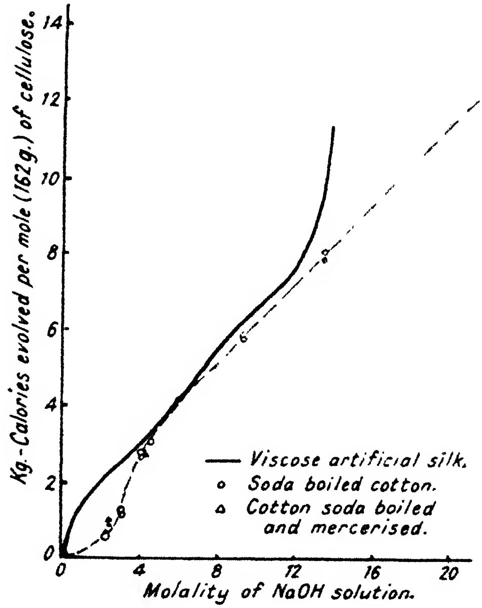
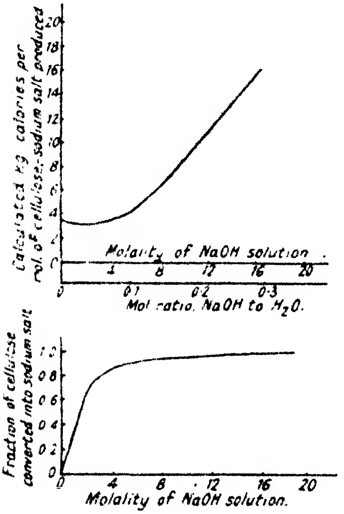


FIG. 204.—Heat of reaction between cellulose and NaOH.

The curve falls below its zero concentration value of 3·25 cals. in the region where the heat of dilution of the alkali is negative, but at high concentrations the heat effect increases rapidly owing to the increasing internal energy of the less hydrated alkali and the large positive heat of dilution of the solution. These considerations apply generally when an acid reacts with a large excess of concentrated alkali.

The fraction of cellulose converted into sodium salt at given concentrations of alkali, calculated from theory, is shown in Fig. 206 ; for the method of calculation the original paper should be consulted. (J.T.I., 1929, *20*, 391.)



FIGS. 205 and 206.—Calculated heat effects for neutralisation and conversion to Na salt.

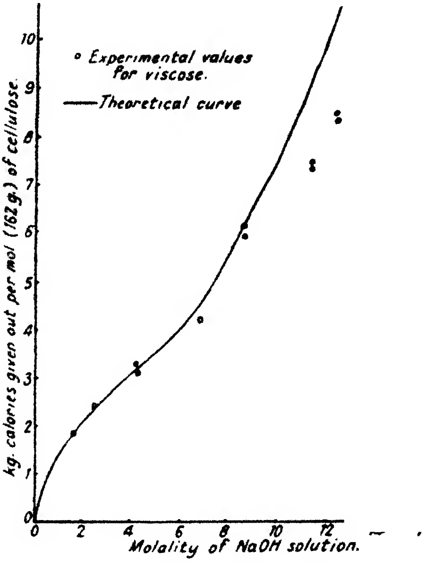


FIG. 207.—Comparison of theoretical and practical data ; the former are derived from Figs. 205 and 206.

The theoretical heat effect per mole of cellulose employed is obtained from the product of this reacting fraction and the total heat effect. The results are plotted in Fig. 207, and compared with the experimental values for viscose. It may be concluded that in the case of viscose and sodium hydroxide, the heat of reaction curve may be explained in terms of the simple theory of salt formation, one mole of sodium reacting with each $C_6H_{10}O_5$ equivalent.

The rapid rise in the evolution of heat at high concentrations of alkali has also been qualitatively considered by Neale as arising from the greater internal energy of sodium hydroxide in concentrated solutions, compared with its state of complete hydration in dilute solution, and the dilution of the strong alkali by water arising from the chemical reaction and water originally bound to the molecule of reacting alkali. The agreement between theory and experiment at low alkali concentrations may indicate that the heat of reaction curve of viscose approximates to the true curve for cellulose when the active mass is identical with the total mass. On this basis, the lower values given by cotton may be explained in terms of an

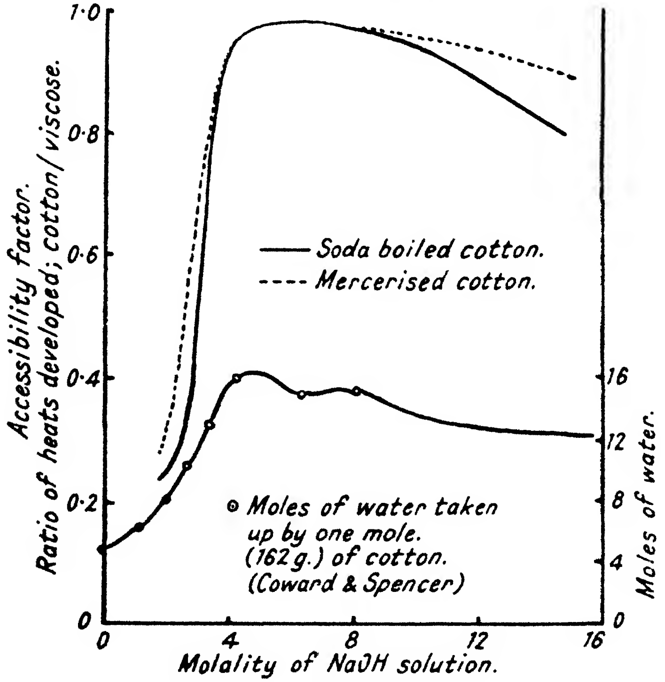


FIG. 208.—Accessibility factor.

"*accessibility factor*"—the fraction of the total number of reactive groups accessible to a given reagent. In this instance, the factor is the number of accessible groups in a given form of cellulose compared with the number in viscose cellulose. This factor will vary with the amount of swelling of the cellulose and therefore with the alkali concentration. The curves of Fig. 204 (see page 342) supports this idea qualitatively, since cotton gives out less heat than the more accessible viscose at low and high concentrations of alkali where the swelling is not very great, but gives the same amount of heat over the concentration range where the swelling of cotton is at a maximum.

Similarly, cotton which has been mercerised, washed and dried, gives out more heat than the untreated cotton in dilute and concentrated solutions of alkali, but all three forms of cellulose react with solutions causing maximum swelling of cotton with the same evolution of heat.

This point is expressed in a more quantitative manner by Neale in Fig. 208, where the accessibility factor (heat of reaction divided by heat of reaction of viscose) is plotted against the alkali concentration.

The graph also shows a comparison with the swelling of cotton as established by Coward and Spencer (J.T.I., 1923, *14*, 32), for the factor increases as the swelling increases and falls again as the swelling falls at high concentrations of alkali.

Tschilikin (Textilber., 1933, *14*, 404) is of the opinion that the heat liberated is not the so-called heat of mercerisation, but is due to the absorption of sodium hydroxide by the cellulosic material. His first results in 1913 showed that during mercerisation with NaOH of 30° Bé. about 4 Kg. calories were liberated per $C_6H_{10}O_5$. The experiment was repeated with washed and dried mercerised cellulose and gave the same result.

In order to establish whether the course of the heat of reaction curve corresponded to that of the absorption of NaOH by the fibre, a specially calibrated calorimeter of the Termochemischen Luginin-Laboratoriums was utilised. The data are referred to $C_6H_{10}O_5$; Egyptian cotton was used throughout. Preliminary experiments showed that with ordinary and with dry cottons the heat of wetting is different. Ordinary cotton with a moisture content of 5·8 % developed 704 calories on wetting in distilled water, whilst the same cotton which had been completely dried developed 1,319 cals. The mercerised dried cotton, on the other hand, developed 2,351 cals. Similar figures were found when the cotton was immersed in 50 % aqueous ethyl alcohol. The amount of heat developed depends on the degree of purity of the cotton, for water-boiled material gave 1,432 calories when immersed in a solution of NaOH containing 31 g. per litre, whereas cotton which has been extracted with alcohol gave 977 calories in a similar solution.

With low concentrations of NaOH, the divergence from the heat of wetting in water is negligible, but with higher concentrations of NaOH there is a considerable difference; in the case of undried unmercerised cotton the heat of wetting in water was 794 cals., and in NaOH solution containing 382 g. per litre it was 6,840 cals.

The results for mercerised and unmercerised cotton run in the same way, but the development of heat is greater in the first case ; at concentrations of about 400 g. and 500 g. per litre the results coincide, the development of heat being influenced by the absorption of water and by the partition of the NaOH between the water and the cotton. Mercerised cotton being more highly dispersed, has a higher absorptive capacity and, therefore, develops more heat. The difference in the development of heat during mercerising of mercerised and unmercerised cotton corresponds to the difference in the heat of wetting. Repeated mercerising does not increase the mercerising effect, yet the heat developed on subsequent treatments is not only the same but somewhat higher.

In the process of mercerisation, the concentration of the NaOH plays a most important part, and with increasing concentration the amount of heat evolved increases also, but Tschilikin's results appear to show that the amount of heat is not dependent on the amount of NaOH which has been absorbed by the fibre. After the maximum absorption of NaOH has been reached the development of heat still continues with more concentrated solutions of sodium hydroxide.

The presence of water plays a very considerable part in the process, for with high concentrations of alkali, the heat of neutralisation is very small compared with the heat of dilution. With a concentration of 491 g. NaOH per litre, dilution of 500 cc. of solution with 15 cc. of water gives rise to 788 calories per gramme, and with a concentration of 604 g. NaOH per litre up to 1,312 calories. In the case of high concentrations of NaOH, the heat of dilution is considerable, and it is possible that some of the heat liberated in technical mercerisation is due to this effect. Tschilikin is of the opinion that the heat of reaction offers no evidence for chemical combination in the relation of $2C_6H_{10}O_5$: NaOH.

The heat of reaction between cellulose and alkali has also been examined by Okamura (Naturwiss., 1933, *21*, 393) employing ramie as the cellulosic material. Measurements were made on the purified and dried ramie in both the native and mercerised modifications. In estimating the true heat of reaction with alkali, it is necessary to correct for the heat of wetting ; this is observed in the following graphs where curves *1* and *2* show the experimental results obtained, whilst curves

3 and *4* show the corrected curves after allowing for the heat of wetting—3·66 cals. per g. for native and 6·09 cals. per g. for the mercerised ramie. (See Fig. 209.)

The mercerised ramie was pre-treated with a solution of 21·6 g. of NaOH per 100 cc. of water, washed and dried. In the case of both native and mercerised ramie the heats of reaction were determined at 25° C. with concentrations of NaOH up to 48 g. per 100 cc. The heat effect of alkali treatment at low concentrations of alkali is quite different for the two materials even after subtraction of the heat of wetting; mercerised ramie gives the greater heat effect. The differences are caused by the different mode of reaction of the two forms of cellulose.

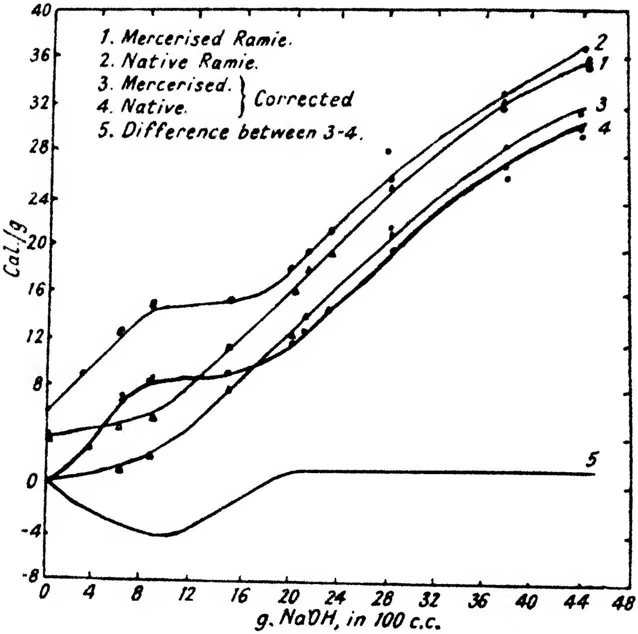


FIG. 209.—Heat of mercerisation.

At a concentration of alkali sufficient for true mercerisation, however, the differences almost vanish and the small residual difference, which may be regarded as the heat of transformation of native cellulose into mercerised cellulose, is constant for a wide range of concentrations.

All the heat effects increase with rising alkali concentration.

The heats of absorption of solutions of lithium, sodium and potassium hydroxides by cotton cellulose have been observed by Morrison, Boyd Campbell and Maass (Can. Res. J., 1938, *B16*, 195) making use of a rotating adiabatic calorimeter. The values obtained with sodium hydroxide in the range 10·7% to 15·2% show good agreement with the figures of Neale, and similar conclusions were reached.

CHAPTER TWENTY-TWO

FURTHER APPLICATIONS OF NEALE'S THEORY

THE swelling of cellulose and the heat of reaction have been described in some detail and it has been shown that according to the views of Neale it is possible to account in a satisfactory manner for the maximum swelling pressure occurring in aqueous solutions of moderate concentration, for the observed alkali absorption, and for the course of the curve when heat of reaction is plotted against alkali concentration. There are, however, further aspects of the mercerising phenomenon which are clarified by the work of Neale.

Swelling and Temperature

Neale (J.T.I., 1929, *20*, 373) calculated the effect of change of temperature on the conditions of equilibrium, by the assumptions already made. As the reaction of salt formation is accompanied by the evolution of heat it should tend to proceed further at lower temperatures. If the appropriate values are substituted in equations (8) and (9), page 329, it is possible to obtain theoretical indications of the variation of the swelling pressure with concentration of alkali at different temperatures. These effects are shown in Fig. 210, from which it appears that as the temperature falls, the maximum osmotic pressure rises, and the maximum occurs at a lower concentration of alkali.

Fig. 211 shows the data of Beadle and Stevens (see page 303) for the observed absorption of water by cuprammonium rayon ; it will be seen that both of the effects take place as predicted. A comparison of the curves, however, shows that the swelling increases more rapidly than the pressure. (The observed curve at 0° C. shows an abnormally low water absorption on account of partial solution of the material at this temperature.)

Neale's predictions for cellulose are in accordance with a mass of evidence collected for the native fibres ; it is well known that lower temperatures compensate for a decrease in concentration of the alkali solution in respect of the mercerising effect. This is shown in Fig. 178 and referred to on page 11.

Transient Swelling

Neale (J.T.I., 1929, *20*, 373) has also investigated the transient swelling of cellulose, i.e. that still greater swelling which occurs when, during the mercerising process, the alkali is removed from the impregnated material by washing with water. This well-known and complex phenomenon can be explained in terms of the osmotic theory of swelling, on the assumption that water diffuses through cellulose more rapidly than does sodium hydroxide or its ions. When the external solution, sodium hydroxide, is suddenly replaced by water, the strong water attraction of the alkali cellulose phase is no longer partially balanced by the opposing water attraction due to the alkali in the external solution. The osmotic pressure or swelling tendency is momentarily greatly increased, and this effect produces a temporary excessive swelling on account of the greater speed of the water molecules entering the cellulose compared with the alkali leaving it. After a little while, however, the alkali leaves the cellulose to such an extent that

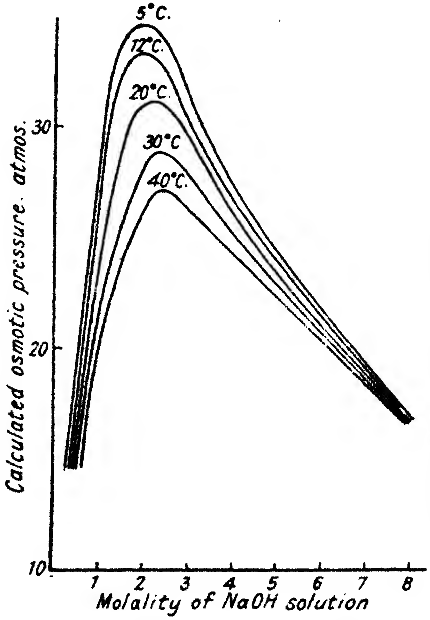


FIG. 210.—Theoretical data by Neale.

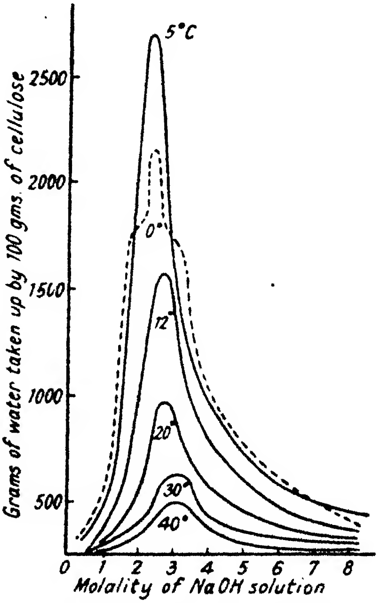


FIG. 211.—Curves by Neale from the data of Beadle and Stevens. (Cuprammonium rayon.)

the osmotic pressure, and hence the swelling, becomes very small.

The experimental evidence consisted in observations of the dimensional changes of strips of sheet cellulose similar to those used for the determination of the absorption of alkali. When

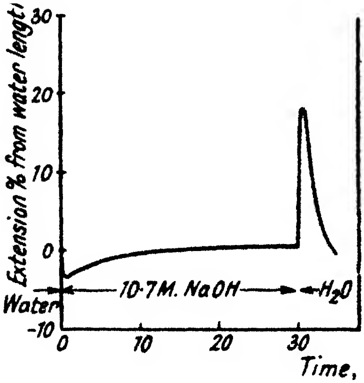


FIG. 212

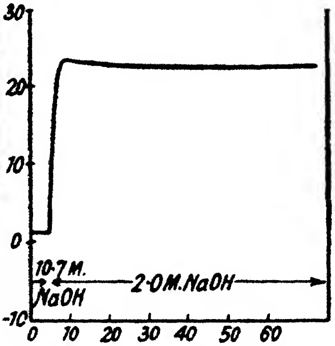


FIG. 213.

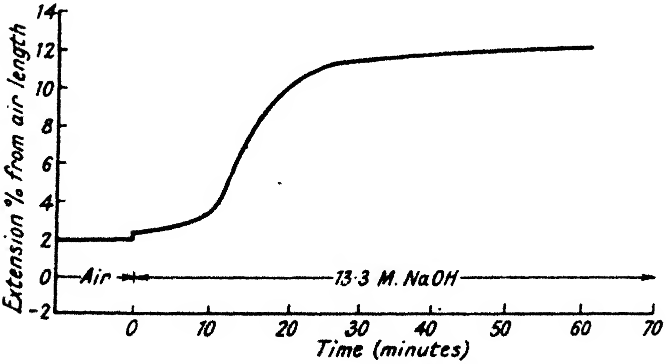


FIG. 214.—Transient swelling.
(Experiments with sheet viscose.)

the changes in length were plotted against time, the effects shown in Figs. 212, 213, and 214 were obtained.

Water-saturated cellulose is far from equilibrium with the concentrated alkali solution, and the system moves towards equilibrium by the diffusion of the two components, water and alkali. The former diffuses from the cellulose to the alkali phase (osmosis) and the latter moves into the cellulose phase. If the diffusion of water is the more rapid process, the cellulose phase will shrink rapidly as water is lost, swelling again as the alkali diffuses in and reduces the activity of water in the cellulose phase below that in the solution, causing water to flow back again into the gel phase, and setting up the final osmotic equilibrium. This is shown in the first part of Fig. 212.

If the strip of cellulose which has reached equilibrium with the concentrated solution of alkali is then transferred to water, as seen in the second part of Fig. 212, the converse behaviour occurs; water first diffuses into the cellulose-alkali phase, causing rapid swelling, and the alkali diffuses more slowly into the solution while the gel contracts.

In Fig. 213, which shows the change from 10·7 to 2·0 *M* alkali, a transient swelling is observed similar to that which takes place in Fig. 212, but the equilibrium swelling is considerable and the contraction slight.

Fig. 214 shows the results of an experiment in which a strip was conditioned over 13·3 *M* alkali and then immersed. Since the cellulose was made isotonic with the alkali solution before immersion, there was no rapid effect due to diffusion of water, and as the water and alkali moved into the gel together, the water following as required after the slowly moving alkali, there was only gradual swelling. The initial " lag " period is probably due to the alkali swelling the outer layers chiefly in the direction of thickness; when the alkali from both sides meet, then lateral expansion proceeds rapidly.

The above data refer to sheet cellulose, but the transient swelling effect is well known in the case of cotton cellulose also. Willows, Barratt and Parker (J.T.I., 1922, *13*, 221) have recorded observations on the contraction in length of single cotton hairs, and transient swelling is also seen from the work of Birtwell, Clibbens and Geake (J.T.I., 1928, *19*, 249) on modified cellulose when a greater proportion of modified cellulose is dissolved by successive treatments with 10 *N* and 1·75 *N* NaOH than by treatment with any single solution.

The commercial and technical importance of transient swelling is particularly evident in the mercerising of rayon where it reaches such a stage that the rayon might be destroyed from a textile standpoint. This may be obviated by the method of B.P. 323,307—the substitution for water of a concentrated aqueous solution of common salt, which has a high osmotic water attraction. This preliminary wash in brine removes the bulk of the absorbed alkali without undue swelling. (See page 187.)

Shrinkage

The decrease in length and the increase in width of native cellulose fibres when subject to swelling agents such as solutions of sodium hydroxide is an example of the anisotropic character of the material. All the mechanical models which have been advanced to clarify the shrinkage phenomenon operate on the basis of the " Nuremberg scissors " or the lazy-tongs principle ; they differ in regard to the points of attachment, which may be fibrous or micellar. The fact that regenerated cellulose behaves in a broadly similar manner to native cellulose shows that the mechanism of shrinkage does not lie in some exclusive property of the native fibres. Van Iterson (Chem. Weekbl., 1933, *30*, 2) has shown that cellophane shows a definite shrinkage in one direction when it is immersed in 5 % NaOH solution.

The contraction of the cotton hairs has been ascribed to the spiral arrangement of the fibrils, but it could also be explained, according to Neale, by the transverse separation of the micelles between points of mutual attachment, on lines drawn roughly parallel to the axis, drawing the points nearer together just as a trellis expands in one direction whilst contracting in another. The effect of tension in reducing the swelling of cotton hairs, and the increased extensibility of mercerised cotton, are corrollary to the fact that the hairs tend to shrink when swollen in alkali. X-ray evidence shows that the old arrangement of the crystallites is lost when the native fibre is swollen in alkali, but may be restored or altered by stretching during washing.

The relative response of the amorphous and crystalline parts of the cellulosic material to the swelling agent may also play some part in the shrinkage effect.

General

The modern idea of the mercerising phenomenon, based on Neale's work, is broadly as follows : The hydroxyl groups on the long cellulose chains attract the water molecules when cellulose takes up water ; the structure expands transversely as some of the mutual secondary valency linkages are replaced by water-hydroxyl linkages. Now in alkali solution, some of the hydroxyl-hydrogen atoms are replaced by sodium atoms and a system of high ionic concentration is established. Owing to osmosis, water tends to enter this system, and more secondary linkages are broken and replaced by linkages with alkali or water. When the alkali cellulose is washed, the sodium ions and the hydroxyl ions diffuse away, and as the osmotic pressure falls the cellulose gel contracts in virtue of its elasticity.

During this contraction the hydroxyl-hydroxyl linkages reform, but not in such great numbers as before, and the orientation of the micelles is more random. The greater proportion of free hydroxyls accounts for the increase in reactivity (see page 272), and in absorptive capacity as discussed in Part Six. The idea agrees with the X-ray evidence of Andress (see page 217) ; the decrease of this high absorptive capacity on drying, particularly at high temperatures, is due to the formation of new secondary linkages on account of the greater amplitude of thermal vibration of the hydroxyl groups as suggested by Urquhart (J.T.I., 1929, *20*, 125).

PART SIX

ABSORPTIVE CAPACITY

CHAPTER TWENTY-THREE

MOISTURE SORPTION

A CONSIDERABLE amount of work has been done on the absorption of water-vapour by native and mercerised cotton; before dealing with this aspect of the mercerised product it is interesting to consider the few available data on the absorption of gases. Most of this work deals with the increase in internal area due to mercerisation. The internal surface of one gram of cellulose is between one million and ten million square centimetres. Kalberer and Schuster (see Meyer and Mark, Z. phys. Chem., 1929, *B2*, 130) found the absorption of sulphur dioxide by mercerised cotton to be twice as great as that of unmercerised cotton, indicating an area twice as large. Osborne (Text. Res., 1935, *5*, 493) experimented on the absorption of carbon dioxide by cotton and from the isotherms, areas of $1{\cdot}4 \times 10^7$ sq. cm. per gram, and $4{\cdot}5 \times 10^7$ sq. cm. per gram, were calculated for unmercerised cotton and for cotton mercerised without tension respectively; the area of mercerised cotton thus appears to be about three times that of the unmercerised material.

Moisture Adsorption

At the time of the discovery of mercerising, the general principles of adsorption were not understood; it was assumed that cellulose was more or less anhydrous, but that the effect of treatment with sodium hydroxide of mercerising strength was to convert it into a hydrate modification—the German term "*hydratcellulose*" still persists although its meaning has been modified.

This reaction was assumed to take place through the initial formation of alkali cellulose which was decomposed by water to yield the hydrate of cellulose. Mercer found as the general result of many experiments that the increase in weight of cotton cloths which had been treated by his "fulling" process was between 4·5 and 5·5%, estimated on the weight of the original material. The latter figure agreed with the formula $(C_6H_{10}O_5)_2 . H_2O$.

It is now generally recognised that the moisture content of mercerised cotton varies with the atmospheric humidity and temperature in the same manner as the unmercerised product. The "hydrate" hypothesis, however, lasted for very many years, and like a large number of other features of mercerisation was responsible for a very large number of publications in the various scientific journals.

Whilst it was well-known that air-dried mercerised cellulose contained more moisture than the unmercerised material, Ost and Westhoff (Chem. Zeit., 1909, *23*, 197) showed that the hygroscopic moisture was driven off at 120° C. in both cases and also that unmercerised cellulose, mercerised cellulose and cellulose regenerated from viscose solution, all had the same chemical composition when dry.

A number of experiments showed that mercerised cotton contained considerably more hygroscopic moisture than unmercerised cotton, but that this could be removed over P_2O_5, by drying in an oven or by distillation in toluene. Analysis showed that all forms of dried cellulose had the formula $C_6H_{10}O_5$. This was in opposition to the old idea that mercerised or regenerated cellulose was actually cellulose hydrate.

Further work on these lines was done by Miller (Ber., 1910, *43*, 3430; 1911, *44*, 78). The moisture of mercerised cellulose in equilibrium with air at ordinary temperatures was readily given off by drying in a desiccator over calcium chloride; it is, therefore, not chemically fixed. Miller gave the following data for water adsorption at 21·5 to 22·5° C. under identical but unrecorded conditions of atmospheric humidity: unmercerised 7·12%; mercerised 10·0%.

Some interesting data on the moisture content of cotton, mercerised with various concentrations of sodium hydroxide, have been obtained by Schwalbe (Z. angew. Chem., 1909, *22*, 197), and these are given below:

MERCERISING AND MOISTURE CONTENT.

Concentration of caustic soda.	Moisture content, based on dry cotton.
0%	6·1%
8%	7·7%
16%	10·7%
24%	11·3%
40%	12·1%

About the same time, Higgins (J.S.C.I., 1909, *28*, 188) made similar observations, but in neither case were the actual conditions of temperature and humidity recorded.

MERCERISING AND MOISTURE CONTENT.

Concentration of caustic soda.	Moisture content based on dry cotton.
0%	6·2%
4·5%	6·37%
8·5%	6·68%
13·5%	8·40%
17·5%	9·41%
22·5%	9·43%
27·0%	9·57%
31·5%	9·69%

Higgins stated that the increase in moisture content with the concentration of sodium hydrate used in mercerising followed the same course as that observed by Hübner for shrinkage and adsorption of dyestuff (J.S.C.I., 1904, *23*, 404). (See page 98.)

Hübner and Wootton (J.S.D.C., 1925, *41*, 10) produced further data on the relationship between the strength of caustic soda used in mercerising and the hygroscopic moisture present in the treated goods ; results are shown below :

MERCERISING AND MOISTURE CONTENT.

NaOH	Percentage of moisture calculated on the dry weight of the yarn.		
	Grey yarn.	Scoured yarn.	Bleached yarn.
0° Tw.	6·62	5·82	5·51
5° Tw.	7·11	6·37	5·92
10° Tw.	6·99	6·17	6·13
20° Tw.	7·56	6·96	6·71
30° Tw.	9·50	9·42	9·64
40° Tw.	10·25	9·91	10·70
50° Tw.	10·85	11·26	11·42
60° Tw.	11·45	10·93	11·20

MERCERISING AND MOISTURE CONTENT.

NaOH	Percentage of moisture calculated on the dry weight of the fabric.		
	Lightly-scoured fabric.	Re-scoured fabric.	Bleached fabric.
0° Tw.	6·13	5·24	4·78
5° Tw.	6·48	6·18	6·21
10° Tw.	6·07	6·12	6·22
20° Tw.	6·52	6·57	6·29
30° Tw.	7·43	7·97	7·71
40° Tw.	8·86	9·30	9·56
50° Tw.	9·37	10·31	10·34
60° Tw.	9·70	10·25	10·44

Here again the conditions of temperature and relative humidity of the atmosphere are not recorded.

The Moisture Relations of Cellulose

It is a well-known fact that cellulose contains a certain amount of moisture even when it feels "dry." When, however, the cotton is dried by heating and then exposed to ordinary cold air, it quickly absorbs most of the moisture it has lost on drying. This property is common to all substances which have large surfaces and exist in the colloid state. The amount of moisture in cellulose varies with the relative humidity of the surrounding atmosphere and with the temperature. It is obvious that the amount of moisture in the cotton is an important factor when buying and selling are considered, as raw cotton and yarns are sold by weight. The accepted regain is therefore fixed at 8·5 %, the moisture being expressed as a percentage of the dry weight. The moisture contained in cotton is also referred to as the moisture of "condition," and the term moisture content strictly refers to the amount of moisture contained in conditioned cotton expressed as a percentage of the weight of the material in its conditioned state.

Whilst both relative humidity and temperature affect the moisture content, the former is the more important, for if it is kept constant the amount of water does not vary over a small range in temperature. On the other hand, there is considerable variation with a change in humidity. This variation has been studied by many observers, but there can be no doubt that our present knowledge of the absorption of moisture by cellulose is largely due to the work of Urquhart and Williams, published in a series of papers in the *Journal of the Textile Institute* since 1924.

In their results of the examination of the moisture relations of cotton, Urquhart and Williams do not refer to the atmospheric conditions in terms of percentage relative humidity, but of relative vapour pressure or p/P, the pressure exerted by the water in the cotton divided by the saturation pressure. As the pressure of the water in the cotton exactly balances the pressure of the water in the atmosphere when equilibrium has been attained, 100 p/P is equal to the percentage relative humidity. If the weight of water taken up by 1 g. of dry cotton is denoted by " a," then 100a is the percentage moisture regain. The results showed that there are two possible values of moisture regain, a lower value if the cotton was initially drier than the atmosphere and a higher value if it had been wetter. The difference between the two sets of observations had been noted previously, but Urquhart and Williams showed that a real hysteresis existed in the case of cotton. The taking up of water was termed " Absorption " and the giving up of water " Desorption."

The moisture regain of cotton definitely depends on its previous heat treatment, heating to a high temperature reducing the capacity to absorb water. The hysteresis shown by soda-boiled cotton is greater than that for raw cotton.

The original method employed by Urquhart and Williams did not yield accurate results for very high or very low humidities, and was later modified (J.T.I., 1924, *15*, 433), by the use of a vacuum device. The cotton was placed in an evacuated bulb with a manometer, known amounts of water were admitted (or removed), and the resultant vapour pressure read directly. The hysteresis did not extend to zero humidity. It was found that the moisture content of soda-boiled cotton is 22·6% at 100% relative humidity ; the measurements were made at 25° C.

Figure 215 may be regarded as representing typical isotherms for cotton at average humidities and temperatures. When the relative humidity is constant at humidities less than 80% the moisture regain decreases as the temperature rises from 10 to 110° C., but at humidities above 80% the regain falls from 10 to 50° C. and increases from 60 to 100° C.

Urquhart and Williams (J.T.I., 1925, *16*, 155) examined the absorption of moisture by cotton mercerised without tension in order to obtain accurate knowledge of the moisture content at all humidities and also the effect of varying the concentration of the mercerising solution.

The material employed was loose cotton which had been boiled in soda before treatment with the mercerising liquor. In the first series of experiments the vacuum apparatus was employed and the results are shown in Fig. 216.

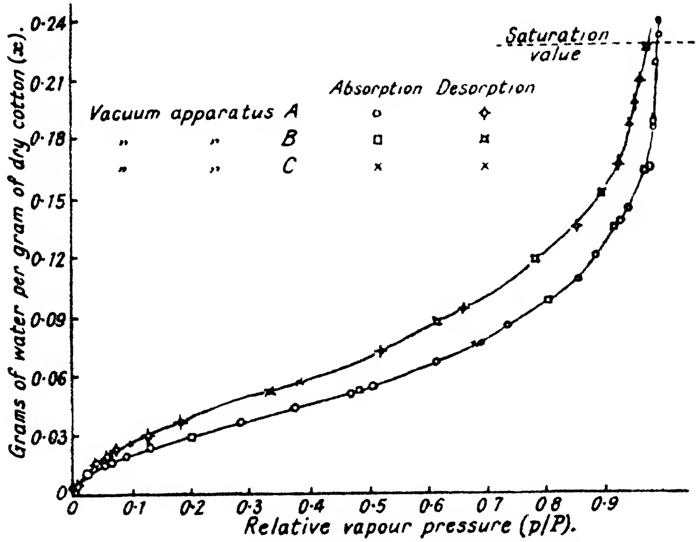


FIG 215.—Absorption and desorption of moisture by soda-boiled cotton at 25° C.

The isotherm previously established for soda-boiled cotton is included in the figure, as a dotted line, so that the increased hygroscopicity may be seen at a glance. The curve is of the same form as that of soda-boiled cotton, but while there is no apparent tendency for the hysteresis loop to close at its upper end, no lower meeting place was found at any measurable pressure above zero. The continuous curves represent the data obtained by mercerising with 15% NaOH solution, but for purposes of comparison the data for mercerising with 28% KOH are also included. The closest agreement between the results is evident.

Urquhart and Williams noticed a tendency for the moisture content of the mercerised cotton to bear a fixed ratio to that of the soda-boiled cotton and this was confirmed by taking readings at each 5% relative humidity, whereupon it became evident that the ratio of the moisture content of mercerised cotton to that of the original soda-boiled cotton at the same relative humidity is appreciably independent of that humidity. The mean values from the nineteen readings were 1·57 in absorbing and 1·46 in the desorption of moisture. These

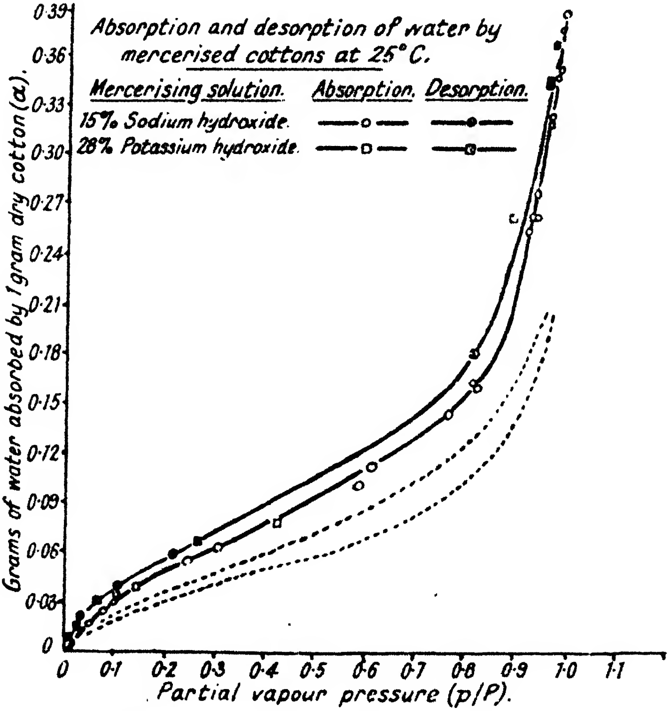


FIG. 216.—Moisture relations of mercerised cotton. (The dotted curve is for unmercerised cotton.)

ratios are therefore indicative of the extent to which the absorptive capacity of the material has been altered by mercerising without tension in 15% sodium hydroxide solution.

The relation between the moisture content of the mercerised material and the concentration of the mercerising liquor was also examined and is shown in Fig. 217, where the two variables are plotted against one another. The curves show maxima at 15% and 25% NaOH; the bottom curve illustrates the relation between alkali concentration and contraction in length of the single hair (Willows, Barratt and Parker—J.T.I., 1922, *13*, 229), while the curve above it represents the increase in diameter of single cotton hairs referred to the wet diameter as shown by Collins (J.T.I., 1925, *16*, 123). The great similarity between these curves points to some definite correlation between the degree of swelling and the absorptive capacity for moisture. It would appear, therefore, that for each mercerisation process there is a ratio which indicates quantitatively the effect of that process on the absorptive capacity. It was shown that this ratio was not dependent on the method of experiment; examination of the data obtained from both the

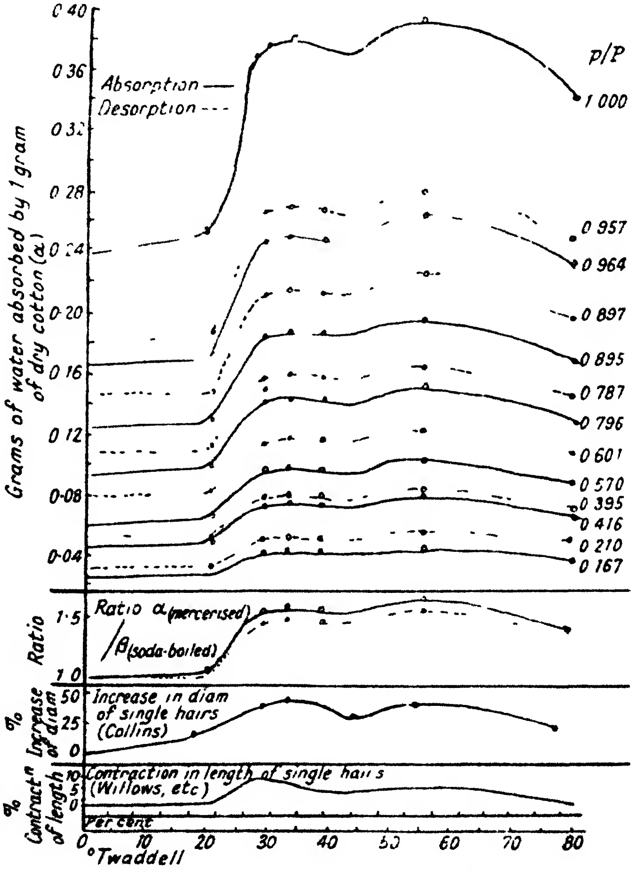


FIG. 217.—Moisture relations of cotton mercerised without tension.

vacuum and desiccator methods and at different temperatures gave the following results :

MERCERISATION RATIOS.

	Absorption.	Desorption.
Vacuum method (25° C.) .	1·57	1·46
Desiccator method (20° C.) .	1·57	1·48

Urquhart and Williams suggested in view of the very close agreement between the hygroscopicities of cottons mercerised with NaOH and KOH, the similarities of absorption and swelling curves and the fact of the ratio of the increase in absorptive capacity being independent of the amount of water absorbed, that the increase in absorptive capacity must be due to an increase in the absorbing surface.

(The absorptive capacity depends only on the area available to an absorbate, whereas the intensity factor or ability to absorb depends on the substance of which the material is composed.)

The similarity between the curves illustrating the swelling of cotton hairs in solutions of sodium hydroxide and those illustrating the hygroscopicity of the mercerised cotton was confirmed by Urquhart in a later publication (J.T.I., 1927, *18*, 55), which was mainly concerned with the effects of mercerising under tension. The applied tension acts in opposition to the swelling forces so that the absorptive capacity of cotton mercerised under tension is considerably less than that of cotton mercerised loose.

The conditions of mercerising under tension were based on mill practice ; a " rope " of yarns, consisting of 100 to 150 strands (depending on the counts) was subjected to a tension of 180 g. per strand in the case of 15s yarn and an attempt made to give other yarns equivalent treatment by varying the tension in inverse proportion to the counts. The general method was to apply the tension after the yarn had been allowed to shrink in the alkali. The time of mercerisation was three minutes.

The reduction in moisture absorption brought about by tension appears to fall with increasing concentration of the mercerising liquor. With cotton mercerised in 15 % NaOH solution, the application of tension reduced the moisture absorption ratio from 1·37 to 1·10, while for the same cotton mercerised with 25 % NaOH under the same tension, the reduction was from 1·22 to 1·16.

The term absorption ratio is preferable to mercerisation ratio ; it is objective and whilst the moisture absorption ratio

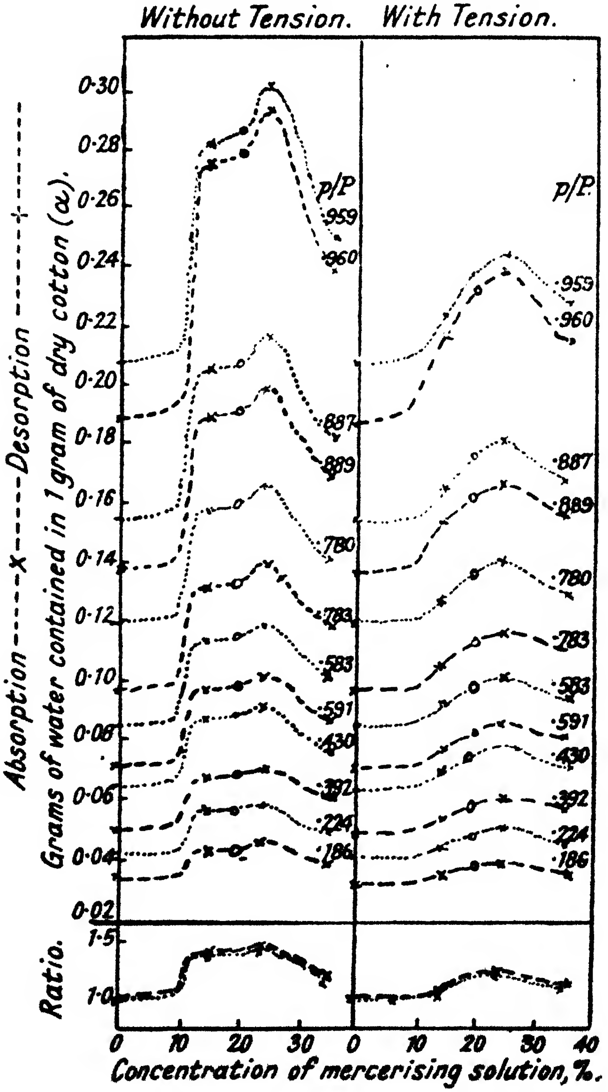


FIG. 218.—Moisture relations of cotton mercerised with and without tension.

is closely related to the increase in affinity for dyes, yet it cannot be regarded as a measure of lustre.

The "lustre ratio" may equally well be regarded as a mercerisation ratio, yet the effect of tension is to increase the lustre and reduce the absorptive capacity.

A small tension is sufficient to bring about the full reduction in hygroscopicity, the application of greater tensions having little extra effect.

Examination of the effect of mercerisation on a large number of cottons showed that there was no essential difference in the response of the various cottons to the process. However the variability in the cottons mercerised in 15% NaOH under tension was much greater than in the cottons mercerised in 25% NaOH solution. From this, it would appear that the concentrated solutions used in common practice give a greater uniformity of product than more dilute solutions.

From the data gathered from treatment of cotton yarns with 15, 20 and 25% NaOH solutions, with and without tension, Urquhart was able to construct curves showing the relation between the hygroscopicity of the mercerised yarn and the concentration of the mercerising solution; between 15% and 25% NaOH, the curves for yarn mercerised loose show one inflexion, but the curves for yarn mercerised under tension show none. The curves are shown in Fig. 218.

Comparison of the data with the results obtained previously for loose cotton, indicated that yarn mercerised without tension occupies a position intermediate between mercerised sliver or roving and yarn mercerised with tension. This is probably due to the fact that in yarn mercerised without tension, the full contraction of the hair is restricted by the constraint of adjacent hairs; the cotton is actually under slight tension.

This is in agreement with the suggestion of Coward and Spencer (J.T.I., 1923, *14*, 32)—see page 312.

In the course of their examination of the reactivity of ordinary and mercerised cottons, Birtwell, Clibbens, Geake and Ridge (J.T.I., 1930, *21*, 85) had occasion to measure the absorption ratios of cotton yarn treated with NaOH and KOH solutions at various temperatures. Fig. 177 represents the results obtained, and these are discussed on page 280.

It will be noticed, however, that there is no great increase in moisture absorption in passing from cotton mercerised at 18° C. to cotton mercerised at −10° C. The curves illustrate that although the absorption ratio is increased, the main effect is that already mentioned as the result of lowering the temperature of the mercerising liquor, i.e. the optimum effect takes place with a lower concentration of alkali. The increase in absorption does not follow the great increase in shrinkage, which is also the result of low temperature mercerising of cotton with NaOH.

In a paper on the effect of processing on the moisture relations of cotton, Urquhart, Bostock and Eckersall (J.T.I., 1932, *23*, 135) record a figure of 1·2 as being normal for a technically mercerised cloth.

The absorption ratios of rayons (more highly dispersed cellulose than mercerised cotton) vary from 2·12 to 1·75 according to Urquhart and Eckersall (J.T.I., 1932, *23*, 163) and are given here for purposes of comparison.

Effect of Drying

When cellulose is formed inside the cotton hair, it is laid down in presence of water and for this reason the free hydroxyl groups will have their high residual valency satisfied by that water. As the hair dries on exposure to the atmosphere after removal from the boll, these groups are freed and there is a tendency for the macro-molecules of cellulose to re-arrange themselves so that the residual valencies of the hydroxyl groups will be mutually satisfied. This is to some extent a more or less permanent arrangement, for whereas the primary desorption curve of cotton taken direct from the boll is irreproducible, yet the absorption and desorption curves after the first drying may be repeated as often as desired. Further, the subsequent desorption curve shows a greatly reduced absorptive power. (See Fig. 219.)

The available surface of cotton is increased as a result of mercerising and as this new surface is formed in presence of water it is reasonable to suppose that it will temporarily exist in the same active state as that of the cellulose in the boll so that an irreproducible primary desorption curve may also be expected for similar reasons. This has been established by Urquhart (J.T.I., 1929, *20*, 125) and by Urquhart and Eckersall (J.T.I., 1930, *21*, 499).

The observation of Knecht (J.S.D.C., 1908, *24*, 107)—see also page 380—that mercerised yarn dyed before drying absorbs more dye from a given bath than the same material dyed after drying was confirmed for direct, sulphur and vat dyes, there being a most pronounced difference between the samples dyed wet and the partially dried samples.

The chief results discussed are shown in the following tables :

Percentage Regain.

Relative humidity .	10	20	30	40	60	80	90
Scoured cotton .	2·0	2·9		4·5	6·2	9·1	11.8
Mercerised cotton .	2·4	3·6		5·6	7·8	11·1	14·3
Viscose rayon . .	3·9	5·7		8·7	11·9	16·9	22·1

Absorption Ratios.

Scoured cotton .	Standard sample of unity.						
Mercerised cotton .	1·2	1·23		1·24	1·26	1·22	1·21
Viscose rayon . .	1·99	2·02		1·95	1·89	1·80	1·80

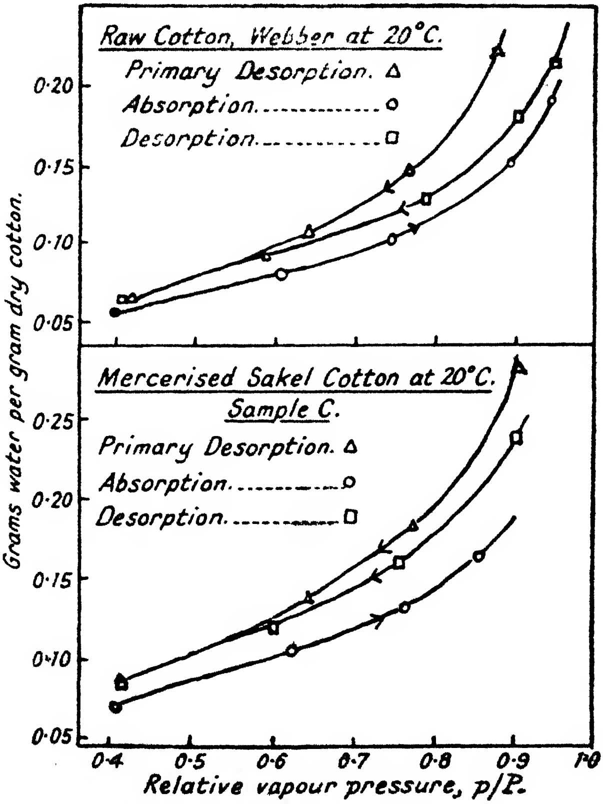


Fig. 219.—Hygroscopicity of cotton.

Theory of Water Sorption

In addition to the possibility of water being held by the hydroxyl groups of the cellulose, there is also the question of capillarity to consider. The retention of water by cellulose is not necessarily part of the same phenomenon as the adsorption of water from the atmosphere. There is a body of opinion which holds that at higher vapour pressures the bulk of the water is held by capillary condensation in the intermicellar spaces.

Bancroft and Calkin (Text. Res., 1934, *4*, 371) pointed out that the work of Davidson (J.T.I., 1927, *18*, 175—see page 218) on the specific volume of cellulose is of importance in considering the manner in which water may be held by cellulose. The specific volume, when measured by the displacement of helium, is 0·638, but the apparent specific volume of a sample of the same material measured by displacement of water is 0·621, so that the disappearance in volume amounts to 12% of the water taken up. This contraction may be accounted for if part of the water is held on the surface of the cotton. Filby and Maass (Can. Res. J., 1932, *7*, 162) found that the volume of the system cellulose-water vapour is much smaller than that given by the component cellulose and condensed water so long as the amount of adsorbed water is below 4%, but with more than 8% of water the density of the absorbed water is the same as that of the normal liquid ; the initial water taken up showed a greater apparent density than that absorbed up to 8%.

Some type of two-phase theory of water sorption is now fairly generally accepted and the development of these ideas may be seen in the work of Urquhart and his collaborators (*supra*) and, in addition, the publications of Pierce (J.T.I., 1929, *20*, 133), Filby and Maass (*supra*), Sheppard (Trans. Farad. Soc., 1933, *29*, 77) and Sheppard and Newsome (Ind. Eng. Chem., 1934, *26*, 285).

Walker (J. Applied Phys., 1937, *8*, 261 ; Text. Res., 1937, *7*, 297) has put forward the following theory as a result of the examination of the insulation resistance of cotton and its relation to the moisture content. Moisture is first adsorbed on dry cotton on the outer hair surface, and it later penetrates by diffusion into the cracks and pits that spiral round the hair. Less than 0·5% of moisture is estimated as being necessary to form a unimolecular layer on pit walls and growth ring surfaces, but about 1% is required to cover all internal surfaces. Below 1% of moisture the rapid increase in resistivity is due to discontinuities in the layer of water adsorbed on the fibril surfaces.

Now Collins (J.T.I., 1930, *21*, 313) has measured the swelling of cotton hairs under various conditions of humidity. It was found that a fairly close parallelism existed between the extent of change in dimensions and the amount of moisture absorbed, between the temperature limits of 20° to 100° C.

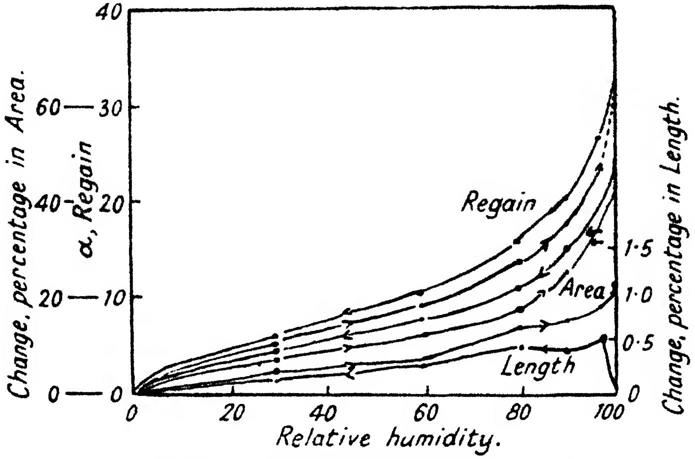


FIG. 220.—Moisture sorption and changes in dimensions.

In passing from dry air to water, the increase in area is about 44% and the increase in length about 1%, when the hair is fully wetted.

These data, and the work of Urquhart, enabled Walker to calculate the effects of moisture absorption. If a monomolecular layer forms over the whole of the fibril surface and one takes 33 concentric layers of fibrils as an average construction of the hair, then on the basis of a water molecule being 3·8 Å in diameter, the total increase in hair diameter will be about 500 Å. This corresponds to 0·4%, which according to Collins (*supra*) is the increase in diameter at 3·6% relative humidity and corresponds to an actual absorption of 1·1 to 1·2% of moisture. It is evident that there must be additional internal surface to accommodate the difference of 0·8% between the observed and calculated amounts of moisture. Walker holds that this additional surface is to be found on the ends of the crystallites which make up the fibrils. He further suggests that multimolecular layers of water condense on the fibrillar surface up to saturation, with corresponding increases in hair diameter throughout the range. For example, if 48 monomolecular layers condense on the fibril surface and one layer on the crystallite ends, then the total moisture absorption of 20·8 % is in close agreement with the observed value and the increase in diameter. The smaller amount of water absorbed on the ends of the crystallites is an assumption in agreement with the lack of hydroxyl groups and the very slight longitudinal swelling.

Each hydroxyl group in the surface of the cellulose is the base of a water chain, with separation between the chains corresponding to the arrangement of the hydroxyl groups on the surface. When the arrangement of the hydroxyl groups is altered, as in the case of dispersed cellulose, they become more accessible, so that increased moisture absorption and increased swelling become possible. The substitution of the hydroxyl groups by acetyl, for example, results in a lower moisture absorption.

Whilst there is considerable opinion that the bulk of the water at higher vapour pressures is held by capillary condensation or volume sorption, it is generally agreed that the primary surface adsorption or chemico-sorption is dependent on the free hydroxyl groups (about 5 % of moisture for native cellulose and 7 % for dispersed cellulose).

Water Imbibition

The retention of larger volumes of water has also received attention in the case of native and mercerised cotton.

In the course of their work on the absorption of caustic soda solutions by cotton, Coward and Spencer (J.T.I., 1923, *14*, 32) measured the water absorbed by cotton hairs after removal of sodium hydroxide. The method involves the use of the centrifuge and experience has shown that this affords one of the best estimates of the degree of swelling of the cellulose. With the particular centrifuge employed, scoured cotton hairs gave a water retention of 50 %. The mercerised samples were washed in water, made neutral with very dilute acid, and then thoroughly washed in running water for one hour. The material was then centrifuged and weighed to determine the water retention before drying. Part of the material was then heated for two hours in a steam oven, then soaked in water, centrifuged and weighed. The remainder was dried for eight hours and similarly treated. The results are shown in Fig. 222, from which it appears that the original water retention of about 125 % falls to some 75 % as the result of drying. The original water retention is influenced by the concentration of alkali used in the mercerising process, but this effect is considerably diminished as a result of drying. The water absorption of the undried hairs is less than the volume of the alkaline liquor

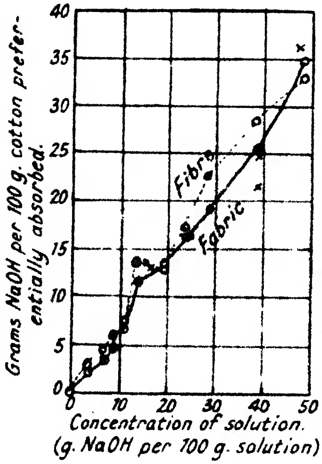


Fig. 221.—Preferential absorption of NaOH.

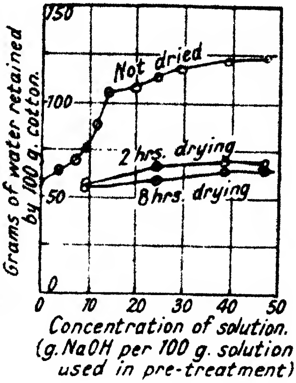


Fig. 222.—Water absorption on mercerising, washing and drying.

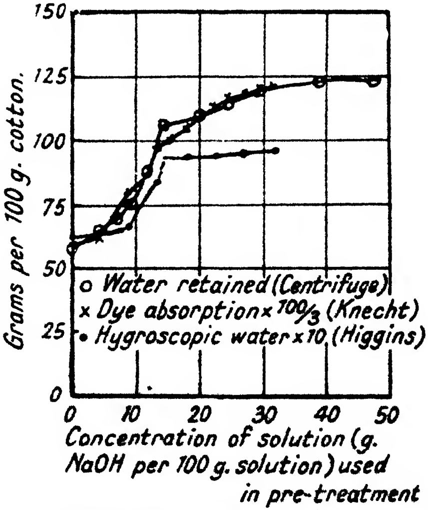


Fig. 223.—Sorption of water, dyestuffs and moisture.

originally absorbed in corresponding experiments (see Fig. 197, page 312), so that considerable contraction of the hair occurs during washing and a still greater contraction on drying. The decrease in water retention after drying is in accordance with the observation of Knecht (J.S.D.C., 1908, *24*, 70 and 107) that whereas mercerised cotton absorbs more dyestuff than unmercerised, yet drying reduces the initial high affinity for dyestuffs of the undried mercerised cotton.

Coward and Spencer have compared the curve of the water retention with that of the absorption of benzopurpurin according to Knecht and obtained close correspondence. The curve of Higgins (J.S.C.I., 1909, *28*, 188) was also included for purposes of comparison, and here again good agreement is obtained, but only up to about 14% NaOH. Higgins' cotton, however, was dried at 60° C. (See Fig. 223.)

A further important observation of Coward and Spencer was that the mercerised and well-washed fibre may be caused to contract somewhat by prolonged boiling in water. For example, a mercerised cotton which after removal of alkali showed a water retention of 108 g. of water per 100 g. of cotton, retained only 88 g. of water after boiling for six hours.

A comparison of the water retention of muslin cloth, treated with acid or alkali, washed and centrifuged (2½ mins. at 7,000 r.p.m. on Coward and Spencer's centrifuge) gave the following results:

WATER RETENTION.

Time in secs.	60° Tw. NaOH (27%)	100° Tw. H_2SO_4 (59·7%)	108° Tw. H_2SO_4 (63·4%)	110° Tw. H_2SO_4 (64·2%)	120° Tw. H_2SO_4 (68·5%)	130° Tw. H_2SO_4 (72·7%)	140° Tw. H_2SO_4 (77·2%)
5 (*a*)		53		183	237	210	225
(*b*)				93	139	146	145
10 (*a*)		53		199	230	228	231
(*b*)				96	143	155	157
15 (*a*)		58		186	254	247	253
(*b*)		58		98	150	168	174
30 (*a*)	87		128				
(*b*)	59		57				

(*a*) Treatment followed by washing only.
(*b*) Fabric dried in air and re-immersed in water for 16 hours.

Bancroft and Calkin (Textile Res., 1934, *4*, 371) made use of a high-speed centrifuge in their work on the absorption of water and of alkali. Experiments on a somewhat similar type of centrifuge have given interesting results.

Water Retention at 12,000 R.P.M.

	Without tension.		With tension.	
	Water retained %	Ratio treated : untreated.	Water retained %	Ratio treated : untreated.
Untreated muslin . .	16·4			
Mercerised and washed at 15° C. . .	87·8	5·35	50·3	3·06
60° C. . .	73·4	4·48	42·6	2·60
100° C. . .	60·6	3·69	42·2	2·57
Mercerised, washed and dried 15° C and re-wet .	56·5	3·44	33·9	2·06
Mercerised, washed at 15° C., dried at 100° C. and re-wet	49·9	3·04	28·2	1·72

These figures show the tenacious manner in which water is retained by swollen cotton cellulose and emphasise in a somewhat striking manner the previous observations of Coward and Spencer and of Knecht on the effect of drying and also of washing at different temperatures.

Champetier's Method

The series of papers (Compt. rend., 1931, *192*, 1593 ; 1932, *195*, 280 and 499) comprised a study of the ternary systems formed by cellulose, water and a compound such as sodium thiosulphate or pyridine which does not combine with cellulose. The cellulose was immersed in the solution and pressed, samples being withdrawn during the pressing operation at intervals, and analysed. As the pressure increased, more sodium thiosulphate (or pyridine) than water was squeezed out and the variation of sodium thiosulphate (or pyridine) content expressed as a function of the water content gives a straight line. By the use of a number of solutions of different original concentrations, a series of such lines may be drawn, and when these are extrapolated the point of intersection " A " indicates an addition compound. This is represented in Fig. 224.

Champetier's results indicate the formation of the following compounds :

Fixation of Water.

Type of cellulose.	Molecules of water per $C_6H_{10}O_5$
Native cellulose . . .	0·5
Mercerised cellulose . .	1·0

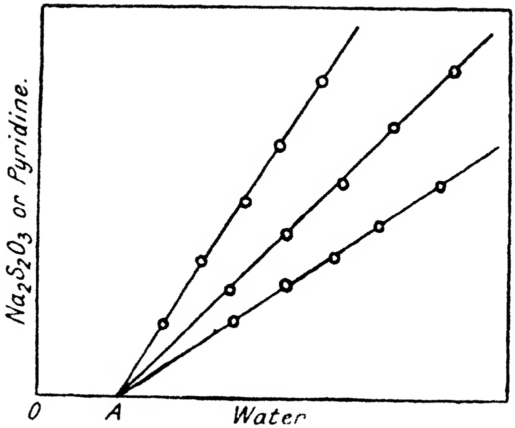


FIG. 224.—Evidence for compound formation from pressure methods.

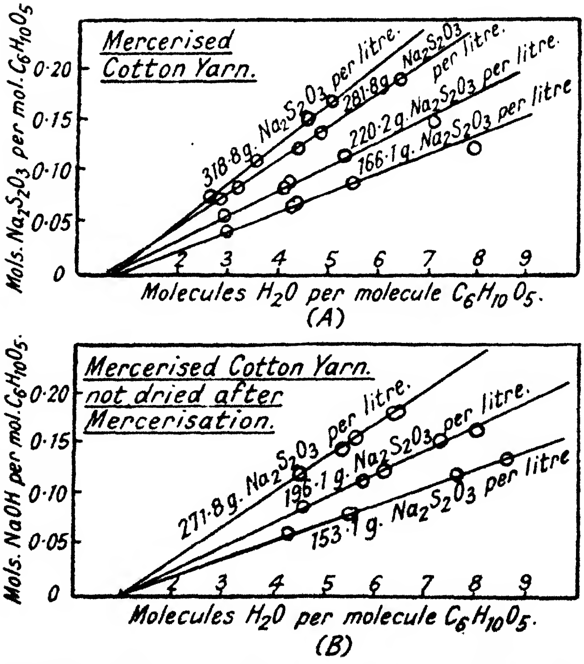


FIG. 225.—Fixation of water according to the pressure method for mercerised cotton.

The general method was repeated by Tankard (J.T.I., 1937, *28*, 263), but with greater pressures, reducing the amount of water associated with 100 g. of dry cotton to some 20 g., compared with some 106 g. of Champetier, so that the amount of extrapolation was considerably less.

The point of intersection indicates the amount of water which would be retained by the cellulose, if sufficient pressure could be employed completely to remove the $Na_2S_2O_3$.

The following results were obtained :

FIXATION OF WATER.

Material.	Molecules of H_2O per $C_6H_{10}O_5$
Ordinary cotton . . .	0·49
Cotton, mercerised and dried .	0·75
Cotton, mercerised and not dried	1·00
Linen	0·55
Linen, mercerised and dried .	1·05
Linen, mercerised and not dried	1·05
Viscose rayon . . .	0·97
Viscose rayon, mercerised (KOH) and dried . .	1·17
Lilienfeld viscose rayon . .	1·10

Tankard suggests that cellulose does not form a limited number of hydrates, but that in each case, there is a maximum amount of water which may be regarded as chemically combined. These results are of considerable interest and could possibly be emphasised by comparison with the extent of mercerisation.

CHAPTER TWENTY-FOUR

ABSORPTION OF DYESTUFFS

THE increased affinity for dyestuffs was one of the first properties of " fulled " cotton to be noticed by Mercer. Although for many years there was no doubt as to the truth of this observation, the state of knowledge was not such as to permit these observations being placed on a quantitative basis.

Minajeff and Schaposchnikoff (Z. Farb. Text. Ind., 1903, *2*, 257; 1904, *3*, 163 and 1905, *4*, 83) carried out a series of quantitative experiments to show how much more dyestuff was absorbed by mercerised cotton than by the unmercerised material. The quantities of Indigo taken up by mercerised cotton and by ordinary cotton were on the average in the ratio of 130 : 100. At least 40% more Indigo is needed to give the same shade on ordinary cotton as on mercerised cotton.

Several experiments with Diamine Blue 3B showed the proportion of dyestuff in mercerised as compared with ordinary cotton to be as 140 : 100. It was also found that in order to match a shade dyed on mercerised cotton with Diamine Blue 3B, it was necessary to use 50% more dyestuff for ordinary cotton.

In the case of Immedial Blue C, again the mercerised cotton was shown to absorb about 40% more dyestuff than ordinary cotton. Some work on mordants also gave interesting results. The amounts of tannin taken up were estimated and the proportion was found to be 140 : 100 for mercerised cotton compared with ordinary goods. Similarly, in the case of mordanting with chromium, it was found that mercerised cotton took up more of the mordant than untreated cotton in the proportion of 148·8 : 100. In all cases the figures refer to cotton mercerised without tension.

The statement that mercerising effects a subsequent economy in dyestuff refers to the fact that a better exhaustion of the dyebath is possible with mercerised cotton; Hübner (J.S.C.I., 1908, *27*, 105) has stated that for the same weight of dye on equal weights of mercerised and ordinary cotton, the same shade is obtained.

Experiments of a partially quantitative character concerned with the depth of dye and the concentration of the mercerising liquor were made by Hübner and Pope (J.S.C.I., 1904, *23*. 404). Bleached yarn was mercerised without tension, washed and then dyed, without previous drying, in a bath of 0·25% Benzopurpurin 4B (estimated on the weight of the yarn) for 30 mins. at the boil. The various hanks were then washed and dried, and the depth of shade estimated by visual examination. The colour was found to increase continuously from the untreated yarn to the yarn mercerised with 25% NaOH solution, in which case it reached a maximum. There was little change in the case of yarns mercerised with solutions containing from 25% to 31·5% NaOH, but as the alkali concentration increased further to 36·5% NaOH, the depth of shade decreased. The maximum dyeing effect at 25% to 31·5% NaOH does not show a sharp maximum for alkali concentration; this may be due to the fact that during the washing of the cotton after the mercerising process, the more concentrated solutions must momentarily exert the effect of a more dilute solution. These results are also discussed on page 98.

ABSORPTION OF DYESTUFFS (Knecht).

Concentration of NaOH %	Benzopurpurin absorbed G. per 100 g. of cotton.
0·0	1·77
4·5	1·88
8·5	2·39
11·0	2·57
13·5	2·95
15·5	3·02
17·5	3·15
20·0	3·27
22·5	3·38
25·0	3·50
27·0	3·56
29·0	3·60
31·5	3·66

Knecht (J.S.D.C., 1908, *24*, 67) made a series of measurements on the absorption of Benzopurpurin 4B from a boiling dye bath by a two-fold Egyptian yarn which had been wetted with boiling water, mercerised under tension with varying concentrations of NaOH solution, and finally dried. In each case 2·5 g. of cotton were dyed for one hour in a bath containing 3 % Benzopurpurin 4B, 5 % sodium carbonate and 10 % common salt in a weight of water equal to twenty times that of the cotton to be dyed.

The quantitative estimation was made possible by Knecht's own method of estimating azo dyes by $TiCl_3$ (J.S.D.C., 1905, *21*, 3).

The weight of absorbed dyestuff increases with the concentration of the mercerising alkali, but the increase is less rapid as the concentration of the NaOH exceeds 13·5 %.

The effect of tension was also examined by Knecht, employing a 22·5 % solution of NaOH.

EFFECT OF TENSION.

	Benzopurpurin absorbed %.	
Unmercerised cotton . .	1·55	1·50
Mercerised with tension . .	2·90	2·86
Mercerised without tension .	3·39	3·54

The first column relates to unbleached cotton and the second to bleached material.

Knecht has investigated the effect of drying on the capacity of the mercerised yarn to absorb dyestuffs (*ibid.*, 107). Bleached American yarn was mercerised in 20 % NaOH solution, washed, acidified and washed again until neutral. One part was then dried for an hour between 100° C. and 110° C., whilst the other remained wet ; both were dyed together for 15 mins. in the boiling bath of Benzopurpurin solution.

EFFECT OF DRYING.

	Weight of absorbed dye
Mercerised, dried and dyed . .	1·16%
Mercerised and dyed without drying	1·74

Similar experiments were made with a singles bleached American yarn, mercerised without tension in 22·5 % NaOH solution, and in this case both Benzopurpurin and Chrysophenin were used for dyeing.

EFFECT OF DRYING.

	Benzopurpurin	Chrysophenin
Unmercerised yarn	0·80%	0·31%
Mercerised and dyed without drying .	2·49	0·97
Mercerised and air dried . . .	1·57	0·77
Mercerised and dried at 110° C. .	1·27	0·54

In another series of experiments, a two-fold bleached Egyptian yarn was employed and mercerised in 16·5 % NaOH solution.

These samples were dyed in a more concentrated bath.

EFFECT OF DRYING.

	Benzopurpurin %	Chrysophenin %
Unmercerised	1·77	0·58
Mercerised and dyed without drying .	3·24	0·96
Mercerised and air dried . . .	3·03	0·92
Mercerised and dried at 110° C. . .	2·51	0·84

The drying of the yarn after mercerising brings about a greatly decreased affinity for direct dyestuffs, and this decrease is greater the higher the temperature of drying.

Some experiments were also undertaken with ordinary untreated cotton, and no difference was observed either by visual inspection or by quantitative examination.

UNMERCERISED COTTON.

	Benzopurpurin absorbed.
Steeped in H_2O for 24 hours and not dried .	1·76%
Air-dried before dyeing	1·79%
Dried at 110° C. before dyeing . .	1·80%

Knecht also showed that by mercerising cotton in the piece and printing it, while still moist, with a 25 % solution of glycerin thickened with British gum, it was possible after drying to conserve the moisture in the printed portions. The piece was then washed with water to remove the glycerin and thickening, and on subsequent dyeing the printed portion showed a greater depth of shade.

Hanson, Neale and Stringfellow (Trans. Farad. Soc., 1935, *31*, 1718) have examined the absorption of Chlorazol Sky Blue FF by various forms of cellulose. In the case of mercerised cotton, the cloth was allowed to shrink without restraint during mercerisation and was air-dried ; this material was found to take up more dye than standard cotton, in a ratio which was roughly independent of the concentration of salt. This ratio of 1·6 approximately is close to that found by Urquhart and Williams for the absorption of water vapour (see page 363). The absorption of Sky Blue FF is shown in Figs. 226 and 227.

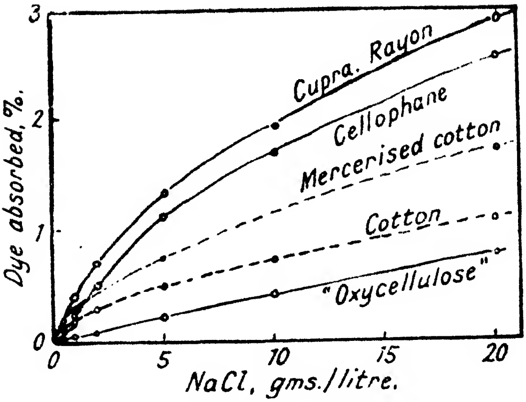


FIG. 226.—Absorption of Sky Blue FF.

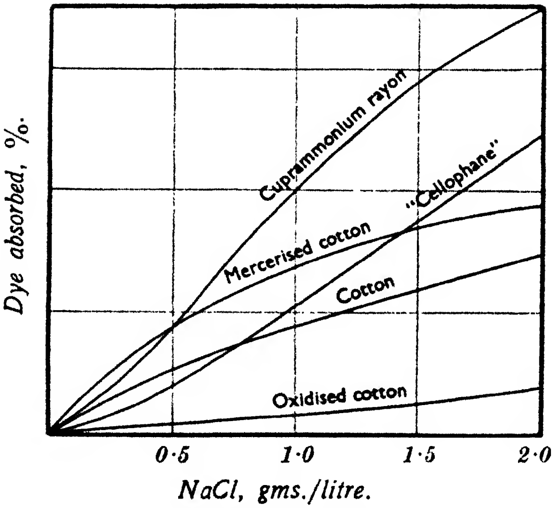


FIG. 227.—Absorption of Sky Blue, FF.

Lindemann (Angew. Chem., 1937, *50*, 157) has described at some length the results obtained by the absorption methods, for instance with iodine and direct dyes, in determining the degree of mercerisation of cotton. As an outcome of this work, a method is described of distinguishing between mercerised and unmercerised cottons by means of mercerisation or "*affinity diagrams,*" prepared by plotting the absorption of direct dyes against the concentration of sodium hydroxide used in mercerising.

A small sample of the material investigated is first examined for the presence of any water-soluble finish, particularly starch, by boiling with water. Any finish which may be discoloured by subsequent mercerisation must be removed by boiling with water and washing several times with distilled water. Wax and similar substances are removed by extraction with ether, and starch is removed by a desizing agent. The material (about 5 to 10 g.) is air-dried overnight and cut into four strips each weighing between 1 and 2 g. One of these strips is used as the control sample and the remaining three are mercerised under tension for 3·5 mins. each at 15 to 20° C. with 10, 15 and 25% solutions of NaOH containing 10 g. of Floranit per litre. The strips are then washed in running water, soured, washed and dried. Next day each strip is weighed to within 1 mg. and dyed separately in closed flasks containing 25 times the quantity of a solution of 120 mg. of chemically pure Chicago Blue 6B and 480 mg. Na_2SO_4 in 100 cc. of water, with vigorous shaking so that the temperature reaches 70° C. in 30 mins., and is then maintained at that temperature for a further 30 mins. The flasks are then cooled rapidly under the tap, the strips removed, each liquor diluted to 20 times its volume and the dye content determined by colorimetric comparison with a solution of 3 mg. of Chicago Blue 6B and 12 mg. Na_2SO_4 in 100 cc. of water. The absolute absorption of dye, calculated in mg. per 100 g., plotted against the concentration of NaOH used in the mercerisation, gives the "affinity diagram," when the dye absorbed is expressed in relation to a value of 100 for the unmercerised strip.

A number of factors, such as the origin of the cotton, the bleaching process, if any, the various dyeing processes and the temperature of drying or finishing, influence the individual affinity diagrams but, nevertheless, a certain type of diagram is always associated with the original state of the cotton when tested by this new method. For instance, if the dye absorption is increased by re-mercerisation with 10 or 15% NaOH solution, then it is concluded that the original mercerisation was equivalent to a treatment with alkali of lower concentration than 10 or 15% NaOH as the case may be. The increased affinity for dyes of cotton mercerised originally with 10% NaOH solution continues to increase in almost a straight line with 15% NaOH up to 1·5 or 2 times the value for the control, whilst the further increase with 25% NaOH is relatively small. If the sample has been mercerised previously with 10% NaOH solution, the affinity diagram does not attain the height of the diagram of the unmercerised cotton, but if the subsequent mercerisation is effected with 15% NaOH solution, then there is a greater increase in the affinity. If, on the other hand, the original fabric has been mercerised with 15% NaOH or stronger solutions, the mercerisation diagram frequently shows a small increase, and as compared with a less mercerised sample, scarcely rises above this value.

Some of these effects are shown in Figs. 228–231.

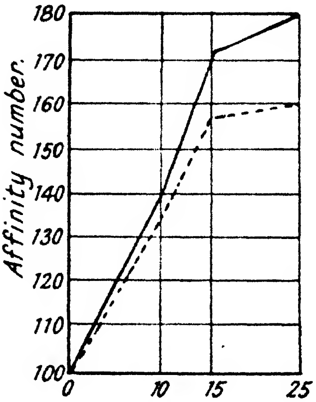
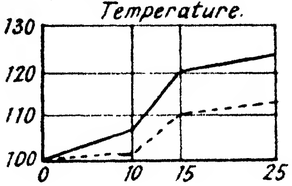


Fig. 228.—Originally unmercerised.


(a) Dried at Room Temperature.

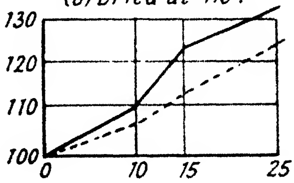
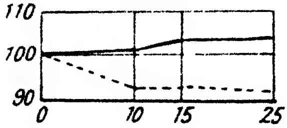

(b) Dried at 110°.

Fig. 229.—Originally mercerised, 10% NaOH.


(a) Dried at Room Temperature.

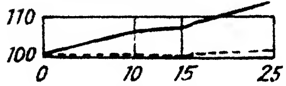
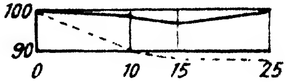

(b) Dried at 110°.

Fig. 230.—Originally mercerised, 15% NaOH.


(a) Dried at Room Temperature.

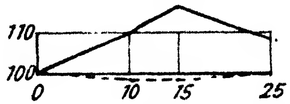

(b) Dried at 110°.

Fig. 231.—Originally mercerised, 25% NaOH.

The *rate of dyeing* has received attention from Boulton and Morton (J.S.D.C., 1940, *56*, 145). Relative dyeing speeds were measured for 0·12% Sky Blue FF and 5% NaCl in 40 vols. at 90° C. The speed of dyeing was estimated by the time required to absorb one-half the equilibrium quantity of dye.

RATE OF DYEING.

Fibre.	Time of half-absorption.
Sakel cotton	1·1 mins.
Sakel, mercerised with tension	0·25 "
American cotton	1·4 "
American, mercerised with tension	0·35 "

These data are taken from a longer list which shows that finer fibres dye more quickly than coarser material, but the complete data do not refer to mercerising. It appears, however, that mercerising under tension produces a fourfold increase in the speed of dyeing and one may reasonably expect further work in the future on mercerising under a wider range of conditions correlated with the velocity of absorption.

CHAPTER TWENTY-FIVE

ABSORPTION OF DILUTE ALKALI

Absorption of NaOH

ONE of the characteristic properties of mercerised cotton is its power of absorbing more alkali from dilute solutions than does unmercerised cotton.

This was first observed by Vieweg (Ber., 1907, *40*, 3876), who gave the following figures to show the relation between the weight of caustic soda absorbed by 3 g. of mercerised cotton wool from 2% NaOH solution and the concentration of alkali used in the mercerising process; the volume of the dilute alkali was 100 cc. and the time of immersion 30 mins.

ABSORPTION OF NaOH FROM 2% SOLUTION.

Material.	NaOH absorbed %
Untreated	1·0
Treated with 4% NaOH solution	1·0
" 8% "	1·4
" 12% "	1·8
" 16% "	2·8
" 20% "	2·8
" 24% "	2·8
" 28% "	2·9
" 32% "	2·9
" 50% "	2·9

Under similar conditions, viscose absorbed 4·5% and cuprammonium rayon 4% NaOH. Vieweg suggested that this might form a useful test of the "degree of mercerisation"; his results are also shown in the lower curve in Fig. 179 on page 286.

This suggestion failed to receive the attention it merits and it was not until the work of Neale (J.T.I., 1931, *22*, 320) that attention was devoted to this easy measurement.

It is necessary to make a compromise in the choice of the concentration of the alkali, for on the one hand high swelling concentrations must be avoided, and on the other hand certain modified celluloses characterised by a high absorption of the basic dyestuff methylene blue will contain a certain proportion of carboxylic acid groups, and as the object of the test is to measure the reactivity of the much more weakly acid hydroxyl groups, a fairly high alkali concentration must be used in order that the reaction with the latter may predominate. Experience showed that 0·5 *N* NaOH, as used by Vieweg, was very suitable.

The actual technique is as follows :

(*a*) *Standard Solutions.*

Decinormal hydrochloric acid is prepared by weight dilution of the constant-boiling acid, and is regarded as the standard. Half-normal sodium hydroxide is prepared by weight dilution of a filtered saturated solution of the pure reagent. The titre of 10 cc. of the half-normal alkali against the decinormal acid is determined within 0·02 cc., methyl red being used as indicator, and will be called the initial titre. As the end point is approached the solution is boiled to remove carbon dioxide and cooled, until the permanence of the colour indicates that the pH is stable at about 5·0.

(*b*) *Determination of the Absorption.*

The moisture present in cotton materials affects the apparent absorption of alkali in two opposite ways, first by diluting the alkali solution and so increasing the apparent absorption, and secondly, decreasing it on account of the fact that the amount of cellulose actually present is less than that assumed. With industrially mercerised cottons it so happens that these opposite effects almost balance, and in general a satisfactory allowance is made if the moisture regain of unmercerised cottons is taken to be 6%, of mercerised cottons 9%, and of regenerated celluloses 12%. Thirty cc. of the *N*/2 alkali are added to a weight of the sample corresponding to 2 g. of dry cellulose, and the whole is shaken, or allowed to stand with occasional shaking, for not less than two hours, preferably in a thermostat at a fixed temperature. Ten cc. of the clear solution are then titrated with the decinormal acid, with the aid of the same carefully calibrated pipette and burette as were used in obtaining the initial titre. Occasionally with very much overbleached samples, it may be necessary to filter the alkali through a coarse sintered glass to remove fragments of cotton hairs.

(*c*) *Calculation of Results.*

To determine the difference in the titre of the alkali due to absorption by the cellulose, the initial titre must be corrected for the dilution by the estimated water content of the sample, and, if thermostat control is employed so that the pipetted equilibrium solution is at a higher or a lower temperature than the decinormal acid, then the obvious small correction for change of volume should be made to the final titre. If the difference between the corrected initial and final titres is x cc. of decinormal acid, then the preferential absorption calculated on the basis of a constant liquid phase volume is $\frac{x}{10} \times \frac{30}{10} \times \frac{162}{2}$ milli-equivalents of alkali per $C_6H_{10}O_5$ equivalent. This figure refers to a constant initial soda concentration, the final equilibrium concentration being, of course, lower as the amount of absorption increases. The absorption calculated as above can be corrected to that obtained when the end concentration is half-normal, if the effect of concentration on the absorption is known. This effect was determined in a series of experiments to be described later, and a curve has been constructed (Fig. 232) giving the correction to be applied in order to obtain the absorption from a solution of end concentration half-normal, when the standard weight of sample and volume of half-normal solution have been used.

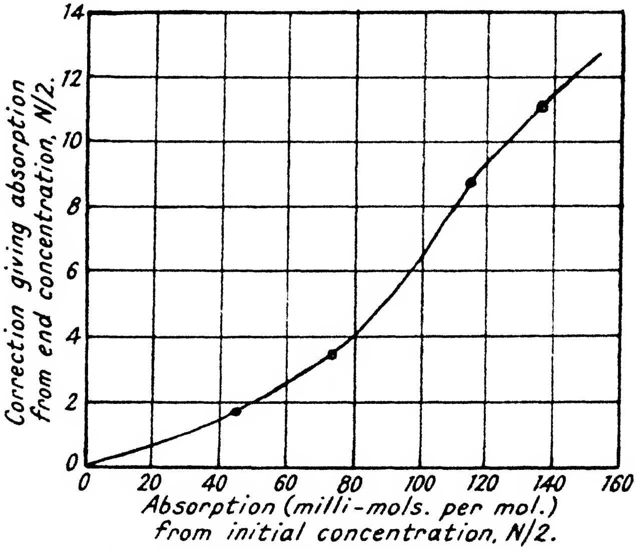


FIG. 232.—Correction of NaOH absorption.

It has been found convenient for the purpose of comparing samples of cellulose to divide this corrected figure by the mean absorption characteristic of natural cotton cellulose that has been boiled with dilute alkali to remove impurities, and call resulting ratio the "soda absorption ratio."

In a series of experiments concerned with the effect of the concentration of the reagent, the onset of mercerisation was quite distinct. Two-gram samples were shaken with 30 cc. of sodium hydroxide solution of concentrations ranging from *N*/4 to 5 *N*, and the change in titre of 10 cc. of the alkali solution enabled the preferential absorption of alkali to be calculated. The results are shown in Fig. 233.

The shape of the curve for alkali treated yarn (25 % NaOH loose) over the whole range, and for the other curves up to a certain critical concentration is typical of a chemical change in a homogeneous system approaching completion as the concentration rises. Neale's interpretation is one of the reaction of accessible hydroxyl groups with alkali proceeding in accordance with the law of mass action.

Above the critical concentrations the absorption curves of unmercerised and of technically mercerised cotton rise more

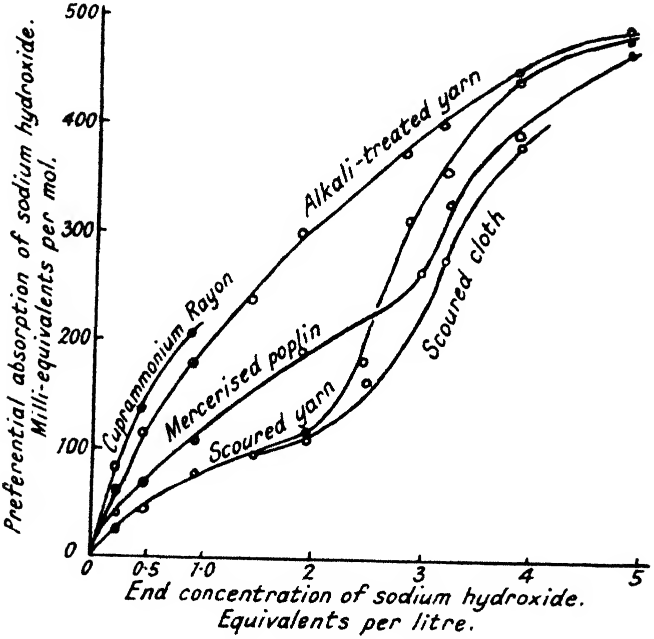


FIG. 233.—Absorption of NaOH.

steeply and finally flatten towards an asymptote, which is practically the same for all the samples. This indicates a rapid increase up to the same maximum in the number of accessible hydroxyl groups, as the reagent swells the cotton and is seen better in Fig. 234, where the absorption values are expressed relative to the absorption of the alkali treated yarn at the same end concentration, since this curve shows no inflexion (see Fig. 233); its absence shows that the absorbing effect remains more or less undiminished when the swollen material is washed and dried at a low temperature.

The scoured yarn shows a rapid rise in absorbing power between 2 and 3 *N*, the poplin cloths both mercerised and unmercerised between 3 and 4 *N*; all samples exhibit much the same absorption from the 5 *N* alkali. This activation is largely determined by those mechanical factors which may restrain the swelling of the cellulose, for the rise in absorption occurs at an appreciably higher alkali concentration for cloth than for yarn. This is in agreement with the work of Coward and Spencer (J.T.I., 1923, *14*, 32), Calvert (1930, *21*, 293), Calvert and Clibbens (1933, *24*, 233)—see pages 47, 94 and 312.

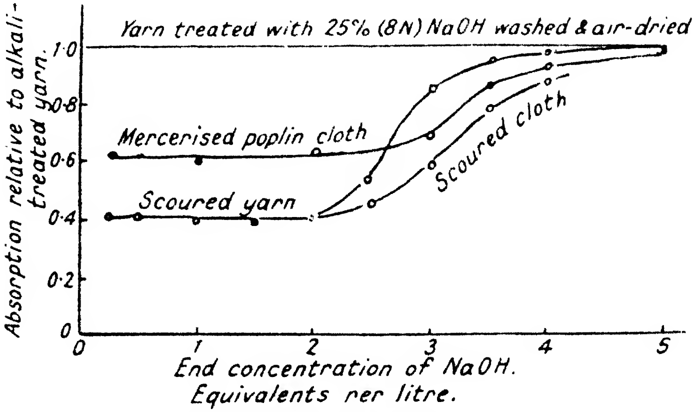


FIG. 234.—Absorption of NaOH, relative to mercerised yarn.

Figure 234 also demonstrates that for the purpose of discriminating between samples of cotton cellulose, the strength of reagent may lie anywhere below 2 *N* NaOH; the *N*/2 reagent adopted by Neale has no swelling action on native cellulose.

The soda-absorption ratios of cottons of different growth were determined from tests made on 2/50's yarn, scoured and washed together. The samples were then air-dried and found to absorb the following amounts of NaOH, corrected to end concentration (*N*/2), as shown on page 388.

Various samples of scoured and bleached sliver, yarns and fabrics all gave values of soda absorption lying between 45 and 48 milli-equivalents per 162 g. of dry cotton. Scoured ramie fibre gave an absorption of 46·8.

The determination of soda absorption ratio is valueless with raw cotton, owing to the interference of other constituents.

ABSORPTION OF NaOH BY VARIOUS COTTONS.
Temperature 18° to 20° C.

Variety of cotton.	Soda absorption.		
	Hair weight per cm. mgms. $\times 10^5$	Milli-equivalents per mole.	Ratio.
Arizona (immature)	107	47·4	1·02
Egyptian Sakellaridis	149	44·0	0·95
Brazilian	164	45·4	0·97
Egyptian uppers	196	44·0	0·95
Peruvian Mitafifi	202	50·0	1·08
Tanguis	212	46·5	1·01
Mean absorption		46·2	

In another series of experiments to show the effect of various concentrations of NaOH in the initial swelling, the method of removing the mercerising liquor was also varied : (*a*) washing in saturated brine after 24 hours immersion in NaOH, (*b*) washing in cold water after 24 hours immersion in NaOH and (*c*) washing in cold water after only 3 mins. immersion in NaOH.

The following figures were obtained :

SODA ABSORPTION RATIOS OF SCOURED 2/40S SAKEL YARN WHICH HAS BEEN TREATED LOOSE WITH SODIUM HYDROXIDE SOLUTION AT 25° C., WASHED, SOURED, WASHED AND AIR-DRIED.

Concentration of caustic soda for pretreatment, g. per 100 g. solution.	Soda absorption ratios (duplicate measurements).						
	In alkali solution 24 hrs., first washed with				In alkali 3 mins., water washed.		
	Saturated brine.		Cold water.				
10	1·28	1·27	...	...	...	...	...
12	1·55	1·57	...	...	...	...	...
13·4	2·28	2·26	...	...	...	...	...
15	2·38	2·39	2·38	2·38	2·45	2·45	2·45
17·5	2·33	2·36	...	...	...	...	...
20	2·40	2·40	2·44	2·47	2·42	2·41	...
25	2·44	2·46	2·66	2·62	2·60	2·61	...
32·4	2·49	2·49	2·68	2·72	2·73	2·71	...
46·2	2·61	2·62	2·72	2·72	2·19	2·19	...

The method in (*c*) was adopted in order to obtain samples comparable in properties with those prepared by Urquhart and Williams (J.T.I., 1925, *16*, 155 ; 1927, *18*, 55) for the estimation of moisture absorption.

The effect of the alkali treatment is seen to rise very rapidly as the concentration increases from 10% to 15% and this is also true of the moisture absorption (see page 364) and of the reactivity to alkaline hypobromite solution (see page 278). The effects are seen clearly in Fig. 235, from which it appears that three mins. immersion is not sufficient at the highest concentration for production of the maximum effect.

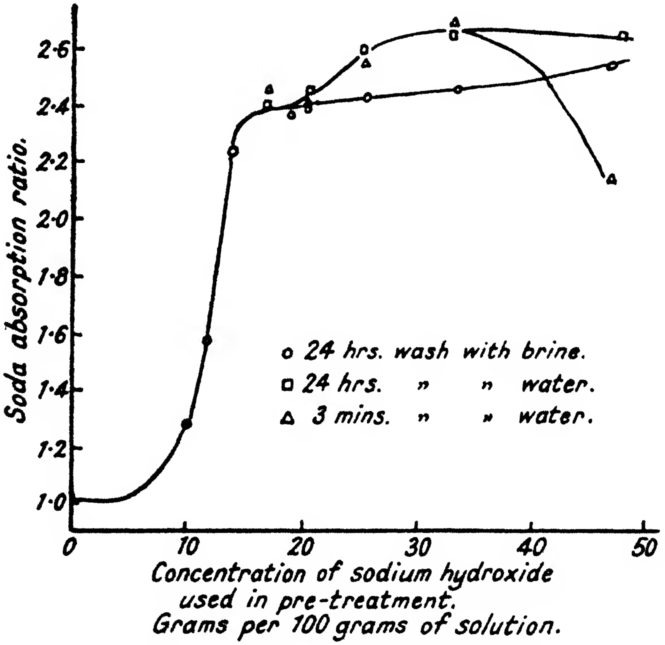


FIG. 235.—NaOH absorption ratios.

This is in agreement with the previous observation of Neale (J.T.I., 1929, *20*, 373) that solutions of sodium hydroxide which are approaching saturation swell cellulose relatively slowly. It will also be seen from the curves that at concentrations above 20% NaOH a more reactive product is obtained by washing with water instead of brine ; this may be attributed to the transient swelling of the cellulose on account of the momentary disturbance of osmotic equilibrium between the external solution and the cellulose (see page 350).

Neale has also made an interesting comparison of the absorptive capacity of the treated product with the extent to which the cotton was swollen in the alkali. The amount of swelling is known for regenerated sheet cellulose (J.T.I., 1929, *20*, 373) and a fair estimate of the amount of swelling of Sakel cotton yarn was afforded by the shrinkage in the alkali solutions of lengths of yarn under load of 0·3 g.

These properties are compared in Fig. 236—the soda absorption ratio relates to yarn which was immersed for 24 hours in the alkali and first washed with brine.

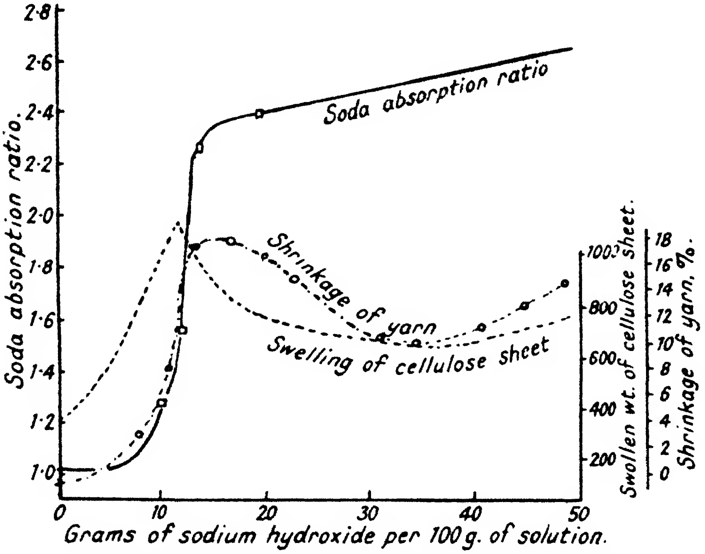


FIG. 236.—Comparison of NaOH absorption, shrinkage and swelling.

Whilst the soda absorption ratio reflects the rapid increase in swelling power between 10 and 14 % NaOH, it is unaffected by the fall in swelling as the concentration approaches 30 %. This is supported by an observation that when scoured yarn is treated with 11 % (3·1 *N*) NaOH at −10° C. the soda absorption ratio is only 2·67, no higher than that obtained at 25° C. in spite of the much greater swelling at the lower temperature —see page 279.

Neale has also shown that the increase in activity caused by solutions of concentration greater than 15 % NaOH is not diminished by removal of the alkali and drying at low temperatures, but on the other hand with concentrations of alkali between 10 % and 14 % NaOH the activation is not wholly permanent. This is seen in Fig. 237.

Curve *A* represents the soda absorption ratio due to treatment with solutions of NaOH as shown on the scale of abscissæ ; it runs horizontally for some time at 1·0 and then rises steeply between 10 and 14 % NaOH to a ratio of 2·4, Curve *B* was constructed from the data of Fig. 233 and represents the results of absorption measurements expressed as the absorption characteristic of scoured cotton relative to that characteristic of the alkali treated yarn of Fig. 233. To facilitate comparison the absorption of the latter sample is regarded as 2·4 units from any solution. Curve *A* thus represents the amount of activation that persists after washing and air-drying, whilst curve *B* shows the increase of reactivity which cotton yarn displays when immersed in NaOH solutions of various concentrations.

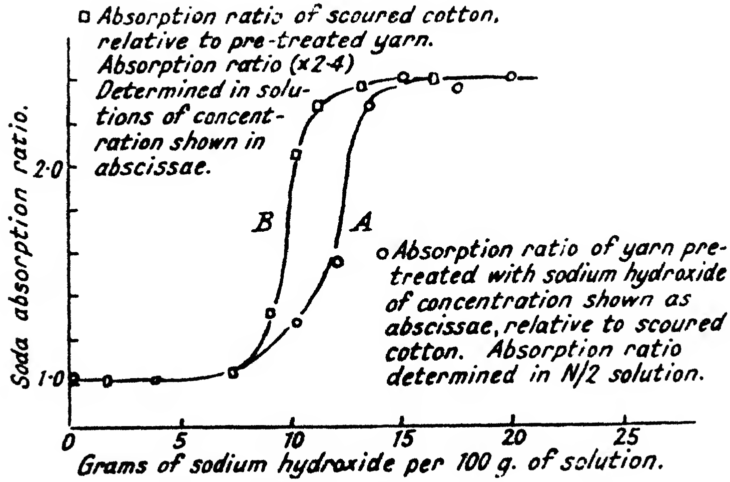


FIG. 237.—Comparison of activation before and after washing and drying.

Other interesting data by Neale show the effect of restraining shrinkage and of the temperature of drying on the absorptive capacity of grey and scoured yarns when treated with 25 % solutions of NaOH. The most remarkable feature of the results is the great decrease in reactivity as the effect of mechanical restraint ; there is also considerable difference between yarns mercerised in the scoured and grey states. It is also seen from the following table that drying at 110° C. decreases the reactivity of the most absorptive samples, but has little effect on the less reactive material mercerised in the grey state with restrained shrinkage.

Bancroft and Calkin (Text. Res., 1934, *4*, 119) also found that drying cotton, both mercerised and unmercerised, at 105° C. decreased the amount of NaOH taken up from dilute solutions.

ALKALI ABSORPTION RATIOS OF YARN MERCERISED WITH 25% CAUSTIC SODA.

	Dried at room temperature.		Dried at 110° C. for 6 hours.	
	Na ratio.	Ba ratio.	Na ratio.	Ba ratio.
Scoured and then mercerised :				
Loose (about 15% shrinkage)	2·55	2·70	2·27	2·52
Loose and restretched . .	2·07	2·10	1·93	1·98
No shrinkage allowed . .	1·96	2·05	1·89	1·99
Cloth mercerised loose . .	2·13	...	...	...
Mercerised in the grey state and then scoured :				
Loose (about 15% shrinkage)	2·09	2·20	1·84	1·97
Loose and restretched .	1·76	1·79	1·76	1·83
No shrinkage allowed . .	1·68	1·73	1·69	1·75

The samples mercerised loose were washed with cold water initially, the rest with hot water.

The yarns whose absorption ratios are given on page 391 were treated in the grey state with 24% NaOH solution, with 4% contraction in length, followed by stretching to the original length, washing, etc., and drying at room temperature. The absorption ratios show that the increase due to mercerisation is relatively constant.

ABSORPTION RATIOS.

Cotton.	Scoured.	Mercerised.
Sakel . . .	0·95	1·57
Egyptian uppers .	0·95	1·57
Brazilian . .	0·97	1·62
Tanguis . . .	1·01	1·63
Arizona . . .	1·02	1·63
Peruvian . .	1·08	1·68

Neale also gives some data on the absorption ratios of cotton yarn treated with swelling agents other than NaOH. With the exception of cuprammonium hydrate, these swelling agents, which have little in common except their ability to swell cotton, produce material of high absorptive capacity.

ABSORPTION RATIOS.

Pretreating solution.		Estimated extent of swelling.	Soda absorp. ratio.	Baryta absorp. ratio.
Sulphuric acid, 65%, for 30 secs. at 20 C.	Loose	Very great, loose yarn approaching complete dissolution	3·20	3·20
	No shrinkage		2·55	2·52
Zinc chloride, 73·3% for 25 hrs. at 20C.	Loose		3·13	3·33
	No shrinkage		2·48	2·36
Cuprammonium hydroxide Cu 5·5 g. per litre. NH_3 88 g. per litre 1 hour at 20° C.	Loose		1·45	1·36
Cuprammonium hydroxide Cu 5·0 g. per litre. NH_3 80 g. per litre 1 hour at 20° C.	Loose	Greater than in 25% NaOH	1·03	1·02
Caustic soda, 25% at 25° C.	Loose	...	2·55	2·60
The untreated 2/40's scoured Sakel yarn		...	1·01	1·01

Absorption of Barium Hydroxide

The absorption of barium hydroxide by cellulose which has been treated with swelling agents gives similar information to that obtained by the absorption of sodium hydroxide from dilute solutions, but since the absorption is greater in amount it may be determined more exactly. The experimental procedure of Neale (J.T.I., 1931, *22*, 349) is similar to that adopted for the soda absorption ratio, but the standard strength of the reagent is $N/4$ and the absorptions are referred to a fixed end concentration of $N/5$.

A weight of the sample containing 2 g. of dry cotton is allowed to stand overnight with occasional shaking in 30 cc. of barium hydroxide solution and 10 cc. are then withdrawn for titration with standard acid. The amount of alkali preferentially absorbed is calculated from the change in titre, with the appropriate corrections for dilution by moisture content and for differences in temperature between the alkali and acid. The standard temperature is 25° C. and the strength of reagent $N/4$.

Fig. 238 shows the results of experiments on the same four samples of cellulose as for Fig. 233, page 389.

Two g. of the material were immersed in 30 cc. of baryta solution, except in the case of rayon, where absorption was also measured in the most concentrated solution in the ratio of 1 g. to 30 cc. The preferential absorptions of baryta as determined are not strictly comparable quantities since they refer to equilibria with solutions of varying concentration. From the data of Fig. 238, however, corrections may be deduced applicable to experiments made with 2 g. of cellulose and 30 cc. of $N/4$ baryta, the observed absorption being converted to that to be expected if the end concentration were always $N/5$. The correction is shown in Fig. 239.

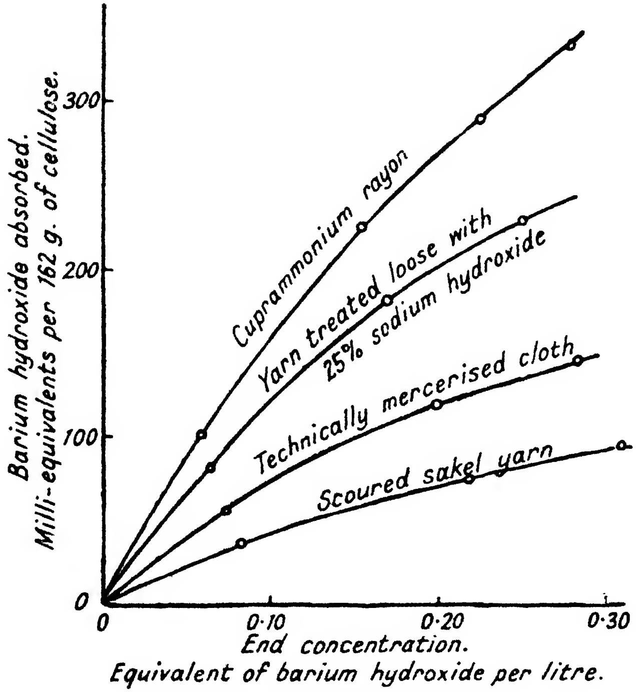


FIG. 238.—Absorption of baryta.

The absorption so corrected to a fixed end concentration is divided by the corrected absorption characteristic of scoured natural cotton (71·0 milli-equivalents at 25° C.), and the quotient is termed the "baryta absorption ratio." Here again it must be emphasised that the baryta ratio cannot be relied upon as a direct measure of any quality of textile merit—it is, however, useful as a test of the regularity of any standard mercerised product.

As in the case of the soda absorption ratio measurements, a number of yarns of different cottons were spun to 2/50s and a portion of each mercerised by wetting, immersing in 24% NaOH solution so as to allow 4% contraction, restretching, washing and air-drying. The samples both grey and mercerised were then scoured together for six hours at 20 lbs. excess pressure in 1% solution of NaOH, soured, washed and air-dried. The baryta absorption ratios are given in the following table, together with the soda absorption figures for comparison.

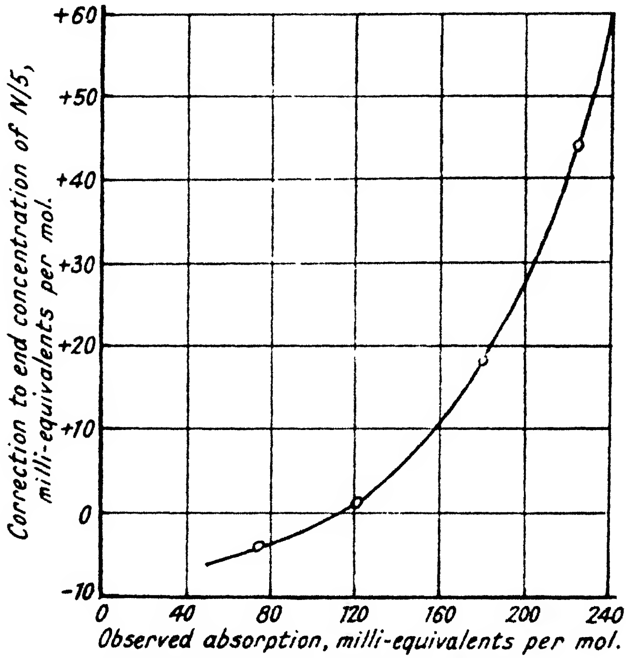


FIG. 239.—Correction of baryta absorption.

The absorption does not vary greatly from one variety to another, and both baryta and soda absorption ratios place the samples in substantially the same order for both mercerised and unmercerised cotton.

Neale also measured the baryta and soda absorption ratios of Sakel yarn, mercerised in the grey and scoured states, with and without tension, in solutions of NaOH of various concentrations. The results are shown in the table (page 400), and also in Fig. 240; the fact that the curves for cotton mercerised in the grey and scoured states cross at high alkali concentrations may be attributed to the local dilution of the

ABSORPTION RATIOS.

Variety of cotton.	Hair Wgt. mg./cm. $\times 10^5$	Scoured only.			Mercerised and scoured.	
		Baryta absorp.		Soda absorp. ratio.	Baryta absorp. ratio.	Soda absorp. ratio.
		Mili-equivalents corrected to end concentration N/5.	Ratio.			
Egyptian Sakellaridis	149	74·0	0·94	0·95	1·57	1·57
Egyptian uppers .	196	75·0	0·95	0·95	1·61	1·57
Brazilian . .	164	77·8	0·985	0·97	1·66	1·62
Tanguis . .	212	78·7	1·00	1·01	1·66	1·63
Arizona (immature) .	107	80·7	1·02	1·02	1·70	1·63
Peruvian Mitafifi .	202	86·5	1·09	1·08	1·66	1·68

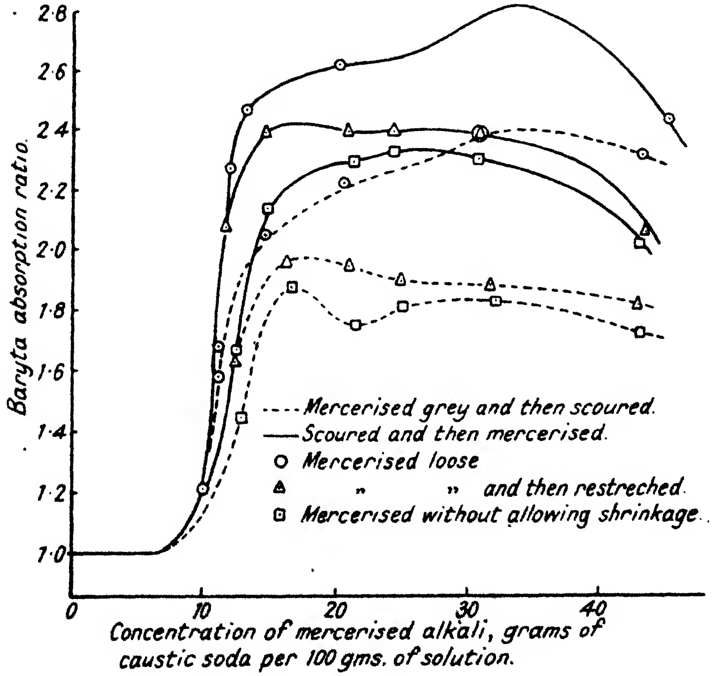


FIG. 240.—Baryta absorption.

ABSORPTION RATIOS OF MERCERISED COTTON.

Concentration of mercerising liquor, g. NaOH per 100 g. solution.	Scoured—then mercerised.						Mercerised grey—then scoured.					
	Loose.		Loose and restretched.		No shrinkage.		Loose.		Loose and restretched.		No shrinkage.	
	Alkali absorption ratios.											
	Na	Ba	Na	Ba	Na	Ba	Na	Ba	Na	Ba	Na	Ba
10·0	1·28	1·21	...	...	...	...	...	...	...	...	...	...
11·6	1·58	1·67	...	...	...	...	1·51	1·57	...	...	...	...
12·5	...	...	1·92	2·07	1·60	1·65	...	...	1·61	1·63	1·41	1·43
13·4	2·28	2·26	...	...	...	...	...	...	...	...	...	...
15·0	...	2·46	...	...	...	...	1·86	2·04	...	...	...	...
16·0	...	...	2·30	2·40	2·07	2·16	...	...	1·95	1·95	1·73	1·85
20·5	2·39	2·62	...	...	...	...	2·02	2·19	...	...	...	...
21·0	...	...	2·30	2·41	2·18	2·28	...	...	...	1·94	1·68	1·75
25·0	...	...	2·34	2·40	2·23	2·34	2·09	2·20	1·85	1·88	1·75	1·79
25·5	2·47	2·61	...	...	...	...	2·13	2·22	...	...	...	...
32·0	...	...	2·28	2·40	2·24	2·33	...	...	1·86	1·89	1·85	1·82
32·4	2·58	2·86	...	...	...	...	2·29	2·39	...	...	...	...
45·0	...	...	1·90	2·06	1·84	2·01	...	...	1·85	1·84	1·76	1·78
46·0	...	2·48	...	...	...	...	2·17	2·34	...	...	...	...

concentrated alkali by the wetting liquor entrained in the grey cotton.

A modification of the baryta absorption test has been described by Edelstein (A.D.R., 1936, *25*, 186) and this differs from that of Neale mainly in that the absorption of a sample of unmercerised cotton, treated in the same manner as the sample under examination, is determined with the absorption of the latter. The results are expressed as the ratio of the absorption of the tested sample to that of the standard unmercerised sample.

The effect of various factors was investigated and it was found that the variables of time of standing above two hours, the concentration of barium hydroxide solution and the temperature did not affect the results ; the test is also applicable to dyed samples. It was established that whereas samples of commercially mercerised yarns gave activity numbers close to 150, commercially mercerised piece goods only gave activity numbers varying from 115 to 130.

Absorption of Copper from Cuprammonium Hydrate Solution

When cotton cellulose has been treated in the loose state with sufficiently concentrated sodium hydroxide solution, the absorptive capacity rises about 2·6 fold, as shown by measurements of the absorption of sodium or barium hydroxide from dilute solutions. The results of a similar swelling process on the capacity to absorb water vapour from atmospheres of varying humidity showed that the increase did not amount to more than 1·7 fold. This difference may be explained on the assumption of different permeability to water and to alkali or on the assumption that the alkalis react with only one of the available hydroxyl groups in the glucose residue, the water with all three, while the swelling treatment leads to a relatively greater increase in the number of free mutually unsaturated hydroxyl groups of the salt-forming type. On this basis, together with the contention of Hess and Trogus (Z. phys. Chem., 1929, *145A*, 401) that the reaction with cuprammonium hydroxide, especially in presence of sodium hydroxide, involves the two non-salt forming hydroxyl groups, the reactivity towards cuprammonium hydroxide should be low.

Brownsett, Farrow and Neale (J.T.I., 1931, *22*, 357) have accordingly measured the absorption of copper from dilute solutions of cuprammonium hydroxide. The results of Hess and Trogus (Z. phys. Chem., 1929, *145A*, 413) indicated that the absorption of copper from cuprammonium containing sodium hydroxide was not dependent to any great extent on the cellulose or on previous mercerisation, but the solutions they employed were of themselves sufficiently concentrated to swell cellulose. The use of a standard reagent too dilute to swell cellulose showed that the absorption of copper is dependent on the pretreatment of the cellulose. The method finally adopted by Brownsett, Farrow and Neale is of technical utility where only small samples of the order of 10 mg. are available.

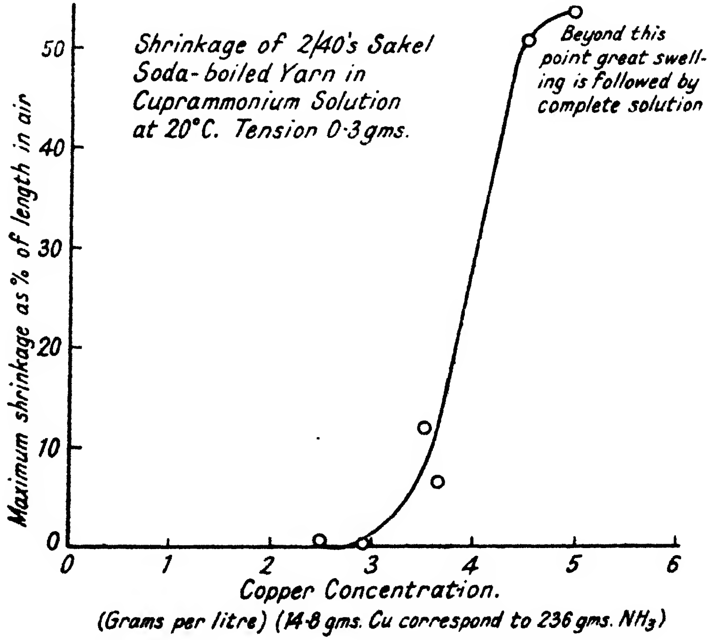


FIG. 241.—Swelling in cuprammonium hydrate.

The choice of the concentration of the reagent was first investigated, taking the shrinkage of 2/50s Sakel yarn as a measure of the swelling of the cellulose. From the results as shown in Fig. 241 it appears that a solution containing less than 2·5 g. of copper per litre has no appreciable swelling action. The solution adopted as the standard reagent had a concentration of 1·85 g. of copper, 28·5 g. of ammonia and 0·02 g. of nitrous acid per litre, and may be prepared from the standard cuprammonium hydroxide solution used for viscosity determinations (see page 242).

About 10 mg. of the sample are weighed on a micro-balance, immersed in a volume of cuprammonium hydroxide calculated on the basis of 15 cc. to 10 mg. of dry cellulose and allowed to stand in the solution for four hours at 20° C. with occasional shaking. The sample is then removed from the liquor, blotted between sheets of filter paper and dried in the oven to drive off the ammonia. The copper is estimated by a method based on that of Baines (J.S.C.I., 1929, *48*, 303), and full details are given in the paper of Brownsett, Farrow and Neale (loc. cit.).

Experiments on scoured cotton yarn gave a mean result of 66·8 milli-equivalents of copper absorbed by 162 g. of dry cotton.

In conformity with the procedure adopted for the soda and baryta absorption ratios, the observed absorption of copper is divided by 66·8, so as to express the copper absorption as a ratio relative to that of scoured cotton cellulose. From the figures on page 404 it will be seen that the copper absorption of scoured cotton rises about 2·6 fold after treatment in the loose condition with 25% NaOH solution. (These determinations fail to substantiate the speculations of Hess and Trogus with regard to the reaction with cuprammonium hydroxide.)

Additions of sodium hydroxide to the cuprammonium hydroxide solution at extreme dilutions of copper indicate that the increase in copper absorption brought about by the addition of sodium hydroxide is still marked, even when the cellulose remains unswollen.

ABSORPTION OF COPPER BY SCOURED COTTON YARNS.

Initial concns. of Cu, 0·00147 N ; of NH_3, 0·25N.

Concn. of NaOH.	Absorption of Cu. (millimoles per 162 g.).		Final concn. of Cu. (equivalents per litre).
0	8·48	8·48	0·00141
0·075	21·0	19·4	0·00133
0·252	29·1	28·5	0·00127
0·540	43·2	43·2	0·00117
0·958	69·0	68·0	0·00099
0·958	79·5	82·9	0·00131

Experiments on the copper absorping power of different samples of cellulose have been done from solutions dilute in copper but moderately concentrated in NaOH. The samples absorbed widely different amounts of copper, but when the copper and ammonia concentrations approached those employed by Hess and Trogus, the differences almost disappeared. Hence it follows that their observation that different forms of cellulose are equally reactive to cuprammonium sodium

COPPER ABSORPTION RATIOS OF VARIOUS SAMPLES OF COTTON CELLULOSE.

NATURE AND PRETREATMENT OF SAMPLE.	Copper absorption millimoles per mole.			Copper ratio.	Soda ratio.	Baryta ratio.
Sakel yarn scoured 1% NaOH for 6 hrs. at 20 lb. excess pressure	65·2		65·2	Taken as	1·01	1·02
	69·5		67·0	1·00		
Technically mercerised cloth	(108		113)	1·67	1·62	1·66
	(108		117)			
Loose scoured cotton pretreated cuprammonium 24 hrs. (5·5 g. Cu per litre)	123		142	1·99	1·45	1·36
Scoured Sakel yarn treated loose with 25% NaOH, air dried	187	178	169	2·66	2·53	2·66
Above wetted and dried fourteen times at 110° C.	145		141	2·14	2·09	2·10
Yarn treated loose with 3N NaOH at −7° C.	205		205	3·07	2·70	2·79
Cuprammonium rayon	222	216	207	3·22	3·20	3·81
VARIATIONS OF MERCERISING PROCESS (all 3 mins. at 25° C.).						
Mercerised grey, then scoured :						
12·5% NaOH. No shrinkage	101		103	1·52	1·41	1·43
25% NaOH. No shrinkage	116		119	1·76	1·75	1·79
25% NaOH. Loose and restretched	122		125	1·85	1·85	1·88
25·5% NaOH. Loose	155		157	2·33	2·33	2·22
Scoured and then mercerised :						
12·5% NaOH. No shrinkage	110		113	1·67	1·60	1·65
25% NaOH. No shrinkage	159		165	2·42	2·23	2·34
25% NaOH. Loose and restretched	157		157	2·35	2·34	2·40
25·5% NaOH. Loose	173		174	2·60	2·47	2·61

hydroxide solutions only applies when the solution possesses sufficient swelling power to bring the least reactive form of cellulose up to the level of the most reactive sample.

The data given in the above table show that the absorption of copper from dilute solutions of cuprammonium hydroxide is broadly similar to the absorption of sodium hydroxide and baryta, except in the case of cotton which has been pretreated with a solution of cuprammonium hydroxide sufficiently concentrated to bring about great swelling. In this instance the sample showed a greater increase of absorptive capacity towards dilute cuprammonium hydroxide than towards the simple alkalis (see page 404).

$NaOH$ and $Ba(OH)_2$

Returning to the question of the absorption of sodium or barium hydroxides from dilute solutions by mercerised cotton, it has been shown that from solutions of the same equivalent concentration, barium hydroxide is absorbed about three times as strongly as sodium hydroxide. Neale and Stringfellow (J.T.I., 1933, *24*, 30) showed that cellulose is actually less highly swollen in barium hydroxide solutions than in water. This behaviour is not consistent with the application to barium hydroxide of the hypothesis of ionised salt formation applied to sodium hydroxide. Experiments were therefore made to analyse the system cellulose-barium hydroxide and also to establish whether in the case of the mixed alkalis they reacted merely as two bases competing for the same acid.

With regenerated sheet cellulose and barium hydroxide it was found that the absorption of the alkali increased steadily with the concentration, but that the absorption of water, and therefore presumably the swelling of the cellulose, decreased. This is shown in Fig. 242.

The curves in Fig. 243 show that as the concentration of baryta is increased in presence of NaOH at a fixed concentration, the absorption of barium increases smoothly and continuously, whilst the absorption of sodium falls. The absorption of barium from the mixed solution is always greater than from the pure baryta solution at the same concentration of barium hydroxide. The effect of barium hydroxide in decreasing the water absorption or in shrinking the cellulose is again seen in the mixed solutions.

Fig. 244 relates to conditions where the concentration of baryta is fixed, whilst that of sodium hydroxide varies. The addition of sodium hydroxide is seen to increase the absorption of barium and the first additions of NaOH—up to 0·2 *N*—exert the greatest effect. Sodium hydroxide soon becomes the predominant alkali and this leads to swelling of the cellulose with increased water absorption, so that the curve of total sodium absorption becomes concave upwards as with pure sodium hydroxide solutions.

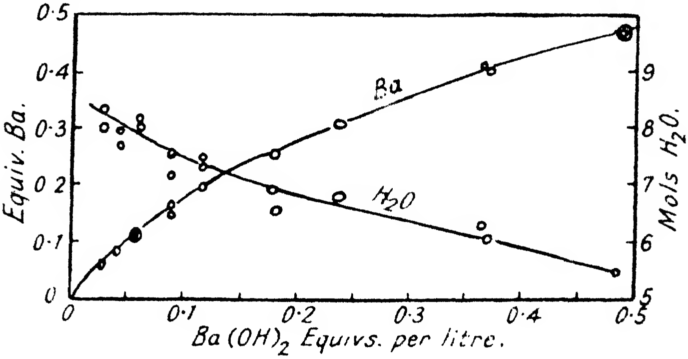


FIG. 242.—Absorption of Ba and H_2O.

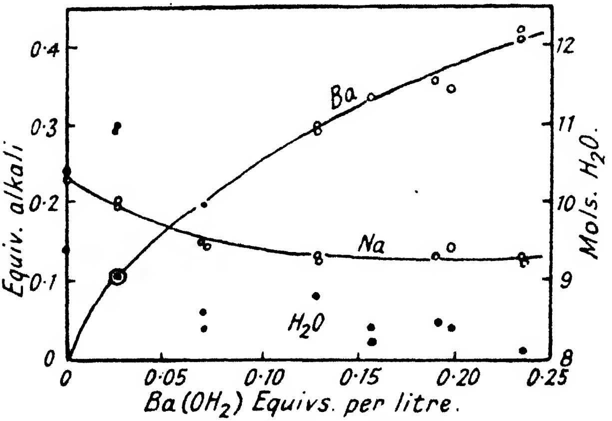


FIG. 243.—Absorption of $Ba(OH)_2$ and NaOH from solutions with constant NaOH and increasing $Ba(OH)_2$.

This behaviour is quite inconsistent with exact similarity of mechanism of absorption of barium and sodium hydroxides, and Neale suggests that the absorption of barium hydroxide by cellulose depends on the ionic product of barium and hydroxyl ions.

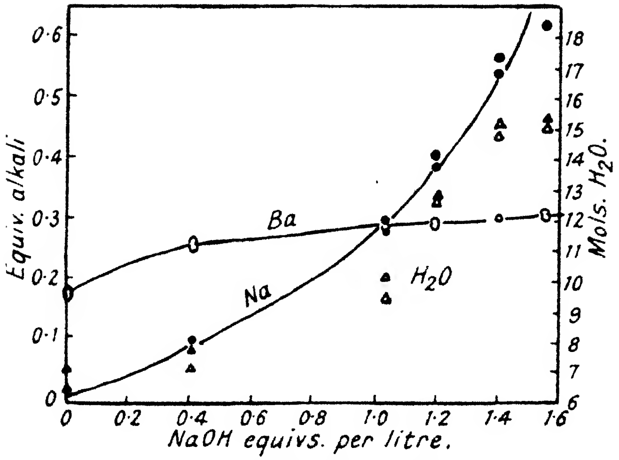


FIG. 244.—Absorption of $Ba(OH)_2$ and NaOH from solutions with constant $Ba(OH)_2$ and increasing NaOH.

General

Neale (J.S.C.I., 1931, *50*, 177) has tabulated the various "activation ratios" of mercerised cotton according to the concentration of alkali with which the native fibre was treated. The columns with reference figures 3 and 16 refer to reactivity ratio and hydrolysis numbers respectively, whereas the remaining data relate to absorption ratios.

ACTIVATION RATIOS.

Conc. of NaOH used in pre-treatment, g./100 g. soln.	17 Water vapour.	3 Alkaline hypobromite.	16 5% H_2SO_4	12 Benzopurpurin 4B	14 0·5 N-NaOH.	14 0·2 N-$Ba(OH)_2$	6 Dilute cuprammonium.
0	1·0	1·0	1·0	1·0	1·0	1·0	1·0
10·0	1·1	1·0	1·1	...	1·2	1·2	...
12·5	1·4	1·3	...	...	1·9	1·9	...
15·0	1·6	1·6	1·7	...	2·3	2·4	...
20·0	1·5	1·6	...	2·2	2·4	2·6	...
25·0	1·6	...	2·2	...	2·5	2·6	2·6
32·5	1·6	...	2·2	...	2·6	2·8	...

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6. Brownsett, Farrow and Neale, J.T.I., 1931, **22**, 357.
12. Knecht, J.S.D.C., 1908, **24**, 107.
14. Neale, J.T.I., 1931, **22**, 320.
16. Schwalbe, Z. angew. Chem., 1908, **21**, 1321; 1909, **22**, 197.
17. Urquhart and Williams, J.T.I., 1925, **16**, 155.

The activation ratios of yarn treated loose with 25 % NaOH solution, washed and dried as under, are also of interest.

EFFECT OF DRYING TEMPERATURE.

	Water vapour.	Alkaline hypobromite.	0·5 *N* NaOH.	0·2 *N* $Ba(OH)_2$
Air dried . .	1·66	1·75	2·55	2·70
Dried at 110° C. .	1·51	1·76	2·27	2·52

The effect of the temperature of drying on the activation of mercerised cotton has also been discussed on page 375 in respect of water-imbibition, and on page 380 in respect of dyestuff absorption.

The activation ratios referred to on the previous page have been considered as follows: water vapour (page 364), alkaline hypobromite (page 278), H_2SO_4 (page 274), Benzopurpurin (page 379), NaOH (page 392), $Ba(OH)_2$ (page 399), and cuprammonia (page 404).

CHAPTER TWENTY-SIX

IODINE ABSORPTION

THE possibility of the absorption of iodine forming a test for mercerised cotton has received attention from many various sources; for example, Cross and Bevan (Cellulose, London, 1895, page 7) state that the "hydrates" of cellulose generally react with iodine in aqueous solution to give an indigo blue coloration, but Hübner (J.S.C.I., 1908, *27*, 105) in his detailed paper on iodine absorption states that no coloration was observed in the case of mercerised cotton treated with a solution of iodine in water.

The absorption of iodine from solution in potassium iodide solution was found to present a simple and satisfactory test of the mercerising process, not only to determine whether the cotton had been mercerised or not, but also the approximate degree of dispersion. Various strengths of solution were employed from $N/10$ to $N/400$ iodine.

With $N/100$ iodine solution, if cotton hanks which had been mercerised with different concentrations of caustic soda were immersed for four hours, a good gradation of colour was obtained according to the degree of mercerisation.

With $N/100$ iodine, 50 g. samples of variously treated cottons were immersed in 500 cc. of the solution for 48 hours. Titration of the residual liquor gave the following results which are compared in the table with the moisture contents:

MOISTURE CONTENT AND IODINE ABSORPTION.

	Moisture %	Iodine absorbed. g.
Ordinary cotton, unbleached	6·12	0·1500
" bleached	5·88	0·1448
Cotton mercerised without tension—		
unbleached	8·535	0·2311
bleached	8·36	0·2108
Cotton mercerised under tension—		
unbleached	7·65	0·2083
bleached	7·45	0·1778

The most important observation of Hübner was that whereas the iodine may be removed very rapidly from unmercerised cotton by washing with water, mercerised cotton behaves differently in this respect. For example, in the case of hanks immersed for a few minutes in $N/10$ iodine solution, after two or three applications of water the brown coloration of both mercerised and unmercerised cotton becomes a chocolate shade. At this stage unmercerised cotton is rapidly decolourised by water, whereas mercerised cotton turns a dark blue colour, which, however, disappears on repeated washing.

Hübner also found that if the quantity of iodine and potassium iodide is increased, the blue coloration of the mercerised cotton after washing is more stable, but it is still possible completely to remove the iodine from the unmercerised cotton. Alternatively, washing with 2 % potassium iodide solution in place of water shows the difference in a pronounced fashion. The solution recommended by Hübner for the detection of mercerised cotton is 30 g. iodine in 100 cc. of saturated potassium iodide solution. A variation of this test is to expose the hanks to the atmosphere without drying, whereupon the iodine rapidly disappears from the unmercerised hank after it is dry, whereas the dark brown colour of the mercerised hank disappears very slowly.

It was also demonstrated that cotton mercerised without tension shows a more pronounced effect than cotton mercerised under tension.

An earlier test utilising iodine was based on the work of Herzberg (Papierprüfung, Berlin, 1902, p. 65) in connection with paper-making ; a solution of zinc chloride and iodine coloured cotton fibres claret-red and wood fibres dark blue. Lange (Bericht des V. Internationalen Kongresses für angewandte Chemie, Berlin, 1903, *2*, 909) made use of a similar solution for the detection of mercerised cotton ; 5 g. potassium iodide and 1–2 g. iodine were dissolved in 12–24 cc. water and then mixed with a solution of 30 g. of zinc chloride in 12 cc. of water. When cotton was immersed in this reagent and subsequently washed with water, the time of decolorising was indicative of the extent of mercerisation of the material, as shown in the following table.

This test was examined by Hübner (J.S.C.I., 1908, *27*, 105) who found that solutions of zinc chloride containing only very small amounts of iodine produce a distinct coloration on mercerised and unmercerised cotton ; the colour reaction was

IODINE TEST.

Treatment.	Time to decolourise.
Unmercerised . . .	Immediately.
3·5% NaOH . . .	2 mins.
6·5% " . . .	8 "
10% " . . .	35 "
14·5% " . . .	6 hours.
18·5% " . . .	10 ,,

found to be influenced by the strength of the zinc chloride solution.

The reagent preferred by Hübner is a solution containing 250 g. of zinc chloride in 300 cc. of water; various amounts of iodine were added to 100 cc. of the above solution and utilised as a test for mercerisation, when it was finally found that a suitable mixture consisted of 20 drops of a solution containing 1 g. of iodine and 20 g. of potassium iodide in 100 cc. of water to 100 cc. of the above-mentioned zinc chloride solution. When the samples are previously wetted and pressed between filter papers and then placed in the reagent, the mercerised cotton is coloured blue, varying in depth according to the concentration of the mercerising liquor, whilst the unmercerised cotton remains almost white.

A large number of variations of the above test have been described and Hübner has described the effect of replacing the zinc chloride by mineral acids and by aluminium chloride.

Harrison (J.S.D.C., 1915, *31*, 198) also made use of the absorption of iodine as a means of following the change produced by the mercerisation of cotton. Previous work on starch (Kolloid Z., 1911, *9*, 5) led to the investigation of the action of sulphuric acid and iodine on cellulose. Samples of cotton mercerised without tension in 45° Tw. NaOH solution were spotted with a 5 % solution of iodine in alcohol and then with sulphuric acid of various concentrations; unmercerised cotton was also subjected to the same treatment and the colour reactions are given in the following table:

COLOUR REACTIONS OF IODINE SULPHURIC ACID.

Concentration of H_2SO_4	None.	70° Tw.	75° Tw.	81° Tw.
Unmercerised .	Brown	Brown	Brown	Brown
Mercerised .	Brownish violet	Brownish violet	Brownish violet	Violet

COLOUR REACTIONS OF IODINE SULPHURIC ACID.

Concentration of H_2SO_4	87° Tw.	95° Tw.	105° Tw.	118° Tw.	130° Tw.
Unmercerised.	Brownish violet	Violet	Bluish violet	Blue	Blue
Mercerised .	Bluish violet	Blue	Blue	Blue	Blue

Attempts were made to obtain a mixture of iodine and sulphuric acid which could be used as a test solution, but in most cases the iodine rapidly separated from solution. The most useful solutions were stable for only a few hours and Harrison states that no special advantage is claimed for these as test reagents for mercerised cotton.

Iodine Test

One of the disadvantages of the iodine test is the fugitive nature of the coloration. Ermen (J.S.D.C., 1931, *47*, 161) attempted to stabilise the coloration by treatment with silver nitrate solution after the washing process, but this was not satisfactory in the case of thick material ; the formation of silver sulphite only resulted in a weak brown colour instead of a deep black. However, on the suggestion of Miss Hibbert, the Indigosols were tried instead of silver nitrate as a means of fixing the iodine stain. Indigosol Black I.B. gave the greatest contrast and Indigosol O 4 B was also satisfactory. The mercerised and unmercerised samples, after treatment with the iodine solution, are washed until the latter is colourless and are then dropped into a boiling solution of the Indigosol whose concentration appears to be immaterial. The oxidation of the Indigosol is almost instantaneous, so that the mercerised sample is deeply coloured, whilst the untreated cotton is colourless. The samples are well washed with cold water and boiling soap solution.

A strong solution of iodine is not advisable and 6 g. of iodine per 100 cc. of saturated iodide solution is adequate.

The test pieces, after mercerisation, should be vigorously stirred in the minimum quantity of cold water, which is replaced by fresh water as soon as it becomes dark brown. The entire washing operation does not take more than five minutes, even in the case of thick cloths.

Cotton material, mercerised under tension, does not show quite as strong a result as a similar material mercerised without tension.

Iodine Absorption Number

The absorption of iodine by cotton has recently received renewed attention ; Garkuscha (Textilber., 1937, *18*, 622) has investigated the influence of the concentration of the iodine solution and found that whereas mercerised cotton absorbs more iodine from strong solutions of iodine, unmercerised cotton absorbs more iodine from very weak solutions. At a certain critical concentration, both unmercerised and mercerised cotton will absorb the same amount. The impurities present in raw cotton also affect the absorption of iodine ; raw cotton will absorb 10 % more iodine than material which has been subjected to solvent-extraction processes.

IODINE ABSORPTIONS.

Concentration of iodine solution.	Unmercerised cotton.	Mercerised cotton.
	mg.	mg.
N/600	3·00	2·36
N/400	4·01	3·10
N/200	5·58	4·56
N/100	9·04	5·53
N/80	9·10	9·70
N/40	14·5	16·75
N/20	21·8	29·2
N/10	30·4	49·2
N/5	46·7	81·2

The method of treatment was to steep two grams of finely divided cotton for one hour at 21 to 22° C. in 40 cc. of the solution ; the absorbed iodine was calculated from the result of the titration of the residual iodine solution with a suitable solution of sodium thiosulphate.

A series of papers by Schwertassek (Textilber., 1931, *12*, 457 ; 1932, *13*, 536 ; 1933, *14*, 73, and 1934, *15*, 269) describes the use of a stronger solution than that recommended by Garkuscha, and it appears to be more sensitive in distinguishing between fully and partially mercerised material.

The solution is prepared by dissolving 5 g. of iodine and 40 g. of potassium iodide in 50 cc. of water. 0·3 g. of finely divided cotton is then placed at the bottom of a weighing bottle and 1·2 cc. of the iodine solution poured over it and thoroughly stirred by means of a glass rod. The small quantity of solution is delivered from a specially graduated 2 cc. pipette. A saturated solution of Glauber's salt (875 g. in 1,200 cc. of water) is used to wash the cotton and iodine solution into a 100 cc. flask and the total volume carefully adjusted to 100·2 cc. The flask is well shaken at ten-minute intervals for a period of one hour, during which time the solution is protected from light.

A pipette whose end is temporarily plugged with glasswool to prevent the cotton being drawn up, is used to withdraw 75 cc. of the liquid, which is then diluted and titrated against $N/50$ sodium thiosulphate solution. The number of milligrams of iodine absorbed by one gram of cotton may then be calculated and expressed as the "*absorption number*."

The course of mercerisation may be followed by means of the iodine absorption number and the results in Fig. 245 refer to cotton treated for 30 mins. at 0° C. with NaOH solutions of various concentrations—full shrinkage being permitted.

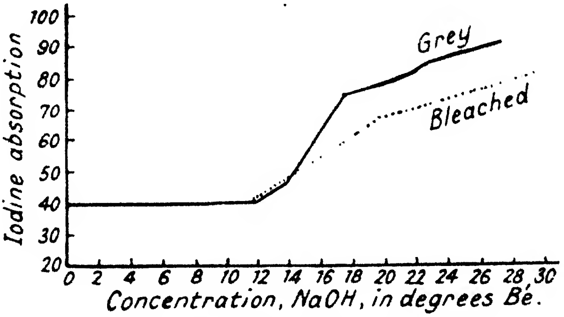

FIG. 245.—Absorption of iodine.

The difference between raw mercerised cotton and bleached mercerised cotton is clearly indicated. The increase in absorption first appears at a concentration of 12–14° Bé., from which point the absorption curve rises rapidly until a concentration of 18–20° Bé. is reached, after which the rise is more gradual.

Further work by Schwertassek showed that the iodine absorption test is not influenced by counts or twist of the cotton. A short boil with dilute NaOH solution was found to reduce the iodine absorption number of raw cottons.

Tests on mercerised cotton dyed with various dyestuffs showed that the test was directly applicable to cotton dyed with the substantive azo dyes, vat, sulphur and Naphthol-AS dyes. The figures for dyed mercerised material are rather lower than those for the undyed mercerised cotton, except in the case of aniline black and the basic colours. In the case of aniline black it is preferable to bleach the material with dilute permanagnate solution before applying the test ; the bleaching reduces the absorptive power and its action on a sample of undyed material of known absorptive number should be ascertained in order to determine the original figure for the dyed

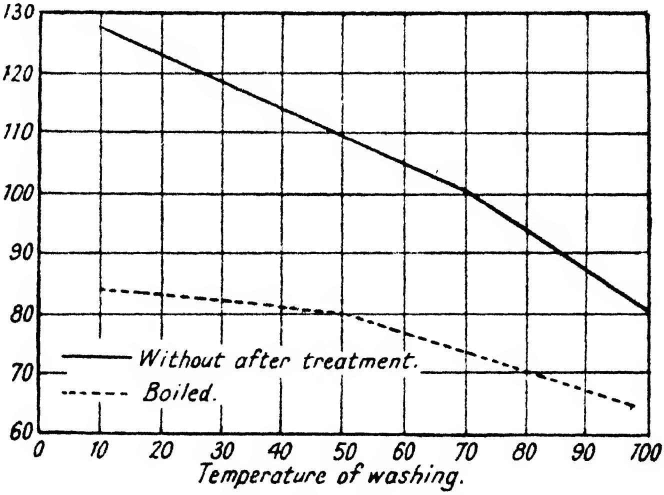

FIG. 246.—Iodine absorption and temperature of washing.

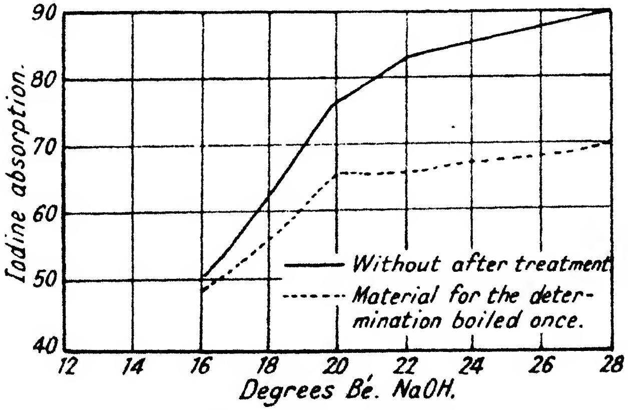

FIG. 247.—Iodine absorption and the effect of boiling after mercerising.

sample. In the case of the basic dyes, the material may be similarly treated with dilute caustic soda.

The lower absorption number of dyed mercerised cotton is not due to the presence of the dyestuff itself, but to the fact that during the dyeing process the mercerised cotton is in contact with boiling liquor. Simple boiling is sufficient to reduce the absorption number of iodine as in the case of water as shown by Coward and Spencer (see page 374). The effect of the temperature of washing is shown in Fig. 246.

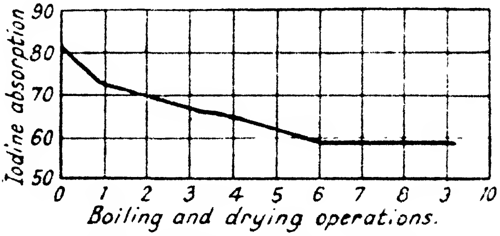

FIG. 248.—Effect of repeated washing on iodine absorption.

Mercerised cotton was thoroughly washed with water of various temperatures from 10° to 100° C. to remove the NaOH and the iodine absorption numbers are shown in the upper curve; the lower curve shows the effect of a second washing treatment from which it appears that the higher the temperature of the first washing process, the less is the further lowering produced by the second boiling process.

The greater the efficiency of the mercerising process, the greater is the effect of boiling. This is shown in Fig. 246.

Schwertassek also found that souring produces a fall in the iodine absorption number of mercerised cotton. The material was mercerised with NaOH of 30° Bé., washed with water at 55° C. and dried in the air. Two samples were then wet with warm water, one of them soured with dilute sulphuric acid, and both thoroughly washed with cold water. The results with two different types of cotton are shown in the following table:

EFFECT OF SOURING.

Treatment.	Iodine absorption.	
	I	II
Mercerised, not soured . .	104·0	81·6
Mercerised and soured . .	100·4	71·6

As might be expected from the previously described work on the absorptive capacity of mercerised cotton, the effect of drying is to reduce the iodine absorption number—the higher the temperature of drying the greater is the drop in iodine absorption number.

The manner in which the iodine absorption number is affected by repeated washings and dryings is of interest and is shown in Fig. 248. After six of these treatments there is no further lowering of the iodine absorption number.

Schwertassek also showed that the bleaching of mercerised cotton resulted in a reduction in the iodine absorption number by an amount more or less equal to that produced by drying at a high temperature.

Before leaving the discussion of the increased absorptive capacity brought about by mercerising, it is important to recall that this offers no *absolute* test of mercerising efficiency or textile merit ; nevertheless the various measures of absorbency have great *comparative* value.

PART SEVEN

THE EFFICIENCY OF THE PROCESS

CHAPTER TWENTY-SEVEN

THE EXTERNAL APPEARANCE

THE greater part of mercerised cotton material has been treated to improve its lustre ; sometimes the increased affinity for dyestuffs and occasionally the improved tensile strength are added requirements, but the importance of lustre in mercerised cotton is fundamental. The reasons for this lustre have been considered (pages 39 and 40) and frequently it is suggested that as lustre is so important a requirement it should form a measure of the degree of mercerising. Many suggested tests of mercerising efficiency depend on the absorptive capacity which increases as the tension during mercerising becomes less and therefore as the lustre falls. Measures of chemical reactivity are also affected by tension, though to a smaller extent.

Lustre is a superficial property, whereas good mercerising is a deep-seated phenomenon ; further, it is possible to produce a temporary lustre by mechanical means such as calendering, schreinering and glazing for piece goods and polishing for yarn. In some cases, owing to the plastic nature of mercerised material, the additive effect of these mechanical processes produces a very high degree of lustre, which is reduced on washing, whereas the lustre of mercerised cotton persists.

Although lustre measurement is not an absolute test of mercerising quality, it forms a very useful relative measure.

Lustre

The lustre of a material is a property which depends on the reflection of light. This reflection may be specular, as from a mirror where the light is reflected in the same plane and at an equal angle with the surface, or it may be diffuse, as from a matt surface where the light is reflected in several planes and at many angles. The greater the proportion of specularly reflected light, the higher is the degree of lustre.

As lustre is associated with the unequal brilliance of the surface in different directions, it may be determined as the ratio of the light specularly reflected to that diffusely reflected. Lustre, however, is essentially a subjective phenomenon and the difficulty arises of how to express this property, for brightness as perceived by the eye is proportional to the logarithm of the intensity and not to the actual intensity of the light. A further complication is due to the eye not being equally sensitive to light of all wave-lengths and this influences the effect of lustre, because in coloured material the diffuse light has penetrated the fibres and suffered selective absorption whereas the specularly reflected light is of the same colour as the incident light. The degree of illumination affects the lustre of coloured materials, and instruments for measuring lustre are less influenced by colour as the light increases in intensity. These factors have been reviewed by Preston (J.S.D.C., 1931, *47*, 136) in discussing the theories of lustre.

The simplest form of fibre structure is a straight cylindrical rod, and light falling along the axis is regularly reflected. Some light is also refracted into the body and undergoes further reflection and refraction. Pelton (Trans. Opt. Soc., 1930, *31*, 184) has shown that from a parallel bundle of such fibres the light will emerge as an annular cone of rays, the maximum lying at the angle of specular reflection in the plane of the fibre and of the incident light ; the fibres appear lustrous.

In the case of cotton, it has been shown by Adderley (J.T.I., 1924, *15*, 195) that the closer the cross-section approaches a circle the higher is the lustre, and Foster (J.T.I., 1926, *17*, 77 ; 1929, *20*, 75) states that this is due to the convolutions of the hair which, together with the shape of the cross-section, control the extent of deviation from the cylindrical or specularly-reflecting form. This has been discussed on page 40.

Yarns of highest lustre are those in which there is the closest approach to parallelism, not only between the hairs themselves but also in relation to the yarn axis. In such circumstances there is minimum diffusion of light and maximum reinforcement of the regularly reflected light from individual hairs.

As Preston (loc. cit.) points out, maximum lustre is produced when the fibrous structure approaches as nearly as possible to a plane parallel pad of fibres. The lustre of a fabric is modified by the structure of yarn and of fabric. In the case of the satin weave, the long floats cause the surface of the cloth to approximate to a parallel pad of fibres, so that the lustre will be at a maximum and can easily be measured at the angle of specular reflection, as the plane of the fibres is the same as that of the cloth. In the plain weave, however, the reflecting surface is divided into three parts, the peak of the loop and the straight inclined portions on each side. The curved portion reflects light in all directions and the two straight portions show specular reflections but in different directions. This accounts for the complicated lustre of fabrics which can only be evaluated by a series of measurements.

Barratt (Trans. Farad. Soc., 1924, *20*, 240) employed a special form of Joly's photometer and arranged the apparatus so that the surface of fibres, yarns or cloth under examination was movable about a horizontal or vertical axis. It was clearly shown that the light reflected from a mercerised fibre in certain positions is concentrated within a small angle of incidence around 67·5°, but with an unmercerised fibre the reflected light is scattered or spread out in a wider angle. The lustre is intensified when a number of fibres are made parallel which gives the enhanced effect in satins with " floats."

Lustre may be accounted for by a single surface reflection, and whilst internal reflection may produce an opalescence it will not have much influence on true lustre.

Examination of a well-mercerised cotton fabric shows a distribution of bright and dull points, but the total amount of reflected light is usually rather less than from the more uniformly illuminated surface of an unmercerised fabric. This is due to the greater transparency (up to 30 %) of the mercerised cloth and the consequent loss of reflected light.

The sharp peaks of Barratt's curves for mercerised cotton show that within a small cone the mercerised fibres reflect more light than the unmercerised and it is to this contrast that mercerised fabrics owe their lustre. The points of light in the fabric are due to the interlacing of the fibres in the fabric and their distribution determines the peculiar beauty of some mercerised fabrics as distinct from the highly lustrous rayon cloths. The small ridges produced by " schreinering " give a similar peculiar lustre.

The early papers of Adderley and Oxley (J.T.I., 1923, *14*, 361) and of Adderley (J.T.I., 1924, *15*, 195) dealt with the apparent brightness of cotton hairs and yarns. Later papers (J.T.I., 1925, *16*, 167 and 352) deal with the measurement of lustre in the true sense and a photometer was employed to measure the amount of light reflected from the test surface for a series of angles of the incidence of light; the angle of reflection was kept constant at 45°.

Where the angle of the incidence is equal to the angle of reflection (45° for Adderley's method and 67·5° in Barratt's apparatus) the effect of mercerising is to cause a more intense reflection and reduce the amount of light scattered at other angles.

Boffey and Derrett-Smith (J. Sc. Inst., 1931, *8*, 256 ; see also J.T.I., 1937, *28*, 293) have also designed an instrument in which the lustre is estimated from observations of the intensity of light reflected from the fabric at a number of angles for different angles of incidence of the illuminating beam.

Ransom and Edelstein (A.D.R., 1937, *26*, 432) made use of a photoelectric photometer arranged so that a sample of yarn or cloth in a fixed position is illuminated at any desired angle with a beam of parallel rays from a tungsten filament lamp. The light reflected from the sample at 45° impinges on a photoelectric cell, the voltage generated being a measure of the reflected light.

A number of readings at different angles of illumination showed that the sample with the highest lustre by visual grading had the highest reflection at 45° and the least at 90°. The *lustre number* was, therefore, defined as the ratio of the light reflected from the sample illuminated at 45° to that when illuminated at 90°. (See page 118.)

The Pulfrich Photometer

LUSTRE MEASUREMENT

In the Pulfrich Photometer the sample to be measured is placed side by side with a standard white plate of barium sulphate which may or may not be tilted with the sample. The sample and the standard are illuminated from the same source and the brightness of the test material is measured by the comparison photometer for a number of tilted positions. In this way it is possible to construct a curve connecting relative brightness with angle of tilt ; in many cases the maximum effect is observed at 22·5°. The angle of incidence is fixed at 45°, but the sample can be both tilted and rotated in its own plane so that measurements can be made in warp and weft directions of a fabric.

Richter's Lustre Value may be measured as follows :—the specimen to be examined is placed in the holder under the right-hand opening of the photometer. With the tilting plate in its normal position (i.e. with the angle of tilt at zero) the left-hand drumhead is turned inwards until both half fields appear equally luminous. If the specimen is coloured, this adjustment may be effected with one of the three light colour filters. The reading of the left-hand drumhead gives the brightness h_0 in the zero position of the tilting plate. The plate should now be tilted through an angle of, say, 10° and the state of identical luminosity re-established by turning the left-hand drumhead. Suppose the reading on the left-hand drum to be h'. The ratio $h' : h_0$ is a direct measure of the lustre of the specimen under examination, compared with the reflective properties of the plate of baryta white; multiplying the ratio $h' : h_0$ with the factor of correction k, which is shown for every angle of tilt in the table on the next page, gives Richter's (Zentr. Ztg. f. Optik u. Mech., 1928, *49*, 287) gloss value η.

$$\eta = \frac{h'}{h_0} \cdot k\ (\delta) \qquad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

The purpose of the factor of correction k (δ) is to eliminate the effect of the inherent lustre of the baryta plate, which, though insignificant, is nevertheless measurable.

Klughardt's Lustre Value γ is commonly used in Germany. Measurements for finding the lustre value in accordance with this method (Ztschr. f. techn. Phys. 1927, *8*, 109) are affected by using the *stationary* plate of baryta white as a standard of comparison. Klughardt's lustre value γ is calculated in accordance with the formula:

$$\gamma = \frac{H'}{H_0} - R \qquad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

in which H_0 is the brightness of the sample in the zero position, H' the brightness in the tilted position, and R a factor of photometric increase in brightness. The R value for any angle of tilt may be obtained from the table.

Klughardt's Lustre Value G (Zentralzeitung, f. Optik u. Mechanik., 1930, *51*, 90) provides a means for denoting the lustre in units which are at equal intervals from a psychological point of view. If a surface has a lustre value of 1 in these numerical units at a certain angle of tilt, and a second surface had lustre 2, that means that the psychological difference of brightness when the samples are rotated from the zero position to this tilted position in each case is as 1 : 2.

The relation between the lustre value G and Richter's lustre value η is

$$G = 10. \ \log \eta \qquad . \quad . \quad . \quad . \quad . \qquad (3)$$

To obtain the lustre value G it is, therefore, only necessary to determine the lustre value η according to the directions described in section 3, and to find the logarithmic value of η in a table of logarithms. The results multiplied by 10 then gives Klughardt's lustre value G. The tables given by Klughardt (Zentralzeitung, f. Optik u. Mechanik., 1930, *1*, 90) can also be used for ascertaining this, and in such a case it is not necessary to find the quotient $h' : h_0$, though it must be mentioned that with these tables it is not possible to determine G with a greater accuracy than 0·5 units, the slight inherent lustre of the plate of baryta white, amounting to 0·2 units at most, being disregarded.

Measuring the Lustre Value η.

The baryta white plate should be placed on the left-hand side of the tilting plate and the specimen to be tested on the right under the Photometer, both being simultaneously rotatable on the tilting plate.

If the sample should exhibit a linear structure on its surface, the revolving object stage should be set at 0° and the specimen inserted with a principal direction towards the lamp.

(*a*) *Zero position.*

If it be assumed that the sample is darker than the plate of baryta white, then to establish the condition of identical luminosity of the halves of the field, the left-hand drumhead must be screwed in to read 80%, the first reading being thus $h_o = 0{\cdot}80$.

(*b*) *Inclined position*, after rotating through an angle of $\delta = 20°$.

If it be assumed for the sake of example that the specimen appears brighter than the plate of baryta white, then to establish the condition of identical luminosity the drumhead on the side of the specimen has to be turned inwards, whilst the left-hand drumhead (on the side of the plate of baryta white) remains at 100. The reading on the right-hand side now shows 92%, i.e. the luminosity of the specimen in relation to the baryta plate is thus $\frac{100}{92} = 1{\cdot}085$. The factor of correction to be taken from the table for $\delta = 20°$ is $1{\cdot}040$; therefore, for $\delta = 20°$, the lustre value is

$$\eta = \frac{1{\cdot}085}{0{\cdot}08} \cdot 1{\cdot}040 = 1{\cdot}41$$

The Klughardt lustre value γ obtained from the equation (4)

$$\gamma = (\eta - 1)\,R \qquad . \quad . \quad . \quad . \quad . \qquad (4)$$

is accordingly

$$\gamma = (1{\cdot}41 - 1)R = 0{\cdot}41 \times 1{\cdot}282 = 0{\cdot}526 = 52{\cdot}6\%$$

TABLE.

	R	k	δ	R	k
0	1·000	1·000	40	1·409	1·006
5	1·083	1·043	45	1·144	0·996
10	1·158	1·046	50	1·409	0·980
15	1·224	1·038	55	1·393	0·969
20	1·282	1·040	60	1·366	0·966
25	1·329	1·033	65	1·329	0·957
30	1·366	1·031	70	1·282	0·938
35	1·393	1·023	75	1·224	0·917

Measuring the Lustre Value γ.

Here, the stationary plate of baryta white is taken as the standard of comparison. When conditions of identical luminosity have been established in the zero position, the reading H_o is observed, and then that for H' in the tilted position. According to this method, the sample considered above gives a reading of 61·2% in the zero position, so that $H_o = 0{\cdot}612$. In the tilted position, luminosity has to be diminished on the side of the specimen to 90·3 so that $H' = \frac{100}{90{\cdot}3}$, i.e. 1·106.

$$\gamma = \frac{H'}{H_o} - R \text{ i.e., } \frac{1{\cdot}016}{0{\cdot}612} - 1{\cdot}282$$

$$\text{i.e. } 1{\cdot}808 - 1{\cdot}282 = 0{\cdot}526.$$

In many cases the highest value for the lustre number occurs at 22·5°.

The Goerz Glarimeter

In this apparatus the intensities of the regularly reflected and the diffusely reflected light are compared with each other. The ray of light is made to assume a parallel direction by means of a lens and the light then falls on the surface whose intensity of lustre is to be measured. The regularly reflected light is made to pass through a prism and then on to a surface which is the plane of comparison. Here it is compared with the illumination which comes from the diffusely reflected light which reaches the plane of comparison through a second prism. The brightness of the two sides of the plane of comparison is equalised by a movable wedge which is turned by a knurled knob; the rotation of the wedge necessary to produce equal illumination of the plane of comparison is shown on a scale attached to the apparatus.

The manufacture of this apparatus appears to have been abandoned about ten years ago, but numbers of them are still in use.

The Comparative Gloss Meter

This instrument is made by the Salford Electric Instruments, Ltd.; a beam of light illuminated the sample at an angle of 45°. By means of a movable photoelectric cell, the reflected light is measured at 45° and at 0°.

Another apparatus utilising a photoelectric cell has been described by Desbleds (Dyer, 1930, ***64***, 515).

Microscopic Examination

The use of the microscope is of very considerable value in the examination of mercerised material, as it is fairly easy to appreciate the difference between the "smooth rod" of well mercerised cotton in cross-section and the bean-shape of the cross-section of unmercerised cotton.

An experienced worker has little difficulty in assessing the value of the mercerised product and diagnosing some of the faults which are apt to arise. Inefficient mercerising is frequently due to inadequate penetration of the alkali, to insufficient tension, and to a combination of these two factors, both of which may be estimated by examination of the cross-section of the yarn.

Fig. 252 shows a cross-section of unmercerised yarn where every fibre has a bean-shaped section and there is an entire absence of the closeness of fit which characterises material which has been well mercerised with tension. Fig. 253 represents a section of material which has been mercerised under tension but where the penetration is poor ; many of the fibres have not been swollen and still preserve their original shape. Although tension has brought the cotton hairs closer together in the yarn, yet there is an absence of that compactness which only comes with good swelling combined with high tension.

In Fig. 254 the swelling is much better but the tension has been inadequate, for the individual hairs are roughly elliptical in section whereas in Fig. 255 the well mercerised material presents sections which tend to be polygonal and bed together in the unmistakable manner characteristic of good swelling and high tension.

In view of the many suggestions for methods of determining the degree of mercerisation in quantitative manner, it is not surprising that a "count" of the rounded cross-sections has been considered. Ermen (Text. Col., 1932, *54*, 227) gives the figure of 80 % rounded cross-sections as indicative of successful mercerising. This method is of limited value owing to its subjective nature even in judging swelling without the added difficulty of tension. As a qualitative test, the shape of the cross-section is very valuable in deciding whether the material has been well mercerised, badly mercerised or not mercerised.

FIG. 249.—Reactivity ratio 1·45.

FIG. 250.—Reactivity ratio 1·22.

FIG. 251.—Reactivity ratio 1·27.

(Cross-sections of warp from mercerised fabric.)

(By courtesy of B.C.I.R.A.)

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FIG. 252.—Cross-section of unmercerised yarn.

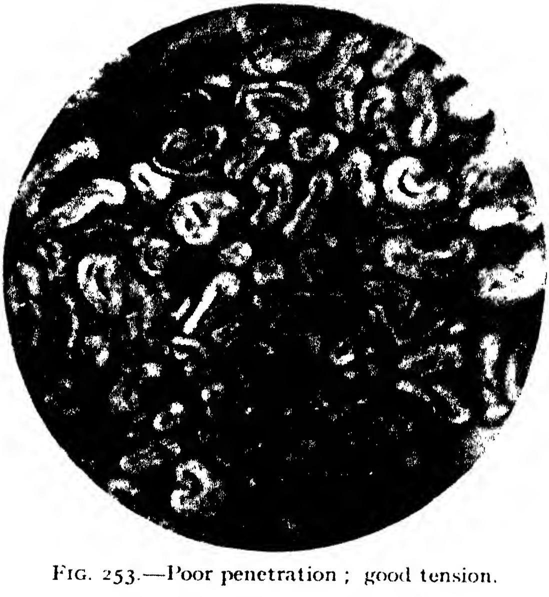

FIG. 253.—Poor penetration; good tension.

(*By courtesy of Miss Alexander.*)

FIG. 254.—Good penetration : poor tension

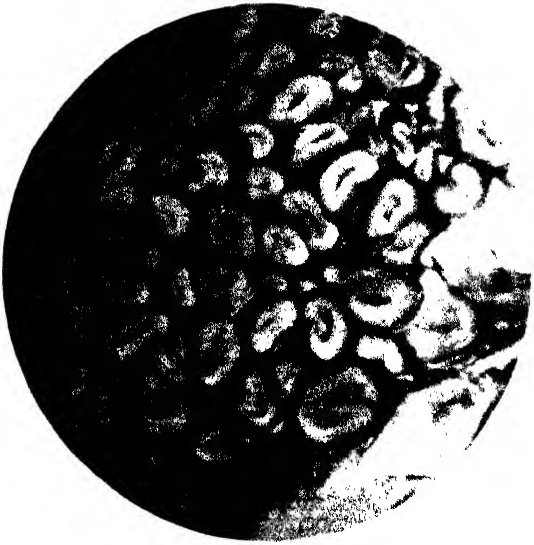

FIG. 255.—Good penetration and good tension.

(*By courtesy of Miss Alexander.*)

PLATE LIV.

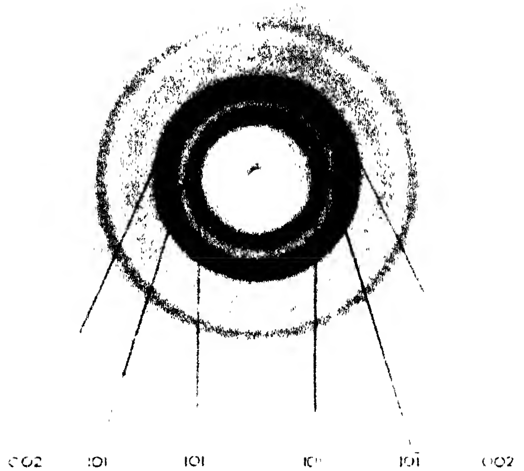

FIG. 256.—Photograph of disorientated native cellulose from an irregular arrangement of cotton hairs.

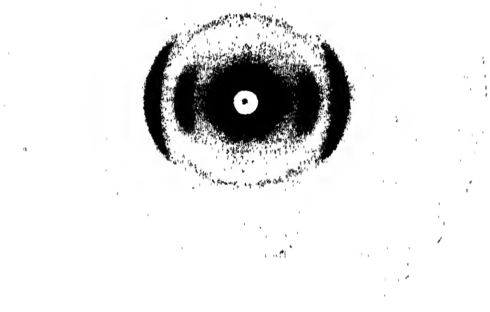

FIG. 257.—Cotton yarn.

(By courtesy of Dr. Astbury, F.R.S.)

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CHAPTER TWENTY-EIGHT

THE INTERNAL APPEARANCE

ALTHOUGH lustre is the prime consideration in mercerised cotton, the improved affinity for dyestuffs is an important matter and must not be unduly minimised; the case of dyestuffs is only one aspect of the general improvement in absorptive capacity which may be regarded as evidence of some change in internal structure.

The maximum increase in absorption of moisture, dilute alkali, dyestuffs, etc., occurs under conditions of minimum tension, so that maximum lustre and maximum absorptive capacity are not concomitant. For this reason alone the interpretation of absorption ratios as a measure of mercerising efficiency needs care. In addition to the effect of tension, the temperature of washing, drying, and any subsequent treatment plays a part in determining the absorptive capacity.

The increase in chemical reactivity is also due to the deep-seated change in internal structure and is similarly affected by tension; the reactivity ratio, however, is not altered by the temperature of drying after mercerisation.

The change from native cellulose to hydrate cellulose has been followed by means of X-ray photographs which provide evidence of the internal change in structure. (It must be remembered, however, that only the crystalline cellulose is considered in the interpretation of the photograph and the 25 to 30% of non-crystalline cellulose does not figure; this, of course, does not affect the question of complete mercerisation as revealed in the photographs.)

X-ray Diagrams

An ordinary photograph presents a visual image of the subject and in any good picture there is not the slightest difficulty in recognising the image depicted. Many X-ray photographs with which we are familiar owing to the advances in modern surgery present a "shadow graph" of the bones of the body and enable fractures, etc., and also the presence of foreign matter to be depicted; this X-ray shadow graph is also an image of the actual subject.

The X-ray photograph of a fibre or a crystal, however, appears to bear no resemblance whatsoever to the subject, for it is in no sense a visual image.

Apart from the absence of an image of a fibre in an X-ray photograph, one of the most noticeable features is the spot in the centre, and this is due to the fact that the main X-ray beam pursues its straight course to the centre of the photograph. It is only the diffracted rays which make the pattern which has to be interpreted later; the main beam would fog the photograph, so it is allowed to pass through a hole cut in the centre of the film, or, alternatively, is absorbed by a small piece of lead.

An understanding of the fibre photograph is based on our knowledge of the structure of crystals where the atoms are in orderly array, arranged in sets of equally spaced, similar, parallel planes. If a parallel beam of X-rays is incident in a direction making a glancing angle θ with any set of planes, then each plane in that set will reflect a small fraction of the incident beam. Any diffraction which occurs must be in a direction corresponding to the reflection of the incident beam from a set of crystal planes. The path difference between reflected beams from the same incident beam and reflected by successive planes at the angle θ, will be $2\,d\sin\theta$—a relationship first pointed out by W. L. Bragg and which forms the basis of the Bragg law.

For any particular setting of a crystal it is not likely that any set of planes will be in the correct position to reflect the light, but if the crystal is slowly rotated about a fixed axis, then a large number of planes will successively come into the reflecting position and the corresponding beams will be diffracted as the crystal passes through the correct setting and so build up on a photographic plate a pattern of spots. The most regularly arranged cellulosic fibres, such as ramie, also give a pattern of spots which is evidence of their crystal structure.

If a crystal is ground up into a very fine powder, then the orientation of the crystalline fragments is at random and a certain number of them will lie with their planes making a correct angle for reflection, and in this case a series of concentric circular rings is built up on the photographic plate.

A bundle of parallel cellulosic fibres gives a rotation type of photograph without the fibres being rotated but, if instead of being parallel, the fibres are crumpled up, then a series of concentric rings typical of the powder photograph appears.

In the case of a bundle of parallel ramie fibres, the same reflections are obtained, but instead of being continuous rings, they now appear as very short arcs.

Experience has shown that all forms of native cellulose give the same reflections in the same relative positions and of the same relative intensities. The presence of definite diffraction rings, arcs or spots shows that cellulose is crystalline, for if it were amorphous, then the pattern would consist of broad bands ("haloes").

Along the equator of a fibre photograph the spots are much broader than along the meridian, which shows that the crystals are much longer than they are broad and have their long axis parallel to the fibre axis.

Whereas the crystalline structure of cellulose is the same for all the native fibres, there is a wide variation among different fibres of the arrangement of the crystals in the cellulose, that is in their orientation.

Before passing on to this point, it might be well to emphasise the relationship between a crystal photograph and a fibre photograph ; a random mass of fibres gives the same type of photograph as a powdered crystalline mass, and a bundle of parallel fibres gives the same type of photograph as a single rotating crystal.

Although the interpretation of an X-ray photograph is a matter for highly specialised knowledge, yet the main characteristic features of photographs of the various forms of cellulose are not difficult to appreciate.

Orientation

The result of orientation is seen most prominently in the diffraction effects due to the *002* planes where they are most intense. The lengthening of the arc is a measure of the disorientation of the cellulose and may be measured micrometrically. The same phenomenon occurs with other spots or arcs, but is not visible in such a striking manner. (This is not the whole story, for spirals also produce arcs—see page 230.)

Another feature of a well-orientated fibre is seen by reference to the photograph of ramie where the clear presence of "outer spots" due to the more complex spectra is, among other factors, evidence of high orientation. The intensities of the higher orders are better defined, giving sharper spots, comparable with a good " crystal " photograph.

Comparison of an X-ray photograph of ramie and cotton shows this distinction in pronounced fashion, as in Figs. 260 and 257.

When well orientated native cellulose is mercerised without tension, the degree of orientation falls, as is seen by comparing Figs. 257 and 260 with Figs. 258 and 261. The effect of tension on orientation is also seen by comparing cotton mercerised with tension (Fig. 259) and cotton mercerised without tension (Fig. 258).

Mercerisation

Reference to good X-ray photographs of native cellulose fibres reveals the presence of two arcs close together and inside the prominent *002* arc. These reflections are from the $10\bar{1}$ plane and the *101* plane, the latter being nearer the centre of the photograph. They are not as intense as the *002* arcs.

In the case of completely mercerised or of regenerated cellulose, the X-ray photograph shows a change in position of these two shorter arcs. The $10\bar{1}$ arc is much nearer to the prominent *002* arc and the *101* arc is nearer the centre of the photograph. This characteristic effect is a feature of dispersed cellulose and super-imposed upon it is the effect of orientation or disorientation, according to the tension.

During the change from native to mercerised cellulose the $10\bar{1}$ and *101* arcs do not move apart but fade out of their old positions and reappear in their new positions. The extent of dispersion of the cellulose can be estimated quantitatively by the intensity of the arcs. Further, in the case of material which is not fully mercerised, then the $10\bar{1}$ and *101* arcs each appear in two positions and even in regenerated cellulose the presence of native cellulose can sometimes be detected. The extent of mercerisation or dispersion may be estimated photometrically, as shown by Schramek (Monatschr. für Textil. Ind., 1934, *49*, 257) and for this purpose it is not necessary to have a complete X-ray photograph but only a section.

In this manner it is possible to produce a graded series passing from native cellulose to 100 % mercerised cellulose where the comparative intensities have been measured and this series may be used as a standard for comparison with other photographs ; the degree of mercerisation may therefore be estimated.

It may be remarked, however, that the quantitative accuracy

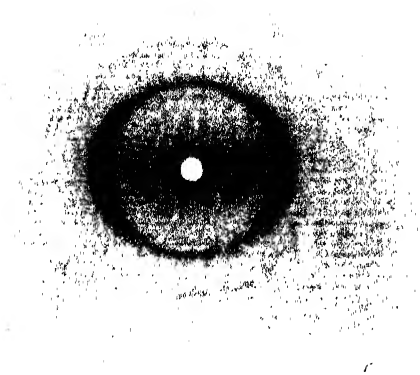

FIG. 258.—Cotton yarn mercerised without tension.

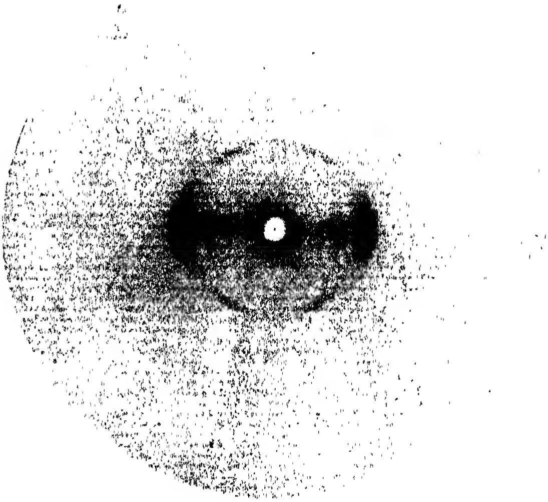

FIG. 259.—Cotton yarn mercerised with tension.

(By courtesy of Dr. Astbury, F.R.S.)

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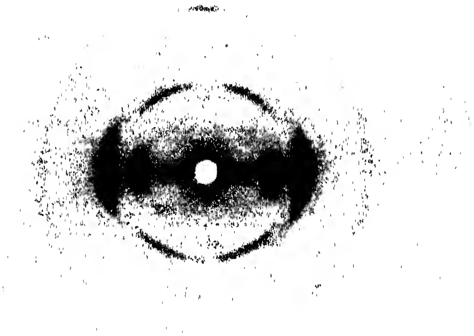

FIG. 260.—Ramie yarn.

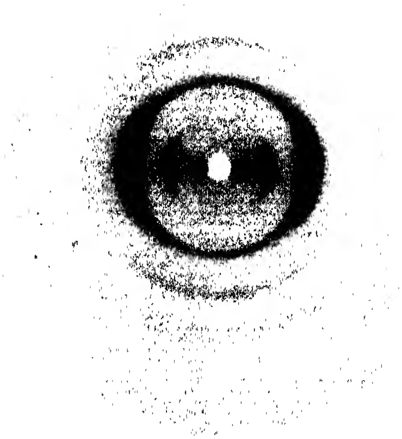

FIG. 261.—Ramie yarn mercerised without tension.

(*By courtesy of Dr. Astbury, F.R.S.*)

of this method is doubtful, for the regular X-ray diffraction pattern arises from the more organised or "crystalline" regions of the fibre structure and it can hardly be doubted that there are varying proportions of less organised material present.

On the basis of these estimations, however, Schramek concludes that in technical mercerising the efficiency seldom exceeds 60–70% for yarn and 35 40% for cloth. These figures show fair agreement with those obtained by the deconvolution count as given on page 47.

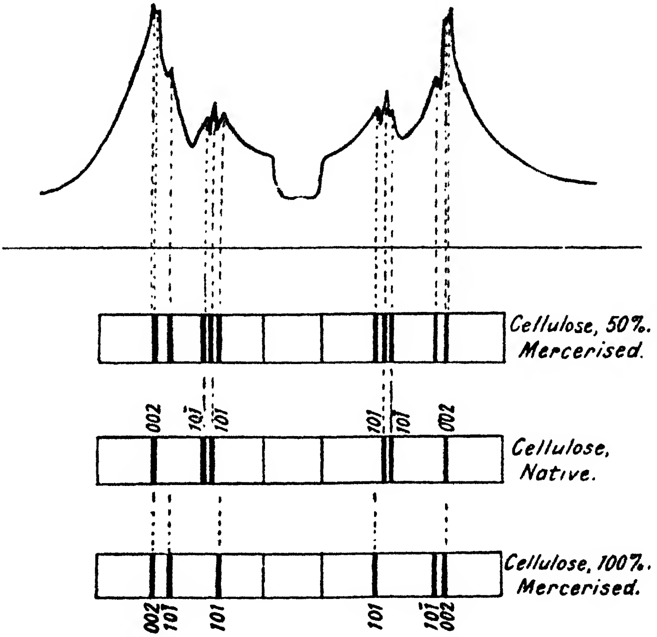

FIG. 262.—Extent of mercerisation.

Fig. 258 refers to cotton yarn mercerised in the laboratory and shows complete conversion to hydrate cellulose ; the yarn was mercerised without tension. Fig. 259 relates to commercially mercerised cotton yarn, and although the effect of tension is seen in the better orientation, the presence of native cellulose is clear.

The relation between the extent of conversion to hydrate cellulose and the lustre has been examined by Schramek (Monat. Text. Ind., 1934, *49*, 257), who used two types of cotton for his experiments—Texas and Mako, the latter being the finer. The cottons were mercerised with tension under such conditions that the original length of the material was restored during the process, hence the lustre should be good. The extent of mercerising was estimated from X-ray photographs.

DEGREE OF MERCERISATION AND LUSTRE.

Texas.		Mako.	
Degree of mercerisation. %	Lustre No.	Degree of mercerisation. %	Lustre No.
0	3·5	0	3·2
15	4·5	10	5·0
40	5·2	45	5·6
70	5·8	70	6·7
90	6·6	90	7·3
100	7·5	100	7·5

It therefore appears that the maximum lustre appears with complete conversion to the hydrate modification.

Many suggestions have been put forward as measures of mercerising efficiency and some of these have been compared with the X-ray method by Schubert (Dissertation ; Dresden, 1932). The broad basis of the investigation was to evaluate the mercerising effect produced by various concentrations of NaOH solution, and not to compare the properties of the same product. For instance, the amount of shrinkage was determined in various concentrations of NaOH, and also the lustre when the cotton was mercerised under tension. These two properties, shrinkage and lustre, do not refer to the same mercerised product, but to the effect which the alkali was capable of producing.

The investigation was carried out on cotton hairs in order to avoid the complications of yarn and cloth structure ; the duration of impregnation with alkali was one hour, after which the shrinkage was measured, and the fibres were restored to their original length before washing out the alkali. The results in the table and in Fig. 263 refers to Mako cotton, but American cotton showed a similar behaviour.

It will be noticed that the average increase in breaking load is some 25% ; the increase of 33% according to Langer's average result (page 103) seems exceptionally high.

It will be seen that shrinkage is not reliable as a measure of mercerising efficiency, as the shape of the curve is different from that of the other properties examined.

Mercerising Values.

Concentration of NaOH %	Shrinkage %	Breaking load of single hair. (g.)	Extension. %	Lustre No.	Degree of Mercerisation. %
0	1·4	8·3	9·9	3·2	0
8·6	2·0	...	...	3·5	0
9·8	3·4	8·6	7·7	3·7	0
10·5	3·7	8·5	8·1	3·7	0
12·0	8·0	9·1	7·3	5·0	10
13·1	13·0	9·5	7·5	5·6	40–45
14·0	16·6	10·0	6·4	6·7	70
14·9	17·9	...	...	7·0	80
16·0	19·6	10·5	6·5	7·5	90–95
17·3	18·8	...	...	7·5	95–100
18·1	18·6	10·2	6·1	7·4	100
19·1	18·3	...	...	7·3	100
20·8	18·2	10·5	6·2	7·4	100
22·0	17·6	10·5	6·4	7·0	100
24·3	17·4	...	...	7·5	100
26·5	17·4	10·4	6·5	7·3	100
28·1	17·2	...	...	7·0	100
30·4	16·0	...	...	6·8	100
32·5	14·8	10·4	7·0	6·9	100
34·2	13·2	...	...	7·1	100
37·3	12·3	10·5	5·7	7·1	100
40·4	10·8	...	...	7·0	100
42·4	9·8	10·4	6·3	6·9	100

This point has been investigated in greater detail by Schramek and Thomas (Monat. Text. Ind., 1938, *53*, 157), who established that whereas the results of lustre, fibre strength and dyeing power measurements follow those of X-ray measurements in a satisfactory manner, the shrinkage curve does not run parallel with the curves obtained by other methods. Hence shrinkage is not a reliable index of mercerisation efficiency in respect of time, temperature, and concentration.

Schramek suggests that the optimum temperature for mercerising is 38° C., which is higher than that generally adopted or advised. Sisson (private communication) finds that complete mercerisation takes place at room temperature (20° C.) when the concentration of NaOH is above 14%. As the concentration falls, the temperature must fall also, so that with 5% NaOH, complete mercerisation is not obtained until a temperature of —18° C. is reached.

Sisson treated cotton hairs with NaOH over a wide range of temperatures and concentrations ; after washing and drying, three types of X-ray diffraction patterns were obtained (*a*) native, (*b*) mixtures of native and mercerised, and (*c*) mercerised cellulose. The results are shown in Fig. 264, where the three types are plotted as areas in a temperature-concentration diagram ; although the boundaries are represented by lines, there is actually a gradual transition from one area to another. No attempt is made to illustrate the ratio of native to mercerised cellulose within the area of partial mercerisation.

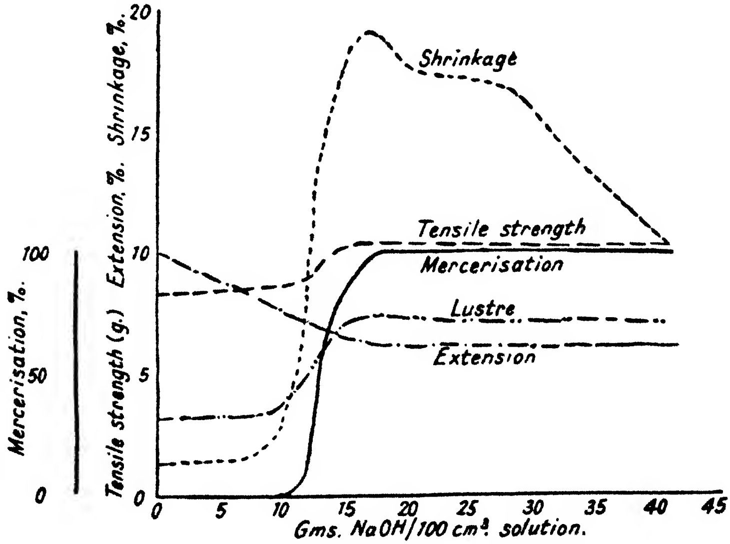

FIG. 263.—Comparison of mercerising effects.

At low temperatures and high concentrations, the area of complete mercerisation is interrupted by a region of incomplete mercerisation, probably due to the formation of hydrates which do not penetrate into the crystalline cellulose lattice.

Sisson also established that with chemically or mechanically damaged fibres, and normal mercerising, the areas of partial mercerisation are considerably reduced. This may be due to cuticular damage in accordance with the work of Willows and Alexander (page 58), Coward and Spencer (page 58) and Calvert (page 92).

The X-ray and the reactivity ratio methods appear to be the only absolute methods of estimating mercerising efficiency in a quantitative manner ; some of the other methods may be used for relative measurements. The X-ray method is the only means of estimating the change in the internal fine structure of the cotton fibre. Nevertheless some of the other methods such as the observations of changes in the form of the fibre, and changes in chemical and physical properties, are useful in indicating qualitative differences between unmercerised and mercerised material.

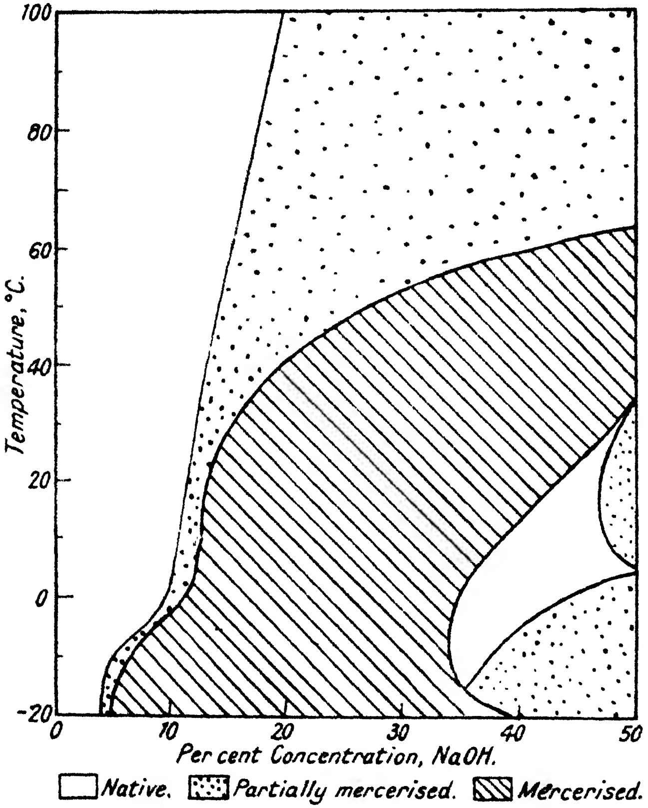

FIG. 264.—Temperature-concentration diagram for the mercerisation of cotton.

As previously stated, the effect of tension which is essential for the production of lustre, is to act against the maximum increase in chemical reactivity or absorptive capacity.

Summary

The following methods have been suggested to estimate the degree of mercerising efficiency:

(1) X-ray analysis, as showing changes in fine structure.
(2) Increased chemical reactivity.
  (*a*) reactivity ratio—page 275.
  (*b*) hydrolysis numbers—page 274.
(3) Absorption methods.
  (*a*) moisture absorption—page 365.
  (*b*) dyestuff absorption—page 379.
  (*c*) absorption from alkaline solution:
    sodium hydroxide—page 387.
    barium hydroxide—page 396.
    cuprammonium hydrate—page 401.
(4) Counting methods:
  (*a*) deconvolution count—page 45.
  (*b*) cross-section count—page 428.
(5) Lustre—pages 118 and 434.
(6) Shrinkage—pages 53 and 97.
(7) Estimate of mechanical properties:
  (*a*) breaking load.
  (*b*) extension.

Consideration of the results from many of these estimates shows that technical mercerising is only moderately efficient even after fifty years of mercerising under tension and one hundred years of mercerising without tension. Putting aside obviously impossible requirements, such as maximum lustre and maximum absorptive capacity in any one sample, and accepting the difficulties imposed by yarn and fabric structure, it is by no means certain that goods of 100% degree of mercerisation would possess enhanced textile merit over those of 40% to 70% mercerisation. Some exceptionally well mercerised materials have met with an unfavourable reception from the public because of their thin "feel" and wiry "handle."

CHAPTER TWENTY-NINE

VARIATIONS IN THE MERCERISED PRODUCT.

VARIATIONS in shade of dyed material knitted from mercerised yarn are fairly common; they may be present as an abrupt change in colour or the variation may be so distributed as to build up a pattern of stripes or diamonds. The shade of dyed mercerised yarn is sensitive to many of the conditions of mercerising, such as impregnation, tension and washing; the drying process too is capable of exerting considerable influence.

Since these factors are known to affect the dyeing quality, it may be expected that many variations in shade are due to lack of uniformity in the hank-mercerising process and some critical methods for investigating this possibility have been described by Clibbens and Geake (J.T.I., 1933, *24*, 255).

Periodic variations in shade are simpler to diagnose than abrupt changes, as they preclude variations in fibre quality, spinning processes and the singeing or " gassing " of the yarn.

The mercerisation of piece goods and the warp-mercerising of yarn are continuous processes, whereas hank mercerising is essentially a discontinuous process; hence local variations are more common with hank-mercerised yarn. The problem was acute for hosiery yarn, owing to the demands of fashion during the period 1930 to 1935, and the B.C.I.R.A. carried out a very careful examination of the faults based on the application of various tests of mercerising efficiency.

Periodicity

It is not possible to examine variations in shade of dyed yarns when a length of the thread is laid flat, nor is it possible to detect a periodic variation; it is necessary to wrap the yarn into a pad under conditions which favour the formation of contrasting areas.

A convenient apparatus for this purpose is a steel rod about six inches long with a circumference of exactly two inches. The yarn is wrapped on this rod under constant tension so that every turn of the yarn is in close contact with the preceding turn to make a smooth and compact wrapping five or six inches long, the compactness being an essential feature in the subsequent detection of bands of colour. Near the beginning of the wrapping an ink mark is made on the yarn before it reaches the rod and the reading of the revolution counter is noted ; a similar mark is made near the end of the wrapping and by noting the reading of the counter again, it is possible to calculate the exact length of yarn between the two ink marks.

Many wrappings from defective knitted material show alternating dark and light bands which may be examined very carefully if the yarn is removed in the following manner.

The surface of the yarn is covered with a strip of adhesive rubber tape of the correct length and width to encircle the wrapping exactly. The rod and covering are slightly warmed and then rolled on a flat surface to ensure even adhesion of the yarn to the tape, which is then cut by a razor at the junction of the two edges of the tape, parallel to the axis of the rod. This pad of yarn with its tape backing may then be pressed flat between damp cloths and mounted on a card. Pencil marks may be traced on the paper on the edge of the pad opposite the centre of each successive light and dark band. The average distance between successive marks is calculated from the pencil tracings and the distance between the two ink marks on the pad is measured. As the length of yarn between the ink marks is known, the length of yarn corresponding to the average distance between successive colour bands may be calculated and this is called the period of colour variation.

In many dyed stockings the mottled or patterned appearance was periodic in the yarn and when the results of the examination of large numbers of stockings were reviewed, it was found that the periods fell mainly into three groups. In the first group the colour bands occurred at intervals which varied slightly in individual cases, but always fell within the limits of 50–54 inches. In the second group, there was also a regular spacing and the interval was slightly less than twice that of the first group, the periods falling within the limits 89–96 inches. In the third group the bands were arranged according to an irregular system but were not all equally spaced and a number of bands at the 50–54 inch interval may be followed by a number at a multiple of this interval. The exact arrangement varies in individual cases, but the effect produced is frequently that of a series of bands of the first group from which some are omitted according to a regular plan of periodicity equal to sixteen times the circumference of the hank.

A local defect across the full width of the hank will affect every turn of the yarn and the defect must occur along the thread at regular intervals equal to the circumference of the hank. This accounts for the periodicity in the first group which corresponds to the length of yarn wrapped in one revolution of the reel, subject to modification by the amount of shrinkage involved in subsequent processing.

The winding of the yarn into a hank for hosiery is mostly done on the Grant system of cross reeling, in which the yarn makes nine complete traverses across the hank width during sixteen revolutions of the reel. This means that at regular intervals of 96 inches the thread will arrive at one and the same edge of the hank so that any defect in the yarn round the whole of one edge of the hank would result in a recurrent defect at regular intervals of 96 inches. This length is a fraction $\frac{16}{9}$ of the hank circumference and subject to variation. This accounts for the second group.

As a result of the method of traverse adopted in Grant reeling, the crossing of the oblique threads produces a hank with a characteristic net-work of diamond meshes. This diamond net-work is completed in sixteen revolutions of the reel, after which the whole of the hank builds itself up on top of the unit pattern. The length of yarn wound during this time is 16 × 54 inches, which is a third period associated with the Grant system of reeling.

It is this interrupted period which is formed by a defective area in the form of a patch on the hank which does not extend across the complete width of part of the length, nor the complete length of part of the width. From the construction of the hank certain of the rounds will miss this area, but the complex pattern will repeat every 864 inches.

Deconvolution Count

A compact wrapping of the dyed yarn is made on a steel rod and is covered with strips of transparent adhesive paper, which is then cut from the rod to yield a pad of yarn in which the variation in shade is shown as light and dark bands.

These bands may be removed and the deconvolution count made on either light or dark regions, or a comparison of the two may be made. The following data refer to yarn from a dyed, mercerised stocking which showed a regular shade variation.

DECONVOLUTION COUNT.

Light Band—		Dark Band—	
No. 1	42	No. 1	63
No. 2	37	No. 2	57
No. 3	32	No. 3	60
No. 4	41	No. 4	68
No. 5	35	No. 5	65
Mean	37	Mean	63

In this case the irregularity in shade is undoubtedly due to imperfect impregnation of part of the hank with the mercerising liquor.

Sudden changes in shade nearly always occur at knots in the yarn and are mainly due to differences between one hank and another. These differences may be avoided by making sure that the yarn is produced from one spinning, one doubling, and one mercerising operation. It is generally possible to decide if the knot marking the change in shade was inserted before or after mercerising, by a comparison of deconvolution counts on the knot itself and on the loose ends of yarn. If the knot was made before mercerising, that part of the cotton hair within the knot will not show deconvolution, owing to the difficulty of penetration of mercerising liquor into the tight knot and also on account of the mechanical resistance to swelling. The loose tails of the knot, however, will have received a treatment which favours deconvolution. The following figures show a comparison between knots inserted before and after mercerising.

DECONVOLUTION COUNT.

The knot made before mercerising	17
The loose ends of this knot	85
The knot made after mercerising	52
The loose ends of this knot	55

If the knot has been made after mercerising there is no significant difference between the knot and its ends and evidence for the origin of the difference in shade must be sought elsewhere. The counts and twist of the yarn may be measured, staple length, the hair weight and the immaturity. Large differences in any of these properties between two yarns of different shades may account for the change in shade.

Shrinkage Diagram

The dyed yarn under examination is wrapped compactly on a steel rod about 6 ins. long and 2 ins. in circumference, and a line is drawn parallel to the axis of the rod on the surface of the yarn.

If the yarn is then unwound from the rod, the ink line becomes a series of spots equally placed along the thread, and the method of investigation is to compare the shrinkages of these equal lengths when they are remercerised without tension. This is done by immersing the unwound yarn in mercerising liquor so that it can shrink freely; the alkali is then neutralised with glacial acetic acid and the yarn washed in water and dried.

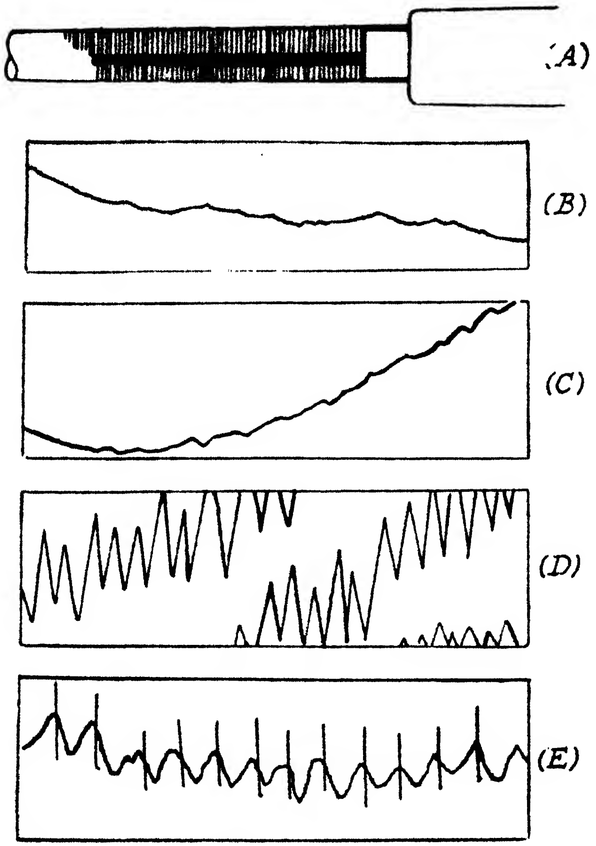

FIG. 265.—Shrinkage diagrams.

The use of glacial acetic acid avoids the additional shrinkage which occurs when water is used, depending on the temperature of the wash water and the rate of removal of the alkali.

The yarn is then wrapped again on a steel rod which is slightly smaller than that employed for the first wrapping, the diameters of the two rods being as nearly as possible in the same ratio as the original to the shrunk length of the yarn. If the shrinkage on remercerising is perfectly uniform and if the diameters are exactly in the specified ratio, then the ink spots would again form a straight line parallel to the axis of the rod ; generally it is not possible to arrange this and the spots spiral round the rod. If the shrinkage during the second mercerising has not been uniform, then changes will occur in the direction of the spiral line and corresponding to the changes in shrinkage.

The yarn is then covered with adhesive tape, as previously described, and removed from the rod to form a flat pad which shows a record of the shrinkage during remercerising and is called the shrinkage diagram. In the case of unmercerised yarn, any irregularities in shrinkage can only be due to irregularities in yarn structure and although the line is not perfectly smooth, there are no very abrupt changes in smoothness. The general angle made with the horizontal by the ink line is of no consequence, as the important features are the changes in slope of the line or a pronounced lack of smoothness.

In the case of mercerised yarns from striped stockings, the indicator line changes its direction at short periodical recurring intervals which coincide with the periods of variation in shade.

Fig. 265B shows the shrinkage diagram of an unmercerised yarn and Fig. 265C the diagram of a level-dyeing mercerised yarn ; these are quite distinct from Figs. D and E which relate to unlevel-dyeing mercerised yarns.

If a yarn contains variations due to uneven impregnation, then the curve in the shrinkage diagram will show a succession of peaks and troughs which coincide with changes in colour and convolution count. If the variation is due to differences in shrinkage, then the shrinkage diagram will coincide with the colour changes but not the deconvolution count. Faulty impregnation and irregular shrinkage may both be detected by the shrinkage diagram but may be differentiated by the deconvolution count. The greater shrinkage on remercerising is associated with the lighter parts of the yarn from whichever cause.

Redyeing

It is possible to obtain useful information about variation in shade of dyed hosiery yarns by stripping the colour and then boiling for one hour in 1 % NaOH solution, washing and redyeing. Clibbens and Geake recommend the use of Chlorazol Brown LFS, the conditions of dyeing being fifteen minutes at the boil in a bath containing 0·02 % of dyestuff, calculated on the volume of the liquor; no salt is added and the ratio of the liquor to cotton is about 200 : 1.

The redyed yarn is washed, dried, wrapped on a steel rod and made into a pad by the usual method. If the pad of redyed yarn is free from periodic irregularity, then the original defect cannot be due to faulty mercerising.

If the variation persists, however, its origin must be sought in the mercerising process. The course recommended is to withdraw further lengths of at least 100 inches from the knitted material, remove the colour and boil for one hour in 1 % NaOH solution. A small skein is then washed, squeezed and immersed in 7·5 *N* NaOH under conditions that allow free shrinkage. The skein is then washed with hot water, redyed and made into a pad. If the irregularity is eliminated or greatly reduced by this treatment, then the original defect lies in the mercerising process.

If the irregularity persists, however, then it is still possible that the cause lies in the original mercerising; in short, a second mercerising is not a cure for all ills. This was shown by treating a hank in such a manner that one third of it was mercerised without tension, one third of it mercerised with tension and the remaining third untreated. The hank was then remercerised with full shrinkage and dyed, when it was found that the intensity of the originally unmercerised portion was the same as that of the part which had been mercerised without tension, but that part of the yarn which had been mercerised with tension remained lighter in shade. This means that the properties conferred upon the yarn by the original mercerising process are retained to a large extent through subsequent mercerising processes under other conditions; this illustrates the irreversible nature of mercerisation. Yarn mercerised under tension dyes a lighter shade than yarn which has been allowed to shrink during the process, and when the former is re-mercerised without tension, it still dyes a lighter shade than the yarn which has only been mercerised once without tension. Experiments on remercerising under tension of a hank treated as above gave results in which the originally unmercerised portion gave the same shade as that mercerised with tension, but the originally shrunk portion dyed more deeply. Hence, by means of these two different remercerising processes, the unmercerised portion of the yarn can be made to dye the same shade as either of the two mercerised portions, but neither treatment is capable of making the two differently mercerised portions equal in dyeing affinity.

Remercerising without tension will produce a reversal of the colour effect, the original wrapping of lustrous yarn containing periodically recurring non-lustrous and light streaks changing to a relatively lustrous wrapping with non-lustrous dark streaks. This characteristic behaviour shows that the original defect was due to non-wetting and this conclusion may be checked by the deconvolution count.

Some irregularities in shade may be due to chemical attack of the yarn, possibly on account of the incomplete removal of acid from hanks that have been soured after mercerising. The presence of degraded cotton may be investigated by redyeing with a basic dye or by using Harrison's silver staining test (J.S.D.C., 1912, *28*, 359) for qualitative indication of the reducing power ; if sufficient material is available, then confirmation can be obtained by comparing the fluidity values in cuprammonium solution of the light and dark coloured parts of the yarn.

Iodine Absorption

The possibility of utilising the iodine absorption test (see page 413) as a means of diagnosing variations in shade of dyed goods due to faulty mercerising has been explored by Schwertassek, Heidler and Kasche (Textilber., 1939, *20*, 433). Faults due to differences in alkali concentrations or to differential penetration of the material can be detected by differences in the iodine absorption numbers even after dyeing or shrinkage with 8·5% NaOH solution. Differences due to variation in tension during mercerisation are not shown by the iodine absorption unless they are accompanied by differences in penetration by the alkali. In utilising these methods it must be remembered that the dyeing and shrinkage processes reduce the iodine absorption value.

Variations in the drying temperature of mercerised material sometimes disappear during the dyeing process and may often be removed by treatment with 8·5% NaOH solution.

APPENDIX

SPECIFIC GRAVITY OF CAUSTIC SODA LYE AT 15° C.

Spec. grav.	Degr. Bé.	Degr. Tw.	100 g. contain g. NaOH	100 cc. contain g. NaOH
1·007	1	1·4	0·59	0·60
1·014	2	2·8	1·20	1·20
1·022	3	4·4	1·85	1·89
1·029	4	5·8	2·50	2·57
1·036	5	7·2	3·15	3·26
1·045	6	9·0	3·79	3·96
1·052	7	10·4	4·50	4·73
1·060	8	12·0	5·20	5·50
1·067	9	13·4	5·86	6·25
1·075	10	15·0	6·58	7·07
1·083	11	16·6	7·30	7·91
1·091	12	18·2	8·07	8·80
1·100	13	20·0	8·78	9·66
1·108	14	21·6	9·50	10·53
1·116	15	23·2	10·30	11·49
1·125	16	25·0	11·06	12·44
1·134	17	26·8	11·84	13·40
1·142	18	28·4	12·69	14·50
1·152	19	30·4	13·50	15·55
1·162	20	32·4	14·35	16·67
1·171	21	34·2	15·15	17·74
1·180	22	36·0	16·00	18·88
1·190	23	38·0	16·91	20·12
1·200	24	40·0	17·81	21·37
1·210	25	42·0	18·71	22·64
1·220	26	44·0	19·65	23·97
1·231	27	46·2	20·60	25·36
1·241	28	48·2	21·55	26·74
1·252	29	50·4	22·50	28·17
1·263	30	52·6	23·50	29·68
1·274	31	54·8	24·48	31·19
1·285	32	57·0	25·50	32·77
1·297	33	59·4	26·58	34·47
1·308	34	61·6	27·65	36·17
1·320	35	64·0	28·83	38·06
1·332	36	66·4	30·00	39·96
1·345	37	69·0	31·20	41·96
1·357	38	71·4	32·50	44·10
1·370	39	74·0	33·73	46·21
1·383	40	76·6	35·00	48·41
1·397	41	79·4	36·36	50·79
1·410	42	82·0	37·65	53·09
1·424	43	84·8	39·06	55·62
1·438	44	87·6	40·47	58·20
1·453	45	90·6	42·02	61·06
1·468	46	93·6	43·58	63·98
1·483	47	96·6	45·16	66·97
1·498	48	99·6	46·73	70·00
1·514	49	102·8	48·41	73·29
1·530	50	106·0	50·10	76·65

SPECIFIC GRAVITY OF CAUSTIC POTASH LYE AT 15° C.

Spec. grav.	Degr. Bé.	Degr. Tw.	100 g. contain g. KOH	100 cc. contain g. KOH
1·007	1	1·4	0·9	0·9
1·014	2	2·8	1·7	1·7
1·022	3	4·4	2·6	2·6
1·029	4	5·8	3·5	3·6
1·037	5	7·4	4·5	4·6
1·045	6	9·0	5·6	5·8
1·052	7	10·4	6·4	6·7
1·060	8	12·0	7·4	7·8
1·067	9	13·4	8·2	8·8
1·075	10	15·6	9·2	9·9
1·083	11	16·6	10·1	10·1
1·091	12	18·2	10·9	11·9
1·100	13	20·0	12·0	13·2
1·108	14	21·6	12·9	14·3
1·116	15	23·2	13·8	15·3
1·125	16	25·0	14·8	16·7
1·134	17	26·8	15·7	17·8
1·142	18	28·4	16·5	18·8
1·152	19	30·4	17·6	20·3
1·162	20	32·4	18·6	21·6
1·171	21	34·2	19·5	22·8
1·180	22	36·0	20·5	24·2
1·190	23	38·0	21·4	26·9
1·200	24	40·0	22·4	26·9
1·210	25	42·0	23·3	28·2
1·220	26	44·0	24·2	29·5
1·231	27	46·2	25·1	30·9
1·241	28	48·2	26·1	32·4
1·252	29	50·4	27·0	33·8
1·263	30	52·6	28·0	35·3
1·274	31	54·8	28·0	36·8
1·285	32	57·0	29·8	38·5
1·297	33	59·4	30·7	39·8
1·308	34	61·6	31·8	41·6
1·320	35	64·0	32·7	43·2
1·332	36	66·4	33·7	44·9
1·345	37	69·0	34·9	46·9
1·357	38	71·4	35·9	48·7
1·370	39	74·0	36·9	50·6
1·383	40	76·6	37·8	52·2
1·397	41	79·4	38·9	54·3
1·410	42	82·0	39·9	56·3
1·424	43	84·8	40·9	58·2
1·438	44	87·6	42·1	60·5
1·453	45	90·6	43·4	63·1
1·468	46	93·6	44·6	65·5
1·483	47	96·6	45·8	67·9
1·498	48	99·6	47·1	70·6
1·514	49	102·8	48·3	73·1
1·530	50	106·0	49·4	75·6
1·546	51	109·2	50·6	77·9
1·563	52	112·6	51·9	81·1
1·580	53	116·0	53·2	84·0
1·597	54	119·4	54·5	87·0
1·615	55	132·0	55·9	90·2
1·634	56	126·8	57·5	94·0

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