THE METHODS OF CELLULOSE CHEMISTRY

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INCLUDING METHODS FOR THE INVESTIGATION OF SUBSTANCES ASSOCIATED WITH CELLULOSE IN PLANT TISSUES

by

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To

MY OLD FRIEND

CHARLES FREDERICK CROSS, F.R.S.

1855–1935

A PIONEER IN CELLULOSE DISCOVERY

AUTHOR'S PREFACE

THE experimental investigation of cellulose in its various aspects —as a chemical substance, as a structural colloidal unit and as a primary constituent of plant cells—necessarily involves specialised methods. These methods, which have been gradually evolved during the last fifty years, are described in a wide literature which includes the standard journals devoted to chemistry, physics, botany and biochemistry, and on the technical side those dealing with textiles, dyeing and colloids. There are, in addition, the publications of institutes and conferences concerned with various aspects of cellulose research. Some of the methods, in more or less detail, have found their way into the text-books on cellulose which have appeared in recent years, but it is nevertheless often difficult for the student, who is commencing work on cellulose, to find easily the experimental details he requires. It is hoped that the present book, compiled from notes made for the author's own students, will assist in removing this difficulty. It should prove useful both to the student about to undertake research in the wide field offered by cellulose and the substances associated with it in the plant world, and also to workers in laboratories controlling and investigating the manufacture of cellulose products.

The purpose of the author has been to give full working details of a selection of the best methods required in each section of the subject, and to illustrate the use and application of the methods by full abstracts of original investigations in which they have been employed. Whilst the need for copying experimental details from a number of journals may be obviated, the student should on no account omit to read the original papers connected with any method he may be using. Such reading will often suggest ideas for improvement or further research. Every effort has been made to select the best methods irrespective of their origin. Thus in the region of normal cotton cellulose prominence has been given to the work of the British Cotton Industry Research Association; in the sections dealing with the Analysis of Wood and with Pulp Processes the work of the American chemists is fully recognised, while in others the methods devised by German and Swedish workers are detailed. The technique associated with the X-ray investigation of cellulose,

so brilliantly developed by Herzog, Mark, Sponsler and Dore and others, has been designedly omitted, as it is essential to gain experience of X-ray methods and their interpretation at first hand.

The author desires to express his thanks and acknowledgments for permission to produce illustrations from publications and for the loan of blocks, to the following: The Director of the British Cotton Industry Research Association, the Director of the Linen Industry Research Association and the Editor of the *Journal of the Textile Institute*. He is also indebted to the following for permission to copy illustrations: The Chemical Catalog Co., Inc., and Drs. Hawley and Wise for Figs. 77, 78, 79, taken from "The Chemistry of Wood"; the Editor of *Industrial and Engineering Chemistry* (Figs. 1, 80); the Editor of *Cellulosechemie* and Dr. E. Heuser (Figs. 66–68); Messrs. Julius Springer, Berlin, and Dr. V. E. Yarsley (Fig. 11); Akademische Verlagsgesellschaft M.B.H., Leipzig, for Fig. 69, from K. Hess, "Die Chemie der Zellulose"; and to Sir Isaac Pitman & Sons Ltd. for Figs. 22 and 23, taken from Faust's "Artificial Silk".

Grateful acknowledgment is also made to Dr. D. A. Clibbens for valuable suggestions in connection with Part I.; to Dr. V. Yarsley in connection with the section on cellulose acetate; to Dr. L. Hall for helpful criticism on the sections dealing with cellulose xanthate and wood pulp processes; to Mr. E. R. Chrystall in connection with cellulose nitrate; and to Mr. L. Hebbs (of Messrs. Cross and Bevan), who has kindly read the whole of the proofs and supplied valuable additions.

The works of A. W. Schorger, K. Hess, and C. G. Schwalbe have also proved of great assistance.

CHARLES DORÉE.

LONDON,
October, 1932.

PREFACE TO THE SECOND EDITION

THE call for a new edition has afforded opportunity for an extensive revision of the whole work. Developments in method over the past ten years, however, have been more in detail than in principle. The bulk of the methods given in the first edition are therefore retained, as well as the general plan of the book. The importance assumed by the chain-molecule theory necessitates the introduction of a chapter devoted to structure and molcular weight determination. In the section on synthetic derivatives two new chapters have been added, one dealing with the general properties of cellulose esters and another treating of the ethers of cellulose. Considerable additional matter relating to the simple and mixed esters has also been included.

The second part of the book has been developed by a more complete treatment of the subject of woodpulps and their analysis, including a full account of British, American and Scandinavian methods and a special section on viscose pulps. The chapters on lignin and the pectic substances have been largely rewritten in the light of recent developments, and new methods have been added in the sections on the examination of plant tissues, hemicelluloses, and wood.

Some general names from the older nomenclature have been retained on the ground that it is difficult, even if necessary, to find better ones. Terms such as oxycellulose, by long usage, convey a definite impression and have a technical meaning, not carried by such expressions as oxidised cellulose. The expression " compound cellulose ", applied as a generic term to the aggregates isolated from lignified tissue, again expresses clearly and shortly the type of product under consideration and may even be justified in that the term compound no longer has the rigid significance formerly assigned to it.

For permission to make use of new matter and diagrams from publications, the author wishes to convey his thanks and acknowledgments to the British Cotton Industry Research Association, the British Standards Institution and to authors of papers and to editors of the following: *Journal of the Chemical Society* (Figs. 47, 48), *Journal of the Textile Institute* (Figs. 33-38), *The Analyst*

(Fig. 75), *Journal of the American Chemical Society* (Fig. 73), *Industrial Engineering Chemistry* (Fig. 70), and the *Paper Trade Journal* (Fig. 77). His thanks are due also to Dr. Clibbens, Dr. Lovecy and Professor E. L. Hirst for help on special points and to Mr. L. Hebbs, both for checking the proofs and for original material in the section dealing with viscose pulps.

CHARLES DORÉE.

AMERSHAM,
February, 1946.

NOTE

Temperatures are expressed in degrees Centigrade throughout.

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PART I

NORMAL CELLULOSE

CHAPTER I

THE PREPARATION OF STANDARD CELLULOSE

CELLULOSE never occurs in Nature except in association with other substances the removal of which requires fairly severe chemical treatment. Its properties, on the other hand, are easily modified by oxidation, by acids and by heat. The production of an approximately " pure " cellulose, therefore, requires methods adequate for the removal of non-cellulosic impurities, but sufficiently restrained to avoid the formation of degradation products.

The purity of any particular sample is measured by its neutrality, indifference to basic dyestuffs, low ash content, resistance to solution in caustic alkalis, minimum reducing power and high viscosity in cuprammonium. The determination of these qualities will be considered in the next chapter. An account is first given of methods which can be recommended for the preparation of cellulose of definitely high standards of purity.

It has been shown that the alkali boil and the bleach (chemic), under proper conditions, do not alter the properties of cotton cellulose. A laboratory normal bleach process is given which can be applied to all types of raw cotton. Alternatively, some commercial methods of preparation are so satisfactory that high-grade calicoes, after suitable purification, can be used as standard cellulose. Cotton linters, as employed for the manufacture of cellulose acetate and nitrate, are also suitable both in form and quality.

The washing of the cellulose after preparation must be very thorough. Cellulose adsorbs and holds tenaciously acids, bases and salts which can only be removed by long contact with repeated changes of water. It is very difficult to remove the last traces of alkali metal ions by washing in water, whereas acid ions can ultimately be eliminated. An acid treatment therefore should conclude the process of preparation.

PREPARATION OF STANDARD CELLULOSES OF THE NORMAL COTTON TYPE

A. From Raw Cotton.—It has been shown that while raw cotton of North and South American, Sea Island, and Egyptian

origin resemble one another in many respects, *e.g.* in possessing an ash content of 1·0 to 1·3 per cent., and ash alkalinity (p. 16) of rather more than 14, Egyptian cotton presents certain differences. It has, for example, when purified, a greater methylene blue absorption value (*e.g.* 0·69 compared with 0·46 for an American cotton). The following process [1] gives a standard cellulose of high purity.

Laboratory Normal Bleach Process.—American cotton in sliver form is given the following treatments :—

(i) A kier boil with NaOH solution of 2° Tw. (0·9 per cent.), for at least 6 hours at 40 lb. per square inch excess pressure.

(ii) A " chemic " in a solution of NaClO containing 1 g. of available chlorine and 10 g. of soda ash per litre.

(iii) A " sour ", which may consist in shaking in a machine for 2 or 3 hours with a large excess of $N/10$ sulphuric acid.

(iv) A wash with cold distilled water in which the material is worked, the centrifuge being used for removal of the wash water. The washing is continued till a little distilled water, shaken for half an hour with the cotton, remains neutral to an iodide-iodate-starch mixture.

A more severe treatment under (i), above, consists of a kier boil of 10 hours with 2 per cent. sodium hydroxide solution at an excess pressure of 40 lb. per square inch.

The following results show the standard of purity obtained by these methods :—

	Copper Number.	Methylene Blue Absorption.	Loss on Boiling in 1 % NaOH, four hours.	Ash Alkalinity.
(*a*) Sea Island cotton given treatments (i), (iii), (iv)	0·02	0·84	—	0·59
(*b*) American cotton given chemic (ii) also . .	0·02	0·45	1·51	—

Preparation of Standard Cellulose from Raw Cotton as recommended by the Division of Cellulose Chemistry of the American Chemical Society.—The original process [2] was modified by Corey and Gray,[3] whose procedure is given. The principle of the method consists in

[1] C. Birtwell, D. A. Clibbens and B. P. Ridge, *J. Text. Inst.*, 1923, **14**, 305T.

[2] *Ind. Eng. Chem.*, 1923, **15**, 748.

[3] A. B. Corey and H. L. Gray, *ibid.*, 1924, **16**, 853, 1130.

a prolonged alkali boil with complete exclusion of air, no bleaching treatment being employed. The apparatus is shown in the figure.

The nickel container is 6·5 in. high by 5 in. wide made of 24-mesh gauze. A nickel chain enables an up and down motion to be given.

Procedure.—A sample of about 75 g. of raw cotton, after hand picking, is extracted for 6 hours with alcohol (95 per cent.), and then for 6 hours with ether.

The cotton is then placed in the nickel basket (Fig. 1) and 3 litres of 1 per cent. NaOH solution (previously boiled to expel air) are added. The solution is boiled for 10 hours, during which 10 litres of fresh 1 per cent. NaOH are introduced. This is done by attaching a flask containing the bulk supply, which is maintained at the

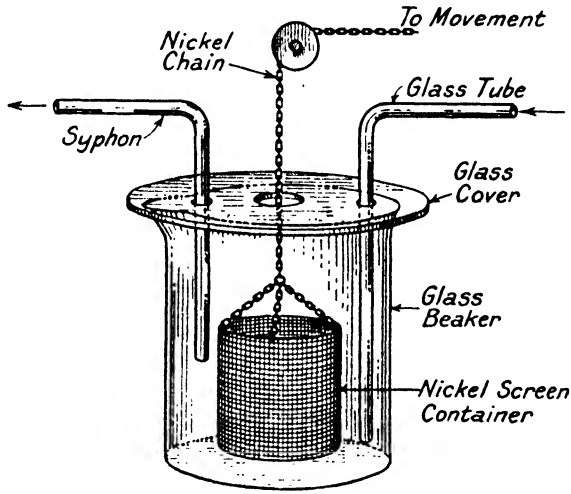


FIG. 1.—Apparatus for the preparation of standard cellulose.

boiling-point, in such a position that the fresh alkali continuously syphons into the beaker containing the cotton. This solution enters at the bottom of the beaker and the old solution is removed at the top by a constant level outflow, the rate being so regulated that it takes 10 hours for the fresh solution to flow in.

When the alkali solution has nearly all passed over, a little distilled water (previously boiled) is put into the flask. This is repeated several times, and finally the flask is filled with boiled water to wash the cotton. This process is continued as long as necessary. The cellulose is then transferred to a suction funnel, washed with three changes of water, immersed for 2 hours in 1 per cent. acetic acid solution and again washed with four changes of distilled water. It is dried in the air.

Such a cellulose should contain about 99·8 per cent. of α-cellulose and 0·05 per cent. of ash.

Cotton Linters.—The short fibre, or nep, left on the seeds after the first ginning constitutes linters. The seed, as received at the mill, may contain as much as 200 lb. of this fibre per ton. The so-called " first cut " yields fibre sufficiently long for use as a stuffing material, the second cut gives a short fibre (about 4 mm.) suitable for the manufacture of gun cotton, cellulose acetate, paper, etc.

According to Hahn and Bradshaw,[1] linters, when purified, have a higher viscosity even than long-staple cotton. They give the following viscosity measurements (time of fall of a steel sphere) in cuprammonium. The samples were prepared by boiling for 4 hours in a 2 per cent. sodium hydroxide solution, air being excluded.

Type of Cotton Fibre.	Relative Viscosity.
Sea Island cotton	80
Long-staple cotton	163
High-grade first-cut linters	280
Good second-cut linters	291
Average mill-run linters	392

The linters may be purified by either of the methods previously given. According to E.P. 438,643 (1935), linters (and other types of industrial cellulose) can be freed from impurities by heating with about 2 per cent. nitric acid for 1 to 4 hours. Treatment with 1 to 3 per cent. caustic soda and a hypochlorite bleach follows.

B. Use of Commercial Cotton Fabric.—Cross and Bevan [2] first pointed out that some commercial bleaching processes are designed to produce a cellulose of high purity. The following results, from their laboratory, show that a calico prepared by the madder bleach process fulfils the requirements of a standard cellulose.

STANDARD MADDER BLEACH CALICO

	Solubility in boiling 3 % NaOH.	Copper Number.*	Ash per cent.	α	β	γ
1. As received .	3·41	0·45	·096	99·5	0·4	0·1
2. Do., malted .	3·14	0·43	·098	100	—	—
3. Do., reboiled in Alkali .	1·66	0·39	0·50	—	—	—

* Uncorrected Schwalbe method.

[1] F. C. H. Hahn and H. Bradshaw, *Ind. Eng. Chem.*, 1926, **18**, 1259.
[2] " Researches on Cellulose ", III. London, 1912.

It requires well washing, with, if necessary, a treatment to remove dress or size and a sour in dilute acetic acid.

A " Standard Tarantulle " calico (Tootal, Broadhurst, Lee Co.) recently employed in research work had copper number 0·04; fluidity (0·5 per cent. soln.), 4·4.

Other commercial calicoes of high grade may also be employed provided that dressing materials can be removed. The following treatment has been found satisfactory for this purpose.

Removal of Dress and Filling Materials.—The cloth is :

(i) Heated for 30 minutes at 60° with shaking in a solution of 1 per cent. sodium hydroxide (20 ml. per g. of cloth).

(ii) Rinsed in cold tap water (ratio 8 : 1) twice.

(iii) Heated for 30 minutes at 60° in 1 per cent. acetic acid solution (ratio 20 : 1).

(iv) Rinsed in distilled water at 60° (ratio 8 : 1).

(v) Rinsed in cold distilled water (ratio 8 : 1) till neutral.

If calcium and magnesium soaps are suspected after (iii) the fabric is boiled for 30 minutes with a solution containing 0·3 per cent. of soap and 0·1 per cent. of sodium carbonate in distilled water. After washing it is soured and washed till the wash water is neutral.

The following values were obtained by the author on a high-grade calico (*a*) before and (*b*) after purification by this process :—

	(*a*)	(*b*)
Ash per cent.	0·13	0·07
Alkalinity of ash *	0·61	0·38

* Milliequivalents per cent.

Two calicoes used in several investigations had the following characters, and are given as indicating a suitable cloth for research purposes where strength measurements are necessary.

	1	2
Weight per sq. foot (oz.)	0·314	0·376
Threads per inch, warp and weft	120	94
Mean fibre length in inches :		
Warp	$1\frac{3}{16}$	$\frac{9}{10}$
Weft	$1\frac{1}{8}$	$\frac{15}{16}$
Bursting strength, lb. per sq. inch	40	45
Ash per cent. (after purification)	0·130	0·055

For the estimation of the percentage of calcium and other hard-water soaps on a fabric the following method gives satisfactory results :—

(*a*) 5 to 10 g. of the fabric are digested, with agitation, for 30 minutes with 20 parts of 1 per cent. acetic acid at 60°, washed and dried to constant weight.

(*b*) The dry fabric is extracted with ether and the extract evaporated to dryness and weighed.

The sum of the loss in weight under (*a*) and the weight of the ether extract in (*b*) is found to account for at least 98 per cent. of the total soaps on the fabric.

An examination of methods in use for the estimation of size and filling on cotton yarns and cloth enables two processes to be recommended [1] :—

(*a*) *A Scouring Method.*—The cloth in loom state (5 g. air dry) is heated for 1 hour at 80° with 1 per cent. NaOH solution (200 ml.), well washed, wrung out in hot water and heated as before in 200 ml. of 0·5 per cent. HCl at 80° for 1 hour. It is then boiled for half an hour with distilled water, dried at 110°, weighed and reduced to ash to estimate any residual mineral matter.

(*b*) *A Malting Method.*—A square of cloth, about 5 g., is taken and five threads pulled out all round so as to leave a fringe (for yarn a bundle of threads is taken). The sample is weighed air dry (moisture on a separate portion) and extracted for 1 hour with chloroform. The solvent is allowed to evaporate and the cloth well washed in hot running water twelve times, wringing out by hand in between. It is then immersed in 100 to 150 ml. of a 0·5 per cent. Diastafor solution and wrung out three times in succession, returned to the solution and heated at 70°, a total immersion of 15 minutes being given. It is then well washed and dried.

These processes result, with cloth in the loom state, in an average loss of 3 per cent. apart from sizing, and this figure is taken as the desizing " blank ". No correction is required for bleached or dyed cloth. The malting process is somewhat better and more consistent than the scouring process.

C. Use of Cotton Wool.—This is a convenient form in which to employ cotton, but many brands are necessarily over-bleached. We have frequently preferred to use a second quality wool, purifying it by boiling for half an hour with *N*/2 alcoholic KOH solution. Boiling with saturated baryta water for several hours should also give a purified product.

Hibbert and Parsons,[2] however, employed a short-fibred mildly bleached American cotton sold for surgical purposes, the analyses of which show a high degree of purity (see table on opposite page).

In the case of technically bleached cotton and cotton wool treated with the kier boil only, without sour (such as is used for the

[1] D. A. Clibbens and A. Geake, *J. Text. Inst.*, 1931, **22**, 465T.
[2] H. Hibbert and J. L. Parsons, *J. Soc. Chem. Ind.*, 1925, **44**, 479T.

	Moisture (at 105°).	Moisture-free Basis.			Furfural.	Viscosity.†
		Ash.	α-Cellulose.	Copper Number.*		
	Per cent.	Per cent.	Per cent.			
(*a*)	4·10	0·10	99·95	0·35	1·02	12·5
(*b*)	4·68	0·11	99·00	0·40	0·51	19·2

* Schwalbe method. † Comparative method.

manufacture of nitro-cellulose), the acid treatment and wash recommended on p. 16, is necessary to ensure a low ash content.

D. Ion-free Cellulose.—Studies on the acid groupings in cellulose (p. 116) require the removal of all cations except hydrogen. Acid washing (p. 16) and electro-endosmosis (p. 129) have been used for this purpose, but it is doubtful whether complete removal of cations can be achieved by either method. In the use of the dyestuff ion from methylene blue hydrochloride the solution is buffered near the neutral point to suppress the competition of the hydrogen ions. This is possible since the absorption of the alkali metals compared with that of the methylene blue cation is small.

E. Miscellaneous Types of Cellulose.—A bleached sulphite pulp, although not so satisfactory as cotton cellulose for critical work, is useful for the preparation of viscose and other esters and ethers. As the physical properties of the products are dependent on those of the original cellulose, it is important, for purposes of repetition, to record the constants of the pulp employed. A good sulphite viscose pulp will contain at least 90 per cent. of α-cellulose together with pentosans and hemi-celluloses. The analytical composition of various types of pulp will be found on pp. 479, 480.

An unbleached pulp may be purified by subjecting it to the stages of the chlorination process for the estimation of cellulose described on p. 352.

Filter papers of low ash content deviate considerably from a normal cellulose, but their reactivity gives them a certain advantage in preparation work, *e.g.* that of cellobiose (p. 205) and of esters and ethers. For investigations connected with the physical and colloidal qualities of cellulose it may be desirable to have a cellulose in sheet form. The commercial sheet known as Cellophane is useful in such cases. It is a cellulose regenerated from viscose and is very uniform in quality. A form specified as " 300 " used in one investigation weighed 2·7 mg./cm.^{2}; copper number (Heyes) 1·1; fluidity (0·5 per cent. soln.), 10.

Mercerised cellulose is described under Chapter V, and cellulose

preparations soluble in dilute alkalis, such as the Cellulose A of Hess, on pp. 283, 285.

The use of cellulose materials which are degraded from the normal, such as filter paper and over-bleached cotton wool, should be avoided for accurate investigation. In cases where a degraded cellulose is required, a definitely changed product should be prepared from a standard cotton cellulose by treatment with acids or oxidising agents under known conditions (pp. 123, 153) so that definite variation from the normal, as measured by viscosity and other constants, may be obtained.

NOTES

1. On the Estimation of Cellulose by Oxidation with Chromic Acid.—This method is now used extensively in connection with β- and γ- cellulose determinations (p. 365), and in micro-methods for measuring alkali-solubility, etc. Brief details are as follows [1] :—

(*a*) *Combustion of Cotton.*—About 0·04 g. is boiled for 1 hour under reflux with 20 ml. water, 10 ml. N-$K_2Cr_2O_7$ and 10 ml. concentrated sulphuric acid. The mixture is well diluted and titrated against $N/10$ ferrous ammonium sulphate

(1 ml. N-$K_2Cr_2O_7$ = 0·00675 g. $C_6H_{10}O_5$).

Example : taken 0·0409 g. of cotton ; found 0·0415 g.

(*b*) *Cellulose in Cuprammonium Solutions.*—10 ml. of solution are weighed into a stoppered conical flask and most of the ammonia driven off by boiling. A slight excess of 2 N-H_2SO_4 is added, the liquid again boiled to displace nitrous acid and finally 20 ml. of N-$K_2Cr_2O_7$ followed by 10 ml. of concentrated sulphuric acid are added. The mixture is boiled for half an hour under reflux, cooled, diluted to 100 ml. and an aliquot portion titrated. A correction should be applied for the dichromate reduced by the cuprammonium, if this contains cane sugar.

Example : cotton in cuprammonium, per cent. . . .	1·061
Found as above	1·068 1·053

(*c*) *Cellulose in Alkaline Solutions of Modified Cotton.*—For details see p. 164.

For a simple and accurate gas-burette method for the estimation of cellulose by oxidation to carbon dioxide with chromic acid, the reference below [1] may be consulted.

[1] C. Birtwell and B. P. Ridge, *J. Text. Inst.*, 1928, **19**, 341T.

2. **On the Compression of Cotton into Plugs for Experimental Purposes.**—The bulkiness of cotton makes it difficult to handle reasonable weights in small vessels, *e.g.* at the bottom of a beaker 1 g. will occupy some 10 ml. and require 10 ml. of liquid for immersion. With the aid of a screw pastille press it is possible to compress the cotton into plugs so that 1 g. occupies less than 0·8 ml. Thus 0·1 g. will form a plug 0·5 cm. in diameter and 0·4 cm. long and 7 g. of cotton in this form can be introduced into a tube of 10 ml. capacity. The plugs keep their shape at ordinary humidities. They expand somewhat in water, but not in organic liquids.[1]

3. **Cellulose Crystals.**[2]—Spindle-shaped crystals of cellulose can be obtained from ramie by the following process :—

Purification of the Bast Fibres.—Portions of 20 g. are shaken out three times with 500 ml. of 2 per cent. NaOH at 30° for 4 hours. After washing the fibres are left for 2 days in 0·3 per cent. chlorine dioxide solution, then 2 to 3 days in 2 per cent. sodium sulphite solution. Further treatment with 2 per cent. NaOH for 3 hours at 60°, washing and treatment with chlorine dioxide is twice repeated. The fibre bundles are then easily separated and freed from pectin, etc.

Separation of Crystals from the Fibre Bundles.—21·7 g. air dry are warmed at 70–75° for 8 hours with a mixture of 6 g. of 6 per cent. H_2SO_4, 88 g. of acetic anhydride and 300 ml. of benzene. The solution is poured off and the fibres washed with benzene and with methanol and then covered with glacial acetic acid. The greater part dissolves as triacetate, but there remain in suspension crystals of cellulose mixed with short pieces of fibre. As the crystals take longer to settle than the fibre, they can, for the most part, be decanted off.

The yield of crystals is not more than 15 per cent. of the crude material. They resemble regenerated cellulose, *e.g.* rotation in cuprammonium (10 mg. mole. $C_6H_{10}O_5$ to 10 mg. mole. $Cu[OH_2]$) is 7·36°, that of cellulose from a diacetate 7·32°. The acetate prepared from the crystals is identical with cellulose triacetate.

[1] A. M. Williams, *J. Text. Inst.*, 1923, **14**, 295T.

[2] K. Hess and G. Schultze, *Ann.*, 1927, **456**, 55 ; H. Ambronn, *Koll. Zeit.*, 1917, **20**, 184.

CHAPTER II

SOME MEASURABLE QUALITIES OF CELLULOSE AND THE DIAGNOSIS OF CHANGE IN CELLULOSE

A good deal of earlier work on cellulose was invalidated through failure to recognise its susceptibility to change, with the result that many useful investigations were carried out on a material which deviated essentially from normal cellulose. It is now recognised that the initial physical qualities of a cellulose persist through a series of changes ; if, for example, the viscosity of a cellulose is low, that of the nitrate and acetate prepared from it will be low, and alternatively, so that it is essential both for purposes of research and of manufacture to ascertain exactly the measurable qualities of the cellulosic material to be employed.

Deviations from the normal found in a sample of cellulose may result from the nature of its growth, the method of its isolation and the action of chemical and physical agencies upon it. They generally result from alterations in the structural balance of the fibre, accompanied by a shortening of the average length of the unit chains, and are revealed by a decrease in the strength and elasticity of the fibres, by a fall in viscosity and by increasing solubility in alkaline solutions. Chemical agents of an oxidising or hydrolytic character bring about the development of reducing properties, indicated by reaction with Fehling's solution. Dispersion of the cellulose, as in mercerisation, is shown by increases in the absorptive power for moisture, dyes, dilute alkalis, etc., and by increased reactivity measured, for example, by rate of change of copper number during hypobromite oxidation.

The more important measurements required for the specification of a sample of cellulose are as follows :—

1. Determination of the percentage of moisture (p. 13).
2. Estimation of the ash (p. 16), and ash alkalinity (p. 17).
3. Estimation of the copper number (p. 26).
4. Determination of fluidity (p. 52).
5. Estimation of the methylene blue absorption value.
6. Estimation of the loss in weight on treatment with sodium hydroxide solutions, which may be either—

(*a*) Loss in weight on boiling in 1 per cent. sodium hydroxide solution for 1, 3 or 4 hours (p. 36).

(*b*) Loss in weight on treatment with 10*N*- followed by 2*N*-sodium hydroxide solution at 15°. This may be coupled with the copper-reducing value of the alkaline extract (p. 165, 167), and the viscosity of the residual cellulose.

7. The determination of tensile strength (p. 73).

8. The ultimate analysis, if required, may conveniently be carried out by a modified micro-combustion method, or, as to carbon, by the wet combustion method (p. 8).

Examples of the employment of these methods will be found in the chapters on Oxycellulose and Hydrocellulose.

The standard methods to be described are based upon older processes. Thus Witz (1882) was the first to describe the methylene blue absorption test, Schwalbe (1907) standardised the technique of the copper reduction value, and Ost (1911) suggested the determination of viscosity as a diagnosis of change. Variations in the conditions employed in making the measurements, however, make the older results only of comparative value. The methods, in any case, are empirical, so that it is necessary to follow a standard procedure in order that results comparable with those of other workers may be obtained. It is very desirable that a set of standard methods should, after due investigation, be agreed upon by all workers on cellulose. Those given are based largely upon the results of the British Cotton Industry Research Association, which has submitted each test to exhaustive scrutiny before adopting it as a standard.

Application and Validity of the Quantitative Measurements.—It is important not to expose the sample to be employed for a series of tests to prolonged drying at a high temperature. A fall in viscosity has been observed even after exposure of cotton to bright sunlight for 6 hours, and a marked fall in viscosity, *e.g.* from 71 to 45 seconds, was observed after heating a purified cellulose at 110° for 24 hours. The bulk material taken for analysis should therefore be dried at a moderate temperature and conditioned in the air. Samples of 1, 2 and 5 g. should then be weighed out into suitable packets or bottles, and the moisture determined on a sample weighed at the same time.

The variation of the viscosity in cuprammonium is by far the most sensitive diagnostic of change in cellulose. It indicates change even before the tensile strength of the material alters to an extent sufficient for direct measurement. The copper number, which indicates the development of reducing property, is neither so sensitive nor so reliable a criterion of change as the viscosity. This is especially the case where the sample, previous to examination, has been treated with alkaline solutions.

The viscosity is not restored to its original value by an alkali boil, and its value therefore reveals initial damage to the cellulose in spite of subsequent alkali treatment. The alkali, however, removes or destroys the substance responsible for the copper reduction, so that a low copper number does not necessarily imply freedom from damage. The following measurements, made on cotton oxidised progressively to an increasing extent, show the changes in copper number and viscosity before, and after, boiling in sodium hydroxide solution.[1]

Copper Number. Boiling for four hours with 1 per cent. NaOH.		Log. Viscosity of a 2 per cent. Solution. Boiling for four hours with 1 per cent. NaOH.	
Before	After	Before	After
0·65	0·09	0·81	0·38
1·07	0·17	0·24	0·02
1·56	0·28	$\bar{1}$·98	$\bar{1}$·71
2·46	0·39	$\bar{1}$·70	$\bar{1}$·53
2·83	0·45	$\bar{1}$·62	$\bar{1}$·45
3·78	0·51	$\bar{1}$·48	$\bar{1}$·35

The viscosity, however, rapidly reaches minimum values. It is most valuable as indicating the initial stages of attack. The copper number, on the other hand, is more useful in giving a measure of marked variation from the normal.

The tensile strength, whether of hair or yarn, is also very sensitive. It is worthy of note that in many cases the alterations produced by chemical attack on yarn and hair strength of the same material are almost identical (see p. 151).

The loss in weight on treatment with 1 per cent. sodium hydroxide solution is not large in the early stages of degradation, but it becomes much greater with progressive attack. With the hydrocelluloses (products formed by acid attack) a definite relation exists between the copper number, the viscosity, the loss in tensile strength, and the loss of weight in alkali respectively, so that the properties of a hydrocellulose can be defined in terms of copper number. This is illustrated by the values on p. 150.

The absorption of methylene blue is more difficult of interpretation, and its value as a diagnostic is much less. A normal cotton cellulose will absorb about 1·0 millimole of methylene blue per 100 g. The degree of absorption depends on the ash, or rather the ash alkalinity, of the cellulose. It is consequently increased by the presence of chemical substances fixed and retained during preparation. An increased absorption is also observed when dilute sulphuric or phosphoric acid is dried into the cellulose at moderate tem-

[1] D. A. Clibbens, A. Geake and B. P. Ridge, *J. Text. Inst.*, 1927, **18**, 278T.

peratures, or when the material is treated with fairly concentrated solutions of sulphuric acid in the cold. Cellulose fixes these acids in such a form that even a drastic kier boil has very little effect in removing them.

The fixation of acid no doubt causes the increased absorption, since volatile acids like hydrochloric acid, when dried into the material, produce an absorption which is usually less than that of the untreated cotton. The absorption value also varies with the H-ion concentration of the dyestuff solution, and modern practice, therefore, recommends a preliminary washing of the samples with dilute sulphuric acid and the use of a solution of methylene blue buffered to *p*H 7. Under these conditions the determination of the absorption value is useful, for example, in following the stages of a purification process. It has also been shown (p. 24) that it is possible to distinguish an increased methylene blue absorption due to oxidation from that due to acid action, by measurement of the absorption of the dyestuff from solutions buffered to *p*H 2·7 and *p*H 7 respectively. Treatment with the dyestuff is also useful for indicating qualitatively the areas on which a fabric may have been damaged by the action of acid or bleach.

Determination of Moisture in Cellulose

General Methods.—In order to estimate the so-called hygroscopic moisture, or moisture of condition, of cellulose, various methods have been employed. These include drying in a vacuum over phosphorus pentoxide at ordinary temperature, drying at the temperature of the water oven (98° to 99°), and drying in electrically controlled ovens at 105° or 110°. Other methods involve the process of distillation of the material with a water-immiscible liquid such as toluene, and the measurement of the water which distils over.

Cellulose undoubtedly undergoes some form of oxidation during prolonged heating in air even at temperatures of the order of 100°, so that prolonged drying is to be avoided. If the temperature is too high, slight decomposition may take place, though an (unpublished) investigation shows that this is not marked below 150°. In some laboratories the practice has always been to dry in a water oven. On the other hand, the electrically controlled oven has many advantages for modern work. The air temperature of 110° should be taken as a standard for cotton materials, and that of 100° or 105° for wood pulps, degraded cellulose, etc. Contact with the walls or shelves of the oven should be avoided, and, ideally, the sample should be suspended in a basket.

The fact that oven drying is as satisfactory as drying in a vacuum at the ordinary temperature was demonstrated by Urquhart and Williams,[1] who carried out comparative tests of the two methods—(*a*) that of drying in an electrically heated oven controlled to 110°, and (*b*) that of drying in a vacuum desiccator containing phosphorus pentoxide, at 15°.

The results showed that with method (*b*) weight continued to be lost during a week, while with (*a*) no appreciable loss of weight occurred after 24 hours.

With raw cottons method (*b*) gave lower results than method (*a*)—*e.g.* 7·02 per cent. on drying at 15° and 7·39 per cent. at 110°. The difference was due to decomposition of non-cellulosic constituents at 110°. This was shown by the following experiment: A sample of cotton sliver was purified by kiering for 10 hours at 40 lb. excess pressure in NaOH of initial concentration 1·7 per cent. The product was washed and dried at 80°. The copper value and viscosity proved it to be a well-purified cellulose. This cotton gave identical values on drying by the two methods—*viz.* 5·66 per cent.

The moisture content of cotton cellulose, under normal laboratory conditions, is fairly constant, and for many purposes may be taken as 6·0 with sufficient accuracy. In all investigations on cellulose it is recommended that the specimens used should not be oven dried. All the quantities required should be weighed out at the same time, and the moisture determined on one of the samples.

Estimation of Water Content by Distillation with an Immiscible Liquid.—The principle of removing water by heating with a liquid such as toluene can be used for fibres, paper and pulp. Fairly large quantities of material are required and accurate measurement of the water obtained is essential.

The apparatus used by Bidwell and Sterling [2] and by Tate and Warren [3] has been put into standardised form by the British Standards Institution (B.S. Specification 756—1937), and is shown in Fig. 2. It is made of Pyrex glass with interchangeable ground joints, B12 and A24. The flask has a capacity of 250 ml. (or 500 ml. in some cases) and the receiver 2 ml. graduated to 0·05 ml.

The weighed sample is introduced into the flask, together with sufficient toluene or other liquid to cover it (usually 75 ml.). The apparatus is then fitted together and the calibrated receiving tube filled by pouring toluene through the top of the condenser. The liquid is distilled off at the rate of two drops per second, until all the water has passed over.

[1] A. R. Urquhart and A. M. Williams, *J. Text. Inst.*, 1924, **15**, 138T.
[2] G. L. Bidwell and W. F. Sterling, *Ind. Eng. Chem.*, 1925, **17**, 147.
[3] F. G. Tate and L. A. Warren, *Analyst*, 1936, **61**, 367.

A little more toluene is poured down the condenser and the distillation continued for a short time. The receiving tube is adjusted to room temperature and the volume of water read off.

Liquids that have been recommended in addition to toluene are *n*-heptane, the non-inflammable tetrachloroethylene, b.p. 121°, and carbon tetrachloride, b.p. 77°.

The estimation of moisture in wood by oven drying is difficult owing to oxidation, the loss of other substances such as turpentine, and to obstinate retention of water. The *TAPPI* standard T3m, 1934, recommends the distillation of 100 to 300 g. of the sample with 500 ml. of toluene. The outlet tube, bent at right angles, passes into a vertical tube acting as a trap. This is joined at the top to a condenser and sealed at the bottom to a graduated tube fitted with a tap. The water which collects under the toluene may either be run into a measure or, better, measured in the tube. Allowance should be made for the difference in shape of the meniscus of water under toluene and water in air.

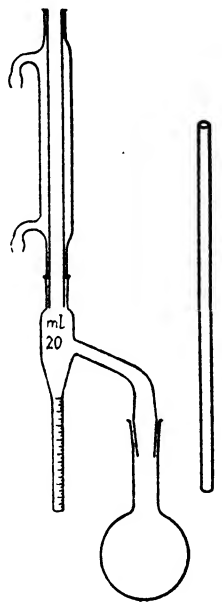


FIG. 2.—Apparatus for the estimation of water by distillation with toluene.

A criticism has been made [1] of all apparatus involving the use of a vertical condenser, *viz.* that it is almost impossible to collect all the water in the measure, some invariably remaining in the condenser. This is due (*a*) to the fact that the water condenses above the toluene and is not thoroughly washed down, and (*b*) because water will adhere to the walls of a glass tube unless the surface is alkaline. To avoid these difficulties the author advises (*a*) a vertical pipette-shaped condenser surrounding the exit tube from the flask which discharges into the lower part of the condenser, and (*b*) that the tube and receiver, after washing with chromic acid, should be rinsed with 5 per cent. KOH solution. In some cases volatile acids are formed during distillation which would again cause fouling of the tube. This can be avoided by adding a little Na_2HPO_4 to the contents of the flask.

A **Moisture Meter** suitable for cotton and other textile materials has been designed by the Shirley Institute, Manchester.[2]

It depends upon the relationship which is shown to exist between moisture content and the electrical resistivity of cotton, viscose

[1] J. A. de Louriero, *J. Off. Agric. Chem.*, 1938, **21**, 645.
[2] E. H. Jones, *J. Sci. Instr.*, 1940, **17**, 55.

rayon, etc. The method consists essentially in pressing a pair of closely spaced electrodes on to the material and measuring the electrical resistance at a number of points. A special electrode system which eliminates variations in resistance arising from variations in shape, size, or initial density of the sample is employed, and the use of a stainless steel anode prevents polarisation errors. A mechanical device enables a constant compressing force of 20 kg. weight to be maintained.

The instrument for measuring resistance is compact, robust and relatively cheap, based on a circuit incorporating common types of thermionic valves. For the normal range of "regain" in cotton *—about 4·5 to 15 per cent.—the instrument measures logarithmically a range of resistance from 9,000 MΩ to 0·17 MΩ on a fairly open scale.

There is, for many textile materials, an almost linear relationship between regain and the logarithm of the resistance. With grey cotton, for example, the resistance increases about 2·8 times for every 1 per cent. decrease in the percentage regain.

The method is quick, accurate to about 0·5 per cent. regain, and does not injure the sample. It can be applied to most textile materials except silk and acetate rayon. The necessary outfit can be purchased. †

Determination of the Ash Content and Ash Alkalinity of Cellulose Preparations

When freed from dirt and other extraneous matter, the residual mineral content of raw, unbleached cotton is about 1 per cent. The same cotton, after a full bleach treatment, concluding with a sour, will show an ash content of 0·1 per cent. or less. The effect of the mineral matter on the absorption of methylene blue is a function of the ash alkalinity, which itself, in the case of cotton, is proportional to the ash content.

To obtain minimum ash and ash-alkalinity it is recommended to shake the material in a machine for 2 or 3 hours with a large volume of $N/10$ sulphuric acid, and to wash until the wash water, after shaking for half an hour with the cotton, remains neutral to an iodide-iodate-starch mixture. In the case of the cotton mentioned above a further reduction of ash to 0·02 to 0·03 per cent. will be effected.[1]

* The regain is the ratio of the weight of water originally present to the oven-dry weight of the sample. The percentage regain is 100 times this figure.

† The Record Electrical Co., Ltd., Broadheath, Manchester.

[1] C. Birtwell, D. A. Clibbens and B. P. Ridge, *Shirley Inst. Mem.*, 1923, **2**, 232; *J. Text. Inst.*, 1923, **14**, 302T.

Procedure.—The following apparatus and materials are required: A 100 ml. stoppered measuring cylinder; $N/100$ sulphuric acid and $N/100$ sodium hydroxide; 0·005 per cent. solution of methyl red. The $N/100$ solutions should be preserved in previously used bottles of resistance glass. The glassware must not be new.

(*a*) *Ash Content.*—About 10 g. of the cellulose, dried at 100°, are placed in a weighed silica, or platinum, dish and ignited gradually before an electrically heated muffle furnace. The ashing is completed by heating in the furnace to a dull red heat controlled to about 750°. The ash is cooled in a desiccator and weighed quickly.

(*b*) *Ash Alkalinity.*—The ash is at once treated with 10 or 15 ml. (accurately delivered) of $N/100$ sulphuric acid, covered with a glass, and warmed for 1 hour. The contents of the dish are washed into the cylinder, the volume made up to 70 ml., 1 ml. of the methyl red added, and the excess acid titrated with $N/100$ sodium hydroxide. As the end-point approaches, the cylinder is stoppered and shaken after the addition of each drop of acid. The correct neutral colour is most sharply observed through a column of the liquid. It is, however, advisable to prepare a " blank " by adding 1 ml. of the methyl red to 70 ml. of distilled water in a similar cylinder. The use of this device has the additional advantage of correcting for any deviation from neutrality of the distilled water.

The results are calculated to milli-equivalents per 100 g. of cotton. For example, an ash alkalinity of 15 means that the ash from 100 g. of cotton would neutralise 15 ml. of a N-acid solution. As the ash alkalinity determination depends upon titrations of the order of 10 ml. of $N/100$ acid, it is a more accurate determination than that of the ash itself, which depends upon the weighing of a few milligrams of hygroscopic material. In many cases the ash content can be estimated from the ash alkalinity.

Another method of expressing the results [1] is to state the alkalinity per gram of ash—that is the ash alkalinity as defined above divided by the ash content—a figure which is appreciably constant for different classes of cotton.

For the estimation of the amount of acid fixed by cellulose, see p. 209.

The Methylene Blue Absorption Value

Carefully prepared normal celluloses have a low absorptive power for methylene blue. The acidic and pectic bodies present in natural cottons raise the amount of dyestuff absorbed. As these are removed the values diminish as shown in the following example [2]:—

[1] R. G. Fargher and M. E. Probert, *J. Text. Inst.*, 1926, **17**, 46T.
[2] C. Birtwell, D. A. Clibbens and B. P. Ridge, *ibid.*, 1923, **14**, 297T.

SAMPLES OF AMERICAN COTTON TAKEN AT VARIOUS STAGES OF A LIME BLEACHING PROCESS

	Methylene Blue * Absorbed Millimoles per 100 g. Dry Cotton.
1. Grey cloth	2·16
2. Lime boil, sour,	1·58
3. ,, ,, ,, ash boil	1·04
4. ,, ,, ,, ,, ,, chemic	1·04
5. ,, ,, ,, ,, ,, ,, ash scald	0·58
6. Processed as 5 followed by chemic	0·57

* Solution not buffered.

It will be noticed that the fall in the absorption occurs after the boil, but not after the chemic.

The methylene blue value is also raised by the presence of mineral matter in the samples, and it varies more precisely with the alkalinity of the ash, as will be seen from the following table, which gives the results obtained on a series of American slivers kier-boiled in the same way and either (A) washed with water or (B) chemicked, soured and washed. The effect of the sour, which reduces ash alkalinity, is marked (Birtwell, Clibbens and Geake, *loc. cit.*):—

	Ash Alkalinity.*	Methylene Blue Absorption.†	Ditto after Laboratory Acid Washing Process.
Samples of A series.	2·69	0·82	0·59
	2·35	0·81	0·60
	1·71	0·78	0·65
	1·52	0·76	0·64
	1·05	0·54	0·51
Samples of B series.	1·19	0·58	0·45
	0·97	0·56	0·46
	0·93	0·53	0·45

* Milli-equivalents/100 g. dry cotton. † Millimoles/100 g. dry cotton.

Egyptian cotton under similar conditions shows a constantly higher value (0·92 to 0·64) than American cotton (0·58 to 0·45). To obtain comparable values in any investigation of progressive change in cellulose the sulphuric acid washing process (p. 2) should be given to all samples (see also under "Absorption from Buffered Solutions").

The H-ion concentration of the solution has a marked effect on the absorption of methylene blue. Determinations by the above process made, using (*a*) a solution of pure methylene blue hydrochloride, (*b*) the same made *N*/10 with regard to excess of free

HCl, (*c*) a solution *N*/100 with regard to excess NaOH, gave the following values :—

(*a*) 0·60. (*b*) 0·26. (*c*) 1·13 millimoles/100 g.

The earlier practice for the estimation consisted in boiling a dilute solution of methylene blue with the cellulose for 5 minutes. The dyestuff present before and after was estimated either by titration with an acid dyestuff, or by colorimetric comparison. A number of precautions are necessary to attain comparable results, and, in particular, a solution buffered to *p*H 7 should be employed. The method recommended for systematic work is first given.

Determination of the Absorption of Methylene Blue from Buffered Solutions.[1]—The cotton is left in contact with the standard solution, which is buffered to *p*H 7, for 18 hours at ordinary temperature. A volume of the solution is then withdrawn and the amount of methylene blue present ascertained by titration with Naphthol Yellow-S solution, one molecular proportion of the acid dye combining with two molecular proportions of the basic dye thus :—

$C_{10}H_4O_8N_2SNa_2$, M.Wt. 358 : 2 $C_{16}H_{18}N_3SCl$, 2 × M.Wt. 320

a reddish-black precipitate being produced.

Reagents and Apparatus Required.—(*a*) *Standard Neutral Buffered Solution of Methylene Blue.*—The "pure" commercial methylene blue hydrochloride (90 to 97 per cent.) is recrystallised three times from twelve times its weight of water. The crystals are air dried, the moisture determined on a sample dried at 110°, and the dye content (99 to 100 per cent.) estimated by titanous chloride.*

The standard solution at *p*H 7 is M/250 in methylene blue, and contains—

Potassium dihydrogen phosphate, KH_2PO_4	6·81 g.
Normal sodium hydroxide solution, *N*-NaOH	29·63 ml.
Methylene blue hydrochloride	1·279 g.
Water	to 1 litre

The acid methylene blue solution is made as follows :—

Methylene blue hydrochloride	1·279 g.
N/5 acetic acid solution	to 1 litre

(*b*) *Naphthol Yellow-S Solution.*—The commercial pure substance is recrystallised from alcohol and water and dried in a vacuum at 70°.

[1] D. A. Clibbens and A. Geake, *J. Text. Inst.*, 1926, **17**, 127T. Also C. Birtwell, D. A. Clibbens and B. P. Ridge, *ibid.*, 1923, **14**, 297T.

* The purity can also be controlled by measurement of the specific conductivity which gradually falls with recrystallisation to 102·2 ohms^{-1} at 25° with a molecular dilution of 200 litres.

A solution of the dye containing 1·5 to 2·0 millimoles per litre is prepared. It is standardised by titration against the standard, or the acid methylene blue, according to which solution is being used for the absorption. The process is as follows :—

Titration of the Naphthol Yellow-S Solution against the Standard Methylene Blue Solution.—The naphthol yellow, when run into the methylene blue, produces at first a reddish-brown precipitate, the colour of the liquid becoming less and less blue, until it finally changes to yellow. This change is largely obscured by the precipitate, which does not readily settle. Pelet-Jolivet, who developed this method, recommends spotting the titrated liquid on to filter paper. The precipitate will be found to remain in the middle of the spot, while the solution spreads around it showing the colour of the dye which is present in excess. Birtwell, Clibbens and Ridge prefer to titrate the methylene blue solution in stout glass tubes of about 50 ml. capacity which fit into the brass buckets of a centrifuge. The approach of the end-point can be detected by observing a drop of the liquid suspended from a glass rod, and when this point is nearly reached the tube is centrifuged for 15 to 30 seconds at about 1,500 r.p.m. with a radius of 19 cm. This separates the precipitate, and the colour of the supernatant liquid is clearly seen.

The change of colour is not very abrupt, but there is little difficulty, after some practice, in fixing the end-point within 0·1 ml. with the solutions prescribed above.

The stout-walled glass absorption tubes are about 11 cm. high by 2·5 cm. external diameter, constricted in the middle. The volume below the constriction is 20 to 25 ml., and above 15 to 20 ml. A stout cover tube, slightly larger and wider, is required, which must fit into the containers of the centrifuge.

Method of Absorption Measurement.—It is advisable to give the cotton a short acid wash by steeping it for 1 hour in $N/10$ sulphuric acid, washing twelve times in water, centrifuging between each wash, steeping in water 3 hours, re-washing and drying in the air.

(*a*) A sample of air-dry material, weighing $2{\cdot}50 \pm 0{\cdot}01$ g. is taken (moisture on a duplicate sample, or, if not greatly changed, a content of 6 per cent. may be assumed). 15 ml. of methylene blue solution is measured into the tube from a burette and the cotton pushed past the constriction and well " worked " with a glass rod in the solution, which will generally be completely absorbed. The rod is left in the tube, which is closed by the cover tube and left for 18 hours at room temperature.

(*b*) The apparatus is then inverted and centrifuged for about 30 seconds at 1,500 r.p.m. About 12 ml. of the solution will be driven into the lower half of the tube, the cotton being retained by the constriction. 10 ml. of this are pipetted out and titrated against the naphthol yellow-S solution as described. The absorption is calculated in millimoles per 100 g. of dry cotton.

With solutions of the concentrations given it is numerically equal to about one-fifth of the titre change. In routine practice it is advisable to adjust the strength of the naphthol yellow-S solution so as to make this agreement exact.

(*c*) The procedure with the acid methylene blue solution is identical with that described above.

Alternative Colorimetric Method.—This method is given for reference purposes. With care the same results are obtained (using M/2,500 solutions of the blue) as with the titrimetric method. The latter is recommended, because the presence of buffer salts affects colorimetric comparison and variations in the final concentration of the methylene blue are of importance in the colorimetric method, but do not affect the titrimetric method.

From 1·5 to 2 g. of cotton are shaken for 18 hours at room temperature with 50 ml. of a solution of methylene blue containing about 0·4 millimole per litre. With normal cotton the concentration of the solution is approximately halved by the absorption which takes place, so that the equilibrium solution is of nearly the same concentration as the standard with which it is compared. The original solution (0·4 millimole per litre) and the comparison standard (0·2 millimole per litre) are obtained by diluting the more concentrated solution of exactly known concentration.

It is generally assumed in colorimetric analysis that the concentrations of two solutions showing equal colour intensity are inversely proportional to the lengths of the columns of fluid in the colorimeter. This assumption has been found to be untrue with regard to solutions of methylene blue when the disparity between the concentrations of the standard and the unknown is large—*e.g.* with solutions whose concentrations stand in the ratio of 1 : 2, the error caused by the assumed proportionality is 10 per cent. Care should be taken, therefore, to have a colorimeter reading for the unknown ranging between 17 and 23 mm. corresponding to a standard solution at 20 mm.

Notes on the Methylene Blue Absorption Method.—1. The great variations in the absorption which arise from acidity or alkalinity in the materials employed are largely obviated by the use of buffered solutions. The alkali dissolved from new glass vessels,

for example, must have been responsible for considerable errors in determinations with the old (unbuffered) solutions. The nature of these errors is shown in the following table (Clibbens and Geake, *loc. cit.*), the same cotton being used in each case.

	Percentage Error in Absorption Measurement.	
	Unbuffered Solution.	Buffered Solution.
1 ml. 0·1 *N*-NaOH added to 1 litre of . methylene blue . . .	+ 26	− 3
1 ml. 0·1 *N*-HCl added to ditto .	− 13	+ 0
Full bleach without laboratory wash	+ 35	− 2
Using new glassware . . .	+ 26	+ 0

2. The relation between *p*H and absorption is approximately linear between the limits *p*H 7·8 and *p*H 2·7 as shown in Fig. 3.[1]

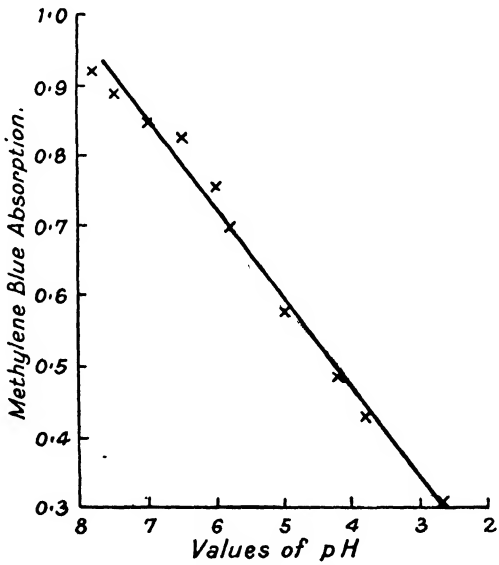


FIG. 3.—Variation in the absorption of methylene blue by bleached cotton caused by the gradual addition of sulphuric acid.

The phosphate ion used in the standard buffer solution is apparently without influence on the absorption of methylene blue, but this is not true of the acidic ions of other buffer solutions. It may be noted that solutions of methylene blue hydrochloride remain acid even after the addition of some quantity of sodium hydroxide. This is due to hydrolysis of the salt.[2]

3. For the measurement of the hydrogen ion concentration of

[1] D. A. Clibbens and A. Geake, *J. Text. Inst.*, 1926, **17**, 138T.
[2] P. Rona and L. Michaelis, *Biochem. Z.*, 1920, **108**, 19.

methylene blue solutions the quinhydrone electrode, tested with M/20 potassium hydrogen phthalate (Clarke, "Determination of Hydrogen Ions", 1922) and compared with a hydrogen electrode in a range of buffer solutions, gives satisfactory results.

4. The results obtained by the standard method on normally scoured and bleached cottons show that for American cotton the value lies between 0·9 and 0·8 and for Egyptian between 1·1 and 1·0. For Peruvian varieties 1·1 is a typical value, while for native Indian types values are higher, ranging from 1·16 to 1·74. Sea Island cotton gives the value 1·0.

From unbuffered solutions the values obtained are lower, being about 0·45 for American and about 0·65 for Egyptian varieties. Mercerisation has very little effect on the absorption, as is shown by the following values obtained with Egyptian cotton fabric which was mercerised under tension.

Treatment.	Absorption Methylene Blue: Millimoles/100 g. Mercerised.	Unmercerised.
Hot soap, pressure boil, chemic .	1·04 ..	1·13
,, open boil, chemic . .	1·39 ..	1·28
,, chemic . . .	1·81 ..	1·95

5. Influence of ash alkalinity on the methylene blue absorption: Since cotton samples taken at any stage from the card sliver onwards are practically free from extraneous matter [1] the ash found affords an accurate measure of their mineral content. The ash content is approximately proportional to the ash alkalinity (p. 16), the value of the latter per gram of ash being about twelve times the percentage of ash in the case of American, Egyptian and Indian cottons.

The methylene blue absorption is also a function of ash alkalinity, as shown in the following table (Birtwell, Clibbens and Ridge, *loc. cit.*, 1923), which gives values for an American cotton, kier boiled and washed with water.

Cotton as Received.		After Acid Washing.†
Ash Alkalinity. Milli-equivs./100 g. Dry Cotton.	Methylene Blue Absorption,* Millimoles/100 g.	Methylene Blue Absorption.
2·69	0·82	0·59
2·35	0·81	0·60
1·71	0·78	0·65
1·19	0·58	0·45
0·93	0·53	0·45

* Solution not buffered. † The ash alkalinity after acid washing was 0·1 to 0·2.

[1] R. G. Fargher and M. E. Probert, *J. Text. Inst.*, 1926, **17**, 46T.

Application of the Methylene Blue Absorption Value to the Differentiation of Oxycellulose and certain Types of Hydrocellulose.—The effect of variations in the H-ion concentration of the methylene blue solution upon the absorption shown by oxycelluloses, whether of the type characterised by enhanced methylene blue absorption or not, is similar to the effect of the same variations on the absorption in the case of normal cotton (Birtwell, Clibbens, and Ridge, *loc. cit.*). Of the hydrocelluloses some show no higher absorption values than those of the original cotton, and with these the effect of change in the H-ion concentration is similar to the

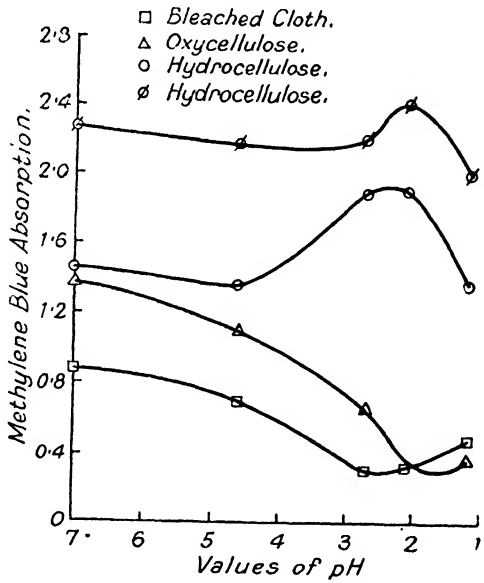


FIG. 4.—Effect of hydrogen ion concentration on the absorption of methylene blue by modified cotton.

effects observed with the normal and oxidised cotton cellulose. There is, however, a type of hydrocellulose, for example, that formed by drying dilute sulphuric acid into cotton, which shows far higher absorption than that of normal cotton. In this type the acid combines in some way with the hydrocellulose and the effect of variations in H-ion concentration on the methylene blue absorption is quite different. Examples can be seen in the table, the values in which are shown graphically in Fig. 4. All the preparations were made from the same sample of cotton. The oxycellulose was prepared by the action of alkali-hypobromite, and the hydrocelluloses by drying 0·1 *N*-sulphuric acid into the cloth at two different temperatures.

Material.	Methylene Blue. Absorption, Millimoles/100 g.				
	Phosphate Buffer, *p*H 7.	Acetate Buffer. *p*H 4·6.	0·2 *N*. HAc. *p*H 2·7.	0·01 *N*. H_2SO_4. *p*H 2·1.	0·1 *N*. H_2SO_4. *p*H 1·2.
Bleached cloth .	0·89	0·70	0·31	0·33	0·48
Oxycellulose .	1·38	1·10	0·66	0·36	0·37
Hydrocellulose (1)	1·46	1·36	1·91	1·92	1·37
,, (2)	2·29	2·19	2·23	2·42	2·02

A large number of oxy- and hydro-cellulose preparations have been examined, especially in regard to values of the absorptions at *p*H 7 and *p*H 2·7 (0·2 *N*-acetic acid). For bleached cotton, and for various oxycelluloses, the ratio of absorption at *p*H 7 to that at *p*H 2·7 is always greater than two, and hydrocelluloses produced by acid attack which gives no increased methylene blue absorption, show the same ratio. With hydrocelluloses formed by drying sulphuric or phosphoric acid into the fibre, or by steeping it in concentrated (above 50 per cent.) sulphuric acid—methods which give products of enhanced methylene blue absorption—the ratio of the value obtained at *p*H 7 to that at *p*H 2·7 is less than 2 and frequently less than 1.

The following table, as an example of this, contains the results of experiments in which M/10 phosphoric acid was dried into the cloth at various temperatures :—

Temperature of drying .	20°	50°	70°	90°	110°	130°
Absorption* at *p*H 7 .	0·89	0·82	0·93	1·39	1·64	1·82
,, at *p*H 2·7 .	0·31	0·52	0·71	1·19	1·70	2·14
Ratio *p*H 7/*p*H 2·7 .	2·9	1·6	1·3	1·2	0·97	0·85

* Millimoles methylene blue/100 g.

Procedure.—To avoid errors due to want of uniformity of material the two absorptions are carried out on the same piece of material. The absorption is determined, using either of the solutions. The cloth is then removed, the excess of dye solution washed away with water, and the sample treated at the boil with successive small quantities of *N*/5 acetic acid until only a slight blue tinge is left—a treatment which has no effect on the absorption of normal or modified cotton. It is washed with water, air-dried, and a second determination made with the other solution.

The following figures show that it is immaterial in which order the values are determined :—

Sample I.		Sample II.	
Absorption at *p*H 7 . .	0·84	Absorption at *p*H 2·7 . .	0·33
Absorption at *p*H 2·7 after stripping	0·30	Absorption at *p*H 7 after stripping . . .	0·82

Determination of the Copper Number

This quantity represents the weight of copper reduced from the cupric to the cuprous state in alkaline solutions by 100 g. of dry cellulose. With normal cotton cellulose the values are of the order of 0·2 and under : any change in the cellulose, whether produced by heat, acids, alkalis or oxidising agents, is revealed by a marked increase in the copper number. The determination of this constant is therefore of great value as a diagnostic, but to obtain concordant results a definite technique must be followed. The test was first introduced by Schwalbe and was gradually brought to a standard process in his hands. The method, however, is long, requires special apparatus, and needs blank corrections, the basis for which is not entirely sound. Knecht and Thompson devised a volumetric method for the estimation of the reduced copper oxide which eliminated some of the objections, and more recently the British Cotton Industry Research Association has added further improvements by substituting for Fehling's solution a solution of copper sulphate kept alkaline by a sodium carbonate-bicarbonate mixture as recommended by Braidy, the cuprous oxide being estimated by the volumetric method of Knecht and Thompson. This process, referred to as the Schwalbe-Braidy method, satisfies the requirements of a method suitable for routine, technical and research work. It is simple and sensitive, with an approximately zero " blank " correction, and with " pure " cotton cellulose minimum values are obtained. It is especially useful in examining the initial stages in the degradation of cellulose, *e.g.* up to copper numbers of about 2·5. A modification (Heyes), which is also described, enables small quantities of cotton (0·25 g.) to be employed. This micro-technique has the advantage of conserving material, and in the present author's hands has proved quite as accurate as the original.

The Schwalbe-Braidy method has been criticised by Hägglund on the ground that the long period of heating involves decomposition of the degraded cellulose with the production of reducing substances. The actual copper number is thus increased to an unknown extent. With products up to a copper number of 2, however, the Schwalbe-Braidy gives values much lower than those of the original Schwalbe

technique. Beyond the value 2 the Schwalbe-Braidy values are about 1·5 times greater. In any case, however, the Schwalbe-Braidy method is not entirely suitable for high copper numbers. The quantities of reagent do not permit the estimation of a higher value than 4·0. The method of Knecht and Thompson is perhaps most suited for values greater than this. Some further criticisms have been made by the American workers.[1]

We have carried out a comparison of the methods described below, using a series of permanganate oxycelluloses prepared in acid and alkaline solution with copper numbers ranging from 1 to 10. In all cases the results given by the Hägglund (p. 36) and the Knecht-Thompson Method I (p. 29), when plotted, give identical curves. The curve for the micro-Braidy (Heyes) method (p. 34) runs almost parallel, but the numbers are 10 to 15 per cent. higher than those of Hägglund. The standard Schwalbe-Braidy (p. 31) usually gives values somewhat lower than those of the micro-Braidy and not very different from the Hägglund values. The cuprous thiocyanate method (p. 30), in our hands, gave low and variable results. Some examples of the values obtained follow :—

Method.	Copper Number.						
Hägglund . .	8·7	7·7	5·3	2·8	2·5	1·5	1·0
Knecht (I) .	9·1	7·5	5·2	2·8	2·5	1·5	1·2
Heyes . .	9·9	8·8	6·5	3·2	3·4	2·4	1·3
Schwalbe-Braidy	—	—	—	2·5	2·8	2·0	—

The use of ceric sulphate has also been suggested. It may be used to titrate the cuprous oxide in the Braidy method without removal of the cloth, and a new process has been based on its use [2] which, however, demands a specified range of conditions.

A. The Original Schwalbe Method [3]

1. The "uncorrected" Copper Number. 2 to 3 g. of the material are placed in a 1·5 litre flask and covered with 200 ml. of water. The flask is fitted with a centrifugal stirrer which passes through the inner tube of a glass condenser which itself is suspended in the neck of the flask by wire. Cork and rubber must be avoided. The water is raised to the boiling-point and 100 ml. of Fehling's

[1] *Ind. Eng. Chem.*, 1925, **17**, 742.

[2] R. B. Forster, *et al.*, *J. Soc. Chem. Ind.*, 1938, **57**, 310T; *cf.* A. H. Best, *Ind. Eng. Chem. Anal.*, 1942, **14**, 145.

[3] C. G. Schwalbe, "Die Chemie der Cellulose", Berlin, 1910, 625; *Ber.*, 1907, **40**, 1347; M. Freiberger, *Zeit. angew. Chem.*, 1917, **30**, 121.

solution introduced. As soon as brisk ebullition has started the time is noted and the boiling continued for exactly 15 minutes. One gram of purified kieselguhr is added and the liquid at once filtered with rapid suction and the residue washed with boiling water till the filtrate is free from copper. The cuprous oxide is dissolved in 6·5 per cent. nitric acid and the mass washed with boiling water till free from copper, and finally with a little concentrated ammonia. The filtrates are concentrated and the copper estimated, preferably by electrolysis, using either a platinum basin as cathode or a rotating platinum cathode.

The Fehling's solution may be made up as follows :—

(*a*)	Copper sulphate, $CuSO_4 . 5H_2O$	82·4 g.
	Water	to 1,000 ml.
(*b*)	Sodium hydroxide	130 g.
	Rochelle salt	346 g.
	Water	to 1,000 ml.

The reagents should be pure and the solution free from dust, etc.

2. The " corrected " Copper Number. It is well known that cellulose and particularly dispersed cellulose, such as viscose rayon and oxy- and hydro-cellulose, absorb bivalent copper from Fehling's solution and that this copper can only be removed by treatment with acids. In the case of cellulose of small reducing power, the absorbed part may easily be greater than the reduced part. The weight of copper absorbed by 100 g. of dry cellulose was called by Schwalbe the " cellulose number " or the " hydrate copper number ". If this is subtracted from the copper number obtained as above, we get the " corrected copper number " which is held to measure only the reduced copper.

The hydrate copper number is determined as follows. It amounts to a " blank " carried out in the cold :—

2 to 3 g. of the material are placed in a flask with 250 ml. of cold water ; 100 ml. of cold Fehling's solution are added, followed by 50 ml. of water. The mixture is shaken 45 minutes, after which 50 ml. of kieselghur suspension is added and the liquid filtered through a double paper. The residue is washed with 1 litre of cold water and then with hot water. It is treated for the estimation of copper as previously described.

3. The " Hydrolysis Number ". The increase in copper number produced on boiling a cellulose with dilute sulphuric acid has been used by Schwalbe [1] as a measure of the reactivity of the cellulose.

3 g. of substance are treated with 150 ml. of 5 per cent. sulphuric acid and the liquid raised to the boiling-point with shaking. The

[1] C. G. Schwalbe, *Z. angew. Chem.*, 1909, **22**, 197.

boiling is continued for exactly 15 minutes, when a solution of 10 g. of NaOH in 25 ml. of water is poured in to neutralise the acid. Fehling's solution, 100 ml. previously heated, is then added and the mixture boiled for 15 minutes, after which the copper is determined as usual. The hydrolysis number is the copper reduced by 100 g. of dry substance. The hydrolysis difference is obtained by subtracting the copper numbers observed before and after hydrolysis.

4. The Standard Schwalbe Method.[1] It is uncertain whether the absorption of cupric copper is the same at the boiling temperature as in the cold, so that the " correction " for absorption is not satisfactory. A further source of error lies in the instability of Fehling's solution. On boiling, auto-reduction to cuprous oxide frequently takes place and a brownish-black precipitate is often observed which may be cupric oxide. The latter is reduced to a minimum by avoidance of any sort of contact with organic matter —cork, rubber, etc. ; but the auto-reduction depends upon conditions of heating—*e.g.* a blank experiment carried out as described on p. 28 gave 8·8 mg. of copper, equivalent (on 4 g.) to a copper number of 0·24, but, by protecting the walls from superheat and by more rapid stirring in one case less than 1/10th and in a second less than 1/100 of this value was observed.

Taking account of these objections, the exact details necessary for producing comparable results were worked out on the lines of the Reichert-Meissl test for volatile fatty acids. The size of flame, type of burner, distance between the flame and bottom of flask, the asbestos shields, etc., are exactly defined. Reference may be made to the work quoted below.

B. The Methods of Knecht and Thompson [2]

(*a*) *Method I.*—The reduction in Fehling's solution is carried out exactly as in the Schwalbe process. The cuprous oxide is, however, estimated as such by allowing it to reduce an equivalent amount of ferric salt to the ferrous condition. The absorbed (cupric) copper, and any cupric oxide that may have been formed from the solution by heating, do not affect the accuracy of the method, which therefore gives in one operation the copper number defined above. At the same time Schwalbe's hydrate copper number can be measured by an estimation of the copper remaining in the filtrates after boiling 100 ml. of Fehling's solution with the cellulose material. The deficiency found represents reduced copper and absorbed copper.

[1] " Die chemische Betriebskontrolle in der Zellstoff und Papier-Industrie ", Berlin, 1922.

[2] E. Knecht and L. Thompson, *J. Soc. Dyers and Col.*, 1920, **36**, 255.

Procedure.—This may be illustrated by an example:

2·7 g. of air-dry oxycellulose was treated as in Schwalbe's process, the boiling being carried out for exactly 15 minutes, and the liquid at once decanted off. After washing with hot water the filter and contents were transferred to a vessel containing an unknown excess (1 or 2 g.) of iron alum dissolved in dilute sulphuric acid. On stirring, the cuprous oxide dissolved rapidly. The solution was filtered, the residue washed, and the ferrous sulphate titrated with permanganate; 56·4 ml. $KMnO_4$ were required, 1 litre being equivalent to 5·50 g. Fe or 6·24 g. Cu.

∴ 100 g. air-dry oxycellulose reduce 13·3 g. of copper.

For the estimation of the unreduced copper the filtrate and washings were acidified with concentrated HCl and made up to 1 litre. A considerable excess of acid must be present, otherwise the tartaric acid interferes with the titration.

50 ml. of the solution with 10 ml. of iron alum (1 litre = 1·242 g. Fe) required on titration with titanous chloride in presence of potassium thiocyanate, 31·9 ml. $TiCl_3$ (1 litre = 1·096 g. Fe). In a blank titration 5 ml. of Fehling's solution with 10 ml. of iron alum required, 46·6 ml. $TiCl_3$. From the difference a copper value of 13·6 is obtained, so that the hydrate copper number would be 0·3. The absorbed copper was also determined directly by titanous chloride, a value of 0·41 being found.

(*b*) *Method II.*—Highly oxidised celluloses are decomposed by sodium hydroxide into substances having practically no reducing value, and the same might happen on boiling with Fehling's solution. The authors suggest the following method, which avoids the necessity of bringing oxidised cellulose into contact with caustic alkali. It is based upon Meade's method of estimating copper by the precipitation of cuprous thiocyanate.[1]

A copper solution is made up as follows:—

Sodium carbonate (anhyd.)	100 g.
Sodium citrate	200 g.
Potassium thiocyanate	125 g.

dissolved in about 800 ml. of water. Then add

Copper sulphate cryst.	18·00 g.

Make to 1 litre. The solution keeps indefinitely.

Procedure.—This may also be illustrated by an example:

1·85 g. of oxycellulose was boiled for 15 minutes with 100 ml. of the above solution, 200 ml. of water, and 8 g. of sodium carbonate.

[1] R. K. Meade, *J. Amer. Chem. Soc.*, 1898, **20**, 610.

The liquid was filtered and the precipitate of cuprous thiocyanate, cellulose, etc., well washed. The precipitate was then warmed with approx. $N/2$ sodium hydroxide, and the cuprous hydroxide formed was filtered and washed free from thiocyanate. The filter and its contents were immersed in a solution of iron alum acidified with sulphuric acid, the solution filtered, and the ferrous sulphate titrated with permanganate.

41·5 ml. $KMnO_4$ were required (1 litre = 5·50 g. Fe). Copper value found, 14·1.

The copper remaining in the filtrate was estimated by adding 150 ml. of hydrochloric acid and 10 ml. of iron alum, and titrating with titanous chloride. The quantity of acid must be sufficient to convert the citrate into free citric acid, otherwise variable results are obtained. 62·8 ml. $TiCl_3$ were required (1 litre = 2·545 g. Fe).

25 ml. of the original copper solution with 10 ml. of iron alum required 42·8 ml. of $TiCl_3$; 1 litre of iron alum = 1·314 g. Fe.

This estimation gave a copper value of 14·5.

C. The Schwalbe-Braidy Method for the Estimation of the Copper Number after Clibbens and Geake [1]

To avoid errors due to the instability and auto-reduction shown by Fehling's solution these authors employ the solution suggested by Braidy,[2] which consists of copper sulphate made alkaline by the addition of sodium carbonate and bicarbonate. It is sufficiently alkaline to prevent precipitation of the copper whilst providing a sufficient hydroxyl-ion concentration to enable the reduction of bivalent copper by modified cellulose to proceed with readiness.

The advantages of the method for standard purposes compared with the others are as follows :—

(i) In the absence of cellulose the " blank " determination is very low and constant, being equivalent to 0·1 ml. of $N/25$ permanganate —*i.e.* a copper number of 0·01 calculated for 2·5 g. of material. This correction should be made to values determined.

(ii) Carefully prepared normal celluloses give very low values (down to 0·005 for scoured cotton fabrics) and the results can be reproduced.

(iii) A slight modification in the cellulose produces a greater change in copper number than is shown by the other methods—*i.e.*, it is a more sensitive diagnostic.

[1] D. A. Clibbens and A. Geake, *J. Text. Inst.*, 1924, **15**, 27T.
[2] *Rev. gén. Mat. Col.*, 1921, **25**, 35.

The following solutions are prepared :—

A. Copper sulphate $CuSO_4 . 5H_2O$ . . . . 100 g.
Water . . . . . to 1,000 ml.
B. Sodium bicarbonate . . . . . 50 g.
Sodium carbonate cryst. . . . . 350 g.
Water . . . . . to 1,000 ml.
C. Iron alum . . . . . 100 g.
Sulphuric acid conc. . . . . 140 ml.
Water . . . . . to 1,000 ml.
D. Potassium permanganate of about $N/25$ strength, 1 ml. being approximately equivalent to 2·5 mgr. of reduced copper.
E. 2 N-sulphuric acid.

Conical glass flasks holding about 105 ml. closed with pear-shaped glass bulbs must be provided, and a water bath suitable for heating them, the flasks being immersed almost to the neck.

Procedure.—(i) 2·5 g. of the cellulose (air dry) are placed in one of the conical flasks.

(ii) The copper solution A is filled into a burette and 95 ml. of solution B are placed in a flask. When ready 5 ml. of A are run into the 95 ml. of B, the mixture raised to the boil and at once poured over the cellulose. Air bubbles are eliminated with a glass rod and the cellulose distributed uniformly through the liquid. The flask is then closed with the glass bulb and is deeply immersed in the water bath, the top of which is covered to prevent cooling by draughts. The heating is continued for exactly three hours, after which the mixture is filtered at the pump and the cellulose, impregnated with cuprous oxide, is washed, first with dilute sodium carbonate solution and then with hot water, till free from soluble copper salts.

(iii) The cuprous oxide is dissolved by treating the cellulose on the filter with the iron alum solution C. A volume of 15 ml. followed by another of 10 ml. is usually sufficient, but a further treatment with 10 ml. may be necessary if the reduction has been considerable. The material is well washed with 2 N-sulphuric acid and the combined filtrates and washings titrated with the potassium permanganate solution D, the end-point being very sharp and stable. Titration with dichromate, using *o*-phenanthroline as indicator has also been recommended.

The following results were obtained on samples of (A) sulphite pulp, (B) the α-cellulose obtained from it, (C) a normal cellulose (author's laboratory) :—

	A.	B.	C.
Ml. $N/25$ $KMnO_4$ . . .	21·8	7·9	0·29
Copper number . . .	2·218	0·804	0·029

Notes on the use of the Schwalbe-Braidy Method

1. The effect of variation in the conditions of working.

(*a*) The *weight of cellulose* to solution must be as specified. The following shows the variation observed in the copper number of four samples of oxycellulose when 1 g. of material to 100 ml. was used :—

Sample No.	Copper Number.			
	I.	II.	III.	IV.
1·0 g. of sample .	0·80	2·21	3·09	3·92
2·5 g. of sample .	0·87	2·33	3·48	4·36

(*b*) The effect of an increase in the *time of heating* on the copper number is illustrated in the following series carried out on a slightly oxidised cotton sample :—

Time of heating in hours .	1	2	3	4	5
Copper number . . .	0·249	0·322	0·354	0·370	0·373

In this case constancy seems to be obtained after 4 hours. The 3 hours recommended in the standard method represents a reasonable compromise.

(*c*) The effect of slight changes in the *temperature* at which the heating is carried out has been investigated by experiments at 90° and 100° respectively, and it is estimated that a temperature variation of 1·5° would cause a variation of 5 to 10 per cent. in the copper number. As the barometric height is liable to a maximum variation in one place of 40 mm., corresponding to a change of 1·5° in the boiling-point of water, it will be seen that for accurate work temperature control would be desirable.

(*d*) The *state of division* of the sample has an important influence especially with pulp. The larger the pieces the higher the copper number.

2. Determination of copper numbers greater than 5·0.

With Braidy's solution under the above conditions complete reduction of 100 ml. of copper solution by 2·5 g. of cellulose would correspond to a copper number of 5·2 (with Fehling's solution under the same conditions the number would be 40). The method, therefore, cannot be used for copper numbers much higher than 4·0. By reducing the weight of material taken to 1 g. values up to 10 can be measured, but when changes of this kind become necessary they should be specified in the report.

3. The following table gives a comparison of the copper numbers obtained with the original and the modified method on a series of hydrocelluloses [1] :—

Method.	Copper Number.					
	Untreated Cotton.	Cotton treated with acid.				
A. Schwalbe (original) .	0·76	1·04	1·06	1·17	1·53	1·85
B. Schwalbe-Braidy .	0·04	0·21	0·43	0·85	1·35	2·34
C. Knecht-Thompson .	0·28	0·35	—	—	—	1·13

D. A Micro-Method for the Determination of the Copper Number [2]

The standard Schwalbe-Braidy method described above involves the use of 2·5 g. quantities of cellulose which frequently limits its application. It has been found possible to scale down the method so as to permit the use of 0·25 g. of cellulose. The results are accurate and the process can be recommended.

Solutions required. (1) 150 g. anhydrous sodium carbonate and 50 g. of sodium bicarbonate dissolved in water to 1 litre.

(2) 100 g. crystalline copper sulphate in water to 1 litre.

(3) 40 g. of ferric sulphate and 100 ml. concentrated sulphuric acid in water to 1 litre.

(4) Potassium permanganate 0·04*N*.

Procedure.—The moisture is determined on 0·25 g. of the sample. A test tube 4 × ¾ in. containing 0·25 g. of air-dry cellulose is weighted by placing it in a roll of sheet lead of such dimensions that one-third of the tube projects above the roll. The mouth of the tube is covered by a glass pear. To 9·5 ml. of solution (1) is added 0·5 ml. of solution (2); the mixture is heated quickly to boiling-point, and poured over the cellulose, allowing to drain for half a minute. The weighted tube is at once immersed in a constant-level water bath filled with boiling water to such a height that the upper surface of the liquid in the tube is below the level of the water, and the bath is covered loosely with a lid. The water is boiled briskly for 3 hours. After the boiling has proceeded for 10 minutes, the sample is stirred with a glass rod to release bubbles of carbon dioxide, and to distribute the cellulose, this stirring being repeated if necessary. At the end of exactly 3 hours the tube is removed from the bath and

[1] D. A. Clibbens and A. Geake, *loc. cit.*

[2] T. F. Heyes, *J. Soc. Chem. Ind.*, 1928, **47**, 90T.

cooled in water. The cellulose and precipitated cuprous oxide are collected at the pump, using either a fritted Jena glass crucible or a Gooch crucible (washing out the reaction tube), and washed with water three times. The crucible and adapter are then attached to a clean filter flask of about 100 ml. capacity. Traces of cuprous oxide are often deposited on the sides of the reaction tube, sometimes enough to form a perceptible mirror. There is also frequently a ring of cupric oxide formed at the surface of the solution in the reaction tube, which may contain some cuprous oxide. Hence the details of the following procedure for the determination of the cuprous oxide :—

1·5 ml. of solution (3) are introduced into the reaction tube, which is shaken for a few seconds till all cupric oxide is dissolved. Without applying any suction the cellulose on the filter is flooded with this solution and the solution allowed to remain there until the darkening, which takes place instantaneously owing to the oxidation of the cuprous oxide to cupric oxide, has passed away. Then suction is applied and the solution drawn into the filter flask ; the vacuum is released and the washing of the reaction tube and irrigation of the cellulose repeated, using 1 ml. of solution (3). The reaction tube is washed out into the filter and the cellulose is washed three or four times with 2 ml. lots of cold distilled water, squeezing the cellulose with a glass rod flattened at the end after each washing. The filtrate and washings are then titrated in the filter flask with 0·04*N*-potassium permanganate, using a 2 ml. micro-burette reading to 0·005 ml. The end-point is sharp, and consists in a change from faint green to colourless owing to the pink of the slight excess of permanganate neutralising the green of the solution. A blank determination is made, using 2·5 ml. of ferric sulphate and as much distilled water as was used in the actual test. The blank is usually 0·025 or 0·03 ml. of 0·04*N*-potassium permanganate. The results are calculated as percentage of copper on the dry material ; 1 ml. of 0·04*N*-potassium permanganate = 0·002543 g. Cu.

If a satisfactory sample of 0·25 g. can be obtained, the results given by the macro- and micro-methods are identical (Heyes), though in our hands the latter has given somewhat higher values. The micro-method increases the usefulness of the test, as it can be applied, for example, to a few threads from a damaged stripe or a tender spot in a cotton fabric. The present author can confirm its accuracy and utility.

E. Method for the Determination of the Copper Number by E. Hägglund

This author [1] critically investigated methods previously in use and finds that the Schwalbe-Braidy (referred to by him as the Koehler-Braidy) gives results about 1·5 times greater than those of the Schwalbe method.* This ratio is not constant even for cotton and sulphite cellulose. The long period of heating in the Schwalbe-Braidy process is considered to produce degradation products which increase the amount of reduction observed.

It was found that the use of Bertrand's solution gives a value, after 3 minutes' boiling, equal to that given by the Schwalbe method in the standard time of 15 minutes. It is claimed that the value given in 3 minutes more nearly represents the reducing power of the material than the values obtained by longer periods of heating.

The Schwalbe-Braidy method is therefore considered unreliable ; the Schwalbe-Hägglund is justified in its accuracy, but is too long and tedious, and a new Hägglund-Bertrand process is therefore suggested as a standard. The following is the technique of the method :—

Bertrand solution I.—62·5 g. of $CuSO_4 . 5H_2O$ per litre.
,, ,, II.—200 g. of Rochelle salt and 150 g. of sodium hydroxide per litre.

The sample is finely divided and sifted. One gram is introduced into a boiling solution composed of 20 ml. each of solutions I and II. The boiling may be carried out in a porcelain dish for 3 to 5 minutes, no special stirring being necessary. The liquid is filtered through a hardened filter paper, the residue washed with hot water and treated with ferric sulphate solution as usual.

We have used the method in work requiring comparative results over a wide range of copper numbers, and can confirm its general accuracy. Its great advantage lies in the economy of time and apparatus effected.

The Loss in Weight on Treatment with Sodium Hydroxide Solutions

This diagnostic forms a part of the Cross and Bevan scheme for the examination of vegetable fibrous materials. The losses in weight shown by the fibres on boiling in a 1 per cent. solution of

[1] E. Hägglund, *Cellulosechem.*, 1930, **11**, 1.

* Schwalbe-Hägglund modification, in which the reduced copper is estimated by ferric sulphate. The statement is true only for Schwalbe-Braidy numbers of 2 and higher.

sodium hydroxide for, (*a*) 5 minutes, (*b*) 60 minutes, give what are called the α- and β-hydrolysis values respectively.

In the examination of cotton celluloses in respect to deviation from the normal standard the following technique [1] is recommended :

About 2 g. of the sample (moisture separately determined) are weighed out and boiled for 4 hours under reflux with 200 ml. of 0·25 *N*-sodium hydroxide solution. The liquid is decanted on to a Gooch crucible, the residue washed with the sodium hydroxide solution, with water, and finally with 0·1*N*-sulphuric acid (sulphurous acid may be used with advantage). The cellulose is collected in the

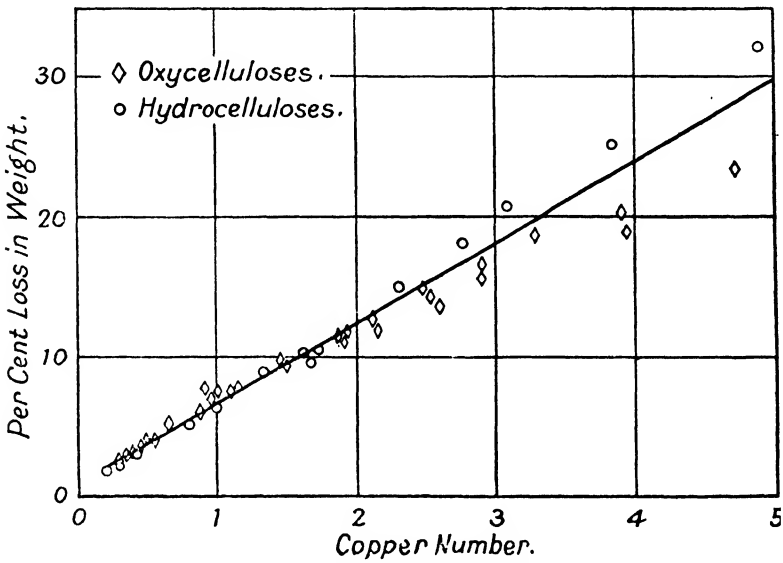


FIG. 5.—Loss in weight of modified cottons on boiling with sodium hydroxide solution in relation to copper number.

crucible and washed with water until the washings are neutral. The crucible and contents are dried for 3 hours at 110°. Under these conditions a " normal " cellulose loses about 1·5 per cent. in weight. An alkali boil for 1 hour is in many cases sufficient for comparative purposes.

In the case of celluloses which deviate considerably from the normal the prolonged drying of the residue to constant weight may lead to change in weight by decomposition or oxidation, so that an unsatisfactory value for the loss in weight due to alkali would be obtained. In such cases the amount of material actually dissolved can be estimated by oxidation with standard dichromate (p. 165).

[1] C. Birtwell, D. A. Clibbens and B. P. Ridge, *Shirley Inst. Mem.*, 1924, **3**, 329 ; *J. Text Inst.*, 1925, **16**, 13T.

The maximum solubility of modified celluloses in the cold, *i.e.* at 15°, has been found to occur with 3*N*-sodium hydroxide, but the maximum possible solubility is obtained by steeping first with 10 *N*-sodium hydroxide, which is then diluted to 2*N*-strength. The technique and value of this 10*N*-2*N*-process is described on p. 165.

Results obtained (*loc. cit.*) for the alkali-boiling loss of cotton modified in the direction of oxy- or hydro-cellulose formation [1] show that this value has almost an equal significance with that of the copper number. If the values for copper number (Schwalbe-Braidy) be plotted as abscissae and the alkali-boiling loss as ordinates, it is found that the figures obtained lie on a straight line for all copper numbers up to 2·5. Above this value the oxycelluloses fall below the line and the hydro-celluloses rise above it, the deviation being greater the greater the copper number (Fig. 5). Typical values are shown in the following tables :—

HYDROCELLULOSE MODIFICATION

Prepared from	HCl at 40°.				H_2SO_4 at 26°.		
Copper number .	1·68	1·75	3·09	4·90	0·30	1·01	1·63
Loss in weight, per cent. .	9·41	10·3	20·5	31·7	2·08	6·02	9·99

OXYCELLULOSE MODIFICATION

Prepared from	*N*/25 Dichromate in *N*/5 H_2SO_4 at 25°.							
Copper number .	0·33	0·48	1·02	1·47	2·13	2·49	2·93	3·93
Loss in weight, per cent. .	2·93	4·20	7·37	9·75	12·6	14·6	16·4	19·9

The loss in weight under these conditions is of the order of six times the copper number.

Solubility in Alkali at Low Temperatures.—The solubility of modified cellulose is greatly increased at temperatures below the normal. It is found [2] that the solubility is a maximum at some definite alkali concentration, and as the temperature is lowered the maximum increases and occurs at a lower alkali concentration. A hydrocellulose, for example, had a maximum solubility at 15°, 0° and −5° of 8·2, 57·5 and 82·6 per cent., and these occurred with solutions of 3·0, 2·75 and 2·5 *N*-NaOH respectively.

[1] D. A. Clibbens, A. Geake andB. P. Ridge, *J. Text. Inst.*, 1927, **18**, 277T.
[2] G. F. Davidson, *ibid.*, 1934, **25**, 174T.

Solubility at $-5°$ was determined by steeping an air-dry weight, equivalent to 1 gram of dry cellulose, in a stoppered bottle with 100 ml. of the alkali solution. The mixture was stirred with the thermometer and when the temperature had fallen to 0° and then to $-2{\cdot}5°$ the bottle was closed and vigorously shaken. When at $-5°$ this shaking was repeated and the contents again cooled to $-5°$. This was repeated three times. The bottle was left for 2 hours to gain room temperature.

The contents were then centrifuged at 2,000 r.p.m. in 40 ml. tubes to get sufficient (say 10 ml.) of clear liquid for the estimation of dissolved cellulose by the chromic acid method.

CHAPTER III

SOLUTIONS OF CELLULOSE AND THE MEASUREMENT OF THEIR VISCOSITY

A USEFUL discussion of the principles underlying the determination of the viscosity of liquids together with a description and criticism of the chief instruments employed will be found in the works of E. Hatschek [1] and G. Barr.[2] The term solution applied to cellulose does not imply true solution. Solutions of cellulose, like those of starch, differ from true viscous liquids in that their rate of flow through capillary tubes is not proportional to the driving pressure. Consequently the " viscosity " of such solutions has no such definite physical meaning as it has in the case of true solutions.

Newton's postulate that the tangential stress set up at any point in the liquid is proportional to the velocity gradient at that point, which accurately defines the flow of most liquids at moderate speeds, is expressed by the relation $F = \eta dv/dy$, where η (the factor of proportionality between stress F and velocity gradient dv/dy) is the viscosity of the liquid. Farrow, Lowe and Neale [3] have shown that in the case of starch pastes the flow is more accurately represented by an equation involving more than one constant such as

$$F^N = \bar{\eta} dv/dy,$$

where $\bar{\eta}$ and N are constants characteristic of the liquid. From this they deduce equations for the total flow, and with the aid of these it is possible to express the results of measurements made in capillary tubes in terms of stress and strain, so as to make them independent of the instrument dimensions and comparable with the data obtained by other forms of viscometer such as the Couette rotating cylinder instrument.

A description of the interchangeable capillary-type instrument with a variable driving pressure and of the Ubbelohde viscometer used by these authors, will be found in an earlier paper.[4] The Couette instrument is described in the later paper (1928).

The instruments commonly used for the measurement of vis-

[1] " The Viscosity of Liquids ", G. Bell & Sons, London, 1928.
[2] " Monograph of Viscometry ", Oxford University Press, 1931.
[3] F. D. Farrow, G. M. Lowe and S. M. Neale, *J. Text. Inst.*, 1928, **19**, 18T.
[4] F. D. Farrow and G. M. Lowe, *J. Text. Inst.*, 1923, **14**, 414T ; *ibid.*, 1928, **19**, 18T ; see also W. Philippoff, *Cellulosechem.*, 1936, **17**, 57–77.

cosity depend upon the flow of liquids through capillary tubes, or on the " falling sphere " principle. The main types are :—

(*a*) *Ostwald Viscometers.*—In these the pressure of a head of the liquid used causes it to flow from an upper bulb through the capillary into a wide reservoir. The viscosity is calculated from the formula

$$\eta = \mathrm{K}td = \frac{\eta_0}{t_0 d_0} \times td,$$

where η is the viscosity, t the time of flow, d density of the liquid, K the constant of the instrument. This constant is determined by measuring the time of flow t_0 of a liquid of known viscosity and density η_0 and d_0. These instruments are easy to make, and give results of the highest accuracy with normal liquids.

(*b*) *Ubbelohde Viscometers.*—These are similar, but the delivery and reception bulbs are identical in shape and capacity and are placed on the same level. An external pressure is therefore required to produce flow, which, of course, can be varied. The effect of the density of the liquid is eliminated and the viscosity is given by the (Poiseuille) formula

$$\eta = \frac{\mathrm{P}\pi r^4 t}{8lV},$$

where P, the pressure in absolute units = pressure in centimetres of water, (p) × 981, V = volume of fluid passing in time t, and l the length and r the radius of the capillary tube. For a particular instrument $\eta = pt \times \mathrm{K}$, where K, a constant, can be determined by means of a standard liquid.

(*c*) *Couette Viscometer.*—In this type viscosity is measured by shearing the liquid between two surfaces. The liquid is placed in the annular space between two coaxial cylinders, the outer one of which is rotated while the inner is suspended by a torsion wire. The necessary experimental conditions, such as temperature and speed of rotation, are rather difficult to obtain, and a good deal of preliminary testing is necessary for satisfactory work.

(*d*) *Falling Sphere Viscometer.*—The measurement of the rate of fall of a metal sphere through a viscous liquid was employed in connection with cellulose solutions by Gibson and Jacobs (1920). The procedure is described on pp. 46, 52 and 69.

In the following sections a selection of methods which have been employed in cellulose investigation will be given. The C.G.S. unit, or poise, is used throughout.

The British Standards Institution [1] use the poise (p) for dynamic

[1] " Determination of Viscosity in Absolute (C.G.S.) Units ", No. 188, revised May, 1937. British Standards Institution, London, S.W.1.

viscosity (η) and the stokes (s) for kinematic viscosity (ν), which is defined as η/d where d is the density of the fluid in g./cm.^{3}. The centipoise (cp) and the centistokes (cs) are considered preferable units unless the viscosities are very high.

It is of interest to note that the value of ν for water at 20° is very nearly 1 cs, and that of η nearly 1 cp.

Although solutions in cuprammonium are generally employed for viscosity determinations the use of quarternary organic bases such as Triton F, which dissolve cellulose, has also been examined (p. 59). The measurement of viscosity in terms of the viscosity of the nitrate prepared under definite conditions, has also proved of value (p. 63).

THE VISCOSITY OF CELLULOSE IN CUPRAMMONIUM

Ost (1911) * was the first to use viscosity measurements in connection with cellulose. Gibson and Jacobs (1920) introduced the falling sphere viscometer. Gibson, Spencer and McCall (1920) and Punter [1] (1920) investigated the connection between kiering conditions and viscosity. Joyner (1922) improved Gibson's technique with the falling-sphere and emphasised the necessity for the exclusion of air and light from the solutions. His work demonstrated the utility of viscosity measurements in characterising a sample of cellulose.

Farrow and Neale (1924) further developed the method of viscosity measurement in connection with change in cotton under chemical and physical attack and as a test of textile quality. Their technique, which is similar to that of Joyner, is somewhat complicated. Clibbens and Geake (1928) introduced a simplified method of viscosity measurement suitable for industrial use which has been adopted as a standard by the British Cotton Industry Research Association, and by the Fabrics Research Committee of the Department of Scientific and Industrial Research [2] (see p. 52). This "rate of flow" principle is now universally employed in technical and research laboratories and the experience gained from the use and testing of some hundreds of standard viscometers has been reviewed by Clibbens and Little (1936).

The Cellulose section of the American Chemical Society [3]

* Full references will be found in the table on p. 43.

[1] R. A. Punter, *J. Soc. Chem. Ind.*, 1920, **39**, 333T.

[2] "The Viscosity of Cellulose Solutions", D.S.I.R. Fabrics Co-ordinating Research Committee. H.M. Stationery Office, London, 1932.

[3] *Ind. Eng. Chem.* (*Anal.*), I., 1929, **1**, 49.

published their recommendations for the determination of the viscosity of cellulose in cuprammonium (1929). A modified falling-sphere method is described on p. 50, and a "rolling sphere" viscometer devised by Clibbens and Little (1936) for use with very small quantities of cellulose is referred to on p. 52.

The composition of the cuprammonium solutions which have been recommended is given in the following table :—

WEIGHTS IN GRAMS PER LITRE

Cu.	NH_3.	
13/14	200	Ost, *Z. angew. Chem.*, 1911, **24**, 1892.
11	200/210	Gibson, Spencer and McCall, *J. Chem. Soc.*, 1920, **117**, 479.
13	200	Joyner, *ibid.*, 1922, **121**, 1511, 2395.
15	240	Farrow and Neale, *J. Text. Inst.*, 1924, **15**, 157T.
30	165	Small, Hahn and Bradshaw, *Ind. Eng. Chem.*, 1925, **17**, 515 ; 1926, **18**, 1259.
15	240	Clibbens and Geake, *J. Text. Inst.*, 1928, **19**, 79T.
15	200	Clibbens and Little, *ibid.*, 1936, **27**, 285T.

With the method used by Joyner (oxidising copper by air in the presence of ammonia solution) it is possible to obtain as much as 30 g. per litre of copper in solution. A certain amount of nitrite is always present, and an important feature of the work of Clibbens and Geake is the discovery that when dealing with *fabrics* the quantity of nitrite present in the cuprammonium must be kept low otherwise satisfactory solution does not take place. The limit of 2 g. of nitrite per litre, formerly accepted, is much too high, and a solution containing less than 0·5 g. should be used, although for some purposes values up to 1 g. per litre may be permitted.

Experience shows, however, that with many forms of cellulose, *e.g.*, pulps, control of nitrite to 0·5 g. is essential if concordant figures for viscosity are to be obtained, and laboratories should rigorously limit the nitrite content to this figure.

The addition of pyrogallol to cuprammonium is said to stabilise cellulose solutions sufficiently to enable them to be filtered, in air, through glass wool, without appreciable change in fluidity.[1] For 0·5 per cent. solutions pyrogallol equivalent to 4 per cent. of the fibre weight is added ; or the cellulose may be soaked for 15 minutes in a 4 per cent. solution of pyrogallol and allowed to dry in air before using.

[1] W. A. White and T. N. Richardson, *J. Text. Inst.*, 1944, **35**, 53T.

A. Preparation of Cuprammonium

1. *Method of Clibbens and Geake* giving a low content of nitrite. The solution now recommended (1936) contains 15 g. of copper, 200 g. of ammonia, and less than 0·5 g. of nitrous acid per litre. A 5 litre wide-mouthed earthenware jar (Fig. 6) is closed by a cork carrying a centrifugal stirrer and air inlet tube of iron. The inlet tube ends in a jet which conducts air into the cone-shaped mouth of the stirrer. Reduced copper passing a 60-mesh sieve is used and the following mixture is placed in the reaction vessel:

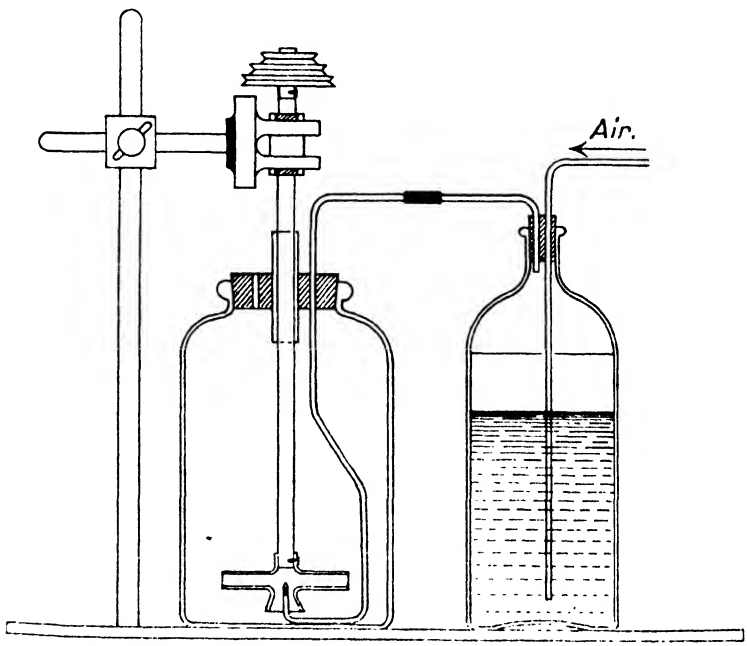


FIG. 6.—Apparatus for the preparation of cuprammonium.

2·6 litres ammonia (0·880); 0·4 litre of water, 3·0 g. of cane sugar and 180 g. of copper.

Air is blown in at the rate of 10 litres per hour through a wash bottle filled with ammonia solution (*d*, 0·90). The approximate copper content obtained can be found by colorimetric comparison of a sample with a standard containing 15 g. of copper per litre, and when the value is distinctly above this, which usually happens in about 5 hours, the solution is allowed to settle for 30 minutes, syphoned off into a stoppered bottle, allowed to settle and again syphoned off. The clear liquid is analysed for copper and ammonia and adjusted to the correct concentration by the addition of water

and ammonia solution. The nitrous acid content is checked by the nitrometer method (p. 46).

The cuprammonium is stored in a blackened bottle fitted with a tubule and tap at the bottom and connected at the top, through a vessel containing alkaline pyrogallol, with a gas holder, *e.g.*, a Kipp's apparatus, filled with nitrogen.

2. *Method of Gibson, Spencer and McCall.*—These authors (*loc. cit.*) recommend the following :—

60 g. of copper sulphate in a litre of hot water, with a few drops of sulphuric acid, is allowed to cool to 50° and ammonia (*d*, 0·88) added until the precipitation of basic copper sulphate is complete, any excess of ammonia being neutralised with sulphuric acid. The liquid is decanted and the precipitate washed with hot water by decantation, after which 200 ml. of 20 per cent. NaOH are added and the whole well shaken. The precipitate is converted into blue cupric hydroxide which is allowed to settle, and then thoroughly washed by decantation. It is collected, washed and dried on a porous plate at 40°. The dried hydroxide is put into an aspirator bottle with 800 ml. of ammonia, containing 200 to 210 g. of NH_3 per litre. The bottle is shaken, the supernatant liquid run off through glass wool and the volume measured. The copper in the solution is estimated and sufficient ammonia added to give a solution containing 11 g. of copper and 200 to 210 g. of ammonia per litre.

3. *Method of Joyner.*—This author used the method of bubbling air through strong ammonia contained in a cylinder packed with copper turnings, about 1 g. per litre of sucrose being added. Solutions containing more than 30 g. per litre of copper can be obtained, but they may contain nitrite (as HNO_2) up to 1 g. per litre.

4. *Electrolysis Method.*—A solution containing about 15 g. of copper and 236 to 245 g. of NH_3 per litre may be prepared by the electrolysis of concentrated ammonia to which 1 g. of cane sugar per litre is added, using copper electrodes and a C.D. of 0·02 amps. per sq. cm. A cooling-jacket is required. The cathode may be a copper tube through which oxygen can be passed to the bottom of the cell. The required concentration of copper is obtained after about 24 hours. The solution, however, will contain up to 2 g. of HNO_2 per litre.[1]

5. *After Cross and Bevan.*—To a solution of copper sulphate ammonium chloride is added and then sodium hydroxide in slight excess ; the blue precipitate is thoroughly washed on a cloth filter, and, when required, redissolved in ammonia of *d*, 0·92. The precipitate, however, may be drained and mixed with sufficient 10 per

[1] F. D. Farrow and S. M. Neale, *J. Text. Inst.*, 1924, **15**, 157T.

cent. solution of glycerol, in contact with which it can be preserved unchanged.

B. Analysis of Cuprammonium

(*a*) *Copper Content.*—Approximately by colorimetric comparison with a solution of known copper content ; by evaporation to dryness and conversion to copper oxide, or by treatment with acidified potassium iodide and titration of the liberated iodine in the usual way. For this purpose the ammonia is boiled off from 25 ml. of cuprammonium, which is then acidified and boiled again. A trace of bromine and re-boiling will remove all nitrous acid. Ammonia followed by acetic acid is then added.

(*b*) The *ammonia* is estimated by adding say 2 ml. to 25 ml. of $2N$-H_2SO_4 and titrating back with N-alkali, using methyl red, allowance being made for the copper present. This requires the subtraction of 0·536 C grams per litre of ammonia where C is the number of grams of copper per litre.

(*c*) *Nitrous Acid Content.*—(i) Nitrometer method : 15 ml. of conc. sulphuric acid are drawn into the nitrometer and carefully covered with 1 or 2 ml. of water before admitting 5 ml. of cuprammonium. During this process the mercury reservoir must be held at its lowest position and each portion of cuprammonium neutralised before admitting the next, otherwise the reaction may be too violent (*cf.* p. 244).

(ii) The volume of cuprammonium solution necessary to decolorise 10 ml. of 0·1 N-potassium permanganate in the presence of excess of dilute H_2SO_4 at 50° can be determined and the nitrite calculated in the usual way.

C. Determination of Viscosity by Falling-sphere Methods

(*a*) **Falling-sphere Viscometer Method by Farrow and Neale.**—1. *The apparatus used* [1] (Fig. 7) consists of a tube G, 1 cm. in diameter, with five etched rings at 5 cm. intervals. The tube is fixed vertically in a thermostat, a $\frac{1}{16}$-in. steel ball is dropped down the axis of the tube, and the time taken to traverse the last 15 cm. is noted. The tubes were calibrated with castor oil, the viscosity of which was found by comparison with benzene, water, and aniline in a series of capillary viscometers. The constants varied from 0·404 to 0·412—that is, the time of fall in seconds of the steel ball through 15 cm. multiplied by one of these factors gives the viscosity of the solution tested in C.G.S. units. The value of the constant calculated

[1] F. D. Farrow and S. M. Neale, *J. Text. Inst.*, 1924, 15, 157T.

from Ladenburg's formula (see Gibson and Jacobs, *loc. cit.*) is 0·437. A solution of sugar, $\eta = 0{\cdot}59$, gave a time of fall of 1·6 seconds, from which the viscosity should be 0·61. The falling-sphere method is,

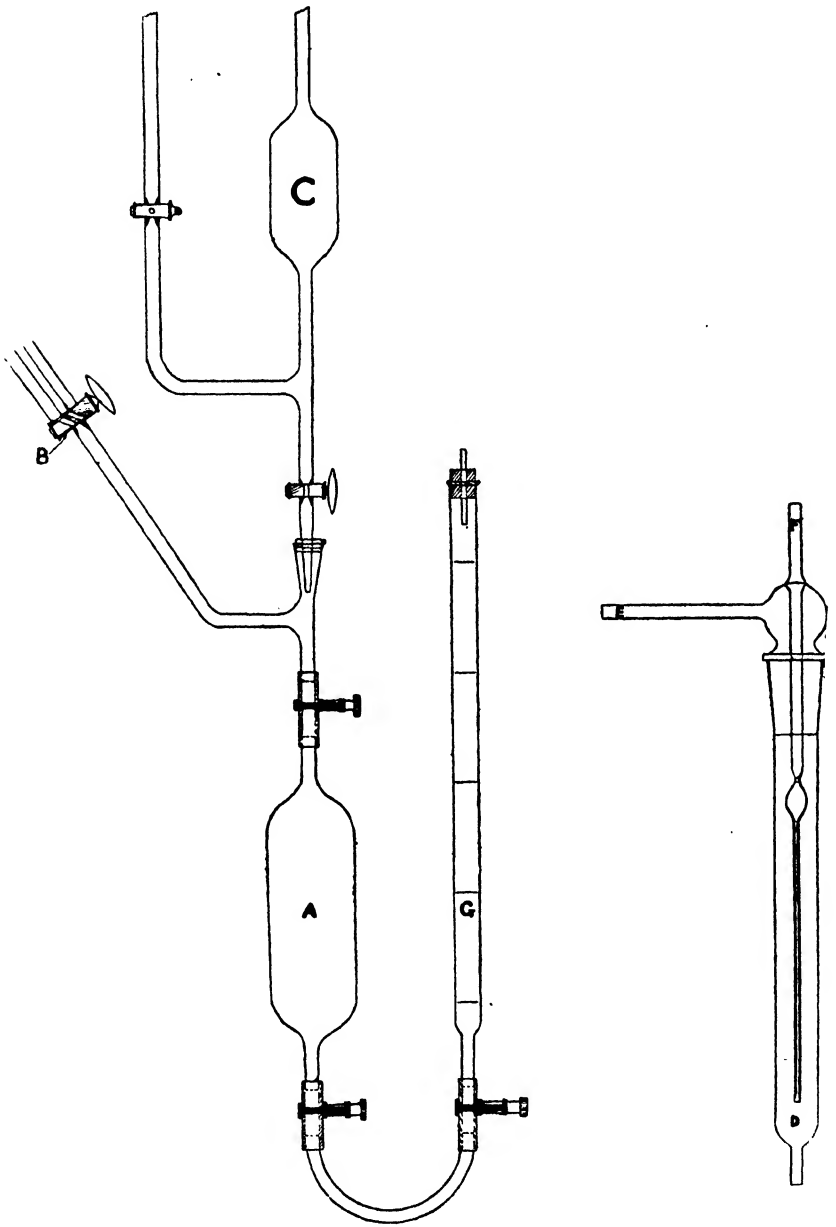


FIG. 7.—Viscosity apparatus of Farrow and Neale.

therefore, not seriously in error even at this high rate of fall. For some comparisons the viscosity was measured in a capillary instrument (D, Fig. 7). This viscometer is evacuated and partly filled with hydrogen before the solution is allowed to enter. The viscometer bulb is filled by connecting E to hydrogen when F is open, and when E and F are both connected to hydrogen the bulb empties itself, the time for this being observed.

2. *Preparation of the Cotton Solution.*—Sufficient cotton to make a 2 per cent. solution is introduced into the bulb A, which is alternately evacuated and filled with hydrogen by manipulating the three way tap B. 50 ml. of cuprammonium are then run into A from the measuring pipette, whereupon A is filled with hydrogen, closed and disconnected. The bulbs are shaken on a bicycle wheel driven slowly by a small motor, the time of solution varying from a few minutes to 2 or 3 days. When solution is complete, the bulb is connected to the viscometer by means of a U-bend and rubber tubing, and the liquid driven over by admitting hydrogen. Two viscometers can be filled from one bulb.

3. *Viscosity Concentration Relation.*—As it is not always possible to use a solution containing the standard amount of cotton, some means of calculating the viscosity of a standard solution from data given by a more, or less, concentrated solution is required. Joyner [1] has given a formula which is a simplification of that of Kendall,[2] but Kendall's equation can be written so as to be applicable directly to solutions made by adding a varying weight of cotton to a constant volume of solvent. It then becomes

$$1 + C/m = B/\log (\eta/\eta_B),$$

where m is the weight of dry cotton in 100 ml. of solvent, η the observed viscosity, and η_B that of the cuprammonium solvent (determined as 0·0152 C.G.S. units, $\log \eta_B = \bar{2}{\cdot}18$), and B and C empirical constants. If $1/m$ is plotted against $1/\log (\eta/\eta_B)$, the graph should be a straight line. The measurements of Farrow and Neale show this to be the case between concentrations of 1·5 and 3 per cent. By using the values of B and C read from the graph, $\log \eta$ is calculated for any value of m. The formula is valid over a wide range of concentration.

To use the relation for evaluating the viscosity at a standard concentration, the value of B may be taken as 11 without serious error. Two equations are then obtained:

$$1 + C/m = 11/\log (\eta_m/\eta_B) \quad . \quad . \quad . \quad (1)$$

and

$$1 + C/n = 11/\log (\eta_n/\eta_B) \quad . \quad . \quad . \quad (2)$$

[1] *Chem. Soc. Trans.*, 1922, **121**, 1511.
[2] *Ann. Physik*, 1907 (IV), **23**, 9, 447.

where m is the weight of cotton in the solution used of viscosity η_m, η_B is the viscosity of the solvent and n is the weight of cotton in a solution of standard concentration whose viscosity, η_n, it is desired to calculate. These may be solved graphically or algebraically.

The table on p. 50, for which the author is indebted to Dr. D. A. Clibbens, is calculated from these equations, the log viscosity of the cuprammonium being taken as $\bar{2}{\cdot}18$.

This table may also be used for calculating log η in 0·5 per cent. solution owing to the following property of the Farrow and Neale equation. Thus, suppose that x is the log viscosity of a 2 per cent. solution and y the corresponding value for a 1 per cent. solution as derived from the equation : then if x is the log viscosity of a 1 per cent. solution, y will be the derived value for a 0·5 per cent. solution. The result of this is that a 2 to 1 per cent. conversion table can be used as a 2 to 0·5 per cent. conversion table by consulting it twice. For example, if the log viscosity of a 2 per cent. solution is 1·00, and this value is sought in the body of the 2 per cent. to 1 per cent. table, the corresponding value for a 1 per cent. solution is seen to be $\bar{1}{\cdot}80$. If this latter value is now sought in the body of the table, the corresponding value in the first column and row is seen to be between $\bar{1}{\cdot}05$ and $\bar{1}{\cdot}06$. This is the actual value of the log viscosity in 0·5 per cent. solution of a 2 per cent. solution for which the log viscosity is 1·00.

The viscosity of a 2 per cent. solution of a carefully bleached cloth should lie between 300 and 10 C.G.S. units (log $\eta = 2{\cdot}5$ to $1{\cdot}0$). The effect of mercerisation is to reduce the viscosity very slightly—*e.g.*, before mercerisation log $\eta = 1{\cdot}86$, after 1·85 to 1·72, with varying conditions of treatment.

The figures in the body of the table are log viscosities in 2 per cent. solution. The values were calculated for a cuprammonium solution containing 240 g. of ammonia per litre with a log η of $\bar{2}{\cdot}18$ and a fluidity of 66. The solvent now recommended with 200 g. of ammonia per litre has a log η of $\bar{2}{\cdot}145$ and a fluidity of 72. This alteration involves a slight change in the values given in the table, although the effect is so small that for most purposes it can be neglected. A correction can be made if required in the following way :—

For a given value of log viscosity in 2 per cent. solution, the corresponding value in 1 per cent. solution is that read from the table *diminished by 0·01*. With this correction the error does not exceed 0·005 in the values for 1 per cent. solutions, and as these values are only given to the nearest second decimal place, the error is then negligible.

(*b*) **A Modified Falling-sphere Viscometer Method.**—Tankard and Graham [1] recommend a falling-sphere method in which : (*a*) The solution is prepared in the tube, as in the rate of flow process, but the capillary and clip for closing the tube during shaking is replaced by an improved stopper of hemispherical shape held down by springs

TABLE FOR THE CONVERSION OF LOG VISCOSITY IN 2 PER CENT. SOLUTION TO LOG VISCOSITY IN 1 PER CENT. SOLUTION

Log η (1 per cent. solution).	·00	·01	·02	·03	·04	·05	·06	·07	·08	·09
$\bar{2}\cdot4$	2·61	2·63	2·65	2·67	2·69	2·71	2·73	2·74	2·76	2·78
$\bar{2}\cdot5$	2·80	2·82	2·84	2·86	2·88	2·90	2·91	2·93	2·95	2·97
$\bar{2}\cdot6$	2·99	1·01	1·03	1·04	1·06	1·08	1·10	1·12	1·14	1·15
$\bar{2}\cdot7$	1·17	1·19	1·21	1·23	1·25	1·26	1·28	1·30	1·32	1·34
$\bar{2}\cdot8$	1·35	1·37	1·39	1·41	1·43	1·44	1·46	1·48	1·50	1·51
$\bar{2}\cdot9$	1·53	1·55	1·57	1·58	1·60	1·62	1·63	1·65	1·67	1·69
$\bar{1}\cdot0$	1·71	1·72	1·74	1·76	1·77	1·79	1·81	1·83	1·84	1·86
$\bar{1}\cdot1$	1·88	1·89	1·91	1·93	1·95	1·96	1·98	0·00	0·01	0·03
$\bar{1}\cdot2$	0·05	0·06	0·08	0·10	0·11	0·13	0·15	0·16	0·18	0·20
$\bar{1}\cdot3$	0·21	0·23	0·25	0·26	0·28	0·30	0·31	0·33	0·34	0·36
$\bar{1}\cdot4$	0·38	0·39	0·41	0·43	0·44	0·46	0·47	0·49	0·51	0·52
$\bar{1}\cdot5$	0·54	0·55	0·57	0·58	0·60	0·61	0·63	0·64	0·66	0·68
$\bar{1}\cdot6$	0·69	0·71	0·72	0·74	0·76	0·77	0·79	0·80	0·82	0·84
$\bar{1}\cdot7$	0·85	0·87	0·88	0·90	0·91	0·93	0·94	0·96	0·97	0·99
$\bar{1}\cdot8$	1·00	1·02	1·03	1·05	1·06	1·08	1·09	1·11	1·12	1·14
1·9	1·15	1·17	1·18	1·20	1·21	1·23	1·24	1·26	1·27	1·29
0·0	1·31	1·32	1·33	1·35	1·36	1·38	1·39	1·40	1·42	1·43
0·1	1·44	1·46	1·47	1·49	1·50	1·51	1·53	1·54	1·56	1·58
0·2	1·59	1·60	1·61	1·63	1·64	1·66	1·67	1·68	1·70	1·71
0·3	1·73	1·74	1·76	1·77	1·78	1·80	1·81	1·83	1·84	1·85
0·4	1·87	1·89	1·90	1·91	1·92	1·94	1·96	1·97	1·98	2·00
0·5	2·01	2·03	2·04	2·05	2·07	2·08	2·10	2·11	2·12	2·14
0·6	2·15	2·16	2·17	2·19	2·20	2·21	2·23	2·24	2·25	2·27
0·7	2·28	2·29	2·31	2·32	2·33	2·35	2·36	2·37	2·39	2·40
0·8	2·41	2·42	2·44	2·45	2·46	2·48	2·49	2·50	2·52	2·53
0·9	2·54	2·55	2·57	2·58	2·59	2·61	2·62	2·63	2·64	2·66
1·0	2·67	2·68	2·69	2·71	2·72	2·73	2·74	2·76	2·77	2·78
1·1	2·79	2·81	2·82	2·83	2·85	2·86	2·87	2·88	2·90	2·91
1·2	2·92	2·93	2·94	2·96	2·97	2·98	2·99	3·00	3·01	3·03
1·3	3·04	3·05	3·07	3·08	3·09	3·10	3·11	3·12	3·14	3·15
1·4	3·16	3·17	3·19	3·20	3·21	3·22	3·23	3·25	3·26	3·27
1·5	3·28	3·29	3·30	3·32	3·33	3·34	3·35	3·36	3·38	3·39

attached to the walls of the tube, somewhat after the manner of the spring wire fastening used for mineral water bottles. (*b*) The tube is 28 cm. long by 1 cm. internal diameter, and a steel ball of $\frac{1}{32}$-in. radius is used. Under these conditions Ladenburg's correction for wall effect is applicable, so that there is no necessity to calibrate each

[1] J. Tankard and J. Graham, *J. Text. Inst.*, 1930, **21**, 260T.

tube. Small variations in the tube diameter ($\pm$ 1 mm.) do not appreciably affect the calculation of wall effect, so that a graph may be prepared of time of fall/log viscosity which applies to all tubes of about 1·0 cm. diameter. Measurements can be carried out over a wide range (down to 1·4 log viscosity with 2 per cent. solutions) and any number of readings may be made with each solution. [N.B.—This claim is not altogether correct. The passage of the sphere produces a channel in the solution which affects subsequent readings.]

The Apparatus and Method of Working.—The 28 cm. tube has one end closed and the other provided with a lip. A mark 5 cm. from the closed end and another 15 cm. higher are etched on the tube. Round steel rods, tapered at each end, 4 cm. long $\times$ 0·55 cm. in diameter, are used for agitating the solution and are adjusted to an equality of $\pm$ 0·01 g. so that they can be interchanged.

The tube is standardised for volume with the steel rod in the tube. The cotton is conditioned at 70 per cent. R.H. (by leaving over a saturated solution of cobalt chloride at 15°), and sufficient is introduced to give a 1 per cent. solution (or 2 per cent. for degraded cotton). The moisture is assumed at 7 per cent. The viscometer is closed with a rubber stopper carrying a short piece of glass tube. A piece of pressure tubing is attached and the viscometer evacuated and closed by a spring clip. The rubber is connected to the cuprammonium and the viscometer filled to within 4 cm. of the top. After mixing with a long steel rod, the weight is introduced and the tube filled completely with cuprammonium and closed with the special stopper. Solution is obtained by rotation for some hours at 1½ r.p.m., light being excluded.

The viscometers are brought to 25°, the tube opened, and a little solution poured out so that the level is about 2 cm. from the open end. This end is then closed with a rubber plug carrying a short glass tube, which dips about 1 cm. below the level of the liquid. The $\frac{1}{32}$-in. steel balls are dropped through this and the time taken to pass between the two etched marks is observed.

The viscosity is calculated from the formula [1]

$$\eta = \frac{2gr^2(s - \sigma)\mathrm{T}}{9l(1 + 2{\cdot}4r/\mathrm{R})(1 + 3{\cdot}3r/h)}.$$

where η is the viscosity of the solution, g, 981, r, radius of the steel sphere ($\frac{1}{32}$-in., 0·0794 cm.), s, density of sphere, 7·81, σ, density of cuprammonium (0·942 for 1 per cent., 0·952 for 2 per cent. solution),

[1] W. Gibson and C. Jacobs, *J. Chem. Soc.*, 1920, **117**, 1479; F. D. Farrow and S. M. Neale, *J. Text. Inst.*, 1924, **15**, 157T.

T, time of fall in seconds, l, distance between etched rings, 15 cm., R, internal radius of tube, 0·5 cm., h, total height of liquid, approximately 26 cm.

(*c*) **The Falling-sphere Method** defined by the British Standards Institution for general use—Publication No. 188 (1937)—is essentially as described on p. 69. Emphasis is laid on the cleanliness of the sphere and of the tube. A tube 32 mm. in diameter will serve for use with spheres of 1/16 to 1/8 in. diameter, and the two reference marks 15 cm. apart should be not less than 5·5 cm. from each end of the tube. If the temperature is controlled to 0·1° the 1/16 in. sphere can be used for the range of viscosities of 1,000 to 12,500 centistokes.

The kinematic viscosity ν is calculated from an equation of the type employed above, which for the same sphere and fall-tube may be simplified to

$$\nu = \mathrm{KT}(s/\sigma - 1).$$

K is obtained by experiment with a liquid of known viscosity.

(*d*) **A Rolling Sphere Viscometer** has been described [1] in which a steel ball 1/32 in. in diameter rolls down a tube 18 cm. × 3·6 mm. in diameter, inclined at 20° to the horizontal. The time of roll (t) in cuprammonium (0·5 per cent. solution) is observed. An equation of the type

$$\mathrm{F} = \mathrm{K}_0/6{\cdot}66t$$

where F is fluidity and 6·66 the difference between the densities of steel and cuprammonium is employed.

There is fair agreement between the results obtained and those given by the capillary instrument for the fluidity range 5 to 15, but beyond that, values given by the rolling sphere method become increasingly low.

Its advantage is that it can be used for comparative purposes with very small quantities of the sample, as a few milligrams only are required for the solution.

D. Viscosity by Rate of Flow Methods.

(*a*) **Rate of Flow Method with the B.C.I.R.A. Standard Capillary Viscometer.**[2]—This method embodies the result of considerable experimental work, and is now adopted as a standard.

A feature of it is that the results are expressed in the form of the reciprocal of the viscosity, or the *fluidity* of the solution under

[1] D. A. Clibbens and A. H. Little, *J. Text. Inst.*, 1936, **27**, 285T.

[2] D. A. Clibbens and A. Geake, *J. Text. Inst.*, 1928, **19**, 77T; D. A. Clibbens and A. H. Little, *ibid.*, 1936, **27**, 285T.

examination, which is usually given in C.G.S. units for a 0·5 per cent. solution of cellulose.

This has many advantages from a technical point of view. The absolute viscosity of a solution of a lightly scoured cotton containing 0·5 g. per 100 ml. is about 1 poise, but more vigorous scouring treatment may reduce this to 0·2 without seriously affecting the quality of the material. A further fall of viscosity from 0·2 to 0·05 is accompanied, however, by a loss of 20 to 30 per cent. in tensile strength. Viscosity changes at different parts of the scale have therefore a different technical significance, and these changes are best brought out when the rate of flow is expressed as fluidity. It has been shown that when fluidity is plotted against the percentage loss of strength produced by chemical action on cotton, a curve is obtained which approximates more closely to a straight line than that given by other methods of expression. Roughly, the same change of fluidity is accompanied by the same change of strength except at the extremes of the scale (p. 163).

Difficulties in working with cuprammonium solutions include first, the necessity of excluding oxygen from any lengthy contact which brings about a marked decrease in viscosity. This is overcome by making the solution in the viscometer. A second difficulty is due to the fact that carefully purified cotton (of consequent high viscosity) and some bleached cotton yarns or cloth often give turbid solutions. This is avoided if the nitrous-acid content is kept below 0·5 g. per litre. Another point is that, since solutions of cotton in cuprammonium differ from true viscous liquids, their apparent fluidity varies with the nature and dimensions of the viscometer. This applies particularly to cottons of high viscosity or low fluidity —*i.e.* for normal cottons ; but it rapidly becomes less accentuated with increasingly severe treatment and in practice may be neglected when the cotton has suffered even slight attack by chemical agents. For such material the fluidity is not seriously dependent on the type or dimensions of the viscometer employed.

Procedure.—(i) *The Cuprammonium Solution.*—Prepared as p. 44.

(ii) *Preparation of the Cotton Solutions and Determination of the Rate of Flow.*—The viscometer (known as the X-type) is shown at A (Fig. 8).* The wide tube has a wall thickness of 0·1 to 0·15 cm., an internal diameter of 1 ± 0·025 cm., and is approximately 26 cm. long. The capillary E was made of Jena KPG precision bore tubing, and is 2·5 ± 0·05 cm. in length ; 0·088 ± 0·001 cm. in internal and 0·6 ± 0·2 cm. in external diameter.

* These instruments, with all accessories, may be purchased from the British Cotton Industry Research Association, Shirley Institute, Didsbury.

The funnel-shaped seal between the wide tube and the capillary is about 1 cm. long, and the overall length of the instrument, excluding the closing devices, is 30 ± 0·2 cm.

Two rings, D and B, are etched at heights of 6·2 and 24·2 cm. (± 0·05 cm.) vertically above the flat end of the capillary E. The top of the tube is closed with a rubber stopper carrying a capillary, the dimensions of which are unimportant. A ring F, about 0·4 cm. below the top, defines the depth of insertion of the rubber stopper, and ensures that a constant volume of solution is enclosed.

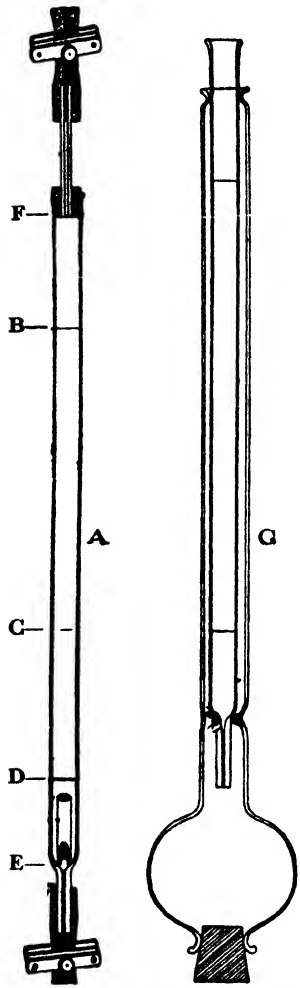


FIG. 8.—Apparatus for measurement of fluidity after Clibbens and Geake.

The steel cylinder formerly used for agitation, which was made from ¼-in. steel rod 2·7 cm. long and about 5·6 g. in weight, volume 0·7 ml., is now replaced by 0·7 ml. of mercury. This is run in from a small burette, after filling the capillary and part of the main tube with solvent, and before the addition of the cellulose. During a measurement it should run out before the level reaches the first timing mark, B.

The internal volume of the instrument is thus about 20 ml., which would require about 0·1 g. of cotton for each determination. The exact capacity is determined by weighing the instrument, both empty and completely filled with water. The weight of dry cellulose required for each determination (equivalent to 0·5 g. per 100 ml. of cuprammonium) is thus fixed once for all for each viscometer. The moisture content of normal and slightly modified cotton may be assumed as 6 per cent.

An examination of 200 instruments constructed within the prescribed limits shows that the mean total volume enclosed when filled for use was 20·3 ml., requiring 0·1015 g. of dry cellulose for a 0·5 per cent. solution. The mean volume flowing between marks B and D was 14·3 ml., and the ratio of the

times of flow between BC and CD varied only between 0·98 and 1·01. The mean Glycerol Calibration Time was 246·5 seconds, with a range between 226 and 268 seconds. The viscometer constant C averaged 1,950, C′ 2,075 and the correction constant K, 465 (see iv).

(iii) *The Process.*—The material must be finely divided. Loose cotton or yarn is cut into pieces not longer than $\frac{1}{16}$ in. and cloth is cut diagonally so as to break down warp and weft threads. The capillary is closed with a short piece of pressure tubing, and the apparatus three-quarters filled with cuprammonium, a few drops of which are run out at the bottom. The necessary weight of cellulose is added and stirred in rapidly with a thin glass rod. The viscometer is then filled completely with cuprammonium and the stopper inserted so that the excess of liquid, displacing all air, overflows through the top capillary and tube, which is at once closed.

The viscometer is wrapped in black cloth and fixed to the spokes of a bicycle wheel driven at such a speed that the mercury or the steel cylinder falls from end to end during a half revolution. The movement is sufficient to cause solution overnight. A maximum rate of four revolutions per minute suffices even for very viscous solutions.

For the measurement of the *rate of flow* the lower clip and rubber tube are removed and the instrument hung in a wider tube in a thermostat at 20°.* After this temperature has been acquired the viscometer is placed in a glass jacket shown at G (Fig. 8), where it rests on three glass points at the bottom. G is supported vertically in the thermostat. The upper clip is opened, and the time necessary for the meniscus to fall from the upper to the lower ring is observed.

(iv) *Standardisation of the Instrument and Expression of Results.*—Since the rate of flow varies with the fourth power of the capillary diameter, the viscometer cannot be made so accurately to specification as to dispense with separate standardisation, which is done as follows :—

A mixture of glycerine and water is prepared containing approximately 64·4 per cent. of glycerine by weight, the specific gravity of which is adjusted to equal 1·1681 in air at 20°, compared with water at 20°. The fluidity of this at 20° is 6·83 reciprocal poises. Its kinematic fluidity $F \times d$ (fluidity × density) will therefore be 7·98 in C.G.S. units. The tube is filled, and the liquid allowed to acquire a temperature of 20°. The time in seconds taken for the meniscus to fall from the upper to the lower ring is then observed.

Alternatively a solution containing about 65 per cent. of glycerine

* For routine work the thermostat can be omitted if the air temperature is near 20°, as a variation of temperature between 18° and 22° has little effect.

is prepared, and its kinematic fluidity measured in a capillary U-tube viscometer. For convenience the time of flow of the solution in the viscometer to be standardised is reduced by calculation to that of a solution of kinematic fluidity 7·98. This corrected time t_G is referred to as the " Glycerol Calibration Time ".

The volume V between the marks B and D, found with sufficient accuracy by running in water from a burette, is also required.

For routine control it is enough to express the viscosity of any cotton solution as the ratio of its time of flow to that of the time of flow of the glycerine. For other purposes it is better to express the results in the form of absolute fluidities (*i.e.*, reciprocals of the viscosities stated in poises). To do this the " constant of the instrument " is divided by the time of flow of the cotton solution.

Constant of the Instrument C'.—The density (d) of the glycerine solution being 1·1681, and its fluidity (F) being 6·83, it can be shown that, if its time of flow in the viscometer is t seconds, the constant of the instrument is given by the relation

$$C' = 1{\cdot}075\ (dFt)$$

provided the rate of flow is not too rapid. The density of the cuprammonium solution is here assumed at 0·93. For the specified instruments C' = 2,000 approximately.

A correction becomes necessary when working with degraded cottons, the solutions of which are very fluid. This involves the kinetic energy of the moving liquid, and may be made by subtracting from the time observed in the instrument an amount which can be calculated (see below). For technical purposes the correction can be neglected, *e.g.* a fluidity of 10 corresponds to about a 10 per cent. loss in the strength of cotton. In this case the time of flow is about 220 seconds and the correction 2 seconds. A fluidity of 20, representing about 20 per cent. tendering, gives a time of flow of 110 seconds and a correction of 5 seconds. On the other hand, observed times of flow of approximately 73, 59 and 50 seconds (corresponding to fluidities of 30, 40 and 50) need a negative correction of 9·2, 14·6 and 20·0 per cent. respectively of the observed time. A corrected equation thus becomes necessary.

Calculation of the General Fluidity Equation.—If F is the fluidity of a true viscous liquid, d its density, t its time of flow in the standard viscometer, then for normal speed of flow

$$Fd = C/t \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where C = the viscometer constant. The viscosity η is then given by

$$\eta/d = 1/Fd = t/C$$

but for rapid flow

$$\eta/d = t/C - k/tol,$$

where k is a constant for a given viscometer and k/t is the kinetic energy correction. The corresponding equation for the calculation of fluidity is

$$\mathrm{F}d = \frac{1}{t/\mathrm{C} - k/t} = \frac{\mathrm{C}}{t - \mathrm{K}/t} \quad . \quad . \quad . \quad (2)$$

where $\mathrm{K} = k\mathrm{C}$ and represents the kinetic energy correction constant. The correction is therefore best applied as a deduction from observed time of flow.

Determination of the Constants C and K.—(i) Since the kinetic correction is very small for the standard glycerol solution, the following relations are used to give a first approximation to the value of C, *viz.* :

$$\mathrm{F}d = \mathrm{C}/t_{\mathrm{G}} = 7{\cdot}98$$

where t_{G} is the " Glycerol Calibration Time ".

(ii) The kinetic energy correction constant K is now calculated from the relations

$$\mathrm{K} = k\mathrm{C} \text{ where } k = m\mathrm{V}/8\pi l.$$

Here V is the volume between B and D, l the capillary length, and m a factor to which (as the result of 100 observations) the value 1·03 is assigned.

Substituting the capillary length, 2·5 cm., and the approximate value $7{\cdot}98t_{\mathrm{G}}$ for C, we have

$$\mathrm{K} = 0{\cdot}131t_{\mathrm{G}}\mathrm{V}.$$

Alternatively, it may be found by observing the time of flow of a second liquid of high fluidity, *e.g.*, water, the fluidity of which at 20° is 99·5 reciprocal poises, and applying equation (2).

(iii) This value of K is now inserted in equation (2), together with the glycerol calibration time t_{G} and the kinematic fluidity of the standard glycerol solution. The corrected constant C is thus obtained which differs by less than 1 per cent. from the first approximation used above.

When working with dilute cellulose solutions the density of the solution may be taken as that of the cuprammonium solvent which for the standard specification is 0·94. Equation (2) can then be written

$$\mathrm{F} = \frac{\mathrm{C}/d}{t - \mathrm{K}/t} = \frac{\mathrm{C}'}{t - \mathrm{K}/t} \text{ where } \mathrm{C} = 0{\cdot}94\mathrm{C}'.$$

It is in this form that the equation is used in practice.

Addition to the Standard Instrument for Observing the Degree of Deviation of Cotton Solutions from true Viscous Fluids and the Necessity

or Otherwise for Correction.—Since cuprammonium solutions of cotton have been shown [1] generally not to be true viscous fluids, but to form a transition stage between plastic solids and true viscous fluids, viscosity measurements have no theoretical significance except in a few cases. The fluidity observed for slightly bleached cotton (and pulp) varies in consequence with the type of viscometer used, as seen from the following values :—

Cotton Solution, Grams per litre.	0·75	1·00	1·25
Absolute viscosity calculated from—			
(*a*) Standard capillary instrument .	1·6	6·8	20·4
(*b*) Falling-sphere viscometer . .	2·8	10·7	33·9

The degree of deviation of the properties of the solution from those of a true viscous fluid may be ascertained by the addition to the instrument of another ring between B and D, say C, so placed that the time, t_1, taken for the meniscus of a true viscous fluid (glycerine, sugar solutions, or oils) to fall from B to C is equal to that, t_2, taken in falling from C to D. The position of the middle ring can be calculated or found by trial. A small correction must be applied for the surface tension of the hanging drop. With the 2 rings in the standard instrument situated 24·2 and 6·2 cm. above the orifice, the position of the middle ring is 12·2 cm. above the orifice, 0·2 cm. being the hanging drop correction. The ratio t_1/t_2 is unity for true viscous liquids. Normally bleached cottons with fluidities about 1·5 have a ratio t_1/t_2 of about 0·7 ; fluidities 2·5 to 5·0 of about 0·8, and in the case of those with a fluidity of about 8·0 the ratio approximates to unity, so that for cottons with a fluidity above 8·0 the abnormal flow is relatively unimportant. Chemically degraded cottons of fluidities 25 to 40 have a t_1/t_2 ratio of just under or sometimes just over unity, since with fast-flowing solutions a considerable kinetic energy correction must be applied. More concentrated solutions (2 per cent.) can be employed in such cases and the fluidities recalculated to the basis of 0·5 per cent.

Note on the Use of Other Liquids for Standardisation.—Benzyl alcohol and phenyl ethyl alcohol have been used in addition to glycerol for calibration purposes. Commercial benzyl alcohol is fractionated, the fraction b.p. 204·9 to 205° (ordinary pressure) being used. With phenyl ethyl alcohol the fraction b.p. 219·3° to 219·8° is retained. Viscosities of these liquids have been measured (Clibbins and Little, 1936, *loc. cit.*) in U-tube viscometers (p. 68). That of

[1] E. K. Carver and H. Folts, *J. Amer. Chem. Soc.*, 1925, **47**, 1430.

benzyl alcohol by comparison with water, and that of phenyl ethyl alcohol by comparison with benzyl alcohol. The following values were obtained at 20° :—

	Density, d	Fluidity, F.	Kinematic Fluidity, Fd.
Benzyl alcohol . .	1·0445	15·25	15·93
Phenyl ethyl alcohol .	1·0190	7·01	7·14

(*b*) **Method for the Viscosity of Wood Pulp.**—The T.A.P.P.I. method (T 206 m, 1935) is practically the same as the B.C.I.R.A. standard, the conditions being slightly less rigid. The tube is 27 × 1·0 cm. in diameter, the capillary 2·5 × 0·09 cm. internal diameter. A cylinder of Monel metal 2·5 cm. long with a notched base is used for mixing. The air-dry pulp is shredded and enough to give a 1 per cent. solution added to the cuprammonium. After shaking 15 hours the time of flow between the two marks 18 cm. apart is noted (t seconds).

Viscosity $= d(t - k/t)/C$, d being the density of the solution (0·96) and C and k constants which are found by using the tube with two liquids of known viscosity, *e.g.* glycerol and water.

Classification of Cellulosic Materials according to Viscosity in Cuprammonium.—This is very desirable in technical specification. In terms of fluidity (0·5 per cent. solution) the best cotton preparations will give values of no more than 1 to 5 reciprocal poises ; normally bleached cottons of about 5 to 10, cotton wools, bleached pulps, etc., 10 to 20, while badly overbleached cotton may show 20 to 30, disintegration beginning between 30 and 40. The effect of mercerisation is negligible. Some rayons may be 30 to 40, but most of them are about 40. This increases with chemical attack up to a value of 60 which indicates almost complete loss of strength. It is now customary to measure the fluidity of rayons in 2 per cent. solution, when the above range of 40 to 60 is reduced to one of 7·5 to 35, which is comparable with the technically useful range in cotton processing.

Fluidity of Cellulose in Organic Bases

Cellulose dissolves in some quarternary organic bases, and Lieser [1] has shown that the minimum concentration of such a base necessary to dissolve cellulose decreases linearly as the molecular weight of the base increases. Some of these bases are available in the U.S.A. under the name of Tritons (Röhm and Haas Co., Philadelphia) and Triton F, dimethyldibenzyl ammonium hydroxide,

[1] P. Lieser, *Ann.*, 1937, **528**, 276.

has been used for fluidity measurements in place of cuprammonium.[1] Optimum solvent concentration is near 2*N*- and at this it has a greater solvent power than any of the other organic bases, such as trimethylbenzyl ammonium hydroxide (Triton B) and cuprietheylene diamine at their optimum. Solution is rapid, and air need not be excluded. Owing to the basic character of Triton F its action on modified celluloses is similar to that of inorganic alkalis, so that fluidity in this solvent, unlike that in cuprammonium, measures total chemical deterioration of the product, including that rendered apparent only after alkali treatment.

The Solvent.—Triton F is concentrated (vacuum) below 60° to about 2*N*-strength, which is then measured exactly by titrating with 0·5*N*-HCl, using methyl red. The stock is then diluted to give a solution 1·96*N*- in dimethyldibenzyl ammonium hydroxide for general use, but 2·1 to 2·25 *N*- are recommended for slightly modified cellulose (Russell *et al*).

Used solvent is recovered by adding a measured volume of *N*-H_2SO_4 to throw out the cellulose and precipitating the sulphate ion with barium hydroxide. The filtrate is exactly adjusted and the clear liquid concentrated by vacuum distillation.

Preparation of the Solution.—To avoid the formation of gelatinous masses, the cellulose sample is finely divided. Solution is effected in a small test tube, with rapid stirring, for which a glass rod 5 mm. diameter is used, bent slightly, so that when attached vertically to the motor, it revolves almost in contact with the walls of the tube. The motor is run as fast as possible without allowing air to be drawn into the liquid: temperature 20 to 25°, or better at $25 \pm 0{\cdot}5°$.

The cotton is weighed to give a 0·5 per cent. solution of anhydrous material. Each particle of cotton quickly becomes gelatinous, and as soon as a transparent solution is obtained, stirring is stopped. With samples of a fluidity of 4, about 3 hours are required, whereas half an hour suffices for those of fluidity 20 to 30. The rate of flow should be measured as soon as possible after solution is complete, with temperature control, if possible, to $\pm$ 0·02°. Air or oxygen has no effect on the viscosity, but a slight increase is shown if the readings are made in nitrogen, *e.g.*, 189 compared with 182 in air or oxygen. With viscous solutions temperature has a great effect on viscosity. Thus with cellulose of cuprammonium viscosities of 20 to 30 cp. the ratio η_{20} to η_{25} was 1·29.

[1] W. W. Russell and N. T. Woodberry, *Ind. Eng. Chem. Anal.*, 1940, **12**, 151; T. Brownsett and D. A. Clibbens, *J. Text. Inst.*, 1941, **32**, 57T.; W. W. Russell and L. N. Hood, *Ind. Eng. Chem. Anal.*, 1942, **14**, 202.

The viscometer [1] used by Russell did not require kinetic energy corrections. It was calibrated with (*a*) glycerol 79·63 per cent. sp. g. 25/25°, 1·20824, viscosity 44·07 cp., and (*b*) sucrose, 59·97 per cent. by weight, *d*, at 25°, 1·28450, viscosity 44·02 cp. Efflux times for cellulose solutions ranged from 20 to 300 seconds, and that of the Triton F alone from 7·7 to 7·9 seconds.

The following formulæ were used :—

$$\omega = Cdt = 0{\cdot}01088t\,; \quad \eta = 1{\cdot}088t$$
$$F = 1/\omega = 1/Cdt = 91{\cdot}92/t$$

Specific Viscosity = (η solution − η solvent)/η solvent,

where ω and η represent viscosity in poises and centipoises respectively, F fluidity in reciprocal poises, C the viscometer constant, *d* the density of the solution (g./ml.), and *t* the efflux time in seconds. The η of cuprammonium was taken as 1·4 and the η of Triton F as 8·4. The viscometer constant was 0·01012, and the density of the cellulose solutions at 25°, 1·075.

Results showed that in the cuprammonium fluidity region 4 to 25 there was a linear relationship between fluidities in cuprammonium and in Triton F. Triton fluidities multiplied by ten give cuprammonium values in the same units with an average error of 9 per cent.

Since Triton F has a fluidity of 11·9 and cuprammonium about 70, the specific viscosity affords a better comparison. Data given show that Triton specific viscosities are about twice the cuprammonium specific viscosities.

Clibbens and Brownsett (*loc. cit.*) have compared the fluidities in cuprammonium and in Triton F of a range of modified celluloses in 0·5 per cent. solution, using the X viscometer (p. 53).

The results indicate that there is no universal relationship, *i.e.* neither solvent is entirely without action on chain-length distribution except with hydrocellulose and some non-reducing oxycelluloses, the curves for which are very close to one another. Treatment with 0·1 *N*-NaOH for 24 hours at 18° has little effect on the viscosity of these, but a marked effect on the alkali-sensitive group, bringing them all nearer to a single relationship. The comparisons of Russell were made on cotton slightly modified in alkaline media over a range for which a general relationship does approximately hold.

A comparison of specific viscosities is given in Fig. 9, values in cupri-ethylenediamine being included. The approach of curves 1′ and 3′ show that the two copper compounds alter the chain-length

[1] M. R. Cannon and M. R. Fenske, *Ind. Eng. Chem. Anal.*, 1938, **10**, 297.

distribution of the alkali-sensitive hypochlorite oxycelluloses in a similar manner and both differ from the action of dilute alkali and of Triton F (*cf.* with curves 1, 3).

The use of cupriethylenediamine has been recommended both for the precise determination of cellulose viscosity [1] and in a rapid method for pulp and paper mill control work.[2] For the latter purpose the wet pulp suspension is stirred for 5 minutes with an equal volume of the solvent (1·0 *M* in Cu) and the viscosity of the

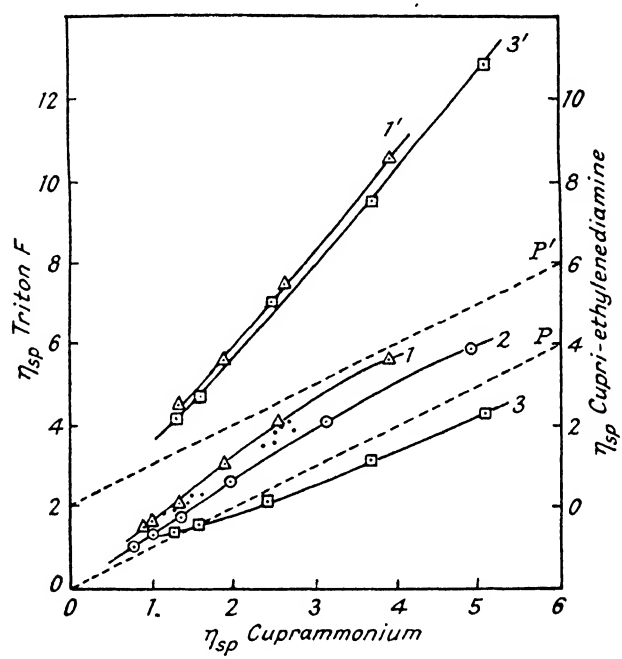


FIG. 9.—Comparison of specific viscosity in (*a*) cuprammonium with that in (*b*) Triton F (1, 2, 3) and (*c*) cupri-ethylenediamine (1′, 3′) of 0·5 per cent. solutions. 1, 1′, Hydrocelluloses; 2, dichromate/H_2SO_4 oxycelluloses; 3, 3′, neutral hypochlorite oxycelluloses. OP line of equal specific viscosities in (*a*) and (*b*) and 2P′ of equal specific viscosities in (*a*) and (*c*).

solution at once measured in a capillary viscometer. The determination can be made in 20 minutes. This solvent, however, is definitely unstable.

The relation deduced by Staudinger that the specific viscosity of the same cellulose at the same concentration in two solvents gives the ratio of the mean molecular weights of the cellulose in the two solvents, was applied by him only to very dilute solutions, such that $\eta_{sp.}$ was below 0·2. The measurements in 0·5 per cent. solution

[1] R. S. Hatch, *Ind. Eng. Chem. Anal.*, 1944, **16**, 104.
[2] R. M. Levy, *et al.*, *Paper Trade J.*, 1944, **118**, *TAPPI Sect.*, 46.

given in Fig. 9 cover a range of $\eta_{sp.}$ from 1 to 10, but a comparison with some of Staudinger's data [1] shows that the ratio of specific viscosities in different solvents at the same cellulose concentration does not vary greatly over a wide range of concentration and specific viscosity.

Nitrate Viscosity of Cellulose and Modified Cellulose

The high or low viscosity of a cellulose is known to persist in the esters derived from it. The observation of Berl (p. 234) that by the use of phosphoric acid instead of sulphuric acid in nitration, a nitrate is formed without alteration in the average chain-length of the cellulose, has given a useful method of measuring the viscosity of a cellulose product, as nitrate, and thus avoiding the reduction in chain-length caused by solution in cuprammonium.

The original method [2] is as follows, the process being carried out in the complete absence of water: The nitrating mixture is either (*a*) 50 to 60 per cent. of concentrated HNO_3; 25 to 35 per cent. H_3PO_4 and 5 to 15 per cent. of P_2O_5. This is allowed to act for less than 5 minutes at 20° or below, giving a product with N, 13·8 per cent., or (*b*) anhydrous HNO_3, 80 per cent.; anhydrous acetic acid 20 per cent., which reacts under the same conditions. The nitrate is pressed and brought into dilute alcohol (1 : 1) at −10° to −30°, washed with this several times, then boiled three times each for 5 minutes with alcohol (95 per cent.) squeezing after each boil. The process takes 45 minutes, and gives soluble nitrates of good stability. Nitrogen content very constant from 13·7 to 13·8 per cent. The nitrate, dried with alcohol and ether (0·25 g.), is dissolved in acetone (100 ml.), or better, in 100 ml. of *n*-butyl alcohol (b.p. 125°) by shaking in a flask with glass beads for 1 to 2 hours. The measurement is made in any ordinary viscometer. Unbleached linters gave nitrate values of 134; linters (N-500), 47 and wood pulps 11–13 centipoises.

A similar technique has been used to determine the nitrate viscosity of modified celluloses.[3] The mixture was prepared from nitric acid of 95 per cent. and phosphoric acid of 89 per cent. strength and adjusted to have the weight-composition HNO_3, 48; H_3PO_4, 50; P_2O_5, 2 per cent. The total acidity was measured by titration with *N*-NaOH solution, using the 4·5 indicator made by British Drug Houses for the titration of phosphoric acid as a monobasic

[1] H. Staudinger *et al.*, *Ber.*, 1937, **70**, 1565, 2508.
[2] E. Berl, *Ind. Eng. Chem. Anal.*, 1941, **13**, 322.
[3] G. F. Davidson, *J. Text. Inst.*, 1938, **29**, 195.

acid and the nitric acid estimated by nitrometer, or by the Devarda method.

One gram of cotton dried over phosphorus pentoxide was steeped in 100 ml. of the acid for 4 hours at 0°, although practically no difference was found at 20°. The product was freed from acid by suction, immersed in a large volume of cold water, and washed until the washings were neutral to methyl red. This occupied some 24 hours. The nitrate was dried in the air and not stabilised.

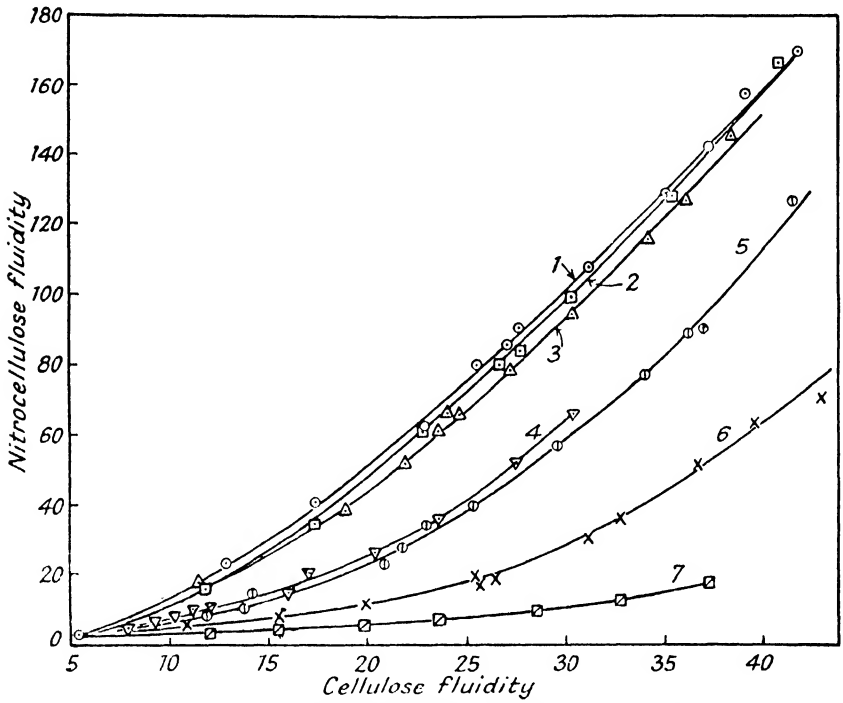


FIG. 10.—Relation between cellulose fluidity (cuprammonium) and nitrocellulose fluidity in cellulose modified by 1-hydrochloric acid; 2-alkaline hypobromite; 3-alkaline hypochlorite; 4-acid hypochlorite; 5-neutral hypochlorite; 6-dichromate + sulphuric acid; 7-dichromate + oxalic acid.

The viscosity was measured in a U-tube B.S. viscometer adapted for pipette filling (p. 66). Results are given in C.G.S. units for 0·25 per cent. solutions at 20°, although unmodified cellulose (cuprammonium fluidity, 5·6) had to be measured in 0·1 per cent. solution. The fluidity of acetone being 310 relative fluidities can be calculated.

About 0·125 g. of nitrate dried in vacuum over P_2O_5 was introduced into a long closed tube, the correct volume of acetone added and solution effected by slow revolution on a wheel over 18 hours. The solution (20 ml.) was then pipetted into the viscometer which

was fitted with a device for raising the liquid by pressure without introducing air or moisture.[1]

Results show that nitration to the maximum of 13·8 is very rapid (6 minutes), but the fluidity falls as the time of nitration is increased, reaching a steady value in about 2 hours, after which there is little change even in 20 hours.

The relation between the cuprammonium fluidity and the nitrate fluidity of all types of modified cellulose is illustrated in Fig. 10. The curves vary with the agent causing the modification, but after boiling under pressure with 1 per cent. sodium hydroxide solution, the relation between cellulose fluidity and nitrate fluidity of all the boiled materials, however modified, is represented by a single curve which is the same as that for hydrocellulose before alkali boiling (Curve 1).

THE VISCOSITY OF CELLULOSE ESTERS

Routine measurements of the viscosity of cellulose acetate, nitrate and lacquers are generally made with instruments of the Ostwald type. The falling-sphere method is also employed for the testing of viscose and acetate solutions, and the Cochius' type (bubble method) is useful for quick works-scale determinations. A special method devised for research work on cellulose acetate, which may be generally useful on account of the rapidity with which measurements can be taken, is also described.

(*a*) **The Ostwald Viscometer.**—The form and use of this instrument may be illustrated by a simple type specified for the measurement of the viscosity of cellulose acetate which is abstracted by permission of the British Standards Institution from B.S. Specification 2 D. 50 (1929).

(i) *Description.*—The instrument shown in Fig. 11 is of the following dimensions :—

Volume of bulb X between marks *ab* is between 18 and 22 ml.

Tube Y, between *b* and *d'*, is 7·5 cm. in length and of such internal diameter (about 5 mm.) that the time of flow of a solution of glycerine of *d*, 1·2526 at 25°/4° from *a* to *b* is between 145 and 175 seconds at 25° (77° F.). Tube Z is 20 cm. long and of such diameter that the volume between *c* and *d* is equal to that between *a* and *c'*.

(ii) *Calibration.*—The instrument is filled up to *cc'* with glycerine of such concentration that the mean time of flow is not less than 60 seconds.

[1] British Standards Institution—"Method for the Determination of Viscosity in C.G.S. Units", revised 1937, Appendix B.

It is then immersed to within 2 cm. of the top in a thermostat at 25° (± 0·1°) and left for 30 minutes with the capillary vertical. The glycerine is then sucked up to a point just above mark *a* and allowed to flow. The time taken for the meniscus to pass from *a* to *b* is determined. Three concordant readings are obtained and the mean value taken.

The viscometer constant K is calculated from the formula $\eta = Ktd$, where t is the time of flow in seconds of glycerine of density d at 25°/4° (determined to four places of decimals) and relative viscosity η; η being ascertained from the following table, given on page 68.

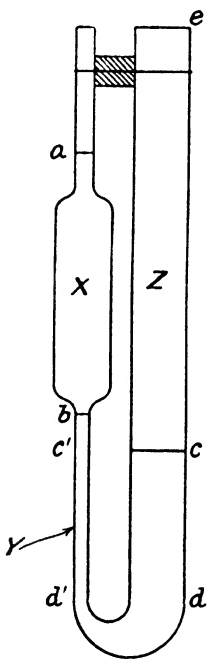


FIG. 11.—Simple type of Ostwald viscometer.

(iii) *Determination of Viscosity.*—The time of flow t_1 of the material under test is determined as above, and the viscosity, η_1, calculated from the formula $\eta_1 = Kt_1d_1$, where d_1 is the density of the material at 25°/4° (determined to two places of decimals).

The British Standards Institution have defined a series of Ostwald Viscometers in publication No. 188,[1] "British Standard Method for the Determination of the Viscosity of Liquids in Absolute (C.G.S.) Units" (revised May 1937). The instruments numbered 1 to 4 cover a range of viscosity between 0·5 and 1,500 centistokes. The illustration, Fig. 12, shows the standard type, Nos. 3 and 4, of which the dimensions in centimetres and millimetres, are shown in a table on page 68, the tolerance allowed being generally ± 10 per cent., except with the capillary (dc), where it is ± 5 per cent.

A modification for pipette-filling is also specified.

The instructions for use are briefly as follows. They are intended to apply to true liquids.

(*a*) Instruments should be cleaned with solvents and with chromic acid mixture and fixed vertically in a bath with accurate temperature control. This is especially important with more viscous liquids. Thus a variation of 0·05° would cause the same error in viscosity (0·05 per cent.) for castor oil (ν = 1,000 cs.) at 20° as would be caused by a change of 0·2° for water (ν = 1 cs.) at 20°.

[1] From the Publications Department, 28 Victoria St., London, S.W.1. Abstract by permission of the Institution.

(*b*) The viscometer is filled through the arm hG to within 0·2 mm. of mark G, when the tube is vertical and the required temperature has been reached. If the tube is wetted above G, or liquid enters the bulb C, time must be allowed for drainage. The liquid is blown or sucked up to a point 1 cm. above mark B, entry of moisture, etc., being avoided—a convenient U-tube device for doing this is described. It is then allowed to flow freely and the time taken for the meniscus to fall from B to C observed. A stop-watch reading to 1/5 second and wound before each test, is used.

(*c*) The instrument is calibrated by first measuring an approximate constant k from the equation

$$k = \nu_s/t_s$$

where t_s is time of flow in seconds with a liquid of known kinematic viscosity ν_s centistokes. The more accurate constant C is then obtained from the relation

$$C = k + c/t_s^2$$

The value of c for instrument No. 3 is 7·0 and for No. 4 11·4, and C, expressed in cs./sec., is the calibration constant of the viscometer.

(*d*) Instrument No. 3 can be calibrated with 60 per cent. sucrose solution, data for which [1] are given in the table on page 69.

No primary standard is available for No. 4. The viscosity of a viscous liquid, *e.g.* castor oil, is measured in a No. 3 tube with constant, say C_3. If the times of flow in Nos. 3 and 4 at the same temperature are t_3 and t_4 respectively, then since—

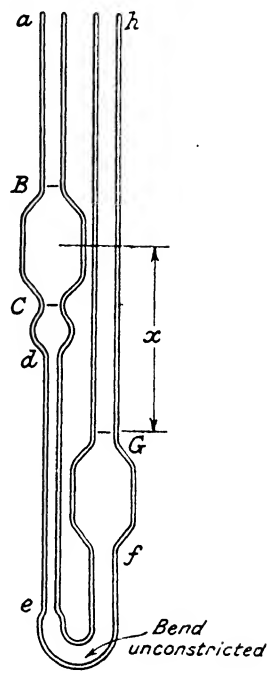


FIG. 12.—Standard Ostwald Viscometer.

$$\nu = C_3t_3 = C_4t_4\,;\ C_4 = C_3t_3/t_4.$$

(*e*) Viscosities are best expressed as kinematic viscosities (ν) in centistokes (cs.).

If t is time of flow in a viscometer of constant C

$$\nu = Ct - c/t.$$

The correction c/t is small with higher viscosities. Thus when $t = 100$ sec. it is less than 0·1 per cent. for No. 4, and less than

[1] Scientific Paper 298, 1917, Bureau of Standards, Washington, U.S.A.

TABLE GIVING RELATION BETWEEN DENSITY OF GLYCERINE AND ITS VISCOSITY

Density at 25°/4°.	Relative Viscosity at 25°.	Density at 25°/4°.	Relative Viscosity at 25°.	Density at 25°/4°.	Relative Viscosity at 25°.
1·2539	108·7	1·2520	96·1	1·2501	84·6
1·2538	108·1	1·2519	95·4	1·2500	84·0
1·2537	107·4	1·2518	94·8	1·2499	83·4
1·2536	106·8	1·2517	94·2	1·2498	82·9
1·2535	106·1	1·2516	93·6	1·2497	82·3
1·2534	105·4	1·2515	92·9	1·2496	81·8
1·2533	104·7	1·2514	92·3	1·2495	81·2
1·2532	104·1	1·2513	91·7	1·2494	80·6
1·2531	103·4	1·2512	91·1	1·2493	80·1
1·2530	102·7	1·2511	90·5	1·2492	79·5
1·2529	102·0	1·2510	89·9	1·2491	78·9
1·2528	101·4	1·2509	89·3	1·2490	78·4
1·2527	100·7	1·2508	88·7	1·2489	77·8
1·2526	100·0	1·2507	88·1	1·2488	77·3
1·2525	99·4	1·2506	87·5	1·2487	76·7
1·2524	98·7	1·2505	86·9	1·2486	76·2
1·2523	98·0	1·2504	86·3	1·2485	75·7
1·2522	97·0	1·2503	85·7	1·2484	75·1
1·2521	96·7	1·2502	85·2	1·2483	74·6

Viscometer No.		3	4
Range (cs.)		30–250	200–1500
Capillary (de)	Length	10	10
	Int. dia.	0·23	0·38
Tube (aB)	Length	7·0	7·0
	Int. dia.	0·7	0·7
Bulb (BC)	Ext. dia.	2·8	3·4
	Capacity	16·0	26·0
Bulb (Cd)	Capacity	1·2	1·4
Bent tube (ef)	Min. int. dia.	0·7	0·8
Tube (Gh)	Int. dia.	0·7	0·8
Bulb (fG)	Ext. dia.	2·8	3·4
	Min. capacity	20·0	30·0
Dimension (x)		5·5	7·0
Dist. between vert. axes		2·0	2·5

0·2 per cent. for No. 3. For routine work therefore the approximate relation $\nu = Ct$ can be employed.

Very full tables giving the density of glycerol will be found in a paper by Bosart and Snoddy.[1]

[1] *Ind. Eng. Chem.*, 1928, **20**, 1377.

VISCOSITY OF 60 PER CENT. SUCROSE SOLUTION IN CENTISTOKES AT 25° FOR A RANGE OF DENSITIES IN G./ML. AT 25°.

Density.	Viscosity.	Density.	Viscosity.	Density.	Viscosity.	Density.	Viscosity.
1·28280	33·22	1·28340	33·70	1·28400	34·18	1·28460	34·69
1·28290	33·29	1·28350	33·77	1·28410	34·26	1·28470	34·77
1·28300	33·37	1·28360	33·86	1·28420	34·35	1·28480	34·85
1·28310	33·45	1·28370	33·94	1·28430	34·43	1·28490	34·94
1·28320	33·53	1·28380	34·02	1·28440	34·51	1·28500	35·03
1·28330	33·62	1·28390	34·11	1·28450	34·60	1·28510	35·11

The dynamic viscosity of water is given in the following table in centipoises and the kinematic viscosity in centistokes.

VISCOSITY OF WATER

t° C.	Cp.	Cs.	t°C.	Cp.	Cs.
12	1·2390	1·2369	19	1·0340	1·0315
13	1·2061	1·2035	20	1·0087	1·0068
14	1·1748	1·1717	21	0·9843	0·9829
15	1·1447	1·1414	22	0·9608	0·9600
16	1·1156	1·1122	23	0·9380	0·9381
17	1·0875	1·0841	24	0·9161	0·9167
18	1·0603	1·0574	25	0·8949	0·8963

(*b*) **The Falling-sphere Method as used for Solutions of Cellulose Acetate and Nitrate.**—(i) The *Viscometer Tube.*[1]—A glass tube 28·5 cm. by 2 cm. internal diameter, shown in Fig. 13, is used. It is fitted with a singly bored stopper carrying a glass tube 7 cm. long and 3 mm. internal diameter, called the releasing tube, which has a small hole blown in the side, 4·5 cm. from its lower end. The wide glass tube may be etched all round its circumference at the points *a*, *b*, *c*, *d*, *e* and *f*, the distance apart being 5 cm., except in the case *a*-*b*, which is 3 cm. Only *c* and *f* are really necessary, and *f* should be at least 5 cm. from the bottom.

(ii) *The solvent employed* is aqueous acetone, prepared by mixing 95 ml. of pure acetone with 5 ml. of distilled water (*d*, 0·8097 at 20°/4°).

(iii) *Procedure.*—A solution of the requisite concentration is prepared by adding the cellulose acetate to acetone in a tube 43 cm. long and 2·5 cm. internal diameter. The tube is securely stoppered,

[1] W. Gibson and C. Jacobs, *Chem. Soc. Trans.*, 1920, **117**, 973. See also p. 50.

shaken, and then rotated on a wheel until the mixture is homogeneous. The viscosity determination is made within 48 hours.

The viscometer is filled, stoppered and clamped vertically in a thermostat, where it is allowed to stand until the solution is quite free from air bubbles, and has reached the temperature of the bath *i.e.*, 20 ± 0·2°.

The stopper is then replaced by the one carrying the releasing tube and a $\frac{1}{16}$ in. diameter steel ball is introduced into the liquid by this means. The time of fall through 15 cm. from mark *c* to mark *f* is observed.

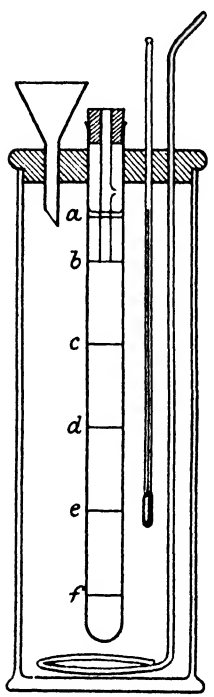


FIG. 13.—Falling-sphere viscometer used for cellulose esters.

(iv) *Calculation of the Result.*—The viscosity in C.G.S. units is $\frac{T(S - S_1)}{T_1(S - S_2)} \times$ viscosity of castor oil in C.G.S. units.

T = time of fall in the cellulose ester solution of density S_1 of the steel ball of density S (about 7·65).

T_1 = time of fall (about 19 seconds) in castor oil of density S_2 (about 0·96).

Viscosity of the castor oil in C.G.S. units 9·65.

The density of acetate solutions ordinarily employed for viscosity measurements may be taken as 0·8 in the above formula. Inserting the values given, the viscosity of a cellulose acetate solution in C.G.S. units becomes very nearly T/2.

Commercial acetates with viscosities below 300 are classed as of low viscosity, between 300 and 400 as of medium, and between 400 and 500 as of high viscosity. Acetates of high viscosity can produce a very thin film, whilst those of low viscosity enable a few coats to give a film of any required thickness.

(*c*) **The Cochius' Viscometer.**—The apparatus consists of a glass tube of 10 mm. bore and 700 mm. long, closed at one end, fitted with a water jacket to maintain constant temperature (20°). The tube is filled with the solution of cellulose ester, so that an air bubble 40 mm. long remains at the top. After standing until the solution is free from air, the apparatus is quickly reversed and the time noted for the large air bubble to pass two graduations 500 mm. apart. The time is taken as a measure of the viscosity.

(*d*) **Method used for the Determination of Viscosity of Solutions of Cellulose Acetates over a Range of Temperature up to 50°.**—To study the viscosity of acetone-soluble acetates over a range of temperature the following method was employed.[1] The apparatus (Fig. 14), consists of a capillary tube of known length and diameter, to which a glass bulb B of known volume is attached by means of a glass joint. The advantage of this joint lies in quick cleaning, and in the use of the same bulb for a series of capillary tubes. The glass-stoppered bottle which contains the solution is

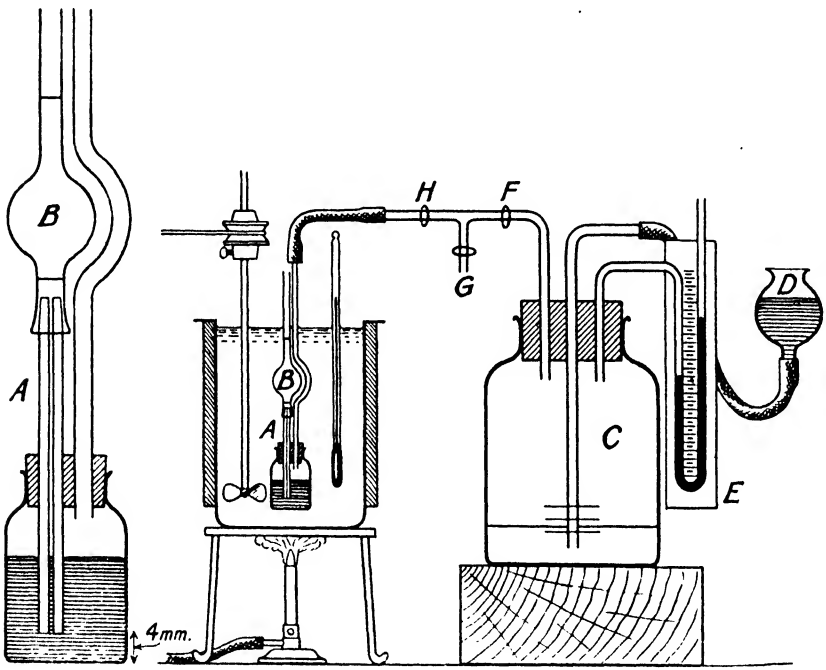


FIG. 14.—Apparatus used for measurement of the viscosity of cellulose acetate over a range of temperature (courtesy of Messrs. J. Springer, Berlin).

fitted with a two-hole rubber plug, in one hole of which the capillary is fixed. The bottle should be about the same capacity as the bulb.

The second hole in the plug serves to connect with the pressure control, a 3-litre flask C partly filled with water to give a uniform pressure. The pressure is adjusted by the bulb D, and is read on the water-manometer E. The movement of the solution in the capillary is controlled by the taps F, G and H.

Before making an estimation the capillary must be left in the

[1] V. E. Yarsley, "Über die Herstellung und physikalischen Eigenschaften der Celluloseacetate": J. Springer, Berlin, 1927. See also Goddard, *Ber.*, 1928, **61**, 586.

thermostat for half an hour. The cocks F and G are closed and D lifted until a sufficient pressure is reached. This varies with each solution and is determined by experiment. The cock F is opened, and the time taken by the solution to fill the volume between the marks on the ends of the bulb B is taken. The cock F is then closed and the pressure reduced by lowering the bulb D. The cock F is again opened and the time taken for the solution to descend between the marks is noted. In this way four readings are made for each determination—*viz.*, the time, t_1, when the volume, V, is forced into the capillary under pressure, p_1, and the time, t_2, in which the same volume falls under pressure, p_2.

At each temperature we have

$$\text{Viscosity} = \frac{(p_1 - p_2)\pi r^4 t_1 t_2}{8Vl(t_1 + t_2)}$$

in which l and r are the length and radius of the capillary in centimetres. As a rule the mean of three determinations at each temperature should be made.

Some experience of the method is necessary to obtain good results. The most important point is the pressure employed, which must be sufficiently large to allow a uniform flow of the solution in the bulb. If the pressure is too high the velocity of flow is too great, and if too low the flow is irregular. The capillary must also be raised 4 mm. from the bottom of the bottle to obtain constant results. The same capillary should be used in a series of experiments, but it is possible to use a larger one if the solutions are of high viscosity. The apparatus is standardised with pure glycerine. Example: Volume of bulb, 2·822 ml.; capillary length 10·00 cm.; diameter, 0·1151 cm.

Viscosity of glycerine at 20·3°, found 8·33; at 26·5°, found 4·93; standard values (Schöttner) are 8·30 and 4·94 respectively.

CHAPTER IV

MEASUREMENT OF THE TENSILE STRENGTH OF HAIR, YARN, AND FABRIC

STRENGTH tests in the case of cotton are carried out on the hair, the yarn or the fabric. The strength of the hair measures the strength of the fundamental unit structure, and for scientific purposes is to be recommended. Its interpretation, however, is by no means simple, the presence of abnormal hairs and variable length making the strength measurement somewhat indefinite.

The strength of a yarn is obviously complicated, depending both upon the strength of the hairs, and many other factors connected with twist, adhesion and extension. The nature of the break has been the subject of much discussion. It was thought that it took place, primarily, through slip of hair upon hair, but it has been demonstrated that quite a large proportion, in some cases 70 per cent. of the hairs, may actually be ruptured.[1]

The strength of a fabric, though industrially important, is even more complex and difficult of interpretation. Reference will be made to the bursting test, the values giving an integrated effect of the action of chemical agents on a fabric.

For further information and references to the literature of the subject the following may be consulted :—

" Mechanisch-und Physikalish-technische Textiluntersuchungen." Heermann, Berlin, 1912.

" The Measurement of the Mechanical Properties of Cotton Materials." Pierce, *J. Text. Inst.*, 1923, **14**, 161T.

" Tensile Tests for Cotton Yarns " : (i) A Survey of Current Tests ; (ii) The Ballistic Test ; (iii) The Rate of Loading. E. Midgley and F. T. Pierce, *J. Text. Inst.*, 1926, **17**, 305, 661T.

" Tensile Tests for Cotton Yarns " : (i) The Dynamics of some Testing Instruments ; (ii) The " Weakest Link." F. T. Pierce, *ibid.*, 342T.

" Influence of Humidity on the Elastic Properties of Cotton." J. C. Mann, *J. Text. Inst.*, 1927, **18**, 253T.

" The Breaking of Yarns and Single Cotton Hairs." G. G. Clegg, *J. Text. Inst.*, 1926, **17**, 591T.

" The Time Factor in Hair Testing." J. C. Mann and F. T. Pierce, *J. Text. Inst.*, 1926, **17**, 182T.

[1] G. G. Clegg, *J. Text. Inst.*, 1926, **17**, 591T.

" A New Machine for the Measurement of Resistance to Wear." W. E. Morton and A. J. Turner, *J. Text. Inst.*, 1928, **19**, 200T.

" A New Autographic Testing Machine for Yarns and Fibres." S. A. Shorter and W. J. Hall, *J. Text. Inst.*, 1923, **14**, 493T.

" The Machines commonly used in the Cotton Industry for the Testing of Materials." E. Midgley, *J. Text. Inst.*, 1923, **14**, 189T ; also G. Osumi and D. Kato, *ibid.*, 1937, **28**, 129T.

The importance of carrying out all tensile strength determinations under conditions of constant humidity must be emphasised. Relative humidities of 66 or 70 per cent. are usually adopted. Accurate work requires a room maintained at constant humidity in which the material is conditioned and the measurements made. A very satisfactory constant-humidity room, electrically controlled, has been described in detail.[1] In the absence of a room, a constant-humidity box has been employed for work with the O'Neill hair strength tester.[2] It consists of a box about 2 ft. × 2 ft. × 1 ft. coated inside with paraffin wax, the front being a sliding panel so that dishes, etc., can be introduced. A circular hole cut in the bottom enabled an O'Neill tube to pass through a small hole in a sheet of rubber and the apparatus was raised a foot above the table, so that, although the hairs are mounted inside the box, the outlet of the tube is manipulated underneath as usual. Constant humidity was maintained by placing two dishes full of calcium chloride solution in the box. A current of air was also passed in, after being conditioned by passing through three bottles full of the same calcium chloride solution. Access to the box was provided by two arm-holes furnished with long oiled-silk sleeves fitting tightly round the operator's wrists. Rubber gloves were worn and the holes closed by elastic doors as soon as the hands were withdrawn.

To obtain satisfactory results with any particular machine experience of its working is required. In cases where a machine is not available a simple device for yarn testing is described which has been found by the author to give useful results of a comparative nature—*e.g.* the dry and wet strengths of rayons (p. 81).

A. Determination of the Breaking-Load of single Cotton Hairs

In all instruments used for this purpose the hair is attached at one end to a rigid support ; the other end is pulled by a hook

[1] R. G. Parker and D. N. Jackman, *J. Soc. Chem. Ind.*, 1925, **44**, 223T.
[2] J. C. Mann, *J. Text. Inst.*, 1927, **18**, 253T.

attached either to a float, the beam of a balance, or a pendulum. The instruments in use then fall into three classes :

(*a*) The Hydrostatic type, of which the O'Neill tester with modifications remains the best.

(*b*) The Balance type, of which the Barratt fibre balance is a good example. The tension is applied by causing a steel solenoid suspended from one arm of the balance to move within a coil under the influence of a current. From the amount of current applied when the break occurs the breaking load of the fibre can be calculated. A similar pattern is the " Deforden " of P. Krais,[1] which is extensively used. Instead of the electrical device a vessel is suspended from the arm of the balance into which water flows from a burette.

(*c*) The Pendulum type, of which the well-known Schopper machine is an example. The Magazine hair tester devised by Balls [2] is somewhat complex. It carries a magazine in which as many as fifty fibres are mounted. These are broken one after the other automatically. An electric spark records the movement of the pendulum as a series of charred lines on a piece of paper, from which, by means of a calibrated scale, the breaking strength of all the fibres is determined.

Illustrations, together with a comparison of the performances of the three typical machines of O'Neill, Barratt and Balls respectively, have been given by Navkal and Sen.[3] The O'Neill instrument has much to recommend it. It is cheap, simple, and independent of mechanical adjustment. A comparison of the performance of the three instruments showed that the fibres are broken at the highest speed in the Balls' machine, the tension being applied at the rate of 0·4 to 0·5 g. per second, whereas the rate is only 0·13 g. per second in the Barratt. The best rate of flow for the O'Neill is that which causes the load to increase at the rate of between 0·023 and 0·037 g. per second. The results of comparative tests show that the values for breaking-load obtained by the O'Neill and the Balls' instruments agree very well, whilst those given by the Barratt instrument are higher. As an example a Dharwar cotton gave—(1) O'Neill (250 breaks), 4·89, (2) Barratt (1,000 breaks), 5·12, (3) Balls (1,000 breaks), 4·66 grams.

The results obtained with the modified O'Neill apparatus,[4] statistically considered, show that for cotton the number of observations required to obtain a possible error of less than 3 per cent.

[1] P. Krais, *J. Text. Inst.*, 1928, **19**, 38T.
[2] W. L. Balls, " Studies of Quality in Cotton ", 1928.
[3] H. Navkal and K. R. Sen, *J. Text. Inst.*, 1930, **21**, 267T.
[4] J. C. Mann and F. T. Pierce, *ibid.*, 1926, **17**, 84T.

varies from 185 in Peruvian to 45 in the case of Sea Island cotton. The mean breaking load in grams varies from 3·1 (Punjab American) to 5·3 (Sea Island) and to a maximum of 6·4 in Peruvian cotton. The tensile strength in dynes/cm.^{2} ranged from $4{\cdot}5 \times 10^9$ in Sea Island varieties to $2{\cdot}3 \times 10^9$ in Peruvian. The finer cottons are thus far superior in tensile strength to the coarser varieties, which may be due to the fact that the cellulose of the primary cell wall has a higher strength than that of the secondary layers, or it may be an example of a general phenomenon bearing out the statement made with regard to quartz fibres " that all fibres seem to show increasing tenacity with a diminution in diameter as though there were a surface tenacity akin to surface tension in liquids ".

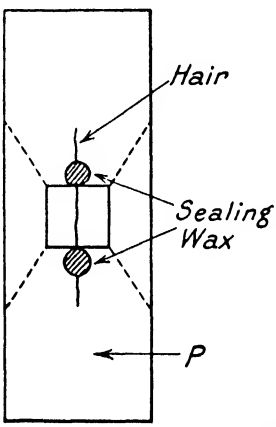


FIG. 15.—Method of mounting cotton hair for testing.

There is no relation between diameter and strength, some cotton hairs being twice as strong as others of different kinds of the same diameter, but an agreement is shown between strength and wall thickness for a given variety of cotton.

It is generally supposed that mercerisation increases the strength of cotton hairs. This is true if shrinking is prevented. If the hairs shrink the increased content of cellulose per unit length causes an increase of strength with a decreased coefficient of variability—*i.e.* the hairs become more uniform in strength on mercerisation.

The effect of relative humidity on the single hair strength of cotton has been shown [1] to be less than generally supposed. The strength at 66 per cent. R.H. compared with strength at 44 per cent. R.H. is of the order of 10 to 15 per cent. greater, but the relation is not linear, the curve becoming parallel to the axis above a R.H. of 66 per cent. and giving no maximum at 80 per cent. R.H., as stated by Willkomm.[2] The R.H. is thus important up to 66 per cent., but above that its effect is negligible.

The relative values obtained for yarn and hair strengths are frequently very similar, as will be seen from the table on p. 151.

(*a*) **The O'Neill Instrument.**—The hair is mounted across a hole 1 cm. in diameter which is cut in a rectangular piece of paper (Fig. 15). One end of the paper is fixed and the other attached to

[1] J. C. Mann, *J. Text. Inst.*, 1927, **18**, 253T.
[2] P. Heermann, " Mechanisch-u.s.w. Textiluntersuchungen ", p. 173.

a cylindrical float, immersed in water. The paper is cut on either side of the hole along the dotted lines shown and the float adjusted to a slight tension on the hair. By allowing the water to flow out slowly (for example, 0·1 g. per second) an increasing tension is put on the hair until breaking occurs.

A *simple form* [1] is shown in Fig. 16.

The cylinder A (Fig. 16) about 50 cm. × 6 cm., contains water supporting the tubular float B, about 1·6 cm. wide. The hair is mounted with sealing wax across the hole 1 cm. wide cut in the slip of paper P (Fig. 15), the ends of which are pinned to the holders K_1K_2. The paper is cut along the dotted lines and water run out from the cylinder until the free 1 cm. length of hair just begins to bear the weight of the float. Water is now run through the capillary jet J into a measuring vessel till the hair breaks.

The breaking load $= Vr^2/(R^2 - r^2)$ grams : V, volume of water run out in ml., r radius of float, R radius of the cylinder in centi-metres.

As the breaking load varies with the time allowed for the hair to stretch to its breaking-point it is desirable to fix some sort of standard time. A rate of 0·5 g. per second is suggested for the O'Neill instrument. For higher speeds a Torsion Balance hair tester [2] can be employed at a standard rate of 2·0 g. per second.

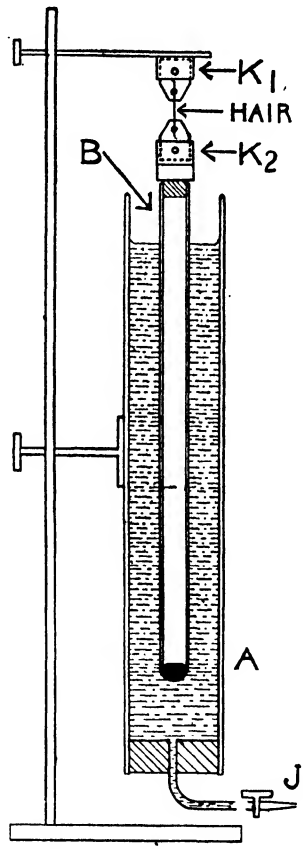


FIG. 16.—Simple form of O'Neill instrument.

This simple apparatus proved unsuitable for very greatly tendered hairs owing to difficulty with the grips. The modified apparatus now described is therefore preferable.

(*b*) **The Modified O'Neill Tester, by Mann and Pierce.**[3]— The modifications consist of an improved upper grip ; the use of calcium chloride solution instead of water, and standardised

[1] P. D. Vincent, *J. Text. Inst.*, 1924, **16**, 281T.
[2] F. D. Farrow and S. M. Neale, *ibid.*, 1923, **15**, 157T.
[3] J. C. Mann and F. T. Pierce, *ibid.*, 1926, **17**, 84T.

dimensions. A complete apparatus as used by Navkal and Sen (p. 75), is shown in Fig. 17.

The Float.—The following dimensions are recommended for the float, as their adoption would make results more accurately comparable :—

Inner diameter of tube (*a*) 4·5 to 5·0 cm. ; length about 30 cm.
Outer diameter of float (*b*) 1·0 to 1·2 cm. ; length about 15 cm.
Free length of mounted hair (*l*) 1·0 cm.

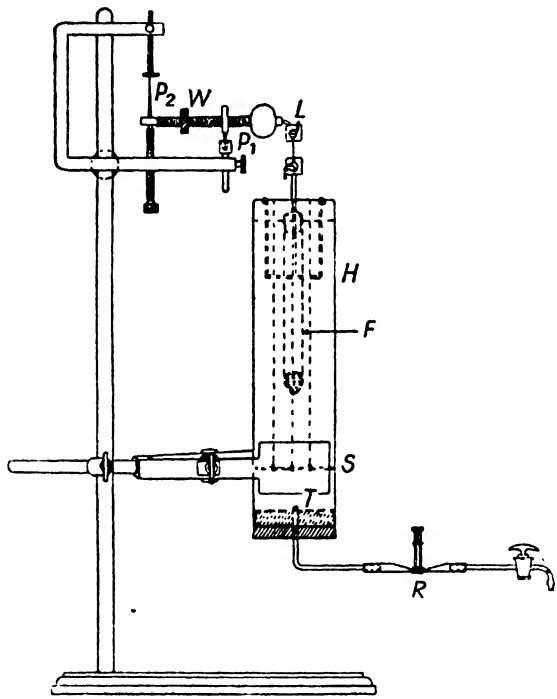


FIG. 17.—Modified form of O'Neill instrument.

The Solution.—When the hairs are broken over a free surface of water, their moisture content may correspond with anything from saturation to the humidity of the laboratory. Any errors that might arise from varying moisture content are avoided by conditioning the test sample of hairs overnight over a 40 per cent. solution of calcium chloride (*d*, 1·272 at 15°), and using the same solution instead of water in the O'Neill apparatus. This gives a relative humidity of 66 per cent.

The Upper Grip.—The greatest source of error in the ordinary form of this apparatus is due to the difficulty of estimating the beginning of tension on the specimen. Ordinary hairs are so

fragile that a " slight " tension, as judged by eye, may be a very appreciable fraction of the breaking load, and it was found impossible to test tendered hairs without the new type of upper grip shown in Fig. 17.

Essentially this consists of a small lever, whose moment can be adjusted by the nut, mounted on two small needles P_1, which rest in point and line depressions on the stand, the third needle P_2 coming to rest against an upper plane stop when a very slight tension is placed on the specimen. Owing to the downward movement of the grip and the delicacy of the lever, it can easily be held in balance, so that the release of two drops of the solution is sufficient to pull it over, with a tension of about 0·005 g.

The nut W is adjusted till needle P_2 just rests on the lower stop; the liquid is run off till P_2 just moves to the upper stop. The hair is now under tension and the liquid, which subsequently is allowed to flow out, is collected. When the fibre breaks the volume is read and from it the breaking load can be calculated, either by the formula below, or by means of a graph obtained in a previous calibration.

The grip at L can be made to take paper mounts or torsion pendulums (small transverse rods). The rate of loading is varied by modifying the jet of the outlet tube, capillary tubing being used for the slowest rate (0·003 g./sec.). A rate of 0·5 g. per second is recommended as a standard.

Calculation of the Breaking Load.—The error due to hair extension is generally neglected, but may be several per cent. unless the dimensions are chosen to reduce it. The hair extends about 7 per cent. of its length before breaking, and the float sinks by this amount. This exaggerates the value of the breaking load.

Let

Breaking load	= F grams.	Outer diameter of float	= b cm.
Length of specimen	= l cm.	Height of liquid at zero	= h_0 cm.
Extension at break	= el cm.	Height of liquid at break	= h cm.
Density of liquid	= ρgm./ ml.		
Inner diameter of tube	= a cm.		

Then the volume of liquid run off and measured.

$$V = \frac{\pi}{4}(a^2 - b^2)[h_0 - h + el \,.\, b^2/(a^2 - b^2)].$$

The load $F = \pi\rho b^2(h_0 - h - el)/4$

$$= \frac{\rho b^2}{a^2 - b^2} \cdot V \cdot \left[1 - \frac{el}{F} \cdot \frac{\pi a^2 b^2 \rho}{4(a^2 - b^2)}\right]$$

$$= \text{factor} \times \text{reading} \times (1 - \text{correction}).$$

The correction can be calculated if e/F is taken as 0·01 at about 60 R.H., a value obtained from the results of Barratt.

(*c*) **Dial Reading O'Neill Instrument.**—These authors [1] find that even the improved O'Neill apparatus is slow in working, owing to the number of measurements required and the necessity for pouring the solution back into the cylinder after each test. The tap, also, may not be shut off at the instant the fibre breaks, making the results too high.

The dial reading apparatus is quick in action and there is no transference of the liquid. A fibre is hung from a hook fixed to a lever-device in which an electric circuit is completed when the fibre is straightened out. The lower end of the fibre is attached to a float suspended in a solution of calcium chloride in one arm of a U-tube. In the other arm is immersed a counterpoise which can be raised slowly by winding a string on a pulley driven from a motor through a gear mechanism. The gear records tension, and recording stops as soon as the fibre breaks. As the counterpoise rises the level of the liquid round the float falls, gradually increasing the tension on the fibre. The results obtained agree within 0·02 to 0·14 g. with those obtained with the Magazine Hair Tester.

(*d*) **The Barratt Fibre Balance.**—This apparatus is shown in Fig. 18. A hook A is attached to one end of the beam of the balance. One end of the fibre is attached to this by a suitable grip; the other is fastened at B to a rigid support C. The screw D enables the distance AB to be varied. The other end of the beam carries a steel rod almost wholly inside a solenoid, the current through which can be varied by means of a resistance. To carry out a measurement the screw D is regulated till the fibre is straightened without appreciable tension. A current is allowed to flow in the circuit and its strength gradually increased till the fibre breaks. The reading of a milliammeter, together with a previous calibration, indicates the breaking load of the fibre.

(*e*) For a description of the **Magazine Hair Tester** reference should be made to W. L. Balls' "Studies of the Quality of Cotton", 1928, p. 355, and to the paper of Navkal and Sen already mentioned.

B. The Breaking Load of Yarns

There are numerous instruments in use for the determination of the breaking load of yarns, such as those of Goodbrand, Avery, Schopper, Mullen, and Baer. A certain amount of practice and experience is required with any particular machine before results

[1] S. S. Sukthankar, N. Ahmad and H. Navkal, *J. Text. Inst.*, 1937, **28**, 129T.

become satisfactory. The significance of the breaking load of a yarn and the factors involved in it have been critically examined and discussed together with the question of the design of suitable machines. The more important contributions to this subject will be found in the list on p. 73.

In yarn testing the length of yarn between the jaws, the temperature and the humidity must be exactly specified. Typical standard procedure is: Length of yarn 40 cm., temperature 20°, relative humidity 70 per cent.; number of breaks 150 to 200.

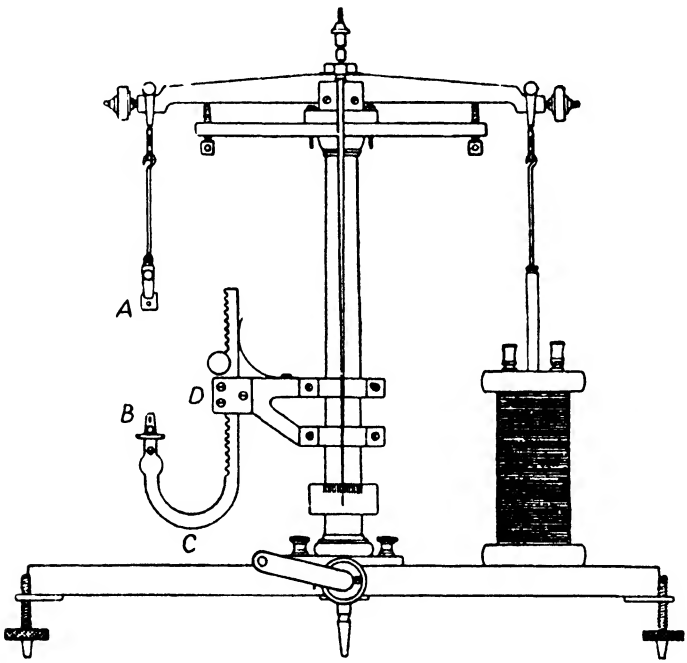


FIG. 18.—The Barratt Fibre Balance.

The author has found the following simple laboratory-made device useful for measuring approximately the comparative strengths of yarns when a better machine is not available :—

Simple Apparatus for Measuring the Breaking-load of Yarns.—The apparatus consists of a tall 150 to 200 ml. beaker loaded with shot, to which is attached a wire handle with a centre loop to which the yarn is fastened by means of a fisherman's bend. The beaker is placed inside a containing vessel, which is lined with cotton wool almost touching the beaker. The other end of the yarn is attached to a cork grip fixed to a retort stand. The grip is raised until the thread bears the weight of the beaker, and the thread is

broken by allowing water to run into the beaker through a Λ-shaped glass tube connected by rubber tubing to a syphon bottle. The rubber tube is held in the hand and the water allowed to flow slowly into the beaker till breakage occurs. The flow of water is stopped by pinching the rubber, and the beaker and its contents weighed.

The average of thirty to fifty breaks will give a fair value for the breaking load.

C. Determination of the Strength of Fabrics

This measurement is of technical importance, and machines are available for measuring the breaking load and extension of fabric and for ripping, tearing and wearing tests.

The bursting strength of a fabric, for the determination of which the Mullen tester is recommended, has been found useful in the study of the action of detergents and bleaching agents on cotton and linen cloths and similar investigations. The Mullen machine has the advantage of rapid working, but to obtain concordant results all tests must be made under identical conditions. The following practical points may be mentioned:

(i) The rate at which the pressure is applied must be kept constant throughout the series of tests.

(ii) The machine is very satisfactory with fabrics made from a uniform thread like rayon, consistent readings being easily obtained, but cotton and linen cloth may show considerable variations in the value of bursts taken from selvedge to selvedge. This must be borne in mind when using test pieces smaller than the full width of the cloth.

(iii) Care must be taken in placing the fabric under the clamp, since stretching in one direction or the other may cause bursts irregularly in warp or weft, giving very different values.

An allowance for the pressure required to bulge the diaphragm is of importance in the case of weak or extensible fabrics.

Since a fabric which stretches necessitates a greater bulge on the diaphragm, it may happen that a fabric which becomes more extensible after some treatment such as washing, may appear to have gained in strength.

The following results if plotted show that the Mullen values ran proportionately with the copper number, and in particular with the fluidity. A standard calico was used.

I. Action of Alkaline Bleach Liquor

Temp. ° C.	Percentage Loss in Bursting Strength (Mullen).	Copper Number.
40	6·5	0·13
60	32·5	0·54
80	36	0·61
95	51	1·84

II. Action of Neutral Bleach Liquor

Percentage Loss of Bursting Strength (Mullen).	Fluidity.	Copper Number.
0	0·715	—
9·4	—	0·17
11·5	1·48	—
32	3·45	—
37·5	—	2·5
42·5	4·55	3·6

CHAPTER V

DISPERSED CELLULOSE—MERCERISED COTTON AND RAYONS

TREATMENT of cellulose fibres with water and aqueous solutions of certain acids, bases and salts, causes swelling. The fibres so treated shrink in length and increase in diameter, at the same time frequently becoming stronger and showing enhanced affinity for dyestuffs. The original patent of John Mercer [1] (1850) shows that he was aware of the general effect of other reagents than sodium hydroxide on cellulose when he claimed that : " My invention consists in subjecting vegetable fabrics to the action of caustic soda or caustic potash, dilute sulphuric acid, or chloride of zinc of a strength and temperature sufficient to produce new effects ".

In some cases the swelling may proceed so far that all rigidity is lost and so-called solution (solvation) of the cellulose takes place.*

The effect on cotton of solutions of sodium hydroxide of 27 to 32 per cent., which are usually employed in practice, is to cause untwisting of the fibre, which swells and becomes cylindrical with considerable shortening. The lumen almost disappears as the walls expand. The cuticle is not apparently ruptured, but adapts itself to the changes and finally sets a limit to further expansion. When the concentration of the sodium hydroxide does not exceed 11 per cent. untwisting alone occurs, at 15·5 per cent. this is followed by swelling, at 17·7 per cent. the two proceed together, while at 27 to 36·3 per cent. the swelling precedes the uncoiling.[2] The increase of tensile strength is about 30 to 50 per cent. when cotton yarn is mercerised without tension. The maximum shrinkage has been found [3] to be 31·3 per cent. with a solution of *d*, 1·320 at 10°. Mercerised with tension the increase in strength is less, but the characteristic lustre is obtained. Cotton *hairs* show a maximum contraction at 13·3 per cent. sodium hydroxide.[4]

The extent to which the mercerising action has proceeded, or the " degree " of mercerisation, is measurable in terms of either—(i)

[1] Eng. Pat. 13296 (1850).
[2] J. Huebner and W. J. Pope, *J. Soc. Chem. Ind.*, 1904, **23**, 404.
[3] P. Krais, *Zeit. angew. Chem.*, 1912, **25**, 2649.
[4] R. S. Willows, T. Barratt *et al.*, *J. Text. Inst.*, 1922, **13**, 229T.

* A summary of the literature dealing with the Swelling of Cotton Cellulose has been given by G. E. Collins, *J. Text. Inst.*, 1924, **14**, 264T. ; and a mathematical examination of the problems by J. R. Katz, *Cellulosechem.*, 1929, **11**, 17. The subject is adequately treated in J. T. Marsh, " Mercerising ", Chapman & Hall, London, 1941.

the contraction produced, or (ii) by the proportion of sodium hydroxide taken up, or (iii) by the increased affinity of the cotton for alkaline hydroxides and for dyestuffs. It varies with the temperature and concentration of the alkaline solution and the time of immersion. Mercerisation, however, takes place very rapidly, and for practical purposes is complete in 3 minutes.

The Contraction of Cotton under the Mercerisation Treatment.—The contraction of cotton *yarn* in relation to temperature and concentration of solution is shown in the table below.

CONTRACTION PER CENT. OF COTTON YARNS ON MERCERISATION

Temperature °C.	Concentration of Sodium Hydroxide Solution.											
	10 per cent.			19 per cent.			24 per cent.			29 per cent.		
	Duration of Mercerising in Minutes.											
	1	10	30	1	10	30	1	10	30	1	10	30
2°	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°	8	8·8	11·8	19·2	20·1	21·1	22·5	22·5	22·5	23·5	23·0	21·0
30°	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°	3·5	3·7	3·8	13·7	14·2	15·5	15·5	15·5	15·5	15·5	15·5	15·4

From Gardner, " Die Mercerisation der Baumwolle ".

The relation between the contraction and the concentration of alkali employed is illustrated by the following results obtained[1] with hanks of cotton yarn of an original length of 200 yards.

Concentration of NaOH : °Tw.	0	1	2	3	4	5	6	7	8	9	10
Contraction per cent.	1·0	1·7	2·1	2·2	2·2	2·4	2·9	3·1	2·9	3·0	2·9

Concentration of NaOH : °Tw.	12	14	16	18	20	22	24	26	28	30
Contraction per cent.	2·7	3·6	4·8	5·6	6·6	14·3	18·4	19·8	20·0	20·9

Concentration of NaOH : °Tw.	35	40	45	50	55	60	65	70	75	80
Contraction per cent.	24·9	28·1	29·5	28·9	28·6	27·3	25·4	24·8	23·6	22·9

[1] J. Huebner and W. J. Pope, *J. Soc. Chem. Ind.*, 1904, **23**, 404.

The increase observed at 20° to 22° Tw. is very marked. The maximum contraction takes place at about 45° Tw.

The contraction undergone by the single cotton hair during mercerisation has also been studied.[1] The hair length was measured under a tension of 50 mg. in each case with the apparatus of Barratt,[2] in which the change in length is magnified about 200 times. The results show—(i) that penetration into the hair is very rapid; (ii) that contraction begins at 22° Tw., and that very great contraction takes place at 30° Tw. and 35° Tw.; (iii) sodium hydroxide solution at 60° Tw. penetrates very slowly, and the time-contraction curves obtained at this strength are abnormal. (iv) The contraction produced by very strong solutions is quite small, the contraction at 86° Tw. being negligible.

The Absorption of Alkali Hydroxide and of Water during Mercerisation.—This problem has been the subject of numerous researches. The early methods employed, *e.g.*, by Gladstone,[3] consisted in treatment of the cotton with sodium hydroxide solution, washing out the excess with absolute alcohol, and then estimating the amount of NaOH remaining in the cotton after drying. The assumption that alcohol is an indifferent solvent, removing only uncombined alkali, is not, however, justified.

Vieweg[4] avoided this difficulty by estimating the amount of NaOH in the solution before and after treatment. He calculated the amount fixed by the cotton from the difference, on the assumption that no water was removed from solution by the cotton. This is not accurate, but it has been found that the general correctness of Vieweg's results is not seriously affected.[5] His absorption curve shows breaks at concentrations of 16 and 24 g. NaOH per 100 g. of solution, and over this range of 16 to 24 per cent. NaOH the absorption is approximately constant, and the breaks seemed to indicate the formation of compounds $(C_6H_{10}O_5)_2$. NaOH and $(C_6H_{10}O_5)$. NaOH. Leighton, taking into account the relative adsorption of water and alkali by cotton and using both gravimetric and titrimetric methods, found a marked difference between the two curves obtained, and considered that the true adsorption curve must lie between them. His curve does not show the inflections previously obtained, but some of the assumptions made are also not justified.

Further work by Vieweg and by Heuser[6] apparently confirmed

[1] R. S. Willows, T. Barratt and F. H. Parker, *J. Text. Inst.*, 1922, **13**, 229T.
[2] T. Barratt, *J. Text. Inst.*, 1922, **13**, 17T.
[3] J. Gladstone, *Chem. Soc. Trans.*, 1853, **5**, 17.
[4] W. Vieweg, *Ber.*, 1907, **40**, 3876; *ibid.*, 1908, **41**, 3269.
[5] D. Clibbens, *J. Text. Inst.*, 1923, **14**, 217.
[6] W. Vieweg, *Z. angew. Chem.*, 1924, **37**, 1008, 1010.

the formation of the compound $(C_6H_{10}O_5)_2$. NaOH which exists in equilibrium in solutions containing 16 to 24 per cent. of hydroxide, but not in the aqueous alcoholic solutions obtained with the alcohol washing method. The other alkali hydroxides also react with cellulose in the same molecular ratio, $(C_6H_{10}O_5)_2$: M.OH. The respective compounds are stable in solutions containing 9 to 11 per cent. of lithium hydroxide, 25 to 35 per cent. of potassium hydroxide and 45–60 per cent. of caesium hydroxide. These ratios represent the limit of chemical combination observed, the higher ratio $C_6H_{10}O_5$: M.OH not having been confirmed (but see p. 92). The swelling of the fibres in various concentrations of alkali proceeds up to the point at which the compound is formed.[1]

Bancroft and Calkin, who have made both centrifugal and X-ray studies of the problem,[2] conclude, however, that there is no definite evidence for the formation in mass of compounds between alkali and cellulose. The results can be interpreted in terms of adsorption, and that part of Vieweg's curve between 16 and 24 per cent. NaOH, which appears to indicate a constant composition, results from a balance between the increase in the amount of alkali and the decrease in the amount of water adsorbed. The curve for the true adsorption of NaOH by cotton is a smooth one.

The X-ray evidence has connected these and other observations with the internal changes taking place in the fibre. When cotton is treated with NaOH of increasing concentrations, washed free from alkali and dried [3] the X-ray pattern is not altered by solutions up to about 12 per cent. NaOH. At 12·8 per cent. the pattern begins to change and at 14·3 to 14·4 per cent. NaOH an entirely new pattern has been produced. This indicates an intramicellar change whereby the interior surfaces become more accessible and allow for greater adsorption. The value of about 14·5 per cent. NaOH is also that at which maximum water absorption takes place (p. 89), and corresponds to the change of direction in the Vieweg diagram.

If the alkali is not washed from the fibres another X-ray pattern,[4] that of " soda-cellulose I, " is obtained. This occurs at 16 per cent. NaOH (Hess) or *ca.* 14 per cent. (Calkin). It would appear that only at and beyond the point of maximum swelling, when the whole of the internal surfaces becomes available for reaction, is extensive compound formation possible. The existence of two phases, cellulose and sodium cellulosate, has been postulated by Hess (*loc.*

[1] E. Heuser and R. Bartunek, *Cellulosechem.*, 1925, **6**, 19.
[2] W. D. Bancroft and J. B. Calkin, *J. phys. Chem.*, 1935, **39**, 1.
[3] J. B. Calkin, *J. phys. Chem.*, 1936, **40**, 27.
[4] K. Hess and C. Trogus, *Z. physik. Chem.*, 1929, **4**, 321 ; 1930, **11**, 381.

cit.), whereas Calkin considers that there is only one, *viz.* cellulose and adsorbed sodium cellulosate. The question is further discussed by Bancroft.[1]

The swelling of the fibres is explained by the fact that the alkali-ion entering carries the associated water with it and distends the cellulose. The ions of lowest atomic volume are associated with the highest number of water molecules, and it has been definitely confirmed [2] that maximum swelling occurs in solutions of the hydroxides corresponding with the fully hydrated ion. Thus with the lithium ion, which is considered to attract to itself 17 molecules of water, a maximum swelling was observed at 6·6 per cent. LiOH, the solution then containing 1 molecule of LiOH to 17 molecules of water. For the other hydroxides the corresponding ratios are : NaOH : $12H_2O$ (15·5 per cent.) ; KOH : $7H_2O$ (38 per cent.) ; RbOH : $6H_2O$ (49 per cent.). The value for NaOH (15 per cent.) has been deduced by Neale from his theory of swelling (p. 90).

The question of the amount of water absorbed by cellulose during swelling under the action of alkalis and salts has been investigated by several workers. By using a suitable centrifuge it has been shown that the interfibrillar liquid can be satisfactorily removed and the composition of the solid phase can then be determined.

Coward and Spencer [3] used a machine with a cage diameter of 8·2 cm., which was run up to 8,000 r.p.m. Samples of cotton weighing 8·5 g. were immersed overnight in 100 ml. of solutions of known composition. The mass was then centrifuged at 7,000 r.p.m. for 7·5 minutes. The amounts of water and NaOH removed from solution were calculated from the weight of dry cotton employed, the weight of the total centrifuged mass and the weight of the NaOH in it (estimated by titration).

The results, illustrated in the following table (*cf.* Fig. 19), show that there is a rapidly increasing absorption of water with increase of concentration of the solution up to 14·3 per cent. NaOH. Beyond this the total weight of solution increases more slowly and the rapidly increasing amount of NaOH absorbed is balanced by a rapid fall in the amount of water absorbed.

It appears that the swelling may be represented approximately by the calculated volume of the absorbed solution. This is shown in the last column of the table, from which it will be seen that from 14·3 per cent. NaOH up to an almost saturated solution (48·8 per

[1] *J. phys. Chem.*, 1936, **40**, 45.
[2] G. E. Collins, *J. Text. Inst.*, 1925, **16**, 123T.
[3] H. F. Coward and L. Spencer, *J. Text. Inst.*, 1923, **14**, 28T, 32T.

cent.) the increase of volume of 100 g. (*i.e.* about 62 ml.) of cotton is constant—*viz.* 177 ± 8 ml. This suggests, again, that the cuticle sets a limit to the swelling. Ordinary cotton retains about 50 per cent. of its weight of water after removal of excess water by the centrifuge. If mercerised with sodium hydroxide and thoroughly washed it retains up to 123 per cent., the amount varying with the concentration of the alkali employed.

Bancroft and Calkin [1] used a Foerst centrifugal machine giving 15,000 r.p.m. with a cup of 2·5 cm. radius. The force exerted was 6,300 times that of gravity, and under it wet cotton retained only 12 per cent. of water, less than half the amount it could absorb from

ABSORPTION OF WATER AND SODIUM HYDROXIDE BY COTTON (Coward and Spencer)

Concentration of Sodium Hydroxide Solution. Grams NaOH per 100 g. of Solution.	Weights absorbed in grams per 100 g. Cotton.			Composition of Absorbed Solution. Grams NaOH per 100 g. Solution.	Calculated Volume of Liquid absorbed by 100 g. of Cotton.
	Total.	Water.	NaOH.		
0·0	52·3	52·3	0·0	0·0	52·3
4·0	73·5	67·9	5·6	7·6	67·4
7·4	99·8	88·7	11·1	11·1	88·6
9·4	133·3	116·0	17·3	13·0	116·0
11·9	177·0	158·0	26·2	14·8	151·0
14·3	222·0	180·4	41·6	18·7	183·0
20·1	220·0	166·8	53·2	24·2	173·0
24·4	239·0	169·5	69·5	29·1	180·0
29·3	236·0	153·1	82·9	35·1	171·0
39·0	251·0	138·1	112·9	45·0	169·0
48·8	288·0	133·0	155·0	53·8	(184)

saturated water vapour. In the case of the cellulose-water-alkali system it was found possible to determine the exact point at which all the supernatant liquid was removed. Water absorption reached a maximum at about 16 per cent. NaOH, but the fixation of NaOH increased steadily with increasing concentration of the solution, the curves showing no evidence of compound formation.

It will be noted from the table above that with solutions of concentration up to 50 per cent. NaOH, the absorption of NaOH amounts to as much as 15 per cent. of the weight of the cotton, and is roughly proportional to the concentration of the alkaline solution. The absorption from very dilute solutions (0·1 per cent. NaOH and under), measured in the same way, is different: the preferential

[1] *Text. Research*, 1934, **4**, 371.

absorption of the sodium hydroxide closely follows the adsorption laws and agrees with the adsorption formula.

The swelling process in the case of regenerated cellulose was studied by Beadle and Stevens [1] using cuprammonium silk monofils, and by Neale [2] using sheet cellulose regenerated from viscose. The results of the former are given in the table on the opposite page, and in the curves (Fig. 19).

Beadle and Stevens immersed the skeins in alkali at varying temperatures, removed the surface liquid with blotting paper, and weighed the skein. The difference between this weight and that of the alkali absorbed, estimated by titration, gave the "hydration" or water absorbed. It will be seen that with a 9 per cent. solution at 5°, hydration is at a maximum.

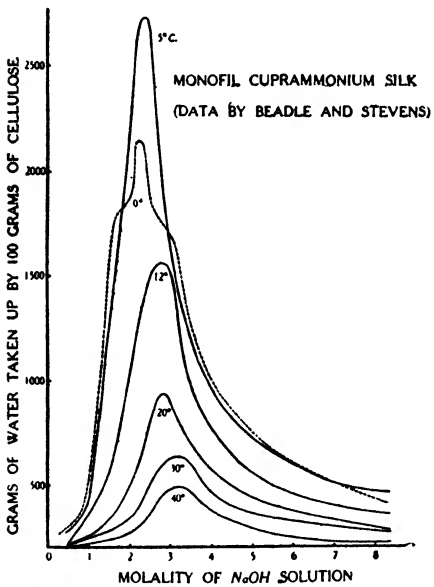


FIG. 19.—Absorption of water by cuprammonium silk from data by Beadle and Stevens (Neale).

The method used by Neale was to take a Cellophane sheet, about 5 cm. square, weighing about 0·2 g., which after washing is placed between filter papers to prevent crinkling and dried first at 80° and finally at 110°.

The sample is put into a bottle with 75 ml. of the sodium hydroxide solution and kept at 25° for 2 days. The swollen sheets are rapidly dried by blotting with filter paper and weighed in stoppered bottles to get the total swollen weight. The alkali absorbed is estimated by standard acid, and the cellulose sheets are washed for several days in water, dried and weighed.

A consideration of the results leads to the hypothesis [3] that cellulose behaves as a weak monobasic acid which forms a sodium salt, according to the law of mass action, to an extent which increases with the concentration of the alkali. Additional alkali is then

[1] C. Beadle and H. P. Stevens, *Proc. Eighth Int. Cong. App. Chem.*, 1912, **13**, 25.

[2] S. M. Neale, *J. Text. Inst.*, 1929, **20**, 373T; *ibid.*, 1930, **21**, 225T.

[3] S. M. Neale, *loc. cit.*

taken up by diffusion into the cellulose phase in an amount determined by Donnan's equation of membrane equilibrium. The unequal distribution of ions which results causes osmosis or movement of water, which distends the cellulose until the osmotic pressure is balanced by the cohesion forces of the gel. During washing with water the cellulose sodium salt is hydrolysed, the osmotic pressure

ABSORPTION OF WATER AND SODIUM HYDROXIDE BY CELLULOSE (after Beadle and Stevens)

Per cent. NaOH in Bath.	Hydration, Cellulose = 100.			Absorption of NaOH, Cellulose = 100.		
	At 5°.	At 20°.	At 40°.	At 5°.	At 20°.	At 40°.
1	217	182	167	3	3	3
2	279	217	192	8	8	8
3	324	241	216	16	14	14
4	426	280	224	24	16	16
5	615	300	230	42	22	17
6	1,380	310	238	83	25	20
7	1,960	380	240	150	36	25
8	2,576	562	261	224	56	30
9	2,699	758	338	256	74	38
10	1,800	920	440	210	98	56
11	1,483	861	458	182	110	66
12	1,310	719	480	170	112	72
13	1,200	620	412	161	102	76
14	1,003	558	360	142	96	78
15	798	500	334	132	88	74
16	762	458	310	128	84	72
17	715	420	300	124	82	71
18	658	400	280	122	82	70
20	590	360	240	110	84	72
22	540	325	220	114	86	73
25	461	280	220	120	86	76

falls, and the cellulose is recovered chemically unchanged, but permanently distorted if the osmotic pressure has been sufficiently high.

Equations have been deduced from this hypothesis by which, for example, the effect of temperature on the variation in the swelling pressure with concentration, can be calculated. The theoretical curves (Fig. 20) show that as the temperature falls the maximum osmotic pressure rises and the maximum occurs at a lower alkali concentration.

The theory accounts for the swelling, and also the fact that it is greater, and the optimum concentration is lower, at low temperatures. Taking the experimental values given above for the absorption of water, those of the sodium hydroxide can be calculated, as

shown in Fig. 21. The theory involves the assumption that the compound formed at high concentrations is $C_6H_9O_5Na$, and not $C_{12}H_{19}O_{10}Na$.

The heat of swelling of cellulose, which has been explained as due to a contraction of volume of the components, has been measured in connection with this hypothesis.[1] The results agree quite well with the assumption that salt formation between alkali and cellulose takes place according to the law of mass action, and, in fact, the ionisation constant of the regenerated cellulose used was determined and found to have the value $1{\cdot}84 \times 10^{-14}$ at 25°.

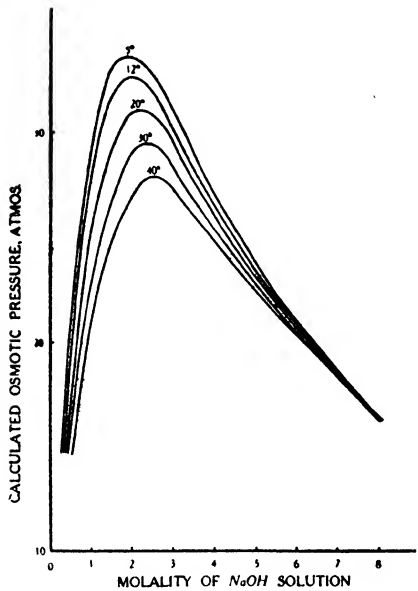


FIG. 20.—Showing variation of osmotic pressure with temperature calculated from the equations of Neale.

The pressure P required to expel the swelling liquid from the swollen substance may be calculated from the vapour pressure h of the swelling liquid by the following equation [2] :—

$$P = -\frac{dV}{di} \cdot RT \log. h$$

(V = sp. volume of the dry unswollen substance, i the amount of swelling liquid in grams absorbed by 1 g. of the dry substance). A close approximation is given by the relation

$$P = -1{,}200 \log. h$$

Neale [3] explains the swelling and mercerisation effects observed by him as follows: In the cotton hair the fibrillar micelles are arranged roughly parallel to the axis. When water is taken up, the hydroxyl groups on the long carbon chains attract water molecules, some of the secondary valence forces are broken and replaced by water-hydroxyl linkages, and the structure expands transversely. With alkali the sodium ions replace some of the hydroxyl hydrogen atoms and a system of high ionic concentration is set up. Water tends to enter this system (osmosis), and more secondary linkages between micelles are broken and replaced by

[1] S. M. Neale, *J. Text. Inst.*, 1929, **20**, 386T.
[2] *Cf.* H. Freundlich, *Kolloidchem. Beiheft.*, 1912, **3**, 442.
[3] *Loc. cit.*, 1929, **20**, 398T.

linkages with alkali or water. When the alkali-cellulose is washed with water the sodium and hydroxyl ions diffuse away, and as the osmotic pressure falls the gel contracts in virtue of its elasticity. Thereby hydroxyl-hydroxyl linkages are re-formed, but not in such numbers as before, and the orientation of the micelles in the mercerised product is more random than in the original cotton. The increased proportion of free hydroxyl groups in mercerised cotton accounts for the enhanced absorption of water and of dyestuffs, and increased heat of reaction with sodium hydroxide. The

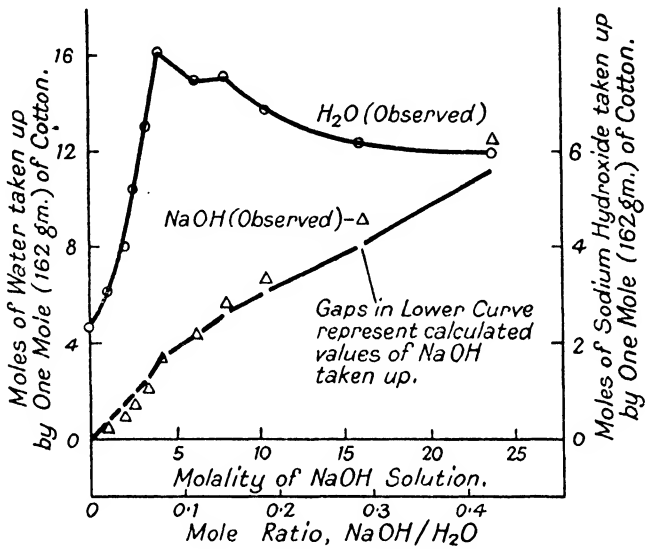


FIG. 21.—Values for the absorption of NaOH by cotton calculated from the data of Coward and Spencer for the absorption of water by cotton, by means of the equations of Neale. Comparison with observed values.

chemical reaction which is the ultimate cause of mercerisation, takes place reversibly, without splitting any of the primary valence linkages which hold the atoms of the micelle together, since the tensile strength [1] and viscosity in cuprammonium [2] are not affected (see table on page 94), nor are the reducing properties developed, which are characteristic of hydrolysis of the oxygen linkage between hexose residues.

Further references to the swelling of cellulose are :—

"The Swelling and Solution Processes of Cellulose and its Derivatives." K. Hess, *Papier Fabrik.*, 1929, **27**, 801.

[1] D. A. Clibbens, *J. Text. Inst.*, 1923, **14**, 217T.
[2] F. D. Farrow and S. M. Neale, *ibid.*, 1924, **15**, 157T.

" Micellar Theorie und Quellung der Zellulose." J. R. Katz, in Hess, *Die Chemie der Zellulose*, Leipzig, 1928, pp. 605–769.

" The Swelling and Degradation of Cotton Cellulose." S. M. Neale, *Trans. Faraday Soc.*, 1933, **29**, 228. J. R. Katz, *ibid.*, p. 279.

The Effect of Mercerisation on the Dyeing Properties of Cotton.— Mercerised cotton, from basic, sulphur, vat and substantive dyes, takes up some 40 per cent. more dyestuff than the original cotton. With mordant dyes some are more and some less absorbed ; with Turkey red there is practically no difference.

EFFECT OF MERCERISATION ON THE PROPERTIES OF SCOURED COTTONS [1]

Variety.	Fluidity.	Copper Number.	Methylene Blue Absorption.	Loss of Weight in NaOH boil per cent.
Egyptian sakel	3·68, 3·70	0·01	1·17, 0·96	1·32, 1·23
,, uppers	3·38, 3·34	before and	1·10, 0·95	1·20, 1·31
Tangiers .	3·47, 3·42	after.	1·24, 1·09	0·84, 1·28
Arizona . .	3·87, 3·67		1·35, 0·98	1·37, 1·30
Peru Mitafifi .	3·52, 3·21		1·03, 0·88	0·88, 1·00

The figures in each column give the values obtained before and after mercerisation.

Knecht [2] has shown that the amount of Benzopurpurine 4B fixed by mercerised cotton increases steadily with the concentration of alkali employed in mercerising, as shown in the table :—

NaOH per cent. in solution .	0	6·5	9·5	11	13	15·5	18	20	22·5	25	26·5	32
Dyestuff fixed per 100 g. . .	1·77	1·88	2·39	2·57	2·05	3·02	3·15	3·27	3·38	3·50	3·56	3·66

The results of Huebner and Pope [3] also show :—

(i) That cold NaOH solution of 1° Tw. considerably increases the affinity for substantive dyes, and from 0° to 18° Tw. the increased absorption roughly varies as the concentration of alkali. (It is interesting to note that boiling with a solution of NaOH of 1° or 2° Tw. has no effect on the dyeing property of cotton.)

(ii) From 18 to 22° Tw. increased dyestuff absorption increases with concentration of alkali more rapidly than under (i) ; it increases

[1] B. P. Ridge, H. L. Parsons and M. Corner, *ibid.*, 1931, **22**, 140T.
[2] E. Knecht, *J. Soc. Dyers and Col.*, 1908, **24**, 68.
[3] *J. Soc. Chem. Ind.*, 1909, **28**, 404.

again more rapidly with alkali at 22 to 26° Tw., and still more rapidly with alkali at 26 to 30° Tw.

(iii) Above 30° Tw. the increase in affinity gradually falls, and between 55° and 70° Tw is very slight, whilst above 70° Tw. there is a decrease in affinity, so that cotton mercerised at 80° Tw. has the same dyeing power as it would if mercerised at 35° Tw.

Methods of Experiment

The methods of investigations employed in this field may be inferred generally from the researches cited.

Methods of Mercerising.—Mercerisation without tension may be effected by working the yarn or loose cotton in the solution for 3 minutes. The temperature should be kept below 25°, and care taken to avoid local changes in the concentration of the solution.

Tension may be applied either (*a*) during the whole time of treatment with sodium hydroxide and subsequent washing out of the alkali, all shrinking being prevented, or (*b*) after the alkali treatment, but before the alkali has been washed out, sufficient tension being applied to stretch the material back to its original length. The lustre is not produced unless tension is applied whilst the alkali-cellulose complex exists.

The tension needed under (*b*) is much greater than that required to maintain the original length during alkali treatment.

The following is a laboratory method that has been employed in mercerising under tension: A glass tube 1 m. long × 3 cm. in diameter is closed at the lower end by a rubber plug carrying a glass tap and a loop of nickel wire, and clamped vertically, the upper end being left open. A rope of yarn of 100 to 150 strands is fastened to the loop, brought out through the open end, and passed over a pulley, below which it is tied to a weight suitable to give the required tension. The weight is supported on blocks. The tube is filled with the alkali solution and the yarn allowed to shrink for 3 minutes. Tension is then applied by removing the blocks from the weight, and the yarn washed for 3 minutes. The tension is removed and that portion of the yarn which has been immersed all the time, is cut off and washed free from alkali. The tension used was 180 g. per strand of 15's yarn or equivalent, this being a usual mill practice.

Measurement of the Degree of Swelling.—The methods used may be, (1) estimation of the increase of weight, as in the examples given on pp. 89, 91. This is specially useful for sheet wood pulp; (2) measurement of the change in diameter and length of the fibres,

microscopically [1] or otherwise, as in the example below. Measurement of the swollen diameter of cottons has been used as a guide to quality.[2]

A simple method for measuring changes of thickness in films is given by Thiessen and Carius.[3]

Measurement of the Swelling Power of Rayon Threads.[4]— The threads of about 50 cm. long are suspended in the swelling liquid and the change of length observed.

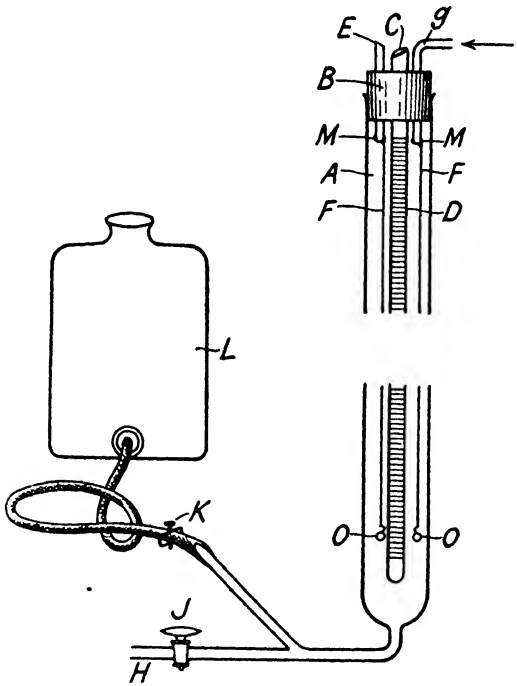


FIG. 22.—Apparatus of W. Weltzien for measuring the swelling of artificial silk threads. (From Faust's "Artificial Silk", by courtesy of Sir Isaac Pitman & Sons, Ltd.)

A glass tube A, Fig. 22, about 70 cm. long, is sealed on to a narrow tube bent at a right angle. This is attached by a Y-tube fitted with taps to a bottle L, containing the swelling solution, and to a supply of dry air. The large tube is closed by a rubber stopper which carries (*a*) a glass tube, C, sealed at the lower end,

[1] E. Heuser and R. Bartunek, *Cellulosechem.*, 1925, **6**, 19; A. Herzog, *Textil. Forsch.*, 1925, **3**, 10.

[2] R. Koshal and N. Ahmad, *J. Text. Inst.*, 1939, **30**, 63T.

[3] P. A. Thiessen and C. Carius, *Koll. Zeit.*, 1925, **36**, 245.

[4] W. Weltzien, *Textilberichte*, 1926, **7**, 338. See also O. Faust, "Artificial Silk," Pitman, London, 1929.

inside which is fixed a millimeter scale 50 cm. long, and (*b*) two or three glass rods with hooks, which support the silk threads.

The large tube is supported vertically. The lower end of each thread to be tested is weighted with a glass bead (say 0·4 g.) and the upper end is fixed to the glass hook. The threads, therefore, hang vertically parallel to the scale and their upper point of support is adjusted to the zero mark. Dry air is then passed through *g* into the large tube, then water, then sodium hydroxide solution, the length of the thread being observed in each case. The changes in length were observed over the following cycle :—

Dry→Water→Sodium Hydroxide solution→Water→Dry

Swelling. Contraction.

Some of the results obtained are shown in the curves (Fig. 23).

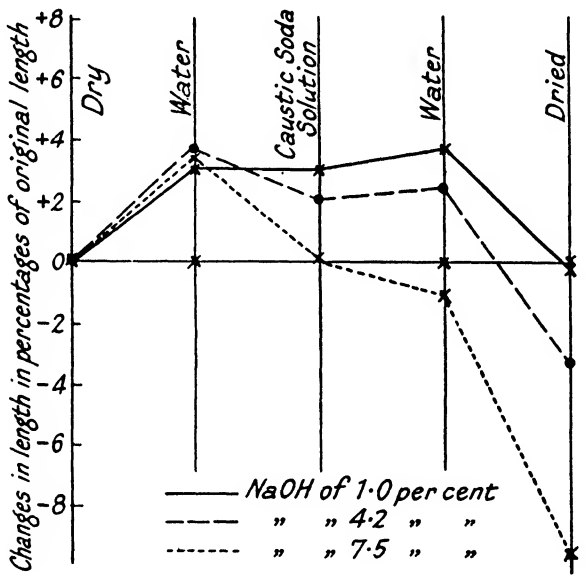


FIG. 23.—Changes in length of artificial silk threads (Weltzien). (From Faust's "Artificial Silk", by courtesy of Sir Isaac Pitman & Sons, Ltd.)

The Reactivity produced by Mercerisation.—The action of swelling agents on cellulose does not produce new properties, but results in an activation of the original ones. The increase in the value of any measurable quality is usually of the order of 1·5 to 1. A summary of these differences and their application has been given by Neale.[1] Of the practical measures of reactivity devised by him the increased absorptive power of mercerised cellulose for sodium

[1] S. M. Neale, *J. Soc. Chem. Ind.*, 1931, **50**, 177T.

and barium hydroxides has been found useful in the examination of cotton and of wood pulp. The following is a brief account of the method :—

The Baryta Absorption of Cellulose.[1]—The moisture regain, say r g. per 100 g. of dry material, is measured and $2(1 + \cdot 01r)$g. of the sample is taken and left, with shaking, for 12 hours in 30 ml. of $N/4$ barium hydroxide solution at 25°. 10 ml. are withdrawn and titrated with $N/10$ HCl, using methyl red.

The titre is corrected (very small) for the fact that the baryta is just below 25° and the acid at room temperature. The initial titre is corrected for dilution by the moisture in the sample. From

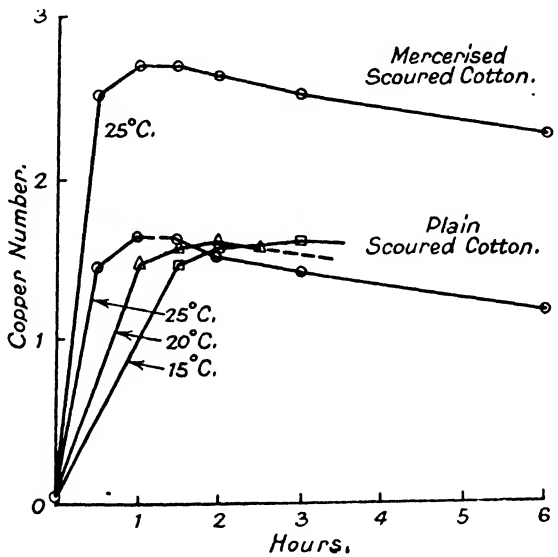


FIG. 24.—The increased activity of mercerised cotton towards sodium hypobromite.

the difference of the two corrected titres the amount of baryta absorbed by 2 g. of dry cellulose is obtained. This is corrected to the absorption anticipated for an end concentration of $N/5$ barium hydroxide by using a graph drawn from the following figures : Ml. observed, 0, 75, 118·6, 183, 226 become at $N/5$ — 0, 71, 119·6, 201, 270 respectively. The corrected absorption in milliequivalents per 162 g. of cellulose, divided by 71, gives the absorption ratio relative to cotton.

Absorption of NaOH is measured in the same way for 2 hours at 25° using 2 g. to 30 ml. of $N/2$ NaOH. The value is corrected as above to an end concentration of $N/2$ from the following figures :

[1] S. M. Neale, *J. Text. Inst.*, 1931, **22**, 356T. See *ibid.*, p. 328, for sodium hydroxide absorption, and *ibid.*, 1933, **24**, 30T for absorption from mixed alkalis.

Ml. observed, 0, 44, 72·5, 114·5, 138 require the addition of 0, 1·6, 3·4, 8·7 and 11·3 ml. respectively.

Reactivity of Cellulose by Hypobromite Oxidation.—Another type of reactivity is illustrated in the diagrams of Fig. 24 which show that the rate of oxidation with sodium hypobromite is more rapid with mercerised cotton than with normal cotton, yet it follows a parallel course. As maximum copper number is attained in 2 hours, and the value is practically independent of temperature, a convenient method for measuring reactivity is based on this reaction.[1]

A stock solution (A) containing 14·4 g. $KBrO_3$ and 60 g. KBr per litre is prepared. To make 1 litre of hypobromite solution (B) 200 ml. of A in a 1 litre measuring flask, are mixed quickly with 200 ml. N-H_2SO_4 and the stopper tied down. After standing, the liquid is cooled and 250 ml. $2N$-NaOH rapidly added. The solution is cooled and diluted to 1 litre. It is very nearly $N/10$ in oxidising value and in free NaOH. It should be used within 24 hours and the strength checked.

For the estimation 2·5 g. of air dry material is treated with 100 ml. of B in a 200 ml. bottle. The mixture is shaken occasionally, over 1·5 hours if temperature is 20 to 25°, or 2 hours if 15 to 20°. The cellulose is filtered off, washed with water, dilute H_2O_2, water, $N/10$ H_2SO_4, and with water till neutral, and then pressed. The copper number is taken without drying or weighing. The value divided by 1·5 is called the reactivity ratio.

All types of normal cotton give copper numbers of about 1·5, so that their reactivity ratio becomes unity. The ratio for cotton mercerised under various conditions ranges from 1·2 to 1·6.

A summary of the values obtained by different methods is given in the following table referred to normal cotton as unity (Neale).

ACTIVATION RATIOS OF MERCERISED COTTON

NaOH used in mercerising g./100 g. soln.	Water Vapour	Alk. NaBrO	5 per cent. H_2SO_4	Benzopurpurin	0·5N NaOH	0·2N $Ba(OH)_2$
10	1·1	1·1	1·1	—	1·2	1·2
12·5	1·4	1·3	—	—	1·9	1·9
15	1·6	1·6	1·7	—	2·3	2·4
20	1·5	1·6	—	2·2	2·4	2·6
25	1·6	—	2·2	—	2·5	2·6
32·5	1·6	—	2·2	—	2·6	2·8

Column 1 gives the ratio of moisture content to that of the original cotton (6·2 per cent.). Column 3 gives the hydrolysis figure of Schwalbe (p. 28).

[1] C. Birtwell, D. Clibbens *et al.*, *J. Text. Inst.*, 1930, **21**, 85.

Tests for Mercerised Cellulose

1. *Reactions with Iodine.*—On treatment with iodine solutions and subsequent washing, mercerised cotton retains a bluish-black colour, whilst normal cotton gradually becomes colourless. Suitable methods are—

(*a*) 20 g. of iodine in 100 ml. saturated KI solution. Immersion for 3 seconds.

(*b*) 1/100*N*-iodine solution ; mercerised cotton after immersion and washing shows colour dependent on the concentration of alkali used in mercerising.

(*c*) 280 g. zinc chloride in 300 ml. of water. To 100 ml. of this 20 drops of a solution of 1 g. of iodine and 20 g. of KI in 100 ml. of water are added. The colours shown by this reagent are given in the table, p. 101.

2. *Dyeing Tests.*—The reaction with Benzopurpurin is characteristic. The test is carried out as follows :—

(*a*) A normal and a mercerised cotton are dyed in a dilute dye bath of Benzopurpurin 4B (pure and free from safranine, etc.). Hydrochloric acid is added till the normal cotton is just turned blue. The mercerised cotton remains red.

(*b*) 5 ml. of Benzopurpurin 4B (0·1 g. per litre) are added to 100 ml. of water. After dyeing, titanous chloride is added to the boiling liquid till an acid reaction is obtained. Cotton remains blue-black and mercerised cotton red.[1]

Another method of differentiating depends upon the fact that mercerised cotton does not acquire any increased affinity for dyestuffs if treated with alkali. Three solutions are prepared : (*a*) Sodium hydroxide of 40° Bé ; (*b*) the same solution diluted 1 : 1 ; (*c*) the solution (*a*) diluted with three times its volume of water. The cloth is spotted with these three solutions, washed, treated with dilute H_2SO_4, and again rinsed. The piece is then dyed with Congo red. If originally mercerised, the spots show no more colour than the surrounding cloth. The following test is also satisfactory :—

3. *Sulphuric Acid-Formaldehyde Test for Mercerised Cotton.*[2]—Cellulose when immersed for 5 minutes in sulphuric acid solutions containing formaldehyde is partially converted into methylene ethers [3] which swell with water and dye deeply with direct dyestuffs. Cotton, after mercerisation, under the same treatment combines with an amount of formaldehyde about 1·4 times greater than that fixed by the original cotton. The reagent is prepared by mixing

[1] A. B. Knaggs, *J. Soc. Dyers and Col.*, 1908, **24**, 112.
[2] H. Mennell, *J. Text. Inst.*, 1926, **17**, 247T.
[3] F. C. Wood, *J. Soc. Chem. Ind.*, 1931, **50**, 412T.

320 ml. of sulphuric acid (120° Tw.) with 260 ml. of formaldehyde (40 per cent.). The sample (together with standard samples of cotton mercerised and unmercerised) is immersed in the reagent for 2 minutes at room temperature. The samples are washed, neutralised with hot dilute sodium carbonate and then dyed with a substantive dye—*e.g.* Chlorazol Sky Blue GW made alkaline with sodium carbonate. If the unmercerised cotton is dyed to about 0·1 per cent. absorption (on the weight of cotton), the mercerised will show a depth of colour equivalent to a 0·8 per cent. dyeing. The depth of shade gives an indication of the degree of mercerisation.

Dyed samples of material can be stripped with hypochlorite or hydrosulphite without interfering with the test.

Examination of Mercerised Cellulose in order to Determine the Concentration of Sodium Hydroxide employed in Mercerising

1. The zinc chloride-iodine solution of Huebner[1] was recommended by him for this purpose, the colours being characteristic. The process may be followed from the table below.

Colours given by Cotton Mercerised at various Alkali Concentrations with Zinc Chloride-Iodine Reagent (J. Huebner.)

NaOH Solution °Tw.	20 Drops of Iodine.*	10 Drops of Iodine.*	5 Drops of Iodine.*
0	Slight red tint	Remains white	Colourless
10	Faint red	Very faint brown	,,
20	Dark chocolate	Darker brown	,,
23	Darker and bluer	Darker and bluer	,,
26	Much darker and bluer.	Much darker and bluer.	,,
30	Dark navy blue	Darker reddish-blue	Faint blue
40	Black	Much darker	Bluer
50	Black	Still darker	Darker blue

* For 100 ml. of the zinc chloride reagent.

2. *A Simple and Reliable Test for Mercerisation.*[2]—This method has advantages over the previous one and requires no comparison samples. It will indicate, if allowances are made for the nature of the material (cotton or linen, yarn or cloth), the concentration of the alkali employed in mercerising.

[1] J. Huebner, *J. Soc. Chem. Ind.*, 1908, **27**, 110.
[2] R. W. Kinkead, *J. Text. Inst.*, 1926, **17**, 213T.

A cutting of the material is soaked for a few minutes in cold methylene blue solution (*ca.* 0·001 per cent.) containing 0·5 per cent. of Na_2CO_3. It is then rinsed and covered with about 10 ml. of a 3 per cent. Na_2CO_3 solution for linen, or a 1 per cent. solution for cotton. Four drops of iodine solution are then added (1 g. of iodine, 20 g. KI to 100 ml.). The liquid is heated rapidly to boiling-point, poured off, and at once replaced by fresh cold Na_2CO_3 solution of strength previously used. Mercerised material becomes reddish-purple; unmercerised remains blue or greenish. The following colours were observed in three-quarter bleached flax line :—

Sodium Hydroxide Solution Degrees Tw.	Colour Change.
0	Bright blue, no change.
20	Slightly more red.
30	Definitely more red.
40–50	Full purple.
60–70	Rather more blue than 50°.

Preliminary removal of dyestuff does not affect the test.

3. *The amount of Benzopurpurin 4B* fixed varies with the concentration of alkali employed in mercerisation, as shown in the figures of Knecht, p. 94.

4. *The hygroscopic moisture content* runs parallel with the degree of mercerisation as indicated by other properties. The following values are given for cotton mercerised without tension. The samples were dried at 60°, conditioned and dried for 8 hours at 100°.[1]

Mercerised in NaOH at °Tw.	0	10	20	30	40	50	60	70
Moisture per cent. . .	6·20	6·37	6·68	8·40	9·41	9·43	9·57	9·69

The term Mercerisation Ratio has been introduced to describe the ratio of the moisture content of the mercerised to that of the original soda-boiled cotton. Using the vacuum-desiccator method of drying, it has been found (*a*) that the mercerisation ratio is independent of the humidity, (*b*) that the variations in the water-fixing power of cotton mercerised at different alkali concentrations, are strikingly similar to the variations in dimensions of the hairs. For example, cotton mercerised in solutions of 15 per cent. NaOH or 28 per cent. KOH, which are known to cause maximum swelling, also shows maximum hygroscopicity.[2]

[1] S. H. Higgins, *J. Soc. Chem. Ind.*, 1909, **28**, 188.

[2] A. R. Urquhart and A. M. Williams, *J. Text. Inst.*, 1925, **16**, 155T; A. R. Urquhart, *ibid.*, 1927, **18**, 55T.

Metallic Salts as Dispersing Agents

von Weimarn considers that all salts that are fairly soluble in water will cause cellulose to swell and dissolve if the correct conditions of temperature, pressure, concentration and time of action are obtained. The results of a number of observers [1] seem to show that the dispersion of cellulose in saturated solutions is a function of the hydration of the ions of the salt. Their specific effect increases in the following order :—

K, Na, Li, Ba, Sr, Ca, SO_4, Cl, Br, I, CNS.

Cellulose is rapidly dispersed in boiling saturated solutions of the halides and nitrate of lithium ; calcium bromide, the iodides of sodium, strontium and calcium, and the thiocyanates of calcium and manganese. Calcium thiocyanate is particularly effective. One per cent. of cellulose dispersed by heating in its solutions forms a clear jelly on cooling.

The solvent action of the thiocyanates has been studied by Williams,[2] who found that a definite balance between the boiling-point, the viscosity and the heat of dilution of the solution of a particular salt must be fulfilled, otherwise solution of the cellulose cannot take place. Thus no solution will take place unless the boiling-point of the thiocyanate solution is above 133°. It must also have a positive heat of dilution not greater than 3,500 calories, and its viscosity must be at least 3·3 times that of water at 20°. In the case of lithium thiocyanate solutions, the correct viscosity is not attained until the concentration of the solution is such that the boiling-point is 165°. The addition of substances such as thiourea, which increase the viscosity without altering the heat of dilution, enables the concentration of the lithium salt to be reduced until the b.p. is about 135°, solution still taking place. A neutral calcium thiocyanate solution, b.p. 133°, dissolves cellulose at 90°. Acids, *e.g.* acetic acid, increase the solvent action, while alkalis inhibit it. A thiocyanate solution of b.p. 140° may be mixed with an equal volume of a solution of calcium chloride of b.p. 140° without altering the solvent power of the thiocyanate. Such a mixture can dissolve 70 g. of cotton or pulp per litre, and threads, vulcanised fibre, etc., can be prepared from it. The regenerated cellulose, however, is modified even when neutral salt solutions are employed.

The solvent action of chlorides has long been known. Cross and Bevan found that cellulose dissolves to a syrupy solution when it is

[1] *E.g.* F. Beck, *Z. angew. Chem.*, 1921, **34**, 113.

[2] H. E. Williams, *J. Soc. Chem. Ind.*, 1921, **40**, 221T ; quoted fully in C. F. Cross and C. Dorée, ' Researches on Cellulose ', IV, London, 1921.

saturated with a 40 per cent. solution of zinc chloride and warmed. Dilution with water gives a white mass containing about 20 per cent. of ZnO, which can be extracted by hydrochloric acid. Filaments have been prepared from similar solutions in the halides of zinc or bismuth, or mixtures of them.

The solvent power of chlorides is increased by employing them in concentrated hydrochloric acid solution.[1] The chlorides of antimony, bismuth, mercury, tin (stannic) and titanium are very effective, whilst those of cobalt, gold, cerium and chromium act as moderately good solvents in the presence of hydrochloric acid.

Regenerated Cellulose—Rayons

The manufacture, properties and identification of the various types of rayon have been adequately treated in a series of works, some of which are mentioned in the Appendix.

It will suffice, therefore, to quote values obtained for the measurable characters of rayons,[2] which are useful as indicating what may be required in an investigation of a particular sample or of a particular process of manufacture.

The measurements being made by the standard methods of the British Cotton Industry Research Association may, in a sense, replace the scattered determinations by various observers and processes which are found in the literature. The names of the different types are given in the original paper from which the table on p. 105 is abridged.

The values for the copper number and alkali solubility of cellulose in the early stages of modification by acids or oxidants have been found (p. 38) to vary proportionally to one another. The figures given show that the regenerated celluloses, viscose and cuprammonium rayons, are very similar, chemically, to oxycelluloses of the same copper number. The ratio of alkali solubility to copper number, in fact, has approximately the same value, about 8, for all the rayons. The methylene blue absorption values enable some light to be thrown on the origin of the rayon. The high absorptions of the Lilienfeld and staple fibre products are probably due to combined sulphuric acid. The former were prepared by spinning viscose into sulphuric acid of 50 to 85 per cent. strength. It has already been explained how the high absorption of methylene blue due to oxidising attack can be differentiated from that due to the action of acids when the conditions have been such that acid is retained in com-

[1] H. G. Deming, *J. Amer. Chem. Soc.*, 1911, **33**, 1515.
[2] B. P. Ridge, H. L. Parsons and M. Corner, *J. Text. Inst.*, 1931, **22**, 117T.

bination (*e.g.* steeping in sulphuric acid of concentration above 50 per cent.). This is done by means of a second dyeing in a solution at *p*H 2·7. In this hydrocelluloses show only a small decrease, or even an increase in absorption, whereas oxycelluloses show a marked decrease. It was found that a fall did, in fact, take place with all the materials examined (Lilienfeld-Durafil, Vistra and Fibro (staple fibres), and viscose silk (A quality)) except with Lilienfeld's Tenasco, in which no significant change was produced. This evidence for the presence of combined sulphuric acid in the yarn was confirmed by the observation that Tenasco was the only yarn in which the sulphur content was not reduced by washing with acid and water.

THE MEASURABLE QUALITIES OF COMMERCIAL RAYONS
(Ridge, Parsons and Corner, 1931)

	Copper Number.*	Loss on boiling † in 1 per cent. NaOH per cent.	Methylene Blue Absorption.‡	Fluidity, 2 per cent. Solution.	Per cent. Ash.	Ash Alkalinity.
Viscoses (17 types) Average	1·0	7·0	1·8	10·0	0·2	—
Viscoses (17 types) Extremes	0·8–1·5	5·8–7·4	1·3–2·3	8·0–14·2	0·06–0·4	1·0–5·0
Staple fibre (2 types)	0·9	8·5	2·5–4·5	4·2–9·7	0·24–0·43	5·5–6·1
Lilienfeld (3 types)	0·8–1·5	11·6	2·1–2·5	2·9–6·3	0·2	2–3
Cuprammonium (7 types)	0·5–1·5	6·7–9·7	1·3–2·2	3·1–7·2	0·08–0·35	2–5
Nitrocellulose (1 type)	2·7	19·4	2·0	16·7	0·43	—
Cellulose Acetate (4 types)	3·0	45·7–48·3	0·8–1·2	53–54	0·09–0·16	2·3–2·6
Esterified Cotton (2 types)	1–1·2	8·0	1·5	4·5–5·8	0·25	4·5–5·3
Cotton Linters (bleached)	<0·5	*c.* 1·5	0·8–1·1	1–4	—	—

* Schwalbe-Braidy. † One hour. ‡ Buffered to *p*H 7.
Values are also recorded for the percentage content of sulphur, copper and iron in each case.

CHAPTER VI

OXYCELLULOSE

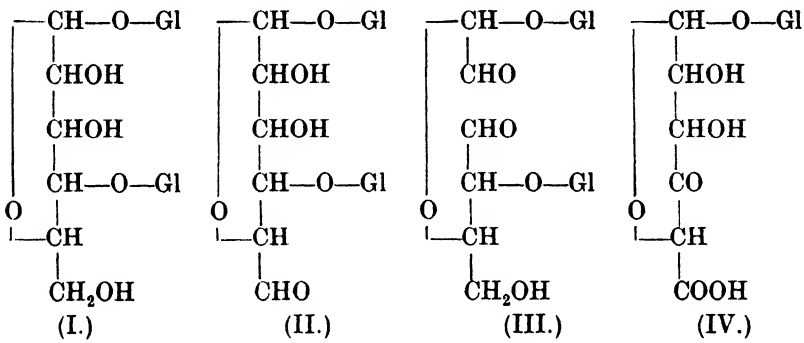
CELLULOSE fibres, when treated with oxidising agents in acid, alkaline or neutral solutions, invariably become tendered. The development of other characteristic properties associated with oxycellulose formation, depends upon the conditions of oxidation. Oxycelluloses prepared in neutral or acid solution may, in general, be described as of the reducing type. They have a high copper number and a low methylene blue absorption value. Those prepared by the action, for example, of alkaline hypobromite solution have the opposite properties, a low copper number and a high methylene blue absorption value. The tendering due to oxidation may not become very apparent until the fibres are treated with alkali. It was observed by Jenmaire in 1873 that vegetable fibres are not appreciably affected by immersion in acid dichromate solutions, but subsequent treatment with hot alkalis produced a considerable loss in strength. Witz,[1] indeed, distinguished oxycellulose from hydrocellulose in that the former, after treatment with alkali, showed a much greater loss of strength than the latter. Measurements which are given on p. 161 illustrate this. There is, however, a considerable resemblance in properties between hydrocelluloses and the reducing oxycelluloses prepared in acid solution. On the other hand, the oxycelluloses of the non-reducing type differ in many respects and stand in a class apart.

The observation of Jenmaire has assumed importance in recent attempts to explain the changes taking place during the oxidation of cellulose. Thus the non-reducing oxycelluloses (alkali hypobromite, alkali and neutral hypochlorite), and also hydrocellulose, at any given fluidity show a considerable and almost equal loss in strength (*cf.* p. 162), while acid-dichromate oxycelluloses, for example, of the same fluidity, show a reduction in strength which is very much less (p. 164). After boiling in alkali, however, the oxycelluloses of the first group suffer only a moderate further loss, while the dichromate oxycelluloses suffer a considerable one, so that on balance the relation between loss of strength and fluidity for all modifications, however prepared, becomes the same.[2] There is thus, in the acid-dichronate oxycelluloses, a latent or potential

[1] G. Witz, *Bull. Soc. Ind. Mulhouse*, 1883, **43**, 334.
[2] D. Clibbens and B. P. Ridge, *J. Text. Inst.*, 1928, **19**, 389T.

loss of strength revealed only by increase in fluidity, which, however, becomes apparent after treatment with alkalis.

The general loss in strength, accompanied by increase in fluidity and solubility in alkalis, is no doubt due to a resolution of the long cellulose chains into shorter units. The oxidation of the primary alcoholic groupings (I) to aldehydic (II) and later (IV) to carboxylic groupings is generally held to account for the development of reducing properties and for the presence of acidic (uronic acid) groupings respectively. The isolation of glucuronic acid from an oxycellulose has been accomplished, and this unit gives rise to the furfural and carbon dioxide observed on hydrolysis (p. 118).



If the decrease in tensile strength and increase in alkali-solubility is a function of the diminution in average chain length, it might be expected that all methods of modification would lead to the same relation between strength and fluidity. The properties of the acid-dichromate and periodate oxycelluloses, which render this generalisation true only after a "levelling up" treatment with boiling alkali, have been explained [1] in the following way: It is, at first sight, difficult to understand why oxidation should bring about the reduction in chain length which is so easily effected by acid hydrolysis. It is necessary to assume that the action of an oxidising agent does not initially lead to a rupture of the chain molecules, but by reaction at centres adjacent to the glucosidic linkages it renders these abnormally sensitive, particularly to alkaline hydrolysis. When oxidation takes place in an alkaline medium, hydrolysis, with shortening of the chains, also takes place and the relation between the strength and fluidity of the product is similar to that observed with the hydrocelluloses formed by direct acid hydrolysis (p. 163). Oxidation in an acid medium, on the other hand, is limited to the development of aldehydic and carboxylic groupings, and to the

[1] G. F. Davidson, *J. Text. Inst.*, 1934, **25**, 174T; *ibid.*, 1936, **27**, 144T.

formation of alkali-sensitive points. The strength of the modified cellulose is not greatly lower than that of the original cotton, although the fluidity in cuprammonium is increased to an amount which should correspond to a considerable loss in strength (p. 137). This anomaly is explained by the alkalinity of cuprammonium which is sufficient to act on some of the alkali-sensitive points and cause a reduction in chain length.

Boiling with alkali leads in most cases to complete reaction of all the alkali-sensitive points and accounts for the further loss in strength observed.

The above explanation is supported by measurements of the fluidity of the oxycellulose nitrates prepared under conditions which are believed not to affect chain length.[1] Modified cellulose samples, each with an original nitrate fluidity of 20, were prepared. This value was almost unaltered after boiling with alkali in the cases of hydrocellulose and alkaline hypochlorite oxycellulose, but became 100 with a dichromate-sulphuric acid oxycellulose and 150 in one prepared with dichromate-oxalic acid.

The relation between strength and nitrate fluidity also is much more nearly the same for all types of modification than is the relation between strength and cuprammonium fluidity (Fig. 41, p. 152).

The solubility (p. 37) of an oxycellulose in dilute sodium hydroxide also bears a definite relationship to the cuprammonium fluidity due, no doubt, to the fact that both are functions of the frequency distribution of chain length. The solubility-fluidity relation should then be independent of the method of modification provided that (*a*) the various chemical agents all produce the same type and proportion of rupture in the chains, and (*b*) that the dilute alkali used for solubility determination has the same effect as cuprammonium in opening up the alkali-sensitive linkage. The behaviour of modified oxycelluloses which do not contain alkali-sensitive centres, and of all types after boiling with dilute alkali, seems to demonstrate the validity of (*a*), but with regard to (*b*) the abnormal relationship between fluidity and solubility shown by acid and neutral hypochlorite and periodate oxycelluloses, indicate that the alkali used in solubility determination and the alkalinity of cuprammonium are not equally effective in the hydrolysis of the alkali-sensitive centres. It would appear [2] that in the case of periodate oxycellulose the cuprammonium hydrolyses weak linkages which are not resolved by the dilute sodium hydroxide employed, although these linkages could be resolved by more prolonged treatment with alkali. On the other

[1] G. F. Davidson, *J. Text. Inst.*, 1938, **29**, 195T.
[2] T. Brownsett and D. A. Clibbens, *J. Text. Inst.*, 1941, **32**, 25T.

hand, the abnormal rise in cuprammonium fluidity shown by acid and neutral hypochlorite oxycelluloses after treatment with dilute alkali, shows that cuprammonium does not resolve all the linkages which are broken by dilute alkali. The use of Triton F as a solvent in fluidity measurement avoids these abnormalities, since its action on the alkali-sensitive linkages is the same as that of dilute sodium hydroxide.

The development of reducing power (measured by copper number, etc.) and of acidity (usually associated with the fixation of methylene blue) is partly due to oxidation of the primary alcoholic group. Another possibility is revealed from a study of the action of periodic acid and of alkaline hypobromite on the alkyl hexosides. Jackson and Hudson [1] found that both reagents open the ring between carbon atoms 2 and 3, periodic acid producing the dialdehyde (III) and hypobromite the corresponding acid. With cellulose, periodic acid formed an oxycellulose of very high reducing power, which on hydrolysis gave glyoxal and erythrose. The formation of these scission products shows that here also ring opening has taken place between carbon atoms 2 and 3 without considerable oxidation of the CH_2OH grouping. Periodic acid oxycellulose (III) is thus the one example of an oxidised cellulose in which the position of the reducing centres is known.

Another explanation of oxycellulose formation [2] assumes that the oxidation of the primary alcoholic grouping precedes the hydrolysis and resolution of the cellulose chains. It is shown that if the hydroxyl groupings are fully acetylated cellulose is not attacked by permanganate at *p*H 11·2 and very slowly either by permanganate at *p*H 1 or by moist ozone. A further suggestion is made (*loc. cit.*) that by simultaneous hydrolysis and oxidation at C_4, a ketonic grouping could be produced (IV) in one or both of the fragments. All these causes may operate in oxycellulose formation.

A moderately oxidised cellulose may be regarded as an association of cellulose units with shorter-chain oxidation products. The prolonged action of such mild reagents as water, baryta, or sodium bicarbonate solutions removes these, leaving behind the less affected units of longer chain-length. The residue resembles the original cellulose, although it may differ in alkali solubility, viscosity, etc. Some experimental results will be seen in the table on p. 111.

Following the discovery of oxycellulose in 1883, a number of oxycelluloses with vaguely defined properties have been described.

[1] *J. Amer. Chem. Soc.*, 1937, **59**, 994, 2049; *ibid.*, 1938, **60**, 989.
[2] C. Dorée and A. C. Healey, *J. Text. Inst.*, 1938, **29**, 38T.

A summary of the literature to 1922 is available.[1] These products, in most cases, are highly oxidised, the fibres being disintegrated to powder form. They are generally insoluble in neutral reagents, but are more or less soluble in caustic alkaline solutions. The soluble portion usually exhibits reducing properties. Some of the oxycelluloses are sufficiently acidic to be soluble, wholly or partially, in sodium carbonate, ammonium hydroxide, pyridine and piperidine.

Modern work has been directed to a study of the earlier stages of the action of oxidising agents on cotton cellulose [2] and has resulted in the recognition of two types of oxycellulose—the acidic type characterised by great absorptive power for methylene blue and capacity for fixing alkalis, but with little reducing power, and the reducing type with high reducing power, low methylene blue value, and excessive loss of weight on boiling with alkalis. The second type, after alkali boiling, leaves a residue similar in chemical properties to the original cellulose. It has become clear that the production of one or other of these types is largely dependent on the acidity or alkalinity of the oxidising solution.

The types usually chosen for experiment, giving a range from the extreme acid (methylene blue) to the extreme reducing (high Cu No.) products are obtained by the action of (1) alkaline hypobromite, (2) alkaline hypochlorite, (3) acid hypochlorite (4) neutral hypochlorite, (5) dichromate and sulphuric acid, (6) dichromate and oxalic acid, (7) periodic acid.

I. Preparation of Typical Oxycelluloses by older Methods

In the following are given details for some of the more typical oxycelluloses that have been described. The details of the first four are taken from a paper by Hess,[3] who had occasion to prepare them according to the methods of the original authors. It was found that by successive extraction of these oxycelluloses with 5 per cent. sodium bicarbonate solution a residue of " cellulose " was obtained, identified chiefly by the rotation in cuprammonium.

(*a*) **Bromine-water Oxycellulose** (Faber and Tollens [4]).—100 g. of linters are shaken for 24 hours with 20 g. bromine and 30 g. $CaCO_3$ in 1·6 litre of water. This treatment is repeated twice more, after which the excess of bromine is removed. After washing (2 per

[1] P. H. Clifford and R. G. Fargher, *J. Text. Inst.*, 1922, **13**, 189T.

[2] C. Birtwell, D. A. Clibbens and B. P. Ridge, *Shirley Inst. Mem.*, 1924, **3**, 321 ; *J. Text. Inst.*, 1925, **16**, 13T ; *ibid.*, 1928, **19**, 349T.

[3] K. Hess and G. Katona, *Ann.*, 1927, **455**, 221.

[4] O. Faber and B. Tollens, *Ber.*, 1899, **32**, 2592.

cent. HCl, dilute acetic acid) the preparation is dried with alcohol. Yield, 79 g., somewhat soluble in water.

(*b*) **Permanganate Oxycellulose** (Nastjukoff [1]).—25 g. of linters are digested with 250 g. of 10 per cent. permanganate solution till the fibres disintegrate (36 hours). The mixture is decolorised with SO_2, filtered, the product washed with 2 per cent. sulphuric acid, with water, and then with methyl alcohol and ether. Yield (air-dry), 19·6 g.

(*c*) **Nitric Acid Oxycellulose** (Cross and Bevan [2]).—25 g. of linters are heated on the water bath for 1 hour with 75 g. of nitric acid (*d*, 1·3). The action is vigorous and the fibres disintegrate. The residue is washed and dried with alcohol and ether. Yield, 19·2 g.

(*d*) **Chromic Acid Oxycellulose** (Vignon [3]).—40 g. of linters are heated (water bath) for 3 hours with a solution of 60 g. of potassium dichromate and 80 g. of conc. sulphuric acid in 3 l. of water. The product is washed with 2 per cent. sulphuric acid, then with water, and dried with alcohol. Yield, 33·7 g.

The following table summarises the properties of these oxycelluloses :—

PROPERTIES OF OXYCELLULOSES PREPARED BY HESS AND KATONA

Method of Preparation.	Yield per cent. of original (air-dry weights).	Analysis.	COOH per cent.	$[\alpha]^{20}$ 435·8 *	Solubility in 2*N* NaOH per cent.	Loss per cent. in conversion to "cellulose" by sodium bicarbonate.	Solubility of this cellulose in 2*N* NaOH per cent.
(*a*) Bromine Aq. (Faber and Tollens)	79	C = 43·5 H = 6·1	1·2	— 3·23	26·8	8·3	12·5
(*b*) Permanganate (Nastjukoff)	78	C = 44·0 H = 5·6	0·9	— 3·28	33·8	5·1	21·9
(*c*) Nitric Acid (Cross and Bevan)	77	C = 43·7 H = 5·7	0·67	— 3·26	22·7	11·5	8·9
(*d*) Chromic Acid (Vignon)	84	C = 43·0 H = 5·2	1·06	— 3·11	40·5	15·3	10·8
Original Linters	—	C = 44·4 H = 6·2	0·43 0·22	— 3·39 to — 3·41	—	[α] 435·8 — 3·36 to 3·43	

* 4 mg. mole $C_6H_{10}O_5$, 10 mg. mole $Cu(OH)_2$, 20 mg. mole NaOH, 1,000 mg. mole NH_3 in 100 ml. of solution (*Ann.*, 1925, **444**, 296, 309).

[1] A. Nastjukoff, *Ber.*, 1901, **34**, 720.
[2] Cf. A. Nastjukoff, *Ber.*, 1901, **34**, 3589.
[3] L. Vignon, *Bull. Soc. Chim.*, 1898, [3], **19**, 811.

II. Preparation of Highly Oxidised Cellulose

(1) **A Permanganate Oxycellulose.**—Knecht and Thompson [1] pointed out that in some of the methods of preparation no account had been taken of the fact that caustic alkalis decompose oxycellulose into substances which have small reducing value, a portion of the product passing into solution. Other oxidation processes are accompanied by hydrolytic treatment, due to the action of hot mineral acids, and in general no attempt has been made to regulate and measure the proportion of oxidising agent consumed.

By the use of permanganate the authors claim that they avoid these disadvantages, and obtain an oxycellulose more active in aldehydic properties, and representing a very high state of oxidation. Their product has frequently been employed in subsequent investigations.

Oxidation of Cellulose with One Atom of Oxygen per $C_6H_{10}O_5$.—30 g. of filter paper is pulped in 600 to 900 ml. of NaOH of 15° Tw. The pulp, mixed with a slight excess of dilute sulphuric acid, is filtered, washed, and, while moist, suspended in 600 to 900 ml. of sulphuric acid of 10° Tw. and rapidly stirred.

12 g. of potassium permanganate (one atom of oxygen per $C_6H_{10}O_5$) is dissolved in the same sulphuric acid and added from a tap funnel over 1 to 2 hours. The solution becomes decolorised after 4 hours, and the pulp disintegrates to a finely divided brown mass. This is separated, suspended in dilute sulphuric acid and decolorised with hydrogen peroxide. The product is washed in water to remove acid and manganous sulphate. It is dried below 40° to prevent it forming a horn-like mass and to ensure a uniform pulp with water. Yield, air-dry, 94·5 per cent.

Oxidation with two atoms of oxygen per $C_6H_{10}O_5$ unit gave a similar but more gelatinous product.

Properties.—The product has no acidic properties, but its aldehydic reactions are very marked. It dyes a deep shade with Schiff's reagent and is very sensitive to alkalis, giving an intense yellow colour on boiling with $N/100$ NaOH, whilst with a 5 N-solution it gives a yellow colour in the cold. The yellow solution gives, on neutralisation, a precipitate of acid cellulose, which has very slight reducing properties, but a distinct affinity for methylene blue. The residue has no reducing properties, and behaves like cellulose, except that it is dyed by methylene blue.

The aldehydic properties are shown by combination with

[1] E. Knecht and L. Thompson, *J. Soc. Dyers and Col.*, 1920, **36**, 251. See also p. 135.

ammonia, hydrazines and hydrocyanic acid. The amount combining is high, *e.g.* 100 g. of oxycellulose took up 56 g. of nitrophenylhydrazine. When stirred with sodium bisulphite of 61° Tw., an increase of temperature is observed and the bisulphite is difficult to remove by washing.

The oxycellulose has a copper value of 14·2 (Schwalbe method). It reduces ammoniacal silver solution, and also the ferric ferricyanide reagent with the formation of Prussian blue in the cold. It reduces methylene blue in the presence of alkali to the leuco-compound. Rosinduline, indigo and indanthrene behave similarly.

Alkali Fractionation.—This oxycellulose has been further investigated.[1] It was prepared from linters with 0·25*N* permanganate and retained the fibrous form. It had copper number, 14; methylene blue absorption, 32; ash alkalinity, 7·9; loss on boiling in 1 per cent. NaOH, 44 per cent. It gave about 1·5 per cent. of furfural. Carboxyl content calculated from furfural 1·4; by CO_2 estimation 1·2, and by direct and by conductimetric titration 1·8 per cent.

It was fractionated by boiling with 0·25*N*-NaOH for 4 hours, when one-half remained insoluble. The insoluble portion was then boiled four times with 2·5*N*-NaOH when again one-half remained insoluble. The properties of the fractions are shown in the table. They acetylated readily like cellulose.

	Per cent. on Oxycellulose.	Cu No.	Uronic Acid per cent.	Yield of Glucose per cent. of Theory	Chain length. Glucose Units.
Oxycellulose . .	—	14	1·2	81	65
A. Sol. in 0·25*N*-NaOH	50	—	nil.	—	—
B. Insoluble „ „ .	50	0·27	—	90	90
C. Sol. in 2·5*N*-NaOH	25	0·23	—	—	35
D. Insoluble „ „ .	—	—	—	—	60

The chain-length determinations were done in several ways, and are approximate. Fraction A contained degradation products which were preferably isolated from the oxycellulose by extraction with 3 per cent. barium hydroxide. They included formic, acetic, lactic and dihydroxybutyric acids with a mixture of C_6-saccharinic acids.

(2) **Dichromate Oxycellulose.**—It has been shown[2] that when dichromate acts on cotton in the presence of oxalic acid the rise in copper number in a given time is very much greater (roughly 100

[1] G. L. Godman, W. N. Haworth, and S. Peat, *J. Chem. Soc.*, 1939, 1908.
[2] D. Clibbens and B. P. Ridge, *J. Text. Inst.*, 1927, **18**, 145T.

times) than it is when sulphuric acid is present. If small volumes of dichromate solution are added at constant temperature to an excess of oxalic-acid solution containing cotton, the copper number resulting is directly proportional to the amount of dichromate added. The relation between copper number and volume of dichromate is strictly linear and this affords a useful method of preparing an oxycellulose of known copper number.

10 g. of cotton in 300 ml. of $N/5$ oxalic acid are treated with x ml. of $N/25$ dichromate solution. This is repeated after each volume is completely reduced till the necessary oxidation is obtained.

(3) **Periodate and Ozone Oxycelluloses.**—These also have very high copper numbers. See pp. 138 and 141.

III. Miscellaneous Methods for the Preparation of Oxycellulose

(1) **Nitric Acid.**—The following table summarises some additional studies of the action of this acid, the temperature in each case being 95 to 100° :—

Observer.	Per cent. HNO_3.	Ratio HNO_3 (100 per cent.) to Cotton.	Time.	Yield per cent. (Insoluble Product).
(*a*) Bull . . .	60	6 to 1	24 hrs.	35
(*b*) Faber and Tollens .	47·5	3·3 to 1	2½ ,,	70
(*c*) Nasjukoff . .	47·5	1·2 to 1	—	90

Product (*a*) dissolved completely in aqueous solutions of ammonia, pyridine, sodium carbonate, and sodium hydroxide. It did not reduce Fehling's solution.

Product (*b*) dissolved in dilute alkalis and in ammonium hydroxide and strongly reduced Fehling's solution. Tartaric acid was observed as a by-product.

Product (*c*) dissolved in boiling ammonium hydroxide and gave a barium salt containing 5 per cent. of barium.

(2) **The Action of Hydrogen Peroxide.**—This was examined by Bumcke and Wolffenstein,[1] who considered that a new product was formed which they designated " hydral " cellulose. The properties of this substance are, however, very similar to those of an oxycellulose. Filter paper is treated with varying quantities of hydrogen peroxide until disintegrated (19 to 90 days at ordinary temperature). A typical product dissolves to the extent of one-third in boiling

[1] G. Bumcke and R. Wolffenstein, *Ber.*, 1899, **32**, 2493; 1901, **34**, 2415.

10 per cent. NaOH solution, giving what the authors describe as acid cellulose. The residue closely resembles cellulose.

(3) **The Action of Ozone.**—The action of ozone is described as an example of a neutral oxidising agent.[1] Ozone acting on moist cellulose at once produces acidity on the fibre, and carbon dioxide is continuously evolved. The residue shows the properties of an oxycellulose (see under (4)). The first stage of the action results in the formation of a cellulose peroxide probably an aldehyde-peroxide.[2] Cotton fibres and viscose silk threads after a short exposure to ozone are able to liberate iodine from potassium iodide and to produce their image on a photographic plate. Ammonium persulphate acts in somewhat the same way.[3]

(4) **Action of Ultra-violet Light.**—Dorée and Dyer[4] have shown that exposure for several days to the rays of an ultra-violet lamp results in the disintegration of the material and the production of an oxycellulose. The following table illustrates this, the properties of an oxycellulose prepared by the action of ozone being included :

	Unexposed Fabric.	Exposed Fabric.	Oxycellulose made by the Action of Ozone.
Loss of weight in 1 per cent. boiling NaOH per cent. :			
Five minutes	0·0	9·5	6·2
Sixty minutes	1·0	13·6	15·5
Copper number	0·62	4·0	8·0
Furfuraldehyde per cent. . .	0·20	1·34	1·5
Methylene blue absorption per cent. .	0·7	1·5	1·6

Numerous researches have been carried out on the action of light on fabrics in the presence and absence of oxygen, water-vapour, etc. With oxygen present, carbon dioxide is produced and the cotton acquires the properties of oxycellulose. Even when exposed in hydrogen the cotton acquires an increased copper number. A typical investigation in which the modern methods of measurement given in Chapter II are employed, is that of Barr and Hadfield.[5]

(5) **Electrolytic Oxidation.**—Oertel[6] prepared an oxycellulose by suspending cellulose in a neutral 15 per cent. solution of

[1] M. Cunningham and C. Dorée, *J. Chem. Soc.*, 1912, **101**, 497 ; C. Dorée and A. C. Healey, *J. Text. Inst.*, 1938, **29**, 27T.

[2] C. Dorée, *J. Chem. Soc.*, 1913, **103**, 1347.

[3] H. Ditz, *J. prakt. Chem.*, 1908 [ii], **78**, 343.

[4] C. Dorée and J. W. W. Dyer, *J. Soc. Dyers and Col.*, 1917, **33**, 17.

[5] G. Barr and J. H. Hadfield, Second Rept. of Fabrics Co-ordinating Committee, 1930, pp. 91–112.

[6] R. Oertel, *Z. angew. Chem.*, 1913, **26**, 246 ; *Diss.*, Hanover, 1912.

potassium chloride which was then subjected to electrolysis. The cellulose was gradually attacked, being finally converted entirely into soluble products. When 60 to 70 per cent. of the cellulose had been dissolved the residual oxycellulose was completely soluble in cold 10 per cent. NaOH solution.

IV. General Properties of Oxycellulose

The general properties associated with an oxycellulose may roughly be classified into three main groups :

A. Those connected with the presence of a carboxyl group ;
B. Those connected with the presence of a carbonyl grouping ; and
C. Those due to molecular chain shortening.

A. Reactions associated with the Carboxyl Grouping.—(i) *Acidity and its Measurement.*—The direct reaction of oxidised cellulose with alkali was formerly used. Schwalbe,[1] for example, employed two methods : (*a*) titration of the material, in water, with *N*/100 NaOH using litmus at ordinary temperature, or phenolphthalein at 80°, the figures being corrected for the alkalinity of the ash, and (*b*) estimation of the amount of barium taken up from a barium hydroxide solution. Results of these authors are given in the table on p. 119.

The direct method was also used by Schmidt [2] with conductimetric titration, and by Lüdtke,[3] who added an excess of calcium acetate before titration, with phenolphthalein as indicator. It has been stated,[4] however, that the direct titration method does not give a satisfactory end-point, " drifting " taking place for several hours, and since cellulose adsorbs or reacts with hydroxyl groupings in alkaline solution, exact results with indicators changing at *p*H values greater than 7 cannot be expected.

The following procedure (Neale, *loc. cit.*) gave good results with non-reducing oxycelluloses and hydrocellulose, stable end-points, lasting over 20 hours, being obtained.

The sample is freed from cations by steeping in cold 2*N*-HCl for 0·5 hour, and washing repeatedly with water till the washings are neutral to brom-cresol-purple (*p*H 5·2 to 6·8). One gram is treated in a stoppered flask with 20 ml. of 50 g./litre NaCl solution and 20 ml. of *N*/50 NaOH. After standing closed for 0·5 hour in the

[1] C. G. Schwalbe *et al.*, *Zellstoff u. Papier*, 1921, **1**, 100 ; *ibid.*, 1922, **2**, 75.
[2] E. Schmidt *et al.*, *Ber.*, 1934, **67**, 2037.
[3] M. Lüdtke, *Z. angew. Chem.*, 1935, **48**, 650.
[4] S. M. Neale and W. A. Stringfellow, *Trans. Faraday Soc.*, 1937, **33**, 881.

cold, four drops of brom-cresol-purple are added and the liquid titrated with $N/50$ HCl. Towards the end of the titration only, the liquid is boiled and a current of air free from CO_2 is passed through.

Heymann and Rabinov,[1] after a full review of existing methods, consider that the use of calcium acetate gives good results, comparable with those of Neale, provided that the cellulose is removed before titration. The concentration of the acetate solution is important, and although decinormal strength is not ideal, and must give results a few per cent. too low, it is recommended, giving what is called the " A " value.

5 g. of cellulose in a steamed-out glass jar with 100 ml. of, *e.g.* $N/10$ (or higher) calcium acetate is left in ice to attain the equilibrium

$$CaAc_2 + \text{Cell. acid} \rightleftharpoons 2HAc + \text{Ca cellulosate},$$

which is reached in 2 hours. The liquid is squeezed out of the fibre and aliquots titrated with baryta water free from carbonate (*ca.* $N/100$), using phenolphthalein.

A purified cotton made cation-free by treating with acetic acid followed by prolonged washing, gave an A value 0·84 ml. of $N/100$ alkali per 2 g. of cotton. A surgical cotton wool treated with $N/10$ HCl and washed till washings had the *p*H of the wash-water had ash-alkalinity zero ; acidity 0·41 ml. as above. A hypobromite oxycellulose treated with HCl to remove cations gave an A value 14·3 ml. as above.

Another method of measuring acidity is to determine the amount of basic ion, *e.g.* Ag or Ca, fixed by the cellulose from salts of the metal with weak acids. The procedure based on an extensive investigation,[2] is as follows :—

(*a*) Silver-binding capacity.—5 g. cellulose in 100 ml. of a silver-salt solution at 25° is left for 1 day to attain equilibrium. 50 ml. aliquots of the original solution and of the solution in equilibrium are titrated by Volhard's method. The salts used may be silver acetate or silver *o*-nitro-phenolate (made by adding excess of silver oxide to *o*-nitrophenol at 70°).

(*b*) Fixation of Calcium ion.—This was determined by steeping the material for 2 hours in a large volume of 0·01 *M*-calcium acetate and washing for 2 hours to remove excess. The Ca fixed was ascertained by electro-dialysis and agreed with the value obtained with Ag ion.

[1] E. Heyman and G. Rabinov, *J. phys. Chem.*, 1941, **45**, 1152, 1167 ; *Trans. Faraday Soc.*, 1942, **18**, 309.

[2] A. Sookne and M. Harris, *J. Res. Nat. Bur. Standards*, 1941, **26**, 205.

(ii) *Amount of Carbon Dioxide evolved on Acid Hydrolysis.*—This property is characteristic of oxycellulose, since cellulose and hydrocellulose give minimal values.[1] It is carried out by distillation with 12 per cent. hydrochloric acid and estimation of the carbon dioxide by one of the methods described on p. 391. The following table shows values obtained by the authors quoted :—

Substance.	Per cent. CO_2H.	Substance.	Per cent. CO_2H.
Oxycellulose (H_2O_2) .	0·29	Oxycellulose (HNO_3) .	0·97 ; 0·83
,, ($KMnO_4$)	0·65 ; 1·04	Cotton Cellulose . .	0·03
,, (CrO_3) .	1·32	Hydrocellulose (Girard)	0·04
,, ($KClO_3$) .	0·66		

(iii) *The Production of Furfuraldehyde.*—This is characteristic of oxidised cellulose, the values being of the order of 1·5 to 3 per cent. The phloroglucide precipitate obtained should be treated with alcohol. Heuser and Stöckigt have shown that the proportion of the precipitate soluble in alcohol is large in the case of hydrocellulose, less with cellulose, and lower still with oxycellulose. The soluble portion is derived from hydroxymethyl furfuraldehyde (p. 379). The furfuraldehyde may arise from uronic acid groupings, but it will be seen from the figures below that the furfuraldehyde obtained (second column) is only in moderate agreement with the amount calculated on the assumption that the source of the CO_2 is a uronic acid (last column).

Oxidising Agent.	Copper Number.	Furfuraldehyde per cent.	CO_2 per cent.	Uronic Acid Anhydride per cent.*	Furfuraldehyde due to Uronic Acid per cent.†
$KClO_3 + HNO_3$[2] .	4·8	0·80	0·62	2·5	0·41
HNO_3[2] . . .	9·6	0·65	1·1	4·4	0·72
CrO_3[3] (2·0 at oxygen) .	25·9	3·56	2·5	10·0	1·67
,, (1·5 ,,) .	28·1	3·27	2·9	11·6	1·93
,, (1·0 ,,) .	24·6	3·06	3·0	12·0	2·00

* 4 × CO_2 per cent. † ⅛ of uronic anhydride per cent.

B. Reactions associated with the Carbonyl Grouping.—(iv) *Phenylhydrazine, etc.*—Most oxycelluloses form coloured compounds with phenylhydrazine and its derivatives, though little

[1] K. Hess, *Cellulosechemie*, 1922, **3**, 61 ; E. Heuser and F. Stöckigt, *Papier Fabrik.*, 1925, **23**, 126.

[2] A. G. Norman, *Biochem. J.*, 1929, **23**, 1359.

[3] H. Hibbert and S. M. Hassan, *J. Soc. Chem. Ind.*, 1927, **46**, 407T.

Properties of Modified Cellulose

Results calculated on Water and Ash-free Samples

Material Examined.	Copper Number.	Yield of Furfuraldehyde.	"α-Cellulose."	Material Resistant to Baryta.	Barium taken up.	Acidity ml. $N/100$ NaOH per gram.		Alkalinity of Ash ml. $N/100$ HCl per gram.	Total Acidity.	Colour with Methyl Orange + NaCl.
						Litmus.	Phenolphthalein 80°.			
		Per cent.	Per cent.	Per cent.	Per cent.					
Cellulose (cotton)	0·28	0·69	98·85	97·8	0·02	1·5	—	0·3	1·8	Yellow
Oxycellulose from cotton (hypochlorite)	11·0	0·26	62·0	59·7	2·18	39·4	40·7	2·0	41·4	Very bright red
Oxycellulose from cotton ($KMnO_4$)	8·03	1·28	61·8	65·6	1·46	27·3	27·0	0·4	27·7	Very bright red
Oxycellulose from cotton (H_2O_2)	5·8	0·94	78·3	77·2	0·34	10·1	11·6	0·3	10·4	Bright red
Hydrocelluloses from cotton (Girard)	3·64	1·24	83·7	75·3	0·10	3·7	4·0	0·9	4·6	Yellow-brown
	6·22	—	—	63·0	—	—	—	—	—	Yellow-brown
Hydrocellulose (Lederer)	5·57	0·76	88·45	76·3	0·17	—	—	—	—	Yellow

reliance can be placed on measurements of the amount of phenylhydrazine fixed. The figures given for different oxycelluloses average 7 per cent.

(v) *Reducing Properties.*—The reduction of Fehling's solution is characteristic. A few values for copper number are given in the following table :—

OXYCELLULOSE PREPARATIONS

Observer.	Source.	Agent.	Copper Number.
Schwalbe and Becker [1]	Cotton	Hypochlorite	11·0
,, ,,	,,	Permanganate	8·0
Schwalbe	Filter paper	Bleaching powder	7·9 ; 7·6
,,	Cotton	Hydrogen peroxide	5·8
Dorée [2]	,,	Ozone	14·96 ; 16·9
Hibbert and Hassan [3]	,,	Chromic acid	24–27
Oertel [4]	,,	Electrolytic	39·5
Davidson [5]	,,	Periodic acid	100 +

(vi) *Other reducing Properties.*—Several other qualitative tests, proposed for oxycellulose, are known to depend upon the reducing property, since they are not shown by the non-reducing oxycelluloses. The more important of these qualitative tests are as follows :—

(*a*) Staining test with silver solution. Harrison [6] proposed a reagent made up of silver nitrate 1 per cent., sodium thiosulphate 4 per cent., and sodium hydroxide 4 per cent. The material to be tested is boiled or steamed in the presence of this solution. Oxycellulose, or hydrocellulose, is indicated by dark stains of reduced silver.

(*b*) Staining test with Nessler's solution. Ditz [7] showed that oxycellulose reduces mercury from Nessler's reagent, giving a grey precipitate. He states that hydrocellulose does not do this.

Birtwell, Clibbens and Ridge (*loc. cit.*) find that a series of oxycelluloses can be placed in the correct order of their copper numbers by the use of these tests, which, however, fail to indicate oxycellulose of the high methylene blue absorption type. The reduction of Nessler's solution is not very sensitive for products with copper numbers below 1, but the reduction of silver solution is quite sensi-

[1] *Ber.*, 1921, **54**, 545 ; *Zellstoff u Papier*, 1921, **1**, 4, 100, 135.
[2] *J. Soc. Dyers*, 1913, **29**, 205. [3] *J. Soc. Chem. Ind.*, 1927, **46**, 409T.
[4] *Z. angew. Chem.*, 1913, **26**, 246. [5] See p. 139.
[6] W. Harrison, *J. Soc. Dyers and Col.*, 1912, **28**, 359.
[7] H. Ditz, *J. Prakt. Chem.*, 1908, **78**, 343.

tive and may be used to indicate products with copper numbers as low as 0·5.

(*c*) Dyeing test with Indanthrene Yellow. Ermen [1] found that oxycelluloses are able to fix Indanthrene Yellow from a hot alkaline suspension of the dyestuff, the oxycellulose functioning in a similar way to hydrosulphite in the preparation of the vat.

On a fabric the test is carried out as follows: A suspension of the dyestuff is made by dissolving in concentrated sulphuric acid and pouring the solution into cold water. The suspension is neutralised and a few drops added to a 10 per cent. solution of NaOH, the fabric to be tested is steeped in the mixture, squeezed and steamed over boiling water. A deep blue stain appears within 1 minute, where oxycellulose is present. The rest of the cloth, if properly bleached, shows no trace of blue for 5 minutes. This test will indicate oxidation which results in copper numbers above 0·5 (Schwalbe-Braidy).

(*d*) Schiff's reagent. The colour is restored by most oxycelluloses, but the test is not very sensitive and does not indicate copper numbers less than 1.

For the qualitative detection of oxycellulose of the reducing type, therefore, tests (*a*) and (*c*) are the most suitable.

C. **Molecular Chain Shortening.**—Properties dependent on alteration in chain-length are—

(vii) *Solubility in Alkaline Solution.*—The solubility in sodium hydroxide is determined either by using a boiling 1 per cent. solution for 1, 3 or 4 hours, or, in the cold, either a 10 per cent. solution or a 10*N*-followed by a 2*N*-solution (p. 165). The α-cellulose value may also be determined. Schwalbe recommends the use of barium hydroxide solution giving

The Baryta Resistance Value.—This represents the residue per cent. of a cellulose preparation which is left after boiling 3 g. for 1 hour with 200 ml. of a saturated solution of barium hydroxide. The residue is washed with water, with 1 per cent. HCl, and then with water. As will be seen, the values do not differ very much from the α-cellulose determinations. Some measurements by Schwalbe *et al.* are given on p. 119.

(viii) *Viscosity or Fluidity* and its dependence on chain-length is discussed in Chapter VIII.

Behaviour towards Cuprammonium.—Pernnetier [2] first observed that oxidised celluloses do not show the bead-like swellings, which are given both by raw and normally bleached cotton, when

[1] W. F. Ermen, *J. Soc. Dyers and Col.*, 1912, **28**, 132.
[2] Pernnetier, *Bull. Soc. Ind. Rouen*, 1883, **11**, 236.

treated with cuprammonium; instead, they swell in a comparatively uniform manner. It has since been shown that a very slight oxidising effect is sufficient to prevent the bead-like appearance, and uniform swelling is shown by both types of oxycellulose and by oxycelluloses which have been alkali boiled. The absence of bead-like formation is thus a reliable test of oxidation.

General Colour Reactions.—The yellow colour shown on treatment with dilute alkali is generally considered to indicate oxycellulose. Oxycelluloses give a blue colour with zinc-chloride-iodine reagent.

Schwalbe and Becker (*loc. cit.*) add a few drops of Methyl Orange to water containing oxycellulose in suspension. An orange-red colour is given, changed to red by the addition of a little concentrated salt solution. They state that hydrocelluloses do not give this reaction.

Dyeing Properties with Direct Dyes.—The behaviour of oxycellulose in regard to direct cotton colours was examined by Saget [1] and by Knecht.[2] They found that oxycelluloses showing a high affinity for basic dyes resist dyeing with direct azo colours, and, in fact, dye less strongly than normal cellulose. Comparative dyeing with these colours thus affords a more sensitive test for oxidation than dyeing with basic dyestuffs. An examination of oxycelluloses of the two types previously described using Diamine Sky Blue FF, Diamine Pure Blue A (0·5 per cent.) and Diamine Bronze G (2 per cent.) has shown that the resistance to direct cotton dyestuffs affords a test for the type of oxycellulose characterised by high methylene blue absorption. The reducing type, however, do not respond to the test.

The whole question has been studied by Neale *et al.*,[3] using chiefly Sky Blue FF on cellulose and its modifications. Assuming that the dyestuff anion is absorbed by the cellulose, an equation is developed connecting the absorption with the concentration of the salt and of dyestuff, which is found to agree with experimental values.

[1] G. Saget, "Mon. Scient." 1892, p. 640.
[2] E. Knecht, *J. Soc. Dyers and Col.*, 1921, **37**, 76.
[3] J. Hanson, S. M. Neale and W. Stringfellow, *Trans. Faraday Soc.*, 1933, **29**, 1167; 1934, **30**, 395, 905; 1935, **31**, 1718.

V. Preparation and Properties of Modified Celluloses obtained by the Action of Oxidising Agents in Solutions of definite Hydrogen Ion Concentration [1]

The experiments of these authors led to the recognition of the two types of oxycellulose. The results, of which a brief account is given, apply only to mildly oxidised cotton in which the structure is still maintained; the investigation was not extended to the powdery oxycelluloses, previously described.

The contrast between the two types is illustrated in the following table, which will serve also to indicate the nature of the measurements required in their examination :—

The Properties of the Two Types of Oxycellulose

	Methylene Blue Type. Alkaline Oxidation.	Reducing Type formed by Acid Oxidation.
1. Absorption of methylene blue .	High	Low
2. Copper number . . .	Low	High
3. Properties of the residue left after boiling with dilute alkali	Very similar to original oxycellulose.	Sometimes closely resembling the original cotton. Viscosity always lower.
4. Loss in weight on boiling with alkali.	Small	Great
5. " Residual alkalinity " * of ash after alkali boiling.	High	Low
6. Yellow colour given with alkali	−	+
7. Reduction of silver nitrate solution (p. 120).	−	+
8. Dye test with Indanthrene Yellow (p. 121) . . .	−	+
9. " Resist " test with direct dyestuffs (p. 122).	+	−

* *I.e.*, after standard washing process of one hour in $N/10$ sulphuric acid followed by washing in water to neutrality.

The reducing type is very soluble in dilute alkalis, and in many cases leaves a residue chemically indistinguishable from the original cotton. The viscosity of the residue, however, is of the same order as that of the original oxycellulose, and the determination of viscosity is thus a valuable diagnostic for over-bleaching in the case of cloth which has been scoured with alkali subsequent to bleaching.

The methylene blue type, whilst very slightly soluble in alkali,

[1] C. Birtwell, D. A. Clibbens, A. Geake and others, *J. Text. Inst.*, 1924, **15**, 27T; 1926, **17**, 145T; 1927, **18**, 135T, 277T.

shows a remarkable affinity for alkali, which it retains in spite of the standard washing treatment of 1 hour with $N/10$ sulphuric acid. The properties of the residue insoluble in alkali, remain substantially those of the original oxycellulose. Many of the other tests are obviously the result of the action of a reducing substance on the reagent used, and, as would be expected, are shown only by the reducing type.

Preparation of Oxycelluloses.—25 g. of cotton were treated with 1 litre of solution until the whole of the oxidising agent was consumed. Five solutions of each oxidising agent were used, the concentrations being $0{\cdot}01N$, $0{\cdot}005N$, $0{\cdot}003N$, $0{\cdot}002N$, $0{\cdot}001N$. Complete reduction under these conditions corresponded to a consumption of 0·32, 0·16, 0·096, 0·064, and 0·032 per cent. of oxygen, calculated on the weight of cotton.

A normal " chemicking " process consumes 0·01 to 0·02 per cent. of oxygen. The oxidising agents employed were chlorine water, acidified permanganate, hypochlorite, and alkaline hypobromite.

Preparation of Hypochlorite Oxycelluloses at various Hydrogen Ion Concentrations.—Samples of cotton weighing 20 g. were treated in stoppered bottles of 200 ml. with $N/25$ NaClO solution containing 1·42 g. of available chlorine per litre, the solution being suitably buffered. The mixture was kept in a thermostat at 25° in the dark, with occasional shaking, until the whole of the hypochlorite had been reduced, the product being then washed with water, dilute acid, then with water again, and finally dried in the air. These conditions correspond to a consumption of 0·32 per cent. of oxygen on the weight of air-dried cotton. The oxidation required from 2 to 14 days.

The $N/25$ sodium hypochlorite was prepared by dilution of a " neutral " solution, which was normal in respect to hypochlorite (the solution was actually alkaline owing to hydrolysis). The normal hypochlorite solution was prepared by passing chlorine into N-NaOH solution until a weight of gas had been absorbed slightly less than the equivalent of the alkali used. A known volume of this was treated with an excess of neutral hydrogen peroxide and titrated to neutrality with $N/10$ sulphuric acid, using methyl red as indicator. The whole of the normal hypochlorite solution was then " neutralised ", previously to 25-fold dilution, by the addition of a volume of $N/10$ sulphuric acid which could be calculated from the observed titration.

The 25-fold dilution was carried out with the following solutions of the acidity or alkalinity recorded :—

Alkalinity or Acidity of Solutions

			*p*H.	
	1. 4M-NaOH (mercerising strength)	$4N$ $\overline{OH}$	14·6*	approx.
	2. M/10 NaOH	10^{-1} N ,,	13	
	3. M/100 NaOH	10^{-2} N ,,	12	
	4. M/10 Na_2CO_3	$10^{-2\cdot8}$ N ,,	11·2	
Buffer Solutions.	5. M/10 Na_2CO_3 + M/10 HCl in volume proportion 5:2	$10^{-3\cdot8}$ N ,,	10·2	Alkaline.
	6. 100 ml. M/5 NaOH + 250 ml. M/5 H_3BO_3 to 1 litre	10^{-5} N ,,	9	
	7. 250 ml. M/5 KH_2PO_4 + 148 ml. M/5 NaOH to 1 litre	10^{-7} N $\overline{OH}$ and $\overset{+}{H}$	7	Neutral.
	8. M/5 HAc + M/5 NaAc in equal volumes	$10^{-4\cdot6}$ N $\overset{+}{H}$	4·6	
	9. M/5 HAc	$10^{-2\cdot7}$ N ,,	2·7	Acid.
	10. M/20 H_2SO_4	10^{-1} N ,,	1	

* Use is made of the *p*H scale for this high alkalinity to secure uniformity.

Hypobromite solutions were also employed, but were much more unstable near the neutral point. Thus the $N/25$ solution at *p*H 9, decomposed to the extent of 30 per cent. in four hours in the dark at 25°, while the equivalent hypochlorite solution lost only 1 per cent. of its available chlorine in 30 hours. The hypobromite solutions, on the other hand, oxidised cellulose far more rapidly than the hypochlorites. Hypobromite oxidation has been found to follow a very characteristic path (Fig. 24, p. 98). The copper number of the product increases rapidly at first, but quickly attains a value which remains practically constant for some time. The absorption of methylene blue, however, increases continuously with time of contact.[1]

Some of the results obtained are given in the tables and diagrams following. The copper numbers were determined by the Schwalbe-Braidy method on 2·5 g. air dry (moisture separately). The methylene blue values were not measured in buffer solution (p. 19), but each solution was adjusted by the addition of acid or alkali to give an absorption value of 0·45 millimole of methylene blue per 100 g. of dry material for a standard American cotton scoured in 1 per cent. caustic soda at 40 lb. for 6 hours and acid washed. The oxycellulose was given the standard acid wash ($N/10$ H_2SO_4 for 1 hour, then to neutrality with water). For the loss in weight on alkali boiling 2 g. of material dry at 110° were boiled with 200 ml. $N/4$ NaOH solution for 4 hours. The residue was washed with $N/4$ NaOH and water, and given the standard acid wash.

[1] D. A. Clibbens and B. P. Ridge, *J. Text. Inst.*, 1927, **18**, 135T; also *ibid.*, 1930, **21**, 87T.

The ash alkalinity is expressed in milli-equivalents per 100 g. of dry material (p. 17). The viscosity was determined by the method of Farrow and Neale,[1] a 2 per cent. solution being used, except with preparations of very low or very high viscosities, when stronger or weaker solutions were employed, the result being calculated to 2 per cent. solution (p. 48). The cotton used was an American cotton cloth, scoured with 1 per cent. caustic soda under pressure, chemicked, soured, and washed. The results of experiments with the three oxidising agents selected are shown in Figs. 25

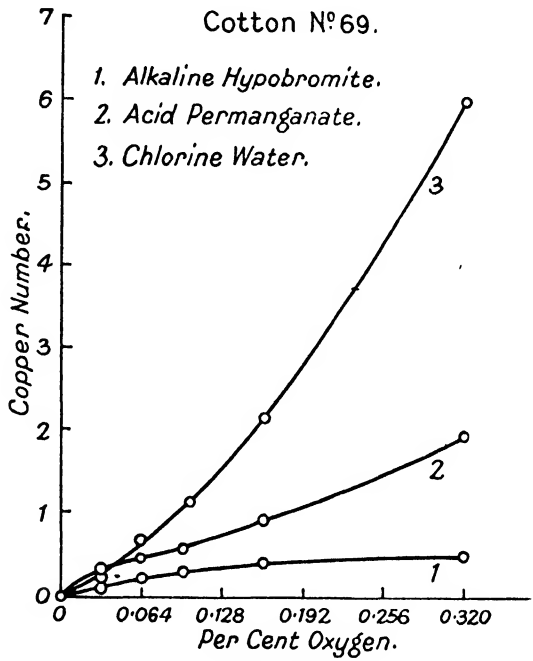


FIG. 25.—Variation in the Copper Number with the amount of oxygen consumed.

and 26. The chlorine series are characterised by high and rapidly increasing copper numbers; the hypobromite series by low copper numbers rising very slowly with progressive oxidation. The second figure shows exactly the opposite relations with respect to methylene blue absorptions. On p. 37 the copper numbers are plotted against the percentage loss of weight on alkali boiling for all three oxycellulose series, irrespective of the oxidising agent used. As the points lie on a smooth curve, the loss of weight on alkali boiling over the range of oxidation examined is determined by the copper number.

Oxycelluloses with a high methylene blue absorption and a low

[1] F. D. Farrow and S. M. Neale, *J. Text. Inst.*, 1924, **15**, 157T.

copper number show only slight loss of weight on boiling in dilute alkali. It might be expected, therefore, that the methylene blue absorption would not be affected greatly by alkali boiling. This is

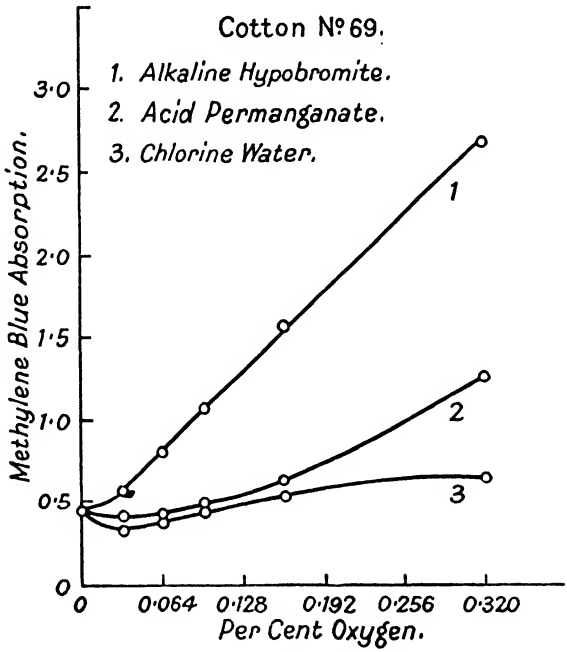


FIG. 26.—Variation in the Methylene Blue absorption with the amount of oxygen consumed.

shown on p. 160 and in the following table, which gives values for three hypobromite oxycelluloses before and after boiling in dilute alkali :—

ALKALI BOIL ON HYPOBROMITE OXYCELLULOSE

Treatment.		Oxycellulose RB3.		Oxycellulose RB1.		Oxycellulose RB2.	
		Copper Number.	Me. Blue Absorption.	Copper Number.	Me. Blue Absorption.	Copper Number.	Me. Blue Absorption.
Before alkali boiling		0·20	1·08	0·35	1·56	0·50	2·95
After alkali boiling	4 hours with 1 per cent. NaOH	0·02	0·95	0·02	1·30	0·09	2·45
	8 hours with 1 per cent. NaOH	0·015	1·12	—	—	0·06	2·65
	8 hours with 2 per cent. NaOH	0·005	1·01	—	—	0·05	2·67

It will be seen that the copper number is so diminished by alkali boiling that the residue cannot be distinguished by this test from the original cellulose. The methylene blue absorption, however, diminishes slightly after the first alkali boil, and subsequent prolonged treatments do not bring about further reduction. In no case do the values revert to those characteristic of the original cellulose (p. 23).

The absorption of methylene blue is well known to depend on the ash alkalinity of the sample (p. 18). Defining the "residual ash alkalinity" as the alkalinity possessed after the standard washing

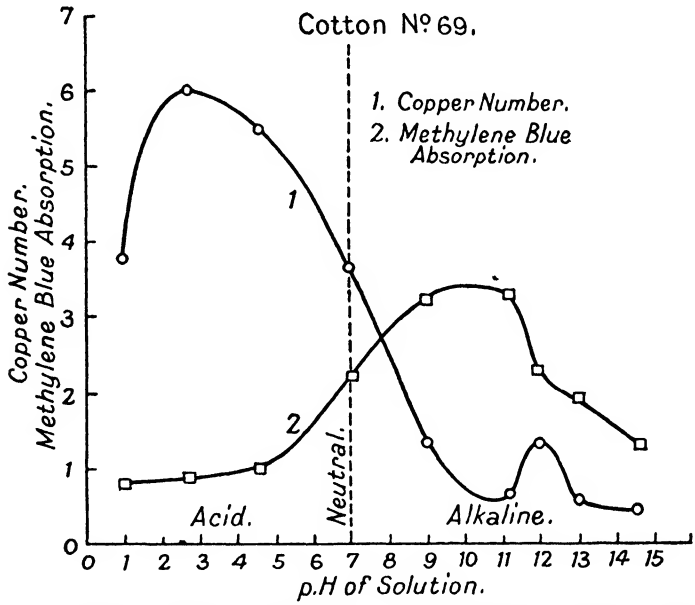


FIG. 27.—The relation between Hydrogen Ion concentration and the properties of hypochlorite oxycelluloses.

process of 1 hour with $N/10$ sulphuric acid, it is found that the residual ash alkalinity of oxycelluloses of the methylene blue type is very high, and is not reduced by further acid-washing treatments. As an example, a cotton sample, after the standard wash, gave an ash alkalinity of 0·6; an oxycellulose made from it with hypobromite, after the standard wash, gave 4·85. This product, after shaking for 18 hours with $2N$-sulphuric acid, showed the value 4·38, and after 14 days' standing with $N/10$ sulphuric acid it still showed the value 4·12.

It was found that the ash alkalinity of these oxycelluloses could be reduced to values even below that of the original cotton by a process of electrolytic washing, the acid-washed material being

suspended in distilled water between two electrodes at a P.D. of 200 volts. The results with a hypobromite oxycellulose are shown in the table :—

Treatment.	Methylene Blue Absorption.	Ash Alkalinity.	Copper Number.
A. Normally acid washed	5·3	4·9	0·79
B. Boiled with N/10 HCl for one hour . .	2·3	0·62	2·90
C. Electrolysed for 6·5 hours	3·3	0·32	0·81

Relation between Hydrogen Ion Concentration and the Properties of Hypochlorite Oxycelluloses.—In the following table are recorded the properties of oxycelluloses prepared, in each case, by the consumption of 0·32 per cent. of oxygen from hypochlorite solutions. The differences are due solely to variations in hydrogen ion concentration.

*p*H.	Copper Number.	Methylene Blue Absorption.	Ash Alkalinity.
14·6	0·42	1·30	1·28
13	0·54	1·91	1·82
12	1·31	2·28	2·57
11·2	0·65	3·26	2·78
9	1·37	3·20	3·18
7	3·64	2·23	2·24
4·6	5·50	1·04	1·23
2·7	6·00	0·90	1·06
1	3·79	0·81	0·98

The values obtained are plotted in the diagram (Fig. 27). It will be seen that the methylene blue absorption rises with decreasing alkalinity and reaches a maximum on the alkaline side of the neutral point (*p*H 11 to 9). It then falls continuously, reaching a minimum at *p*H 3. The copper number curve is the reverse of this : from a minimum value at *p*H 11 it rises continuously to a maximum value at *p*H 2 to 4. At the extreme points *p*H 1 and *p*H 13 other factors have to be considered.

It is interesting to note that a solution so slightly alkaline as *p*H 9 produces an oxycellulose with a copper number which has already fallen far below its maximum value. Also " the very great change in the properties of these oxycelluloses from the maximum to the minimum occurs almost entirely within the range *p*H 5 to *p*H 9 (N/100,000 hydrogen ion to N/100,000 hydroxyl ion), a range

so small, and so near the neutral point, that the results obtained with unbuffered solutions are purely fortuitious". Obviously, for hypochlorite oxycelluloses prepared in strictly neutral solution, the measurement either of the copper number or the methylene blue absorption would afford a delicate test for oxidising attack, but for oxycelluloses prepared in very slightly acid or alkaline solution the

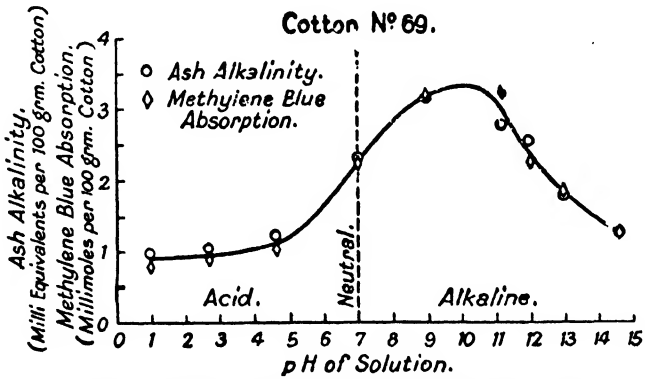


FIG. 28.—The relation between Ash Alkalinity and Methylene Blue absorption of hypochlorite oxycelluloses.

measurement of either property, taken alone, might lead to an entirely wrong conclusion as to oxidising attack.

The relation between methylene blue absorption and residual ash alkalinity of these hypochlorite oxycelluloses is remarkably close, and Fig. 28 shows a curious parallel between the two values when plotted against hydrogen ion concentration.

Viscosity of Oxycelluloses in Cuprammonium.—Measurements on samples prepared under conditions of *p*H which would

VISCOSITY OF HYPOCHLORITE OXYCELLULOSES

Oxygen consumed per cent.	Prepared at *p*H 2·7 Reducing Type.	Prepared at *p*H 12. Methylene Blue Type.
0·0	3·2	3·2
0·6	2·77	1·44
0·9	1·66	0·67
0·16	0·27	−0·16
0·32	−0·37	−0·36

produce either type of oxycellulose show that, when the extent of oxidation becomes considerable (*e.g.* a consumption of 0·32 per cent. of oxygen), the same fall of viscosity results, whatever the hydrogen

ion concentration. In the earlier stages, however, an alkaline hypochlorite (*p*H 12) produces a much greater fall in the viscosity of cotton than that of a similar solution of *p*H 2·7. The results are given in the foregoing table as log. viscosities in 2 per cent. solution.

The following table illustrates the important point previously mentioned, *viz.* that, although the effect of alkali boiling may be to produce a residue chemically similar to the original cotton, the viscosity of the residue demonstrates the change due to oxidation. Each line refers to a different oxycellulose :—

Copper Number.		Log Viscosity in 2 per cent. Solution.	
Before Boiling.	After Boiling.	Before Boiling.	After Boiling.
0·10	0·02	1·46	1·30
0·20	0·04	0·48	0·39
0·35	0·11	−0·25	−0·27
0·50	0·15	−0·63	−0·76
5·32	0·71	−0·65	−0·76
7·30	1·01	−0·86	−0·92

The Rate of Oxycellulose Formation.—Clibbens and Ridge [1] have studied the rate of oxycellulose formation with hypochlorite and other solutions, defining the term as the rate of consumption of oxygen by a cotton cellulose, or as the rate of change of any property which varies continuously with progressive oxidation—*e.g.* viscosity or copper number.

Two methods of experiment were employed : (i) Strips of cloth (acid-washed) were immersed in the solution contained in a glass bottle and previously heated to 25°, at which all measurements were made. The bottle was stoppered and kept in a thermostat in diffused light, and the contents occasionally shaken. Samples were removed at intervals, rapidly washed with water and dilute hydrogen peroxide, and finally given the standard acid wash. The products were air-dried, the moisture content being taken as 6 per cent.

(ii) A circulating apparatus was employed in order that fairly large quantities of material could be oxidised with a high ratio of liquor to cotton, so as to avoid a serious fall in the concentration of the oxidising agent.

An earthenware jar of about 10 litres capacity, containing an electric heating lamp, a thermo-regulator, and a glass circulating pump, was connected at the bottom to a second earthenware jar

[1] D. A. Clibbens and P. B. Ridge, *J. Text. Inst.*, 1927, **18**, 135T.

made in three sections, of which the lowest and largest was exactly similar to the vessel containing the pump. The three sections fitted into one another by means of ground rims and flanges, the two upper compartments being relatively shallow and possessing perforated bottoms, also of earthenware. Cotton to be oxidised was placed in the middle compartment, which could conveniently accommodate 100 g., and 9 to 10 litres of the oxidising solution were poured into the vessel containing the pump, whence it divided itself between this vessel and the lower section of the second jar. The heating lamp and temperature regulator being adjusted to maintain a temperature of 25°, liquid was pumped from these reservoirs into the top perforated compartment, from which it percolated through the cotton in the middle section before finally returning to the reservoir formed by the lowest section; the action of the pump was so regulated that the cotton was always covered to a depth of about ¼ in. with liquor, and a continuous circulation of the oxidising solution through the material was maintained in this way. The results obtained showed no great difference between the two methods of working. The following liquids of the stated *p*H values were employed:—

1. *M*/10 NaOH . . . . . *p*H 13
2. *M*/100 NaOH . . . . . *p*H 12
3. *M*/10 Na_2CO_3 . . . . . *p*H 11·2
4. 100 ml. *M*/5 NaOH + 250 ml. *M*/5 H_3BO_3 diluted to 1 litre . . . . . *p*H 9
5. 730 ml. *M*/5 H_3BO_3 + 270 ml. *M*/20 $Na_2B_4O_7 \cdot 10\ H_2O$ . . . . *p*H 8
6. 940 ml. *M*/5 H_3BO_3 + 60 ml. *M*/20 $Na_2B_4O_7 \cdot 10\ H_2O$ . . . . *p*H 7·1
7. 250 ml. *M*/5 KH_2PO_4 + 148 ml. *M*/5 NaOH diluted to 1 litre . . . . . *p*H 7
8. *M*/5 HAc + *M*/5 NaAc in equal volumes . . . *p*H 4·6
9. *M*/5 HAc . . . . . *p*H 2·7
10. *M*/20 H_2SO_4 . . . . . *p*H 1

Experiments on the rate of consumption of oxygen from hypochlorite solutions are summarised in Fig. 29.

The ordinates show the time necessary for the consumption of half the total available chlorine which may be taken as a measure of the rate of oxidation. The position of the last point representing the most alkaline solution (*N*/10 NaOH) shows that here the rate of oxidation is very slow. The fall in the curve between *p*H 13 and *p*H 11 shows that the rate rapidly increases with diminishing alkalinity.

With acid solutions between *p*H 4 and *p*H 6, a rapid increase in

the rate of oxidation also occurs. At the neutral point the rate reaches a sharp maximum. It will be noticed that it is roughly ten times that of a slightly alkaline liquor at *p*H 9, or a slightly acid one

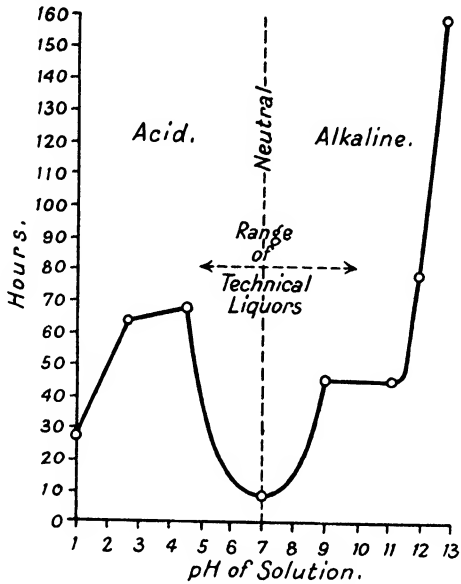


FIG. 29.—The rate of consumption of oxygen by cotton from hypochlorite solutions of varying *p*H values.

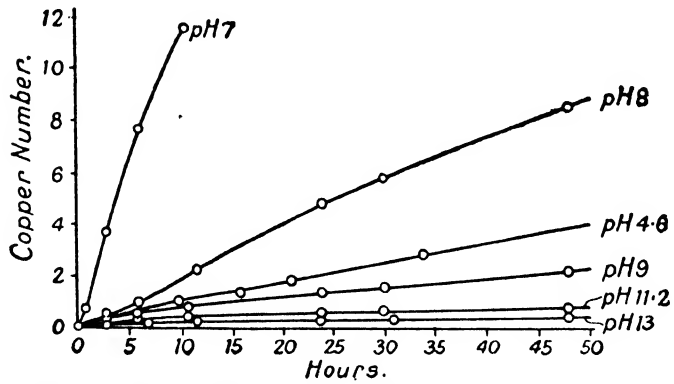


FIG. 30.—Rate of change in the Copper Number produced by hypochlorite solutions of varying *p*H.

at *p*H 4 to *p*H 6. The intense activity of neutral hypochlorite solutions is well known, but, in order to see whether the buffered solutions exerted a catalytic effect, experiments were made in this region both with a phosphate buffer No. 7 and the boric acid solution No. 5. The curves obtained, however, were of the same general

form. The rapid action with neutral hypochlorite solutions can best be explained at present, as due to the relatively high concentrations of both hypochlorous acid and hypochlorite ion which exist simultaneously in such solutions.

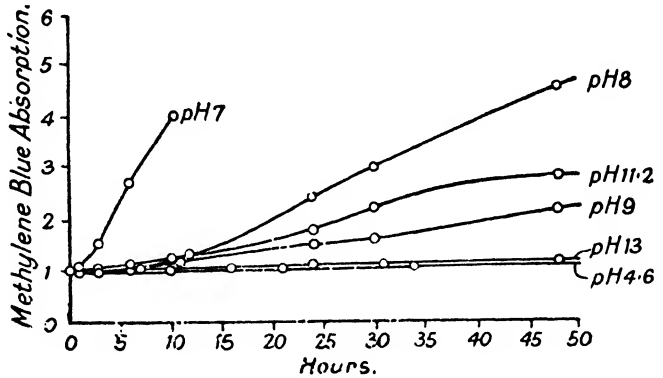


FIG. 31.—Rate of change in the Methylene Blue absorption produced by hypochlorite solutions of varying *p*H.

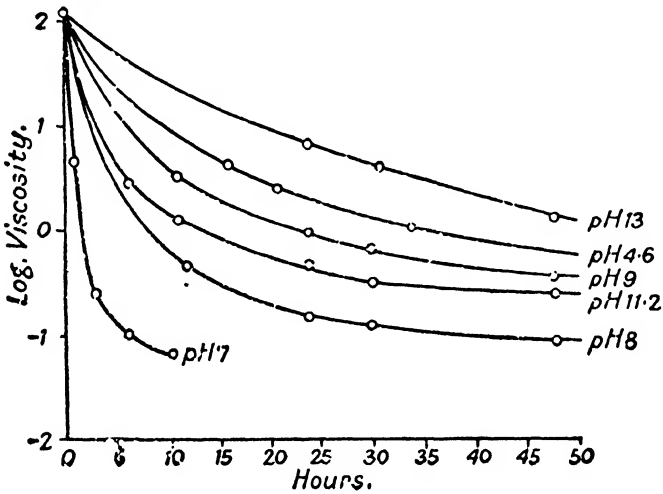


FIG. 32.—Rate of change in the Viscosity produced by hypochlorite solutions of varying *p*H.

Rate of Change in the Properties of Cotton treated with Hypochlorite Solutions of Varying *p*H Value.—These experiments had to be carried out by the first method described above. The results (Figs. 30, 31 and 32) show (*a*) that the rate of increase of the copper number is extremely slow with alkaline liquors between *p*H 13 and *p*H 11·2. Even after 50 hours the copper number is not seriously raised. With less alkaline solutions, *p*H 9 and *p*H 8, the

rate of increase rises fairly rapidly and becomes very high at the neutral point before again falling with hypochlorous acid solutions at *p*H 4·6. Similar results were obtained for the methylene blue absorption and the viscosity measurements which are given in the diagrams.

Effect of Permanganate Solutions of Graded *p*H Value on Cotton Cellulose

Potassium permanganate is well known to react differently with organic substances in acid and alkaline solution. A series of experi-

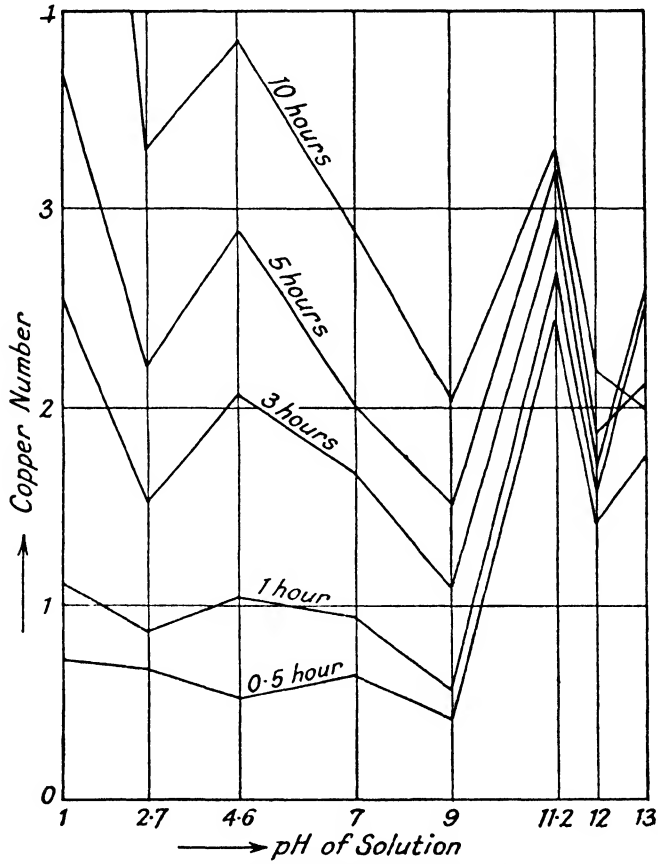


FIG. 33.—Changes in the Copper Number produced in cotton by the progressive action of potassium permanganate solutions of graded *p*H value.

ments [1] on similar lines to those just described, carried out with permanganate solutions of graded hydrogen ion concentration at 25°, show that the activity of permanganate is least in solutions at

[1] C. Dorée and A. C. Healey, *J. Soc. Dyers and Col.*, 1933, **49**, 290.

*p*H 9. The curves giving the relation between *p*H and copper number (Fig. 33) and between *p*H and methylene blne absorption (Fig. 34) illustrate the results obtained. The curves for solubility number (10*N*–2*N*-NaOH) are of the same shape as those for methylene blue absorption.

On the acid side of *p*H 9 the products are of the reducing type, and on the alkaline side of the methylene blue type. The great

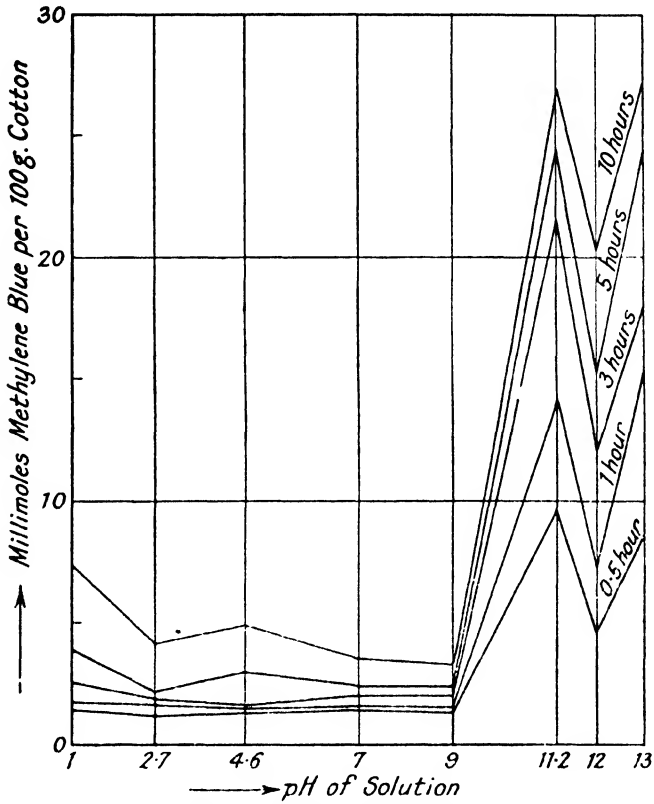


FIG. 34.—Changes in the Methylene Blue absorption value produced in cotton by the progressive action of potassium permanganate solutions of graded *p*H value.

activity of permanganate buffered to *p*H 11·2 with sodium carbonate is worthy of note. In the preparation of highly oxidised products it was found that 0·5 atom of permanganate oxygen per $C_6H_{10}O_5$ unit was consumed by cotton in *N*-NaOH solution in 25 minutes, whereas in *N*-H_2SO_4 10 hours were required. The copper number of the product formed in alkaline solution was 3·7, reduced by boiling in 1 per cent. NaOH to 2·3.

The copper number of the product formed in acid solution was

12·0, becoming 3·1 after boiling with NaOH. The action of alkaline permanganate thus resembles that of alkaline hypobromite.

Progressive Oxidation with Chromic Acid.—The action of chromic acid has been examined [1] for comparison with that of periodic acid (p. 138). A mixture of dichromate (1 equiv.) with sulphuric acid (2 equivs.) was employed at 20° in a solution 0·2*N* with respect to the former and 0·4*N* to the latter : ratio of cotton to solution 1 g. to 100 ml. giving a maximum available oxygen of 1·6

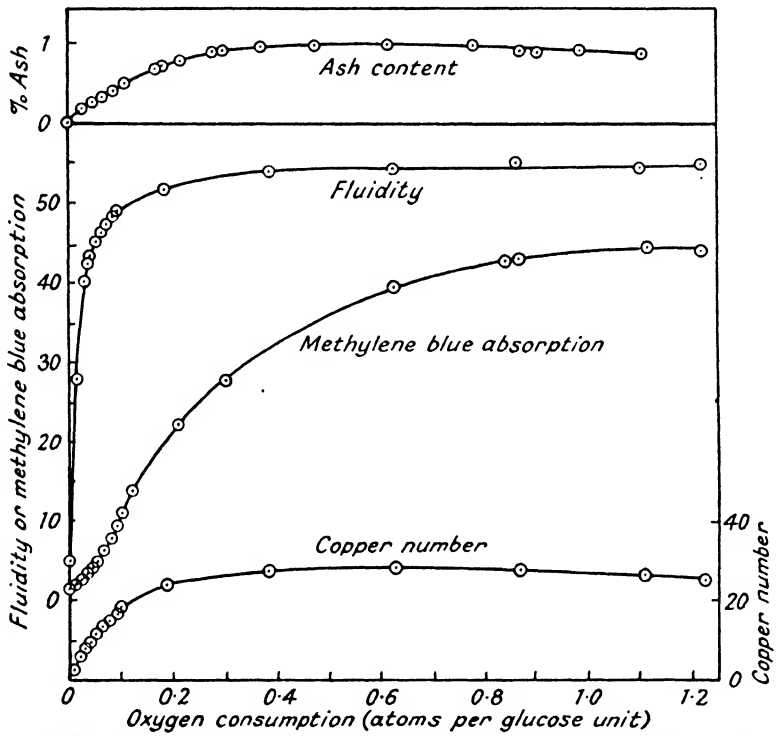


FIG. 35.—The progressive oxidation of cotton cellulose with chromic acid.

atoms per $C_6H_{10}O_5$. Concentration changes were measured by titration with ferrous iron using phenylanthranilic acid as indicator.

Some of the results are given in Fig. 35. By coincidence the values for loss in weight per cent. in 0·25*N*-NaOH at 100° for 6 hours follow almost the same curve as that shown for fluidity, *e.g.* at 0·4 atoms of oxygen both quantities have the same value 53. The course of the reaction is very different from that produced by periodic acid, and most other oxidising agents, in that all the measurable qualities of the oxycellulose, including copper number and

[1] G. F. Davidson, *J. Text. Inst.*, 1941, **32**, 132T.

methylene blue absorption, increase up to a point (0·4 atoms of oxygen) after which their value becomes constant.

Complications arise in that chromium is fixed during oxidation. The results can be explained by the assumption that the action of the chromic acid is confined to the inter-crystalline regions of the cellulose.

Oxidation with Periodic Acid.—The extreme alkali-sensitive oxycelluloses include, in order of sensitivity, products formed by dichromate-sulphuric acid, dichromate-oxalic acid (p. 161) and periodic acid. The table below illustrates the changes in cuprammonium fluidity, nitrate fluidity and breaking load shown by such preparations in the earlier stages of oxidation (consumption of 0·002 to 0·01 atom of oxygen per $C_6H_{10}O_5$) after boiling for 1 hour with 0·25*N* sodium hydroxide.[1]

PROPERTIES OF MODIFIED CELLULOSES BEFORE AND AFTER ALKALI BOILING

	Cuprammonium Fluidity.		Cellulose Nitrate Fluidity.		Relative Breaking Load.	
	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)
Original yarn	5·3	6·1	3·33	5·0	100	100
Modified with HCl (200 g./litre) at 20°	15·9	16·5	31·4	35·1	79·7	74·5
	27·0	27·3	86·8	88·5	50·8	46·6
	33·6	34·1	123·8	123·0	34·6	29·1
Modified with 0·005*M* KIO_4, 0·005*N* in H_2SO_4 at 20°	17·4	16·1	4·0	34·6	96·4	83·9
	27·6	25·9	5·1	77·5	90·3	64·8
	35·8	34·3	7·8	124·0	84·4	45·8
	42·5	41·0	9·9	166·8	74·1	26·9
Modified with dichromate and oxalic acid	15·3	16·6	5·2	33·9	97·9	86·5
	29·6	30·6	10·8	101·6	90·9	53·3
	41·7	39·6	26·5	157·4	76·6	24·4

(*a*) Before and (*b*) after boiling for 1 hour with 0·25*N*-NaOH.

Periodate oxycelluloses, prepared over the above range of progressive oxygen consumption, show a rapidly increasing cuprammonium fluidity, whereas the nitrate fluidity hardly differs from that of the original cellulose. The strength also is only slowly reduced. After alkali-boiling, however, the nitrate fluidity increases by some 10 to 15 times its original value, and the strength rapidly decreases, although not quite to the extent shown by dichromate oxycelluloses.

[1] G. F. Davidson, *J. Text. Inst.*, 1940, **31**, 81T; *ibid.*, 1941, **32**, 109T.

This sensitivity is also shown by the increases observed in nitrate fluidity after boiling with water, or by treating with dilute borax, sodium carbonate, or soap solutions, or with 0·1*N*-NaOH at 20°.

The periodate oxycelluloses fall into line with the generalisation that there is a unique relation between cuprammonium and nitrate fluidities for all types of modified cellulose after they have been boiled with dilute alkali. There is, however, no unique relation between strength and nitrate fluidity, although this might have been expected on theoretical grounds.

The copper number of periodate oxycelluloses shows a linear relationship with oxygen consumed over the above range. Its value is rapidly reduced by boiling dilute alkalis, and after a pressure boil with 0·25*N*-NaOH becomes of the same order (about 0·1) as that of the original cellulose. The action of alkali on the reducing groups is not, however, directly associated with its action on the alkali-sensitive centres.

The results obtained by oxidation with periodic acid at the higher oxygen consumption of from 0·1 to 1·2 atoms per glucose unit (Davidson, *loc. cit.*, 1941), are given in the table and in Fig. 36. The

PROPERTIES OF PERIODIC ACID OXYCELLULOSES

Oxygen atoms per $C_6H_{10}O_5$.	Fluidity in Cupram-monium.	Copper Number.	Per cent. loss in Weight on treatment with		Nitrogen in Nitrate per cent.
			0·1*N*-NaOH, 24 h. at 20°.	0·25*N*-NaOH, 6 h. at 100°.	
0·0308	45·8	10·2	5·5	32·1	13·6
0·0765	54·5	21·7	14·7	43·0	13·4
0·1260	56·3	33·4	22·4	51·2	13·3
0·3860	60·0	67·4	41·0	66·1	12·3
0·6580	63·5	89·1	67·0	—	10·5
0·8330	67·9	110·8	—	—	—
0·9500	69·2	120·9	—	—	—

methylene blue value remains almost unchanged. The copper number increases to values previously unrecorded (approximating to 40 per cent. of that of glucose) at 1 atom of oxygen consumed. The linear relation with oxygen consumption observed above, however, no longer holds. The initial steep rise in cuprammonium fluidity slows down after 0·2 atoms of oxygen have been consumed to a limit of 72 set by the fluidity of the solvent.

The loss in weight on treating with 0·25*N*-NaOH for 6 hours at 100° is very considerable, being 60 per cent. at 0·3 atom of

oxygen rising to 85 per cent. at 1·0 atom consumed. The loss on boiling for 6 hours with water is almost proportional to the oxygen consumed, reaching 65 per cent. at 1 atom of oxygen per glucose unit. The solubility values are only somewhat greater than this when the products are steeped in 0·1*N*-NaOH at 20° for 1 day.

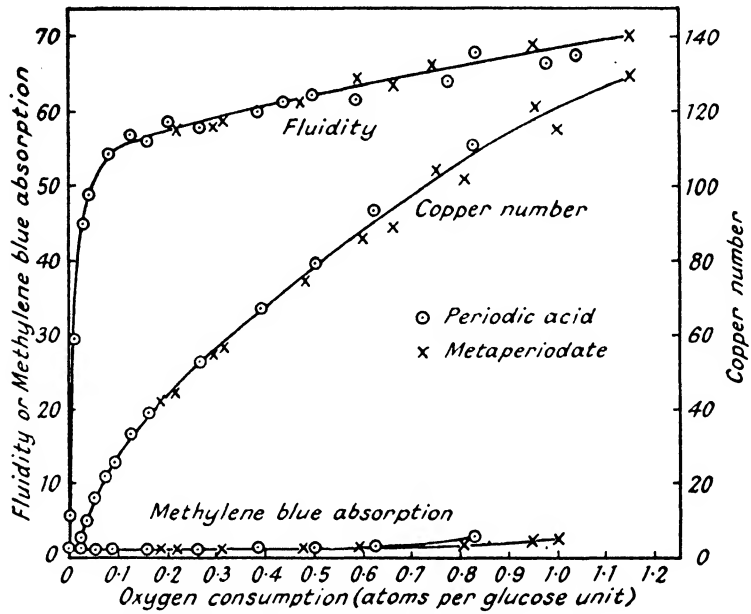


FIG. 36.—The progressive oxidation of cotton cellulose with periodic acid.

The main reaction with periodic acid at carbon atoms 2 and 3 of the glucose unit may be expressed by the equation

$$\begin{matrix}(2)\ \text{—CHOH} \\ \quad\ \vert \\ (3)\ \text{—CHOH}\end{matrix} + H_5IO_6 \rightarrow \begin{matrix}\text{—CHO} \\ \\ \text{—CHO}\end{matrix} + HIO_3 + 3H_2O$$

The salts of periodic acid, described as metaperiodates, act in solution as primary salts of the acid, and in dilute solution have a *p*H of about 5·3. The oxidising action of the acid and of the salt on cellulose are practically identical—except at the limit of oxidation—and either may be used.* Carbon dioxide and formic acid are by-products of the oxidation which is also accompanied by swelling, and, in the case of sheet cellulose, an increase in thickness and contraction in area.

Procedure.—Periodic acid solutions are prepared from the pure acid; or sodium metaperiodate with the equivalent of H_2SO_4 may be

* Sodium paraperiodate has also been recommended as it is cheaper (*J. Chem. Soc.*, 1942, 184).

used. For oxygen consumption up to 0·01 atom per $C_6H_{10}O_5$ solutions of 0·005*M*- to 0·01*M*- KIO_4 with 0·005*N*- H_2SO_4 respectively, are employed at 20°, with about 20 g. cellulose to 1 litre of solution. For higher oxygen consumption periodic acid solutions up to 0·25*M*- (0·5*N*- as oxidising agent), or 0·1*M*- solutions of sodium metaperiodate with 1 g. of cellulose to 100 ml. of solution are used.

To estimate the concentration of the periodate solutions 25 ml. are mixed with 10 ml. of saturated sodium bicarbonate solution and

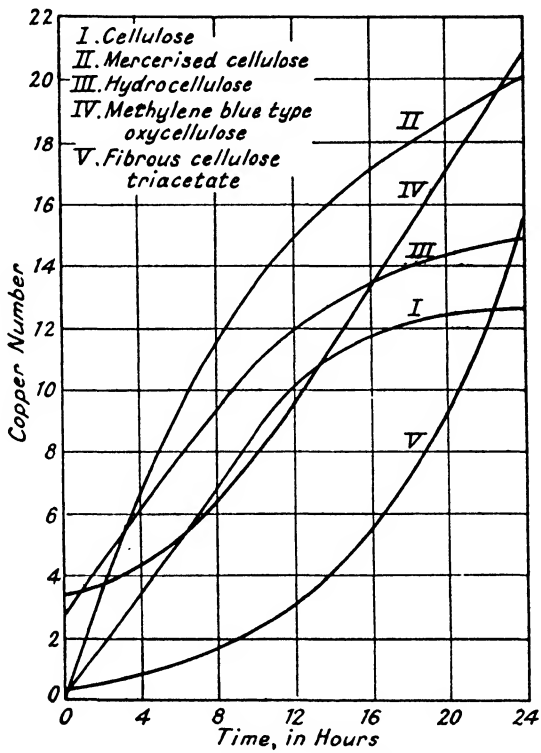


FIG. 37.—The progressive action of Ozone on cellulose and its derivatives. Copper number-time curves compared.

10 ml. of 10 per cent. KI. The liberated iodine is titrated with 0·02*N*- arsenite solution.

The nitrate, prepared as on p. 63, is soluble in acetone completely only at oxygen consumptions up to 0·02 atom per $C_6H_{10}O_5$. Beyond that it becomes increasingly insoluble (2 to 10 per cent.).

The Progressive Action of Ozone on Cellulose and Modified Cellulose.—This has been studied [1] as an example of a neutral oxidising agent forming no mineral by-products which might

[1] C. Dorée and A. C. Healey, *J. Text. Inst.*, 1938, **29**, 27T.

influence the reaction. Ozonised oxygen (2 g. O_3 per 100 g. of gas) was used throughout. In the presence of moisture acidity develops on the fibre, carbon-dioxide is produced and the oxycellulose formed is of the reducing type (Fig. 37).

Ozone has little action on cellulose, or mercerised cellulose, when less than 15 per cent. moisture is present, the copper number produced in 3 hours being below unity. With increasing water-content both forms of cellulose show a curious copper number maximum

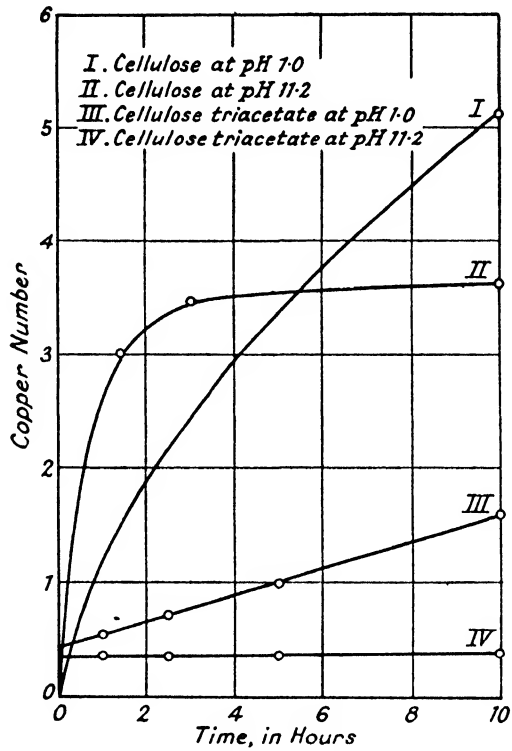


FIG. 38.—The progressive oxidation of cellulose and cellulose triacetate with 0·04-*N*-potassium permanganate.

(3 hours' exposure) of 4·2 and 6·8, respectively, at 50 per cent. water-content, but thereafter up to 200 per cent. moisture the copper number produced remains at about 2·8 and 5·1, respectively, for the same time of exposure.

Typical results of progressive oxidation are given in Fig. 37. The increase in copper number of normal cellulose (I) is almost directly proportional to time over the first 12 hours, the value rising one unit per hour. Mercerised cellulose (II) shows a greatly increased rate.

The methylene blue absorption, however, is small, and not very different in all cases. Hydrocellulose (III) resembles cellulose in reaction, the copper number/time curves running almost parallel at a distance apart (2·5 units) approximately equal to the difference between the original values. This contrasts with the behaviour of a methylene blue type oxycellulose (IV) of copper number 3·25, which developed a copper value of 5·8 in 6·5 hours, whereas the original cellulose (I) of copper number 0·15 reached the same value in the same time. Beyond that point, however, oxidation shown by curve (IV) was rapid, and ran parallel with that of the triacetate (V). The methylene blue absorption of this oxycellulose was reduced by oxidation with ozone.

Complete acetylation afforded some protection against ozone action over the first 12 hours, but after this the rate of increase in copper number (calculated on the cellulose content) was rapid. For comparison the oxidising action of acid and alkaline permanganate solutions of *p*H 1 and *p*H 11·2, respectively, was examined. The results (Fig. 38) show that the triacetate, as with ozone, is slowly attacked by the acid permanganate, but there is no oxidation at all with alkaline permanganate. The methylene blue values were not increased in either case, and the reagents had no effect on the acetyl content.

These results seem to indicate that reducing groupings which are not capable of further oxidation (perhaps ketonic) can be formed in the absence of free hydroxyl groupings.

Nitrogen Peroxide Oxycellulose.—By the action of NO_2 gas (0·6 to 0·9 parts) on cellulose at 20° or below for 50 hours, it is claimed [1] that oxidation of the terminal carbon atom takes place, giving rise to an oxycellulose which has a CO_2 equivalent of not less than 13 per cent. It is soluble in 2 per cent. sodium hydroxide.

[1] Eastman Kodak Co., U.S.P., 2,232,990 (1941).

CHAPTER VII

HYDROCELLULOSE

THE fact that cellulose is very sensitive to the action of aqueous acids, losing strength and fibrous structure and becoming increasingly soluble in alkalis, was early recognised. Girard,[1] in 1875, began a series of investigations into the properties of cellulose, modified in this way by acids, for which he introduced the term "hydrocellulose". His methods of preparation have been largely followed by succeeding investigators.

The term hydrocellulose is used to cover all types of acid-modified cellulose, which may vary in form, according to the extent of acid treatment, from fibres to friable powders.

Examination of hydrocelluloses formed under definite conditions has shown that there is a homogeneity about all types, whatever their method of preparation. The copper number and viscosity of all hydrocelluloses, for example, are connected by a simple relationship (p. 154), enabling one value to be deduced from the other. In the light of the chain-molecule theory the formation of hydrocellulose is due to hydrolysis of glucosidic linkages in the cellulose chains, resulting in shorter chains constituted on the same structural plan. The shorter chains vary in length so that hydrocellulose must be regarded as a mixture of cellulose fragments, similarly constituted, but differing in size. The opening up of the primary valence bonds of the cellulose brings about the loss in strength observed,[2] and the unmasking of reducing groups with the shortening of the chains, leads to the development of solubility in alkalis and increase in copper number.

Recent investigation (p. 172) confirms this view. A hydrocellulose preparation was separated[3] into a fibrous part and a powdered part. The average chain-length of the former was about 200 glucose units, and of the latter 50 to 100 units. Glucose in maximum yield was the sole product of hydrolysis, and the same methylated sugars were obtained as with cellulose.

Hydrocelluloses are thus intermediate between cellulose and the cellulose dextrins of chain-length 20 to 25 glucose units (p. 202).

[1] A. Girard, *Compt. rend.*, 1875, **81**, 1105; *ibid.*, 1879, **88**, 1322; *Ann. Chim. Phys.*, 1881 (v.), **24**, 337.

[2] *Cf.* H. Staudinger *et al.*, *Ber.*, 1937, **70**, 1565.

[3] W. N. Haworth, S. Peat and P. Wilson, *J. Chem. Soc.*, 1939, 1901, 1905.

I. Preparation of Girard's Hydrocellulose

(*a*) **By Drying Small Quantities of Acid into Cellulose.**—The usual method is to soak cotton in 1 per cent. solutions of hydrochloric, sulphuric, or phosphoric acids. The excess of acid is squeezed out, the material allowed to dry in the air, and then heated at 60 to 70°. Preparations made in this way are frequently referred to as Girard's Hydrocellulose.

(*b*) **By Immersion in Acids.**—Cellulose is converted by the stronger acids on simple immersion. Using sulphuric acid (*d*, 1·453), cotton is soaked for 12 hours at 15°, or with hydrochloric acid (*d*, 1·091) for 24 hours. The use of acids over a range of temperatures is described on p. 153.

(*c*) **By the Action of Moist Gaseous Acids.**—By treatment with moist hydrochloric acid gas in the cold, cellulose is converted into hydrocellulose in 1 hour. Viscose rayon gives a product with special properties (p. 147).

(*d*) **By the Action of Organic Acids.**—Cotton is immersed in 5 per cent. solutions of oxalic, tartaric, citric acids, etc., dried in the air and heated in closed vessels at 100°. Oxalic acid effects a satisfactory conversion, but the others, including acetic and formic acids, produce only a moderate change.

II. General Properties and Reactions of the above Hydrocelluloses

(i) **General Properties.***—Hydrocelluloses thus prepared are friable powders, generally white in colour. If quite free from acid they remain colourless when dried at 100°, but if a trace of acid is present they turn brown. As will be seen, acid is often retained in a very stable condition.

(ii) **Colour Reactions.**—A blue-violet colour is given by the zinc chloride-iodine reagent and by potassium iodide-iodine. The colour is washed away by water. They are said not to react with Schiff's reagent.

The behaviour of hydrocelluloses towards dyestuffs is variously described in the literature, the divergencies being probably due to the different amounts of acid retained by the preparations.

(iii) **Reducing Properties.**—Hydrocelluloses reduce ammoniacal silver nitrate and Fehling's solutions. Schwalbe [1] and others have given the copper numbers of many hydrocellulose preparations,

* See "Hydrocellulose": A summary of the Literature, P. H. Clifford, *J. Text. Inst.*, 1923, **14**, 69T.

[1] *Ber.*, 1907, **40**, 1347, 4523; *Z. angew. Chem.*, 1910, **23**, 924.

the results varying from 3 to 10. A method[1] for the estimation of aldehydic groups in hydrocellulose involves oxidation at 0°, with iodine at *p*H 10·6, and measurement of the iodine consumed. A correction is required for side reactions. Results can be confirmed by titration of the carboxyl groups formed with silver *o*-nitrophenolate (p. 117).

(iv) **The Action of Water, Alkalis and Alkaline Earths.**—When boiled with water the copper-reducing substance passes into solution and the reducing value of the residue falls. A preparation with a copper number 5·4, for example, after 70 hours' treatment with water,[2] gave a copper number 0·8. This product could again be converted into hydrocellulose by acid treatment.

Alkaline solutions dissolve considerable quantities of hydrocellulose; *e.g.*, Schwalbe [3] found that Girard's hydrocellulose dissolved to the extent of 52 per cent. on boiling for 10 minutes with 15 per cent. sodium hydroxide solution, while the hydrocellulose prepared from viscose cellulose (p. 147), dissolves completely in a cold 8 per cent. solution.

On prolonged boiling with milk of lime hydrocellulose yields calcium *iso*-saccharinate among other salts.[4] The liquors are concentrated and calcium *iso*-saccharinate crystallises out. It contains Ca, 10·05 per cent. If boiled with the equivalent of oxalic acid the free acid is liberated. The filtrate is concentrated and seeded with a crystal of the acid (m.p. 92°).

The baryta resistance value and the amount of barium taken up by hydrocelluloses have been determined as in the case of oxycellulose (see table, p. 119).

(v) **Esterification.**—Hydrocellulose reacts with esterifying agents with greater ease than cellulose, and in the commercial preparation of esters a preliminary treatment of the cellulose with acid is frequently given. The nitrates of hydrocellulose have lower viscosity and increased alcohol solubility compared with those made from cellulose under the same conditions. Berl and Klaye,[5] for example, prepared nitrates under similar conditions, each containing 13·3 per cent. of nitrogen. The solubility in alcohol of the nitrate from hydrocellulose was seven times as great as that of the cellulose

[1] A. R. Martin *et al.*, *J. Res. Nat. Bur. Stand.*, 1941, **27**, 449.
[2] E. Heuser and H. Herzfeld, *Chem.-Zeit.*, 1915, **39**, 689.
[3] C. G. Schwalbe, *Z. angew. Chem.*, 1909, **22**, 155.
[4] J. J. Murumow, J. Sack and B. Tollens, *Ber.*, 1901, **34**, 1427; C. G. Schwalbe and E. Becker, *J. prakt. Chem.*, 1919, **100**, 19; *cf.* G. L. Godman *et al.*, *J. Chem. Soc.*, 1939, 1910.
[5] E. Berl and R. Klaye, *Z. ges. Schiess-und Sprengstoffwesen*, 1907, **2**, 381; *cf. Mon. Sci.* (4), **24**, 103.

product, but the viscosity of the cellulose nitrate was 150 times as great as that of the hydrocellulose nitrate.

III. The Hydrocellulose of Knoevenagel and Busch[1]

This hydrocellulose is completely soluble in dilute alkaline solutions, and may be useful in experimental work. The following directions are given by Hess (*loc. cit.*) :—

75 g. of viscose rayon, air dry, are treated with CO_2 to remove air and then saturated with HCl gas, moisture being excluded, after which the material is left for 15 hours at room temperature. It is then put into ice water, the acid neutralised with bicarbonate, and the product washed and dried. A yellowish fibrous mass (53 g.) is obtained which powders easily. It is taken up in 400 ml. of 10 per cent. NaOH, and the solution centrifuged to remove any suspension. Ammonia gas is then passed to saturation, the temperature being kept below 10°. The fine white precipitate is easily separated by centrifuge from the mother liquor. The solid is washed with 25 per cent. ammonia, centrifuged, etc., until the liquid becomes colourless. The ammonia is then cautiously removed by water. The water is added the first few times without too much disturbance of the sediment as the fine suspension formed settles with difficulty. When the bulk of the alkali has been removed this danger becomes less and washing is continued till the odour of ammonia almost disappears, the last traces being neutralised with acetic acid. The residue is washed with alcohol and with ether, and dried (vacuum) at 100°. Yield, 20·3 g.

An analysis gave C, 44·7 ; H, 6·35 ; ash 0·16 per cent. $C_6H_{10}O_5$ requires C, 44·4 ; H, 6·22.

For further purification 8 g. are shaken for 12 hours with 50 ml. of *N*-NaOH, air being excluded. The liquid is centrifuged and the residue washed free from alkali, taken up in 2*N*-NaOH, and saturated with ammonia gas. The sodium hydroxide is removed by treatment with 25 per cent. ammonia solution, using a good centrifuge.

Another preparation was made by treating a viscose rayon for 2 hours only with HCl gas. 20 g. of rayon gave 18 g. of product, which, after purification as above, gave 10 g. of dried hydrocellulose. C, 44·45 ; H, 6·32 ; ash 0·41 per cent.

[1] E. Knoevenagel and H. Busch, *Cellulosechem.*, 1922, **3**, 47 ; E. Heuser and v. Neuenstein, *ibid.*, 1922, **3**, 101 ; K. Hess, *Ann.*, 1923, **435**, 142.

IV. The Properties of Hydrocelluloses prepared under exactly known Conditions of Acid Treatment[1]

These authors, pointing out the uncertainties in the concentration, etc., of the acid employed by previous workers, find that a wide range of hydrocelluloses can be obtained, and reproduced, by the action upon cotton of a large excess of acid at temperatures between 20° and 100° (the "acid steeping method"). In view of the technical importance of the effects of small quantities of acid when dried into cotton fabrics, hydrocelluloses were also prepared for comparison in this way (the "acid drying method").

Methods of Preparation.—(i) *By Steeping in Acid Solutions at* 20° *and* 40°.—40 g. of cotton were treated with 1 litre of the acid solution, the vessel being kept in a thermostat and care taken to ensure thorough wetting. The product was washed with distilled water and dried in the air.

For special purposes, such as the measurement of hair strength, more prolonged washing was required, for although a neutral wash water is soon obtained, this gives no guarantee that acid has been eliminated. In these cases the hydrocellulose was allowed to steep in water for periods of 1 to 3 days and centrifuged between changes until the water, after steeping, was not more than $10^{-5}N$- in mineral acid. Methyl red (*p*H 4·2 to 6·3) can be used for this purpose.

(ii) *Boiling with Acid.*—With very weak solutions of acid of boiling-point approximately that of pure water, the cotton was boiled with fifty times its weight of the acid under reflux. With acids of 0·001*N*- concentration the ash alkalinity of the cotton had first to be reduced by the standard acid-washing process with 0·1*N*-sulphuric acid.

(iii) *Impregnation with Acid and subsequent Heating.*—With this treatment it is difficult to obtain an even action. The following was found fairly satisfactory :—

Cotton cloth was wetted out in a large volume of acid and mangled between rubber rollers until the weight was double the air-dry weight (two and a quarter times in the case of phosphoric acid); it was then allowed to "dry" overnight in the air and heated on a rotating glass frame inside an electric oven maintained at the required temperature for the necessary time. This procedure yielded reasonably uniform and reproducible results when the concentration of acid was not less than 0·025*N*-, but with acid as dilute as 0·01*N*- no method was found which yielded uniform results over a considerable area of cloth. The cotton was washed

[1] C. Birtwell, D. A. Clibbens and A. Geake, *J. Text. Inst.*, 1926, **17**, 145.

with cold dilute acid and water before impregnation and heating, in order to reduce the ash alkalinity, but even after this treatment the residual ash-alkalinity varied from 0·5 to 1 milli-equivalent per 100 g., and when 0·01*N*- acid solutions were used the amount of acid present on the cloth (1 milli-equiv. per 100 g.), was of the same order of magnitude as the residual ash alkalinity.

Methods of Measurement.—(i) *Breaking Load.*—Yarn tests were made on a Goodbrand single thread tester on 40 cm. lengths at 20° and R.H. 70 per cent., 150 breaks in each case. Hair-breaking loads at 20° and R.H. 66·3 per cent., 200 breaks being made on the modified O'Neill apparatus (p. 77).

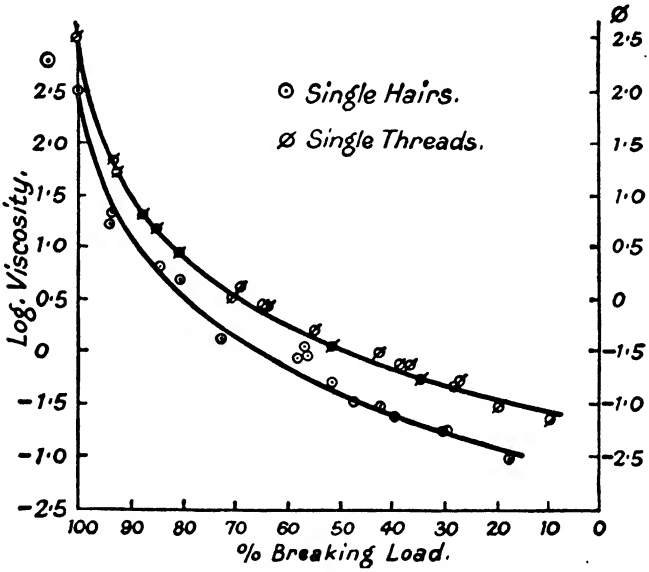


FIG. 39.—Relation between the breaking load and viscosity of cotton tendered by acids.

(ii) *Copper Number.*—The Schwalbe-Braidy method on 2·5 g.

(iii) *Viscosity.*—As Farrow and Neale (p. 46). Two per cent. solutions were used unless the viscosity was very high.

(iv) *The Methylene Blue Absorption.*—On 2·5 g. samples, using methylene blue at *p*H 7. Results expressed in millimoles of methylene blue per 100 g. of dry material.

(v) *Loss of Weight on Alkali Boiling.*—Method, p. 37.

(vi) *Phosphorus Content.*—The samples were moistened with dilute sodium carbonate solution before ignition, and the phosphorus estimated by the method given on p. 213.

The general results obtained were derived chiefly from hydrocelluloses prepared by the acid-steeping method, but on the whole

they applied also to those made by the acid-drying method. The more important conclusions are as follows :—

(i) The general character of the changes produced in cellulose by the action of acids is the same whatever acid is employed.

(ii) The fall in the tensile strength of cotton caused by the action of acids, under any conditions of treatment, is accompanied by a fall in viscosity and a rise in reducing power.

(iii) A definite relation exists between loss of tensile strength and viscosity (Fig. 39). The same fall in viscosity corresponds to the same loss of strength, irrespective of the mode of acid treatment.

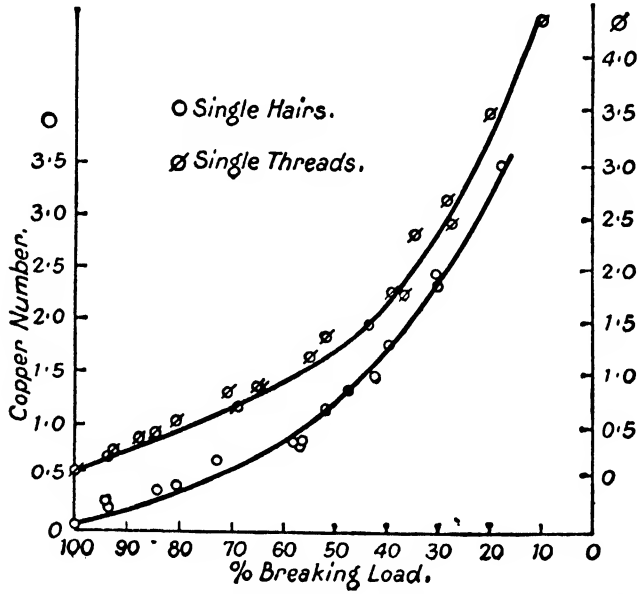


FIG. 40.—Relation between the breaking load and the copper number of cotton tendered by acids.

For example, a treatment which causes the viscosity (log η) to fall to the value 1 produces a loss of 10 per cent. in strength ; a loss of 80 per cent. in strength corresponds to log $\eta = \bar{1}$.

(iv) A definite relation (Fig. 40) exists between the strength and the copper number of any hydrocellulose ; for example, a diminution of 10 per cent. in breaking load corresponds to a rise of 0·25 in copper number, a decrease of 80 per cent. in breaking load to a rise of 3·5.

(v) A definite relation exists between the viscosity of a hydrocellulose and its copper number (Fig. 41). A given viscosity always corresponds to the same copper number irrespective of the conditions of acid treatment. The relation between these two

quantities can be expressed with reasonable accuracy by a simple equation.. By this relation it is possible to differentiate between hydrocelluloses and those oxycelluloses which are otherwise indistinguishable from them, since hydrocellulose formation conforms strictly to the equation, whereas oxycellulose formation does not.

(vi) The increased absorption for basic dyestuffs shown by preparations made with sulphuric and phosphoric acids is due to the presence of combined acid which cannot be removed by severe

CHANGES PRODUCED IN A 40's COMBED WARP YARN STEEPED IN ACIDS UNDER VARIOUS CONDITIONS

Acid Treatment.				Breaking Load per cent. on Untreated Material.		Copper Number.	Log Viscosity in 2 per cent. Solution. Log η.
Acid.	Concentration.	Time Hours.	Temp. °C.	Single Thread.	Single Hair.		
H_2SO_4	100 g./lit.	48	20	93·3	93·4	0·20	1·33
,,	200 ,,			84·7	80·4	0·42	0·69
,,	300 ,,			70·3	56·3	0·80	0·02
,,	400 ,,			51·4	47·1	1·34	$\bar{1}$·53
,,	500 ,,			34·1	29·9	2·32	$\bar{1}$·23
,,	600 ,,			19·5	17·6	3·48	$\bar{2}$·98
,,	700 ,,			9·7	—	4·36	$\bar{2}$·85
,,	500 ,,	4		68·5	72·5	0·66	0·12
,,	500 ,,	12		54·5	51·5	1·15	$\bar{1}$·70
,,	500 ,,	24		38·5	39·5	1·76	$\bar{1}$·38
HCl	200 ,,	4		64·0	58·0	0·85	$\bar{1}$·94
,,	200 ,,	12		42·5	42·0	1·46	$\bar{1}$·49
,,	200 ,,	24		27·0	30·0	2·44	$\bar{1}$·22
H_2SO_4	0·01*N*	0·25	100	92·5	94·0	0·26	1·22
,,	0·01*N*	0·5		87·5	84·0	0·37	0·82
,,	0·01*N*	1		80·7	—	0·52	0·45
,,	0·01*N*	2		64·5	56·0	0·85	$\bar{1}$·95
,,	0·1 *N*	1		36·1	—	1·74	$\bar{1}$·37
,,	0·2 *N*	2		27·9	—	2·65	$\bar{1}$·17

alkaline treatment. The increased absorption due to oxycellulose formation can be distinguished from that due to the action of sulphuric and phosphoric acids by absorption measurements made from acid methylene blue solution.[1]

(vii) The rate of attack on cotton by acids is best measured by the change in copper number. The increase of copper number, with increase of time of treatment, is governed by the rule that the copper number is increased by 50 per cent. when the time of treatment is doubled. This rule, expressed as an equation, enables the

[1] D. A. Clibbens and A. Geake, *J. Text. Inst.*, 1926, **17**, 127T.

velocity constant to be calculated. The mean temperature coefficient of hydrocellulose formation between 20° and 100° is found to be 2·3—*i.e.* the copper number resulting from given treatments is increased 2·3 times by a rise of temperature of 10°. As both tensile strength and viscosity have been correlated with the copper number these quantities also can be calculated from the copper number.

(viii) The addition of neutral salts to hydrochloric acid has a very great effect in increasing the rate of the attack of this acid, especially when the concentration of the salt is high.

The experimental methods and results will readily be grasped

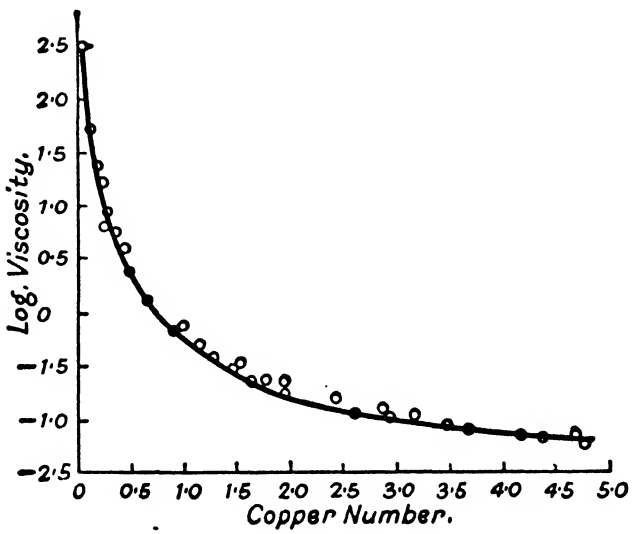


FIG. 41.—Relation between the viscosity and the copper number of cotton tendered by acids.

from an examination of the tables and curves which appear on p.p. 149 to 153.

The values are plotted as curves in Figs. 39, 40, 41.

It will be seen from Fig. 40 that the copper number as a measure of tendering is most sensitive in the later stages of acid attack when the loss in breaking load is between 50 and 100 per cent., whilst the viscosity (Fig. 39) is most sensitive in the early stages corresponding to the first 20 per cent. loss in breaking load.

The copper number and viscosity (log η) of a number of hydrocellulose preparations are given in the table on p. 153.

In spite of the wide variation in the conditions under which these hydrocelluloses were prepared, all the points connecting viscosity with copper number lie on or near the same smooth curve.

Treatment of Cotton.				Copper Number N_{Cu}.	Log Viscosity in 2 per cent. Solution. Log η.	Log Relative Viscosity V.	$N_{Cu}V^2$.
Acid.	Concentration gms. per litre.	Time, Hours.	Temp. °C.				
HAc	6	1	100	0·13	1·74	3·56	1·7
H_2SO_4	50	48	20	0·15	1·66	3·48	1·9
,,	100	24	20	0·17	1·37	3·19	1·7
,,	12·25	24	40	0·20	1·39	3·21	2·1
HCl	0·036	1	100	0·26	1·10	2·92	2·2
HAc	60	1	100	0·29	0·83	2·65	2·1
H_2SO_4	200	24	20	0·31	0·94	2·76	2·4
,,	0·49	0·5	100	0·37	0·82	2·64	*2·6*
H_2SO_4	49	20	40	0·45	0·60	2·42	*2·6*
,,	49	24	40	0·46	0·61	2·43	*2·7*
HCl	0·365	1	100	0·495	0·39	2·21	*2·4*
H_2SO_4	100	192	20	0·52	0·38	2·20	*2·5*
,,	0·49	1	100	0·52	0·45	2·27	*2·7*
HCl	100	24	20	0·58	0·26	2·08	*2·5*
H_2SO_4	500	4	20	0·66	0·12	1·94	*2·5*
,,	100	384	20	0·77	1·99	1·81	*2·5*
HCl	200	4	20	0·85	1·94	1·76	*2·6*
H_2SO_4	0·49	2	100	0·855	1·95	1·77	*2·7*
HCl	0·73	1	100	0·88	1·87	1·69	*2·5*
,,	100	48	20	0·91	1·84	1·66	*2·5*
HAc	60	6	100	0·95	1·76	1·58	*2·4*
H_2SO_4	100	24	40	1·00	1·89	1·71	*2·9*
,,	500	12	20	1·15	1·70	1·52	*2·7*
HCl	36·5	24	40	1·23	1·65	1·47	*2·7*
,,	100	96	20	1·28	1·58	1·40	*2·5*
H_2SO_4	400	48	20	1·34	1·53	1·32	*2·4*
HCl	200	12	20	1·46	1·49	1·31	*2·5*
,,	100	5	40	1·52	1·47	1·29	*2·5*
H_2SO_4	4·9	1	100	1·74	1·37	1·19	*2·5*
HCl	200	24	20	2·44	1·22	1·04	*2·6*
H_2SO_4	500	48	20	2·62	1·17	0·99	*2·6*
,,	9·8	1	100	2·65	1·17	0·99	*2·6*
HCl	200	2	40	2·87	1·13	0·95	*2·6*
,,	3·65	1	100	3·17	1·07	0·89	*2·5*
,,	100	24	40	3·67	2·93	0·75	2·1
H_2SO_4	24·5	1	100	4·15	2·87	0·69	2·0
HCl	7·3	1	100	4·22	2·88	0·70	2·1
,,	100	960	20	4·47	2·83	0·65	1·9
,,	200	5	40	4·68	2·89	0·71	2·4
,,	300	48	20	4·70	2·76	0·58	1·6

Mean of values in italics—2·6

It is of importance to note that the copper number-viscosity relation obtained for the acid-tendered cottons is very different from that obtained for certain oxycelluloses which otherwise closely resemble hydrocelluloses, this difference affording a method of distinction.

Use of the Copper Number-Viscosity Relation as a Criterion of Acid Attack on Cellulose.—From the results given on p. 153 it is possible to deduce an equation connecting the viscosity and the copper number values.

If η is the absolute viscosity of a 2 per cent. modified cellulose solution, and η_0 is the absolute viscosity of the cuprammonium solvent (0·0152 poise), then η/η_0 may be called the "relative viscosity" of the solution, and the quantity log η, generally used, may be replaced by log η/η_0, designated by the symbol V, so that—

$$V = \log \eta/\eta_0 = \log \eta - \log \eta_0 = \log \eta + 1{\cdot}82.$$

If the copper number is denoted by N_{Cu}, the copper number-viscosity relation for the hydrocelluloses described above is represented with fair accuracy by the equation—

$$N_{Cu}V^2 = 2{\cdot}6.$$

In the table the hydrocelluloses are arranged in order of increasing copper number and the product $N_{Cu}V^2$ is calculated for each preparation. It will be seen that for values of the copper number between 0·4 and 3·0 the product is reasonably constant, the mean value for forty-two preparations being 2·6. For hydrocelluloses with copper numbers outside these limits the product becomes less than 2·6, but the range within which the equation is valid is technically the most important, corresponding to loss of tensile strength (breaking load), varying roughly between 15 and 75 per cent. of that of the untendered material.

The following table contains values of the product $N_{Cu}V^2$ for a series of oxycelluloses [1] covering a similar range of copper number. Prepared from the same yarn by the action of hypochlorous acid, they could not, by other means, be distinguished with certainty from hydrocelluloses. The values of $N_{Cu}V^2$ leave no doubt, however, that the modification in this case is not due to acid attack, which would lead to the constant number 2·6.

YARN OXIDISED WITH HYPOCHLOROUS ACID

Copper Number, N_{Cu}.	Log Viscosity in 2 per cent. Solution, Log η.	Log Relative Viscosity, V.	$N_{Cu}V^2$.
0·36	1·37	3·19	3·7
0·55	0·96	2·78	4·2
0·88	0·38	2·20	4·3
1·76	$\bar{1}$·92	1·74	5·3
3·39	$\bar{1}$·44	1·26	5·4

[1] C. Birtwell, D. A. Clibbens and B. P. Ridge, *J. Text. Inst.*, 1925, **16**, 13T.

A further series of results shows that for any particular value of the copper number the viscosity of the product will be lower if the change is produced by acid attack than it will be if produced by the action of oxidising agents. This applies only, however, to oxycelluloses of the reducing type.

Hydrocelluloses formed by acid impregnation and subsequent heating, give a value of about 2·8 for $N_{Cu}V^2$ in all cases when the temperature of drying does not exceed 70°. For higher temperatures values ranging from 1·9 at 90° to 1·1 at 130° are obtained. Other changes than those of hydrocellulose formation take place under these conditions, one being the combination of the acid with the hydrocellulose. The effect of this, incidentally, is to cause an abnormally high methylene blue absorption. The cellulose is also degraded by the drying in of acid at a high temperature, dextrins and other soluble reducing products being formed. This is shown by the reduction in the copper number of the product after thorough washing.

The Methylene Blue Absorption of Hydrocelluloses.—A decreasing absorption of methylene blue is the normal effect of the action of acids on cotton ; an enhanced absorption, which is sometimes observed, being a property of hydrocelluloses produced by relatively high concentrations of sulphuric or other acid. The high absorption is due to retention of acid.

The following table illustrates the phenomena observed with sulphuric acid steeping. When the absorption is determined at *p*H 7 a steady fall in absorption value is shown by products formed with increasing acid concentration, but the value rises again beyond an acid concentration of 500. A similar, but more marked, effect is observed when the absorption is determined at *p*H 2·7.

COTTON STEEPED IN SULPHURIC ACID AT 20° FOR FORTY-EIGHT HOURS

H_2SO_4 grams per litre	0	100	200	300	400	500	600	700
Methylene blue absorption								
at *p*H 7	0·89	0·82	0·83	0·82	0·79	0·79	0·94	1·30
at *p*H 2·7	0·31	0·28	0·26	0·25	0·27	0·36	0·72	1·76

With lower concentrations of sulphuric acid at higher temperatures, no rise of methylene blue absorption is observed, but only a steady fall. The same steady fall is observed when cotton is steeped in hydrochloric acid under any conditions.

Hydrocelluloses formed by impregnation with sulphuric acid and

heating also show an initial fall in the absorption of methylene blue followed by a rapid rise as the concentration of acid increases, this rise beginning at a concentration of 0·1*N* to 0·5*N*. At 70° the rise is definite at 0·1*N*. With products made at 110° absorption measurements at *p*H 2·7 show a greatly increased value even with acid as dilute as 0·025*N*.

Hydrochloric acid, when similarly dried into cloth, depresses the absorption below that of the untreated cloth in nearly all cases, except under such drastic conditions as *N*-acid at 90°, when a rise in absorption occurs. Phosphoric acid, on the other hand, gives similar results to those obtained with sulphuric acid.

Relation between the increased Methylene Blue Absorption and the Amount of Acid fixed by the Hydrocellulose.—As an accurate method for the estimation of phosphoric acid is available (p. 213) experiments were carried out by impregnating cloth with 0·1*M*-phosphoric acid, heating for 2 hours, and estimating the acid present after prolonged washing. Some results are given below.

CLOTH IMPREGNATED WITH 0·1*M*-PHOSPHORIC ACID AND HEATED FOR 2 HOURS

Temperature of Heating.	Methylene Blue Absorption.		H_3PO_4 Content. (M. Moles/100 g.).
	At *p*H 7.	At *p*H 2·7.	
(untreated)	0·89	0·31	0·00
50°	0·83	0·52	0·35
70°	0·93	0·71	0·79
90°	1·39	1·19	1·80
110°	1·64	1·70	2·62
130°	1·82	2·14	3·31

PHOSPHORIC ACID HYDROCELLULOSE SUBMITTED TO HOT ALKALINE TREATMENT

Treatment.	H_3PO_4 Content (M. Moles/100 g.).
Prolonged water washing	3·31
Boiled 4 hours with 1 per cent. NaOH solution .	2·81
„ „ 5 „ NaOH solution .	2·67
„ „ 1 „ KOH in amyl alcohol (b.p. 137°) .	2·86
„ „ 15 „ NaOH solution .	2·11
Sealed tube at 140°, 4 hours with 5 per cent. NaOH .	2·46

It will be seen that the absorption at *p*H 2·7 is proportional to the acid content of the hydrocellulose except in the early stages. That this acid is tenaciously retained is shown in the second table on p. 156.

V. The Rate of Acid Attack on Cotton

This was investigated [1] by steeping yarn in solutions of suitable acid concentration at 20°, 40° and 100° for times varying from 0·1 to 40 days, and measuring the copper number of each sample. A rule has been deduced which holds with fair accuracy—*viz.* that when the time of action of any given acid treatment is doubled the copper number of the resulting product is increased by 50 per cent. This may be expressed by the equation—

$$N_{Cu} = KT^{0.6},$$

where T is the time of treatment and K a constant under the defined conditions. If the time is measured in days, K is equal to the copper number which results from an acid treatment lasting 1 day. This is illustrated by the following results for hydrocelluloses formed by acid steeping :—

	Time in days.	1	4	8	16	
H_2SO_4 100 g./litre at 20°.	Copper No., N_{Cu}.	0·17	0·36	0·52	0·77	
	Constant, K	0·17	0·16	0·15	0·15	Mean 0·15
	Time in days.	0·208	0·229	1·0		
HCl 100 g./litre at 40°.	Copper No., N_{Cu}.	1·52	1·54	3·67		
	Constant, K	3·90	3·73	3·67		Mean 3·77

The mean value of K gives the most satisfactory measure of the rate of acid attack under any conditions of concentration and temperature. The method, however, was not applied to hydrocelluloses with copper numbers above 4.

The Effect of the Concentration of Acid on the Rate of Attack on Cotton.—This is best determined by direct measurement of K, *i.e.* the copper number produced in 1 day. The results obtained with hydrochloric and sulphuric acids at 20°, 40° and 100° show that the rate of hydrocellulose formation is practically the same for solutions of the two acids of equal molar concentrations,

[1] C. Birtwell, D. A. Clibbens and A. Geake, *J. Text. Inst.*, 1924, **15**, 161T.

hydrochloric acid being always slightly more active. Below a concentration of 3-molar, K is almost proportional to the concentration, but above this the curves become steeper, *i.e.* the rate of attack increases more rapidly than the acid concentration. Hydrochloric acid at 20°, and concentration 8-molar, is nearly six times as active as that of acid of concentration 4-molar.

The temperature co-efficient of the rate of hydrocellulose formation was calculated from the velocity constants measured for the range 20 to 40° for sulphuric acid, of concentrations 0·5, 1·02, and 2·04-molar, and for hydrochloric acid at 2·74 molar, the values found being 2·2, 2·5, 2·4, and 2·5 respectively for an interval of 10°. A similar value, 2·2, was found for the higher range of 60 to 100°. The average value is thus 2·3, which implies that the copper number resulting from the action of a solution of either acid, for a definite time, is increased 2·3-fold for a rise of temperature of 10° within the range 20 to 100°.

The presence of *neutral salts* appears greatly to increase the rate of attack. Thus the rate of attack of 0·1 molar hydrochloric acid at 60° was increased three-fold by making the solution 3·9-molar in sodium chloride. These results may have a bearing on the action of concentrated solutions of zinc and magnesium chloride on cotton.

The Rate of Attack when Cotton is Impregnated with Dilute Acid and Heated.—Quantitative measurements are obviously more difficult to carry out under these conditions. In the case of sulphuric and phosphoric acids continued heating produces only a gradual rise of copper number, and the fall of viscosity also is very slow after the initial effect. The rise of copper number caused by doubling the time of heating does not exceed 10 per cent., and is generally very much less. Impregnation and subsequent heating for 2 hours at temperatures ranging from 50 to 130° with the same two acids produced copper numbers rising to a maximum at 70 to 90°. Beyond this point temperature has little or no effect.

The type of result obtained is shown in the table.

COPPER NUMBERS OF CLOTH IMPREGNATED WITH DILUTE ACIDS AND HEATED FOR 2 HOURS AT VARIOUS TEMPERATURES

Concentration of Acid.	Temperature of Heating.					
	50°	70°	80°	90°	110°	130°
H_2SO_4, 0·5*N*	3·79	4·57	—	—	—	—
H_2SO_4, 0·1*N*	1·60	3·65	3·21	3·44	3·54	—
H_2SO_4 0·025*N*	0·30	1·56	—	2·01	2·12	—
H_3PO_4, 0·1*M*	0·74	1·23	—	1·55	1·45	1·67

Hydrochloric acid, when dried into cotton, shows a different behaviour, which is no doubt a function of its volatility. The copper number of the cellulose increases at first with increased temperature of drying, passes through a maximum, and then falls again as the temperature, and the volatility of the acid, simultaneously become high.

From the table it will be seen that the maximum copper number is reached at about 70° (2·6 with acid 0·25*N*), and yet the cotton can be heated with 0·25*N*- acid at 90° without appreciable tendering, while the same acid at 70° causes loss of strength of the order of 70 per cent.

CLOTH IMPREGNATED WITH HYDROCHLORIC ACID AND HEATED FOR 2 HOURS

Concn. of Acid.	Temperature of Heating.	50°	70°	90°	110°
0·1*N*-HCl . .	Copper number .	2·06	3·60	2·89	3·21
0·025*N*-HCl .	,, .	0·96	2·56	0·10	0·20

The Rate of Depolymerisation.—This has been examined by Staudinger.[1] Cotton of original polymerisation value 1650 was treated with solutions of *N*-acids for periods up to 226 hours. Depolymerisation was rapid, *e.g.* with HCl, etc., it fell to half value in 1 hour and with acids of the type of H_2SO_4 in 5 hours. After this time depolymerisation slows up and in about 20 hours comes to a standstill. Mechanical properties are not seriously affected till the value falls below 700, but at 600 damage is very marked. With weak acids, such as formic and phosphoric acids, the value never becomes less than 1,000 units after 20 hours, but with the strongest acids the value falls to 250 and with sulphuric acid to about 500.

VI. THE ACTION OF ALKALINE SOLUTIONS ON MODIFIED CELLULOSE

Behaviour of Hydrocellulose and Oxycellulose on Boiling with Dilute Alkali.—The effect of boiling with dilute alkaline solutions has been examined[2] with a view to deducing the cause of the original modification—*i.e.* whether it was due to the effect of acids or of oxidants. The treatment consisted in boiling for 6 hours

[1] H. Staudinger, *Ber.*, 1937, **70**, 1565.
[2] D. A. Clibbens, A. Geake and B. P. Ridge, *J. Text. Inst.*, 1927, **18**, 277T.

with 1 per cent. sodium hydroxide solution either (*a*) under atmospheric pressure, or (*b*) at 20 lb. per square inch excess pressure.

Some of the results obtained with process (*b*) are given in the following table :—

CHANGES IN THE PROPERTIES OF MODIFIED COTTON AFTER BOILING WITH ALKALI *

(A)—*Oxycelluloses*

Method of Preparation.		Copper Number.			Methylene Blue Absorption.			Viscosity (Log η, 2 per cent.)		
		Before Boiling N_B	After Boiling, N_A	Ratio N_A/N_B	Before Boiling, M_B	After Boiling, M_A	Change $M_A - M_B$	Before Boiling, V_B	After Boiling, V_A	Change $V_A - V_B$
N/25 Hypochlorite (neutral *p*H7) at 25°.	1	1·02	0·22	0·22	0·96	—	—	0·95	$\bar{1}$·96	0·99
	2	1·41	0·34	0·24	1·01	1·18	+ 0·17	0·46	$\bar{1}$·57	0·89
	3	2·02	0·47	0·23	1·08	—	—	$\bar{1}$·98	$\bar{1}$·39	0·59
	4	3·22	0·66	0·21	1·36	1·66	+ 0·30	$\bar{1}$·56	$\bar{1}$·12	0·44
	5	4·58	0·79	0·17	1·51	1·89	+ 0·38	$\bar{1}$·34	$\bar{1}$·09	− 0·25
N/25 Hypochlorous Acid (*p*H 4·6) at 25°.	1	0·65	0·09	0·13	1·02	0·90	0·12	0·81	0·38	0·43
	2	1·07	0·17	0·17	1·04	1·02	0·02	0·24	0·02	0·22
	3	1·56	0·28	0·18	1·06	1·06	0·00	$\bar{1}$·98	$\bar{1}$·71	− 0·27
	4	2·46	0·39	0·16	1·10	1·21	+ 0·11	$\bar{1}$·70	$\bar{1}$·52	− 0·17
	5	2·83	0·45	0·16	1·08	1·30	+ 0·22	$\bar{1}$·62	$\bar{1}$·45	− 0·17
	6	3·78	0·51	0·14	1·18	1·48	+ 0·30	$\bar{1}$·48	$\bar{1}$·35	− 0·13
N/100 Sodium Hypobromite (*N*/10 in NaOH) at 25°.	1	0·29	0·03	0·11	1·14	1·04	0·10	0·78	0·55	− 0·23
	2	0·39	0·04	0·11	1·32	1·18	0·14	0·33	0·05	− 0·28
	3	0·51	0·07	0·14	1·66	1·56	0·10	$\bar{1}$·81	$\bar{1}$·65	− 0·16
	4	0·63	0·12	0·19	2·16	2·08	0·08	$\bar{1}$·45	$\bar{1}$·33	− 0·12

(B)—*Hydrocelluloses*

Hydrochloric Acid at 25°.	1	0·41	0·06	0·16	0·92	0·88	0·04	0·50	0·58	+ 0·08
	2	0·67	0·13	0·19	0·90	0·91	+ 0·01	0·21	0·13	.0·08
	3	1·22	0·30	0·25	0·97	1·04	+ 0·07	$\bar{1}$·65	$\bar{1}$·63	0·02
	4	2·17	0·57	0·26	0·89	1·10	+ 0·21	$\bar{1}$·23	$\bar{1}$·26	+ 0·03
	5	3·22	0·85	0·27	0·88	1·24	+ 0·36	$\bar{1}$·09	$\bar{1}$·18	+ 0·09
	6	4·13	1·22	0·29	0·85	1·38	+ 0·53	$\bar{2}$·95	$\bar{2}$·96	+ 0·01

* The same sample of cotton was employed throughout.

The following differences are observed: Oxycelluloses, after boiling with alkali, show a marked fall in viscosity, differing in this respect from hydrocelluloses and normal cotton. The deviation from the normal viscosity is much greater for neutral hypochlorite oxycelluloses than for others.

Exactly the same results are observed with the residue left after the treatment employed in the determination of copper number by the Schwalbe-Braidy method, hydrocelluloses showing no change in viscosity and oxycelluloses a considerable decrease. The viscosity change observed after treatment of a modified cellulose with alkali constitutes one of the best methods for deciding whether the modification has been produced by oxidants or by acid action.

The other properties do not afford such a sharp distinction

The copper numbers of modified celluloses, for example, are reduced to about one-fifth of their original value as a result of alkali treatment under atmospheric pressure and to about one-tenth of their original value by a similar treatment under increased pressure.

The methylene blue absorption of modified cellulose rises after alkali boiling, the only exceptions being in the case of modified celluloses with copper numbers less than 1. Even hydrocelluloses which have an initial high absorption for methylene blue, due to combined sulphuric acid, show a further rise of absorption on alkali boiling. The figure for the percentage loss of weight on boiling for 4 hours with 1 per cent. sodium hydroxide at ordinary pressure is about six times the copper number when the latter does not exceed 2·5. This is independent of the manner in which the modification is produced, but with products having copper numbers above 2·5, hydrocelluloses experience a greater, oxycelluloses a smaller loss of weight. The relation between the loss in weight and the copper number is shown in Fig. 5 (p. 37).

The Effect of Hot Dilute Alkalis upon the Strength of Cotton already slightly Modified by Acids or Oxidising Agents. —Witz in 1883 observed that cotton tendered by oxidising agents suffered a further loss of strength on treatment with hot dilute alkalis, but that hydrocellulose did not show this phenomenon. The following results [1] are to some extent in agreement. Cotton yarn was modified by various agencies between two kier boils (6 hours 1 per cent. sodium hydroxide, 20 lb. pressure), and the strength of the material, both of the modification and the product after the second kier boil, was determined. The results are given in the following table :—

Loss of Strength Per cent.*

Per cent. Loss of Strength of Boiled Yarn after Modification only.	Boiled Yarn after Modification and Re-boiling.				
	Modified with Acid.	Modified with Alkaline Hypochlorite.	Modified with Neutral Hypochlorite.	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

* Given as single thread breaking load. The loss in strength of the single hairs was proportional to this.

† The concentration of acid employed did not, alone, produce any tendering effect under the conditions of experiment.

[1] D. A. Clibbens and B. P. Ridge, *J. Text. Inst.*, 1928, **19**, 390T.

It will be noted that the cotton modified with acid shows very little additional loss of strength. This is also the case with cotton oxidised with alkaline hypochlorite, which contrasts strongly with the neutral hypochlorite where a 20 per cent. loss by oxidation is converted into a 61 per cent. loss after boiling with alkali. The loss is far greater in the case of the modifications produced with dichromate and oxalic acid.

Milder treatments, such as boiling with 1 per cent. sodium hydroxide, or sodium carbonate, or soap solutions, for 6 hours, showed that again the additional loss of strength was very considerable, and it is pointed out that cotton materials might suffer chemical change during bleaching, printing or dyeing, which would not produce a harmful loss of strength until the goods were laundered. Some typical results are shown in the table below.

	Breaking Load (mean of 200).	Copper Number.	Approximate Loss of Weight per cent.
Kier boiled yarn, untreated .	100	0·02	0
Do. oxidised with dichromate .	84·0	6·70	2
Do. do. and boiled 1 per cent. NaOH 6 hours 20 lb. . .	22·7	0·45	37
Do. do. and boiled 1 per cent. NaOH 6 hours open . .	25·6	0·87	31
Do. do. and boiled 1 per cent. Na_2CO_3 6 hours open . .	31·5	2·00	19
Do. do. and boiled 0·1 per cent. soap and 0·2 per cent. Na_2CO_3 6 hours open . . .	33·5	2·85	10
Do. do. and boiled 1 per cent. soap 6 hours open . . .	35·4	3·51	6
Do. do. and boiled water 6 hours open	45·1	6·10	2

The results of Witz are thus substantially confirmed in that hydrocelluloses do not experience the great additional loss of strength shown by oxycelluloses; but from this the oxycellulose formed by alkaline hypochlorite solutions, which is of the non-reducing type, must be excluded.

Effect of the Alkali Boil on Fluidity.—Similar results were obtained in a study of the relation between cuprammonium fluidity and strength of modified cotton after alkali boiling (*loc. cit.*). Neither the strength nor the fluidity of cotton tendered by acids or by alkaline hypochlorite is greatly affected by boiling, but in the case of other oxidising agents the tendering and fluidity are greatly increased. Unlike the change in strength, however, the rise in fluidity is com-

paratively little with cotton oxidised by dichromate. In consequence of this the fluidity of modified cotton yarn after boiling corresponds with the same loss in strength whether hypochlorite or dichromate has been used.

In the diagnostic sense it appears that the measure of the fluidity of cotton attacked by dichromate indicates, not the immediate loss of strength, but a potential loss which is realised only when the material is boiled with alkali (p. 107).

" These effects afford a strong vindication of the use of fluidity as a strength control, since material which would lose half its

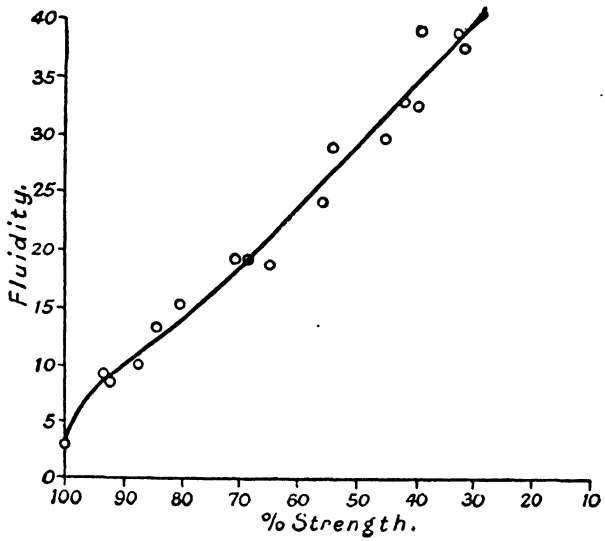


FIG. 42.—Relation between breaking load and cuprammonium fluidity of cotton yarn modified by acid action.

strength on laundering might be passed as satisfactory in a direct tensile test, whilst being rejected as unsatisfactory by the fluidity measurement." [1]

The losses in strength (single thread) in cotton yarn corresponding to increasing fluidities caused by oxidation attack followed by kier boiling (1 per cent. NaOH, 6 hours, 20 lb. pressure) are given below :—

Fluidity *	10	20	30
Loss of strength per cent. .	10	30	58

These values are, within the limits of experimental error, independent of the oxidising agent used, whether hypochlorite, neutral

[1] D. A. Clibbens and B. P. Ridge, *loc. cit.*, 394T.

* Fluidity values are given throughout as in 0·5 per cent. cuprammonium solution and log viscosity values in 2 per cent. solution. Unit, the poise.

or alkaline; or dichromate, acidified with sulphuric or oxalic acid.

The value of fluidity measurements as giving the most reliable early indication of change may again be emphasised. The copper number determination is of very little value as a guide to loss of strength. A curve showing the relation between loss of strength and fluidity in the case of cotton modified by any acid treatment is given (Fig. 42). It is almost identical with the corresponding curve for modifications produced by alkaline hypobromite or neutral or alkaline hypochlorite.

The significance of the fluidity of the nitrate (p. 64) prepared under conditions which are said not to involve alteration in chain-length has been discussed (p. 234). It is found [1] that there is a definite relation between cuprammonium fluidity and nitrate fluidity for each type of modification (Fig. 10) but, as will be seen, not the same for each type. After boiling with 1 per cent. sodium hydroxide (20 lb. excess pressure, 6 hours), however, the relation becomes constant for all types, and is identical with the curve given by hydrocellulose before alkali boiling (Fig. 10, curve 1).

The Action of Sodium Hydroxide Solutions on Modified Cotton Cellulose at the Ordinary Temperature.[2]—All modified celluloses become "soluble" in alkaline solutions. Using the term "solubility" to mean the percentage weight of the material which dissolves under stated conditions, it is found that the maximum solubility of modified cotton at 15° occurs in 3*N*-sodium hydroxide (Fig. 43). On either side of this point the solubility rapidly decreases. If, however, the modified cotton is first treated with more concentrated solutions of 6 to 10*N*, and the alkali is subsequently diluted, a much greater percentage weight can be brought into solution.

The conditions of maximum solubility for modified cotton at 15° were found to be, first steeping in 10*N*-NaOH, and then diluting with water to 2*N* while still in contact with the cotton. This process is referred to by the authors as treatment with 10*N*–2*N*-sodium hydroxide. As an example a hydrocellulose of copper number 3 which dissolved in 3*N*-solution to the extent of 6 per cent., dissolved to the extent of 30 per cent. in 10*N*–2*N*-solution. These results are illustrated in Fig. 43.

The direct method of determination of "solubility" by washing and drying the residue left after the action of alkali is, in the light

[1] G. F. Davidson, *J. Text. Inst.*, 1938, **29**, 195.

[2] C. Birtwell, D. A. Clibbens and A. Geake, *J. Text. Inst.*, 1928, **19**, 349T; G. F. Davidson, *ibid.*, 1934, **25**, 174T; 1936, **27**, 112T.

of these facts, not likely to be satisfactory. Washing with water obviously involves treatment of the material with alkaline solutions of diminishing strength. The solubility is therefore obtained by estimating the amount of material in solution by means of the volumetric dichromate process used for α-cellulose determination.

Estimation of the Solubility of Modified Celluloses in 10*N*—2*N*-*Sodium Hydroxide Solution.*—2·5 g. are steeped in 25 ml. of 10 *N*-solution for 15 minutes, the liquid then diluted to 2*N* and the whole allowed to stand for 1 hour at a temperature controlled within

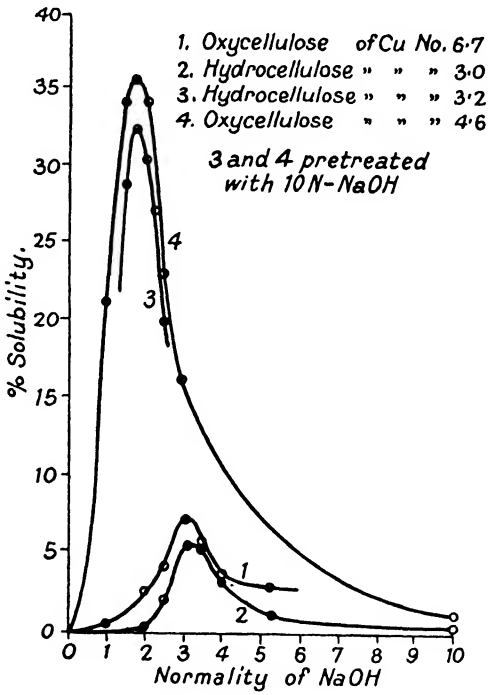


FIG. 43.—Solubility of modified celluloses in sodium hydroxide solutions with, and without, pre-treatment with 10*N*-solution.

one degree. The liquid is filtered, preferably through a fritted glass filter, a preliminary separation being effected by centrifuging when filtration is difficult. The filter is of the "inversion" type, 4 cm. in diameter, and made of Jena glass with glass filter disk of the coarsest grade. It is dipped into the bottle containing the mixture, and the solution drawn off into a second vessel.

To 10 ml. of the filtered solution, approximately neutralised with sulphuric acid, 25 ml. of *N*-potassium dichromate are added—or less if the solubility is small—followed by 10 ml. of concentrated sulphuric acid, the total volume being adjusted, roughly, to

55 ml. with water. The mixture is boiled under reflux for 1 hour, cooled, made up to 100 ml. with water, and 20 ml. portions titrated with $N/10$ ferrous ammonium sulphate. This solution is standardised before use with dichromate solution. From the volume of dichromate consumed, the weight of cellulosic material (as $C_6H_{10}O_5$) is calculated.

The effect of the temperature of extraction on the results is very marked, as is shown by the following figures :—

Per cent. solubility, $10N$–$2N$ of Hydrocellulose at	10°	15·5°	16°	17°	20°	25°
(*a*) Cu number 3·27 .	33·3	30·2	—	28·6	22·3	15·8
(*b*) Cu number 2·27 .	17·1	—	14·3	—	—	6·5

Unmanufactured cotton gives maximum solution in $10N$–$2N$-NaOH without continuous shaking. Cloth or yarn, however, must first be disintegrated and then shaken continuously for maximum effect. The cloth is cut diagonally into shavings about $\frac{1}{16}$th inch wide, and the shavings rubbed between the hands. The standard filtration method recommended is necessary, because these modified cottons give opalescent colloidal solutions, and the greater the extent of change the more viscous the solution and the more gelatinous the undissolved residue becomes.

It must also be mentioned that the insoluble portion tenaciously retains the soluble cellulose. Thus after steeping cotton in alkali the lye run off contained 0·5 per cent., whilst that squeezed off contained 0·8 per cent. With wood pulp the figures were 0·3 per cent. and 2·3 per cent. respectively.

A micro-method [1] has been developed from the above process. The material is boiled for 6 hours with 2 per cent. NaOH, washed free from alkali, dried, and disintegrated. Exactly 0·1 g. (air dry) is put into a $5 \times \frac{5}{8}$ inch tube fitted with ground glass stopper, and is treated with 1·0 ml. of $10N$-NaOH in a bath kept at 15°. A vacuum flask is suitable. After 15 minutes 4 ml. of water are added to dilute to $2N$- strength and the tube is replaced in the bath at 15° for 1 hour and occasionally shaken. A small fritted glass filter is attached to the lower end of a 2 ml. pipette and immersed in the liquid. The pipette is filled by suction and the 2 ml. of liquid run out into 10 ml. of $N/2$ dichromate containing 230 ml. of H_2SO_4 per litre. After 1 hour in a boiling water bath the solution is titrated with $N/10$ ferrous ammonium sulphate solution. If *b* ml.

[1] C. R. Nodder, *J. Text. Inst.*, 1931, **22**, 416T.

are required and a ml. is the equivalent of 10 ml. of $N/2$ dichromate the so-called " solubility number " will be 1·688 (a—b).

The solubility number is the percentage of cellulose (calculated on the air-dry weight of the material after the preliminary alkali boil), which is dissolved by the 10N–2N-treatment. The method has proved useful in routine work. We have used it for considerably modified celluloses, omitting the preliminary boil. Instead of the fritted glass filter we prefer to use a piece of wide glass tube about 1 inch long, packed with glass-wool, and fastened to the lower end of the pipette with rubber.

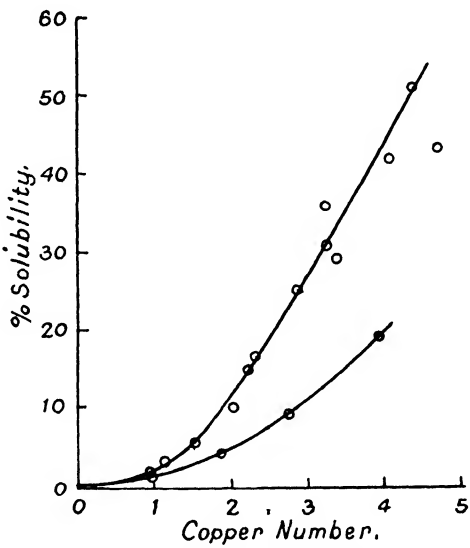


FIG. 44.—Relation between solubility in 10N–2N-NaOH and the copper number of cotton modified by hydrochloric acid solution at 20°, or by boiling $N/10$ sulphuric acid (upper curve). Lower curve shows solubility of hydrocelluloses from mercerised cotton.

The " Reducing Value " of the Alkaline Extracts.—The term " reducing value " is introduced [1] to define the amount of copper reduced by 75 ml. of the alkaline solution obtained by the standard method above calculating the result to the basis of 100 g. of dissolved cellulose. The difference between this value and the copper number is that whereas the former is carried out on a fixed weight of cotton, the latter is carried out on a fixed volume of a solution the cotton content of which varies.

75 ml. of the alkaline filtrate are placed in a conical flask, of capacity little greater than 100 ml. and mixed with 11·3 ml. of 10N-

[1] C. Birtwell, D. A. Clibbens and A. Geake, *loc. cit.*

sodium hydroxide. Carbon dioxide is passed in until the gain in weight amounts to 6·9 g., after which 5 ml. of the copper sulphate solution and sufficient of the carbonate-bicarbonate solution, used in the Schwalbe-Braidy method, to bring the volume to 100 ml., are added. The subsequent procedure follows the usual course, except that a wad of scoured cotton fibre is placed above the filter paper to prevent choking. The weight of cellulose in the 75 ml. is found from the dichromate analysis.

Relation between the " Solubility " of Modified Cotton in 10*N*–2*N*-Sodium Hydroxide and the Nature and Degree of the Modification.—(*a*) *The Relation between the Copper Number and Solubility.*—With hydrocelluloses the solubility is completely defined when the copper number is known ; for example, products

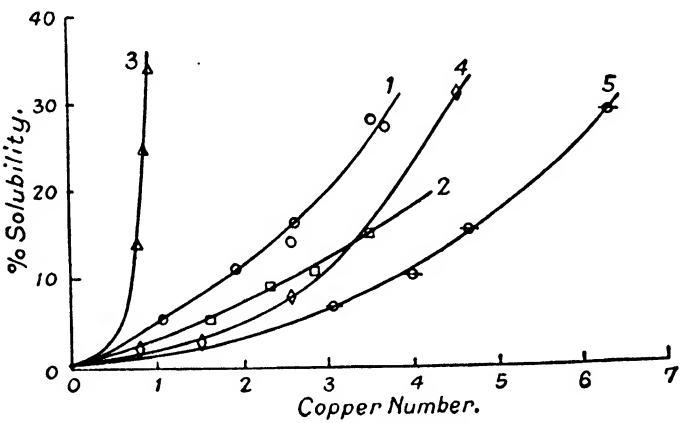


FIG. 45.—Solubility in 10*N*–2*N*-NaOH of oxycelluloses formed by the action of solutions of (1) neutral hypochlorite ; (2) HClO ; (3) NaBrO ; (4) $K_2Cr_2O_7$ + H_2SO_4 ; (5) $K_2Cr_2O_7$ + $H_2C_2O_4$.

obtained by the action of 20 per cent. hydrochloric acid at 20° for several days, or by the action of 0·5 per cent. sulphuric acid at 100° for several hours, with equal copper numbers gave the same solubility (Fig. 44, upper curve). With oxycelluloses (Fig. 45) there is no general relation between solubility and copper number, but with the same oxidising agent under the same conditions, for varying times, the copper number does define solubility.

It is noteworthy that although the reducing substances present in modified cotton dissolve to a certain extent in alkali, they do not completely account for the loss in weight on extraction—*e.g.* a modified cotton boiled with *N*/4 caustic alkali had its copper number reduced almost to zero, but its solubility in 10*N*–2*N*-NaOH actually increased. An example is given in the following table :—

Effect of Boiling for 4 Hours with 1 per cent. NaOH on the Properties of Modified Cellulose

Properties of Modified Cotton before and after Boiling.

Copper Number.		Fluidity.		Per cent. Solubility in 10*N*–2*N*-NaOH.		Reducing Value of Extract.	
Before.	After.	Before.	After.	Before.	After.	Before.	After.
2·27	0·80	—	33·9	15·3	19·2	4·1	2·1
3·27	1·12	—	—	31·1	38·7	4·2	2·6
4·41	1·43	—	41·7	51·4	63·8	4·6	2·0
2·56	0·65	—	31·6	14·5	18·2	—	3·2
5·80	0·43	—	38·3	35·9	32·7	9·7	3·2
0·61	—	—	—	8·0	9·6	2·3	1·0

The first three are Hydrocelluloses ; the last three Oxycelluloses.

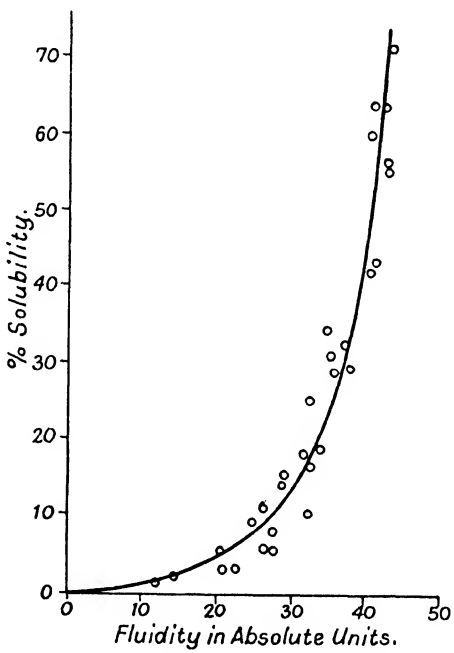


Fig. 46.—Relation between the solubility in 10*N*–2*N*-NaOH and the fluidity of all types of modified cottons.

(*b*) *The Relation between the Fluidity and Solubility.*—A very clear relationship exists between the solubility of cotton modified in any way and the fluidity of the material in cuprammonium (Fig. 46).

(c) *The Relation between the Copper Number of the Modified Cotton and the Reducing Value of the Alkaline Extract.*—Hydrocellulose extracted with 10*N*–2*N*-NaOH gives extracts the reducing values of which are roughly 4, irrespective of the nature and extent of the acid attack. This was observed, for example, in two samples with copper numbers of 2 and 4, and solubilities of 10 and 50 per cent., respectively. The reducing values of the extracts from oxycelluloses vary with the nature of the attack. Cotton oxidised in neutral hypochlorite solutions gives an extract with a reducing value of about 8, those formed by the action of hypochlorous acid give a value of about 12, and those formed by dichromate-oxalic acid of 16 to 20. It will be noted that oxycellulose extracts have very much higher reducing values than those from hydrocellulose, but alkaline hypobromite oxycelluloses and all modified celluloses which have been boiled with alkalis must be excluded from this generalisation. The high reducing value can, however, be used to distinguish between the reducing oxy- and the hydro-celluloses.

These relations do not apply to cotton which has been mercerised before modification. If an oxy- or hydro-cellulose of a certain copper number is prepared from mercerised cotton, its solubility is much less than that of a product of the same copper number made from unmercerised material (Fig. 44).

Solubility in Alkalis at lower Temperatures.—The solubility of modified cellulose is greatly increased at lower temperatures.[1] Solubility is a maximum at a definite alkali concentration and as the temperature is lowered the maximum increases and occurs at a lower alkali concentration. A hydrocellulose, for example, had maximum solubility at 15°, 0° and — 5° of 8·2, 57·5 and 82·6 per cent., and these occurred with solutions of 3·0, 2·75 and 2·5*N*-NaOH respectively.

Maximum possible solubility varies among the different bases. Thus at 15° the maximum attained is in the order

$$\mathrm{LiOH} < \mathrm{NaOH} < \mathrm{NMe_4OH},$$

but at 0° and —5° the order is

$$\mathrm{NMe_4OH} < \mathrm{LiOH} < \mathrm{NaOH}.$$

The actual maxima (per cent. dissolved) at 15° for a slightly modified oxycellulose were LiOH, 5·1 (*N*-3·5); NaOH, 10·5 (*N*-3·0) and NMe_4OH, 13·4 (*N*-2·5). At 0° the maxima were NMe_4OH, 43·4 (*N*-2·25); LiOH, 46·5 (*N*-3·0); NaOH, 68·2 (*N*-2·75) and at — 5° NMe_4OH, 65·1 (*N*-2·25); LiOH, 85·6 (*N*-2·75); NaOH, 89·7 (*N*-2·5).

[1] G. F. Davidson, *J. Text. Inst.*, 1934, **25**, 174; *ibid.*, 1936, **27**, 112.

The solvent action of potassium hydroxide is much lower (*e.g.* a maximum of 7 at 15° and 18 at −5° at 4·5 *N*-KOH), and much less affected by temperature.

The solubilities were determined by the standard procedure given on p. 38. In the case of potassium hydroxide, however, if the liquid and the cellulose were both cooled to − 5° before mixing, the solubility, except around the maximum, was much greater than that observed with the above procedure, *e.g.* with 3·5*N*-KOH the figures were 16 and 8 per cent. respectively.

The increased solubility gained by treating with, say, 5*N*- solutions, followed by dilution, was confirmed, the maximum with NaOH being at a dilution to 2–2·3*N*-. If the mixture is cooled to −5° solubility is greater, but much lower than the solubility obtained directly without pre-treatment. The following figures for the solubility of an oxycellulose (fluidity 34) illustrate these points:—

NaOH:*N*-	1·75	2·0	2·25	2·5	2·75	3·0	3·5
15° (*a*) .	1·0	1·4	2·5	4·4	7·8	10·5	6·3
(*b*) .	17·9	22·8	23·8	19·9	15·4	10·4	5·6
−5° (*a*) .	3·3	35·6	72·4	85·2	77·4	65·2	20·7
(*b*) .	18·0	22·9	28·0	30·7	38·0	29·7	16·3

(*a*) Solubility in normality shown, and (*b*) value found when pre-treatment with 5*N*-NaOH is given before dilution to the normality shown.

VII. Tests for Modification in Cellulose and Methods by which Oxycellulose and Hydrocellulose can be Distinguished

The presence of oxy- or hydro-cellulose may be recognised by the following qualitative tests: (*a*) With iodine solution cellulose gives a yellow changed to blue by sulphuric acid. Oxycellulose gives an immediate blue destroyed by sulphuric acid. (*b*) A piece of cotton and the piece to be tested are dyed in Benzopurpurin 4 B, rinsed in dilute sulphuric acid and washed in water till the red colour of the normal cotton reappears. Any oxidised parts will be bluish-black. (*c*) Indanthrene yellow is dissolved in concentrated sulphuric acid, the solution poured into water and neutralised. A few drops of the suspension are added to 10 per cent. NaOH solution and the fabric is steeped, removed and squeezed slightly. It is placed over a beaker of water boiling vigorously. In 1 minute a deep blue stain appears where oxy- or hydro-cellulose is present. Unchanged cellulose shows no change for 5 minutes. If the fabric

is washed, soured with acetic acid and scoured in soap, the unaffected parts wash light while the changed parts remain coloured. (*d*) The presence of red copper oxide after boiling with Fehling's solution shows modification.

With certain reservations oxycellulose and hydrocellulose may be differentiated—(1) by the change in viscosity after boiling for 6 hours with 1 per cent. NaOH solution. Oxycelluloses show a marked fall in viscosity, hydrocelluloses and normal cotton do not. The residue left after the determination of the copper numbers shows similar changes to those produced by the alkali boil and it may, conveniently, be used (p. 160); (2) by the determination of the reducing value of the extract obtained in the $10N$–$2N$-NaOH treatment (pp. 165, 167, 169). Hydrocelluloses have a value 4; oxycelluloses of the reducing type have values of 8 to 20; (3) an approximate differentiation between damage caused by oxidation and that caused by acid attack can be obtained by the use of methylene blue at *p*H 2·7 and *p*H 7·0 as described on pp. 25 and 218.

The following points of difference have been recorded for highly modified products:—

(*a*) The evolution of carbon dioxide during hydrolysis from oxycelluloses, but not from hydrocelluloses (p. 118).

(*b*) When methyl orange is added to a suspension of the material in water an orange-red colour is given by oxycellulose, changed to red by the addition of brine. Hydrocellulose does not give this test.

An Examination of Hydrocellulose in the light of the Chain Molecule Theory [1]

The hydrocellulose, prepared by the action of HCl, was a white powder, iodine value 1·3; copper number 3·3. Extraction with water failed to remove reducing material. It was soluble (30 per cent.) in aqueous NaOH (15 per cent.). Uronic acid residues were absent.

Acetylation.—Hydrocellulose (20 g.) was added to a mixture of glacial acetic acid (200 ml.), containing chlorine, and acetic anhydride (100 ml.), containing SO_2, with stirring, temperature below 10°. After 20 hours at room temperature the solution was diluted with twice its volume of glacial acetic acid and poured into tepid water. As acetylation was found to be incomplete, the product was treated with pyridine (200 ml.) and acetic anhydride (200 ml.), and then purified by adding light petroleum to its solution in chloroform

[1] H. C. Carrington, W. N. Haworth, E. L. Hirst and M. Stacey, *J. Chem. Soc.*, 1939, 1901.

containing alcohol. Yield, 32 g.; $[\alpha]^{17°}_{5780}$ −20° (chloroform, *c.* 1·0); iodine number, 0·6; acetyl content, 43·2 per cent.

The acetate was not homogeneous. 22 g. were stirred with cold acetone (500 ml.) for 2 hours and the liquid centrifuged. The insoluble portion (fraction I) would dissolve in acetone at 50°. The part soluble in cold acetone gave fractions II and III by precipitation with ether and light petroleum.

The properties of these fractions are given below. Viscosity in *m*-cresol at 20° (*c.* 0·4 g./100 ml.); [α] in chloroform-alcohol.

Fraction.	Weight, g.	Per Cent. Acetyl.	$[\alpha]^{20°}_{5780}$.	$\eta^{20°}_{sp.}$	Apparent mol. wt.	Apparent chain-length.
I . .	7	39·1	− 19°	0·31	22,300	77
II . .	3	44·0	− 20°	0·25	18,000	63
III . .	11	43·5	− 21°	0·27	19,500	68

Methylated Hydrocellulose.—10 g. of the acetate in 200 ml. of warm acetone were treated with 30 per cent. sodium hydroxide (320 ml.) and methyl sulphate (120 ml.), one-third being added at once, together with enough alkali for deacetylation. The mixture was stirred for 30 minutes before adding the rest of the reagents over 1 hour. After heating at 80° to remove acetone the solid was washed. Yield, 6·3 g. Boiling with ether removed colour. The total product, fractionated from chloroform by light petroleum (84 g. of methylated hydrocellulose) gave the following :—

Fractions.	Weight g.	M.p.	$[\alpha]^{20°}_{5780}$.	Per cent. OMe.	$\eta^{20°}_{sp.}$	Apparent mol. wt.*	Apparent chain-length.
I .	4	207–210°	− 5°	42·5	0·172	8,800	44
II .	5	205–210°	− 5°	43·5	0·239	12,200	59
III .	60	209–212°	− 7°	45·0	0·214	10,000	54

* $K_m = 1 \times 10^{-3}$.

Fraction III could not be separated into fractions and had the composition $C_9H_{16}O_5$—that of trimethyl cellulose.

Hydrolysis of Methylated Hydrocellulose.—65 g. of fraction III were added to concentrated HCl (300 ml.), the mixture stirred, cooled to 0° and saturated with HCl gas. The solid dissolved to a viscous syrup which, after 3 days at 0°, became more mobile. Air was blown through the solution at 15°, an equal volume of water added, and the acid neutralised with barium carbonate. The filtrate was extracted with 1·2l. of chloroform in 6 portions, the extracts giving a syrup (43 g.), which was boiled 10 hours with 2 per cent.

methyl-alcoholic HCl (1 litre). The solution was neutralised with silver carbonate and the methylated methyl glucosides (A) obtained on evaporation.

The aqueous solution left after chloroform extraction was taken to dryness at 50° (low pressure), and the residue extracted thoroughly with boiling chloroform. The extract (23 g.) was converted to methyl glucoside as above (product B).

Product A was distilled and refractionated, giving,

Fraction.	Weight, grams.	B.p. (bath)/0·5 mm.	$[n]_D^{19°}$.	Per cent. OMe.
A I . .	0·9	117–120°	1·4460	61·2
A II . .	0·3	120–125°	1·4506	57·1
A III . .	4·15	125–135°	1·4580	52·0
A IV . .	5·55	130–140°	1·4585	52·1

The remainder (38 g.), distilled directly from the flask, b.p. 130–140°/0·5 mm., $n_D^{15°}$ 1·4578. On hydrolysis it gave crystalline 2 : 3 : 6-trimethyl glucose. Residue negligible.

Product B similarly gave a main fraction $n_D^{19°}$ 1·4580, but a small residue required remethylating, after which it distilled at 135–40° with $n_D^{20°}$ 1·4575.

From refractive index and methoxyl content A I contained 0·9 g. and A II 0·15 g., or 1·05 g. in all, tetramethyl methylglucoside, or 1·62 per cent. After correction this indicates a chain-length of 70 glucose units, that derived from the iodine value being 95 units.

A hydrocellulose of the fibrous form was also examined.[1] It was made by soaking cotton sliver in hydrochloric acid (5 per cent.), and had Cu No. 2·6. It was separated into (A) fibre (ash 0·2 ; moisture 4·5 per cent. ; Cu No. 1·7), and (B) powder (ash 5·5 ; moisture 1·3 per cent. ; Cu No. 5·4) in small proportion. (A) had an apparent chain-length (end group) of 200 glucose units, and (B) one of 70 units (iodine value). Distillation with hydrochloric acid proved the absence of uronic acid groups, and the following test for enolic groupings was negative. The dry material was immersed in dry methyl alcohol, and then in dry ether containing diazomethane. After 2 days at −10° the product was washed with methyl alcohol and dried. No methoxyl groups were present, indicating the absence of enolic groupings.

The "solvent" action of alkali was investigated, and showed that the solubility was inversely proportional to chain-length.

[1] W. N. Haworth, S. Peat and W. J. Wilson, *J. Chem. Soc.*, 1939, 1904.

The Action of Aqueous Alkali on Hydrocellulose.—The fibre and the powder (1 g.) were respectively boiled with 100 ml. of the solution for 1–6 hours. The loss per cent. on the original material is given.

0·25*N*-Sodium Hydroxide

Time of boiling (hours).	1	2	3	4	5	6
Hydrocellulose powder .	23·4	34·6	39·4	39·6	38·8	40·4
Hydrocellulose fibre .	9·0	10·5	10·4	12·6	11·8	11·8
Cotton linters . .	1·2	2·4	2·0	2·0	3·0	3·4

2·5*N*-Sodium Hydroxide

Time of boiling (hours)	1	2	3	4	5	6
Hydrocellulose powder .	49·5	57·9	57·6	60·0	57·0	57·3
Hydrocellulose fibre .	15·2	16·9	15·3	17·9	16·5	17·3
Cotton linters . .	1·7	2·2	2·6	3·2	2·7	2·9

The copper number of the hydrocellulose fibre was 1·7. The values found after each of the above treatments, and after boiling with water, are given below :—

Copper Numbers

Time of boiling (hours).	1	2	3	4	5	6
Water, Cu No. . .	1·86	1·50	1·56	1·55	1·54	1·38
0·25*N*-NaOH Cu No. .	0·45	0·44	0·34	0·35	0·31	0·29
2·5*N*-NaOH Cu No. .	0·26	0·13	0·14	0·17	0·14	0·13

These results confirm the observations of former workers [1] that a residue resembling cellulose is obtained by extraction of modified celluloses with alkaline solutions. Actually the longer chains are left showing minimum values for copper number. That complexes of shorter chain-length are still more soluble was shown (*loc. cit.*) by a comparison with the cellodextrins.

Action of Alkali on some Cellodextrins.—100 g. of cotton were added gradually to a cooled mixture of acetic acid (375 ml.), acetic anhydride (375 ml.) and sulphuric acid (10 ml.). After leaving at 15° overnight, the mixture was kept at 30° for 4 days. The dark

[1] *E.g.*, E. Heuser and H. Herzfeld, *Chem. Zeit.*, 1915, **39**, 689; C. G. Schwalbe and E. Becker, *J. prakt. Chem.*, 1919, **100**, 19.

liquid was centrifuged and the bulk poured into water, the precipitate washed, dried, and extracted with boiling methyl alcohol. The cellodextrin acetates obtained were fractionated by light petroleum from chloroform. The two main fractions had iodine numbers corresponding to chain-lengths of 12 and 18 glucose units. The former was completely dissolved on boiling in 0·25*N*-NaOH for 4 hours, the latter was soluble as to 96 per cent. at this concentration, and completely soluble in 2·5*N*-NaOH.

IX. Products of the Cellulose-Dextrin Type

A number of these acid-degraded products of cellulose have been recorded, some of which had technical applications. They are colloidal and form an ill-defined group, the members of which are usually named after the authors who first described them. Schwalbe and Becker made a comparative examination of some of the more important. A summary of their results is given in the accompanying table, followed by the methods of preparation employed :—

Material.	I. Cellulose Number (p. 28).	II. Copper Number (Corrected).	III. Hydrolysis Number* (Corrected).	IV. Hydrolysis Difference.	V. Solubility in Alkali per cent.
Cotton wool . .	0·23	0·20	2·70	2·5	8·6
Guignet cellulose .	2·78	10·76	7·26	−3·5	70·1
Flechsig amyloid .	1·78	18·36	26·67	8·3	99·4
Parchment from cotton	2·06	7·11	17·63	10·5	70·1
Ekström's acid cellulose	2·43	11·20	30·40	19·2	100·0

* For the hydrolysis number see p. 28.

Guignet Cellulose.[1]—5 g. of cellulose are kneaded for 15 minutes with 85 ml. of sulphuric acid (62·5 per cent.), and the mass allowed to stand for 5 hours with working. About 170 ml. of water are then added, the mass stirred and filtered through a linen filter. The residue is washed with water.

If free from acid the product may be dried at 105°. In water it dissolves to a milky solution which filters easily and is not affected by boiling. If taken to dryness the residue will again dissolve in water. The solution is coagulated by small quantities of acids, salts, or alcohol. The copper number is reduced by hydrolysis.

Flechsig's Amyloid.[2]—5 g. of cotton are treated with sulphuric acid, prepared by mixing 30 g. of H_2SO_4 (92 per cent.) with

[1] C. Guignet, *C.R.*, 1889, **108**, 1258; C. G. Schwalbe and W. Schulz, *Zeit. angew. Chem.*, 1913, **26**, 499.

[2] *Zeit. physiol. Chem.*, 1882, **7**, 524.

10 g. of water. The temperature must be kept between 6° and 30°, so that the addition of the cotton may take 1–2 hours. A syrup-like mass results, which on adding water is resolved into white flocks and a milky liquid. On filtering a great deal is lost in colloidal solution. The residue is washed by decantation till free from acid,* and dried below 95°.

Cellulose Parchment.—The properties of this vary with the cellulose employed—*e.g.* whether filter paper or cotton wool.

(*a*) Filter paper is dipped for 20 seconds into sulphuric acid containing 78 per cent. H_2SO_4, rapidly removed, allowed to drain for 10 seconds and washed in water until free from acid. (*b*) 1 g. of cotton wool is brought into 9 ml. of the above acid, to which, after 10 seconds, 200–250 ml. of water are added.

Ekström's Acid Cellulose.[1]—5 g. of cotton wool, in the course of 45 minutes, are brought into 18 g. of 78 per cent. sulphuric acid. The mass is diluted with 29 ml. of water and pressed between linen. If it is shaken with a small amount of water a sticky mass is formed; a large amount of water gives a parchment-like product. If ground with water a colloidal solution is obtained. Like cellulose parchment, acid cellulose colours potassium iodide-iodine reagent blue without the addition of sulphuric acid. It has no acidic properties, and may be dried up to 95°.

* Salt solution might avoid loss and will remove sulphuric acid more rapidly than water.

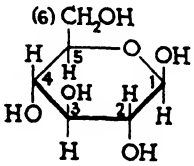
[1] Ger. Pat., 207354 (1906).

CHAPTER VIII

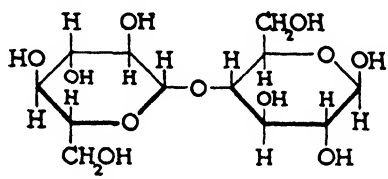
THE STRUCTURE AND APPARENT MOLECULAR WEIGHT OF CELLULOSE AND ITS MODIFICATIONS

THE interpretation of results is of even more importance than their accumulation. The concepts of cellulose structure developed during the past 15 years, although not decisive, have proved of the utmost value in explaining and co-ordinating experimental facts. They have been fully described elsewhere, and only a short summary need be given as a prelude to details of the methods used for the measurement of chain-length and molecular weight.

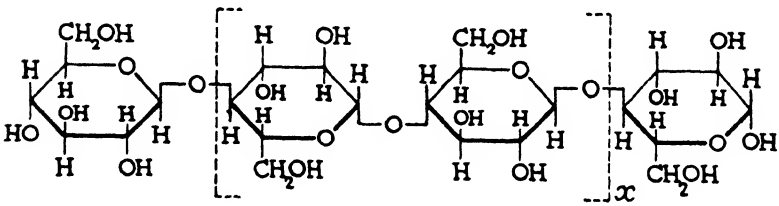
The chemical unit of cellulose is anhydro-β-glucose (I), and these units are linked 1 : 4 ; 1 : 4 as in cellobiose (II) to give a long series which forms the cellulose unit chain (III).



(I) β-glucose



(II) Cellobiose (β-form)



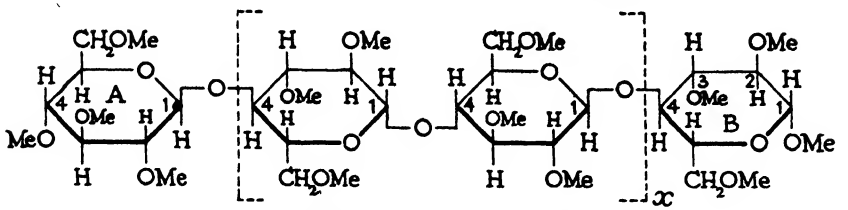
(III) Cellulose

The connection of cellulose with glucose and cellobiose becomes apparent. Further, the chain has two ends, the one A (IV), linked at the 1-position, and the other B, at the 4-position. The end group B, unlike A, has the reducing group at position 1 free, and to this the constant reducing properties of normal cellulose are due. With certain assumptions their measurement (copper number, iodine number) affords an indication of the number of glucose units in the chain.

The "end group" method,[1] now generally employed for the determination of chain-length, depends upon the characterisation

[1] W. N. Haworth and H. Machemer, *J. Chem. Soc.*, 1932, 2270, 2372 ; *ibid.*, 1939, 1888.

of end A. If the cellulose chain is fully methylated (IV), and then



(IV) Methylated Cellulose

hydrolysed, all but the end groups give 2 : 3 : 6-trimethyl glucose. The end groups have one more hydroxyl grouping, and each could give a tetramethyl glucose. The additional methyl in group B, however, is in the reducing position 1, and is removed during hydrolysis. The additional methyl group in end A at position 4 is not affected by hydrolysis, so that for every cellulose chain one molecule of 2 : 3 : 4 : 6-tetramethyl glucose is obtained, thus giving a measure of the number of units in the chain.

The chain theory accounts for the formation of the so-called oligosaccharides. Intermediate stages in the acetolysis of cellulose to cellobiose were early shown to yield a trisaccharide.[1] A cellotetraose and a cellohexaose were later isolated,[2] and the cellotriose was shown to be a cellobiosido-glucose. The application to cellotriose and cellotetraose of the "end group" technique showed[3] that they were formed from 3- and 4-unit glucose residues respectively, in chains joined by 1 : 4-linkages as in cellulose. Cellulose, in fact, can be resolved successively into cellodextrins of chain-length $(C_6)_{25}$ . . . $(C_6)_{10}$, and then to reducing sugar units $(C_6)_6$, $(C_6)_4$, $(C_6)_3$, $(C_6)_2$ and $(C_6)_1$, without any indications of discontinuity.

Measurements of the molecular rotation of oligosaccharides (Freudenberg *et al.*, *loc. cit.*) indicated that the value of this property increased regularly with each extra glucose unit, making it apparent that the chains are formed definitely of β-glucose units all linked in the same way. By inference the same applies to the enormously longer chain of cellulose and its modified products, in particular of hydro-cellulose, so that there is one structural unit and arrangement only in cellulose and the polysaccharides derived from it.

The constant association of xylan with cellulose in the plant

[1] J. C. Irvine and G. J. Robertson, *Chem. Soc. Trans.*, 1926, **128**, 1488; H. Ost, *Z. angew. Chem.*, 1926, **39**, 1117.

[2] L. Zechmeister and G. Toth, *Ber.*, 1931, **64**, 854.

[3] W. N. Haworth, E. L. Hirst and Thomas, *Chem. Soc. Trans.*, 1931, 824; K. Freudenberg, *et al.*, *Ann.*, 1932, **494**, 41.

world make it possible that some glucosan units in the chains can be replaced by xylan, especially as, except in length, the xylan structure isolated is of the same dimensions, and identical with that of glucose.

A classification based on comparative measurements of chain-length of cellulose and its degradation products is given in the following table : [1]—

	No. of Units in the Chain Molecule.	Length of Chain Molecule A.	Appearance.	Type of Flow in Cuprammonium Deviation.*
Eu-colloidal α-cellulose.	500–2,000	> 2,500	Long fibres, fibrillar micro-structure	Marked
Meso-colloidal α and β-cellulose	50–500	250–2,500	Short fibres	Slight
Hemi-colloidal β-cellulose.	10–50	50–250	Powder	None
Oligosaccharides γ-cellulose.	1–10	50	Powder or crystalline	None

* From the Hagen-Poiseuille Rule.

The X-ray data (1921–35) led to the concept of cellulose as a crystal structure made up of a unit pattern or " cell " of four glucose units joined along the *b* axis to form the chains. The glucose units are linked as in cellobiose, and are held together along the *b* axis by primary valence forces constituting a chain which forms the axis of the cellulose fibre. The units are connected laterally through the oxygen atoms by secondary valence forces. The original model of the crystal unit given by Meyer and Mark, in which the parallel chains are all oriented in the same direction, is still valid, but a revision, on the basis that the orientation of the chains alternates has been found [2] to agree more closely with the X-ray data. In this model the cellobiose chains forming the *b* axis have principal valency distances C : C, 1·54A, and C : O, 1·45A. They are connected along the *a* axis by residual valencies of hydroxyl groups which themselves are distant 2·6A from one another and arranged so that each set parallel to the plane *ab* is orientated in opposite directions.

The effect of mercerising is to move the molecular chains further apart as will be seen from the following measurements :—

[1] H. Staudinger, *Ann.*, 1936, **526**, 72.
[2] K. H. Meyer and L. Misch, *Helv. Chim. Acta*, 1937, **20**, 232.

	Native Cotton.	Mercerised Cotton.
a . . .	8·35A	8·1A
b . . .	10·3A	10·3A
c . . .	7·9A	9·1A
β . . .	84°	62°

For the more complete explanation of cellulose as a crystal structure the concept of the micelle was introduced. This assumes that cellulose is composed of rod-like units—micelles or crystallites—held together by so-called micellar forces to form fibrils. Their arrangement may roughly be likened to that of the rows of bricks forming a wall in which one covers the junction of two others, and all are connected by means of a cementing substance. The X-ray data seem to require that only a part, some 75 per cent. or more, of the cellulose is truly crystalline. The other part is amorphous, or does not respond in the same way as the definitely crystalline part, and the existence of such a cementing or connecting substance in cellulose is supported by other evidence. The crystallites are, however, not cemented in the physical sense, since they can readily move into definite orientation. In native cotton fibres the micelles run spirally round the axis (*cf.* Fig. 51), whilst in ramie and some other fibres they run parallel to it. When cellulose is regenerated, as in rayons, the orderly arrangement has gone. It can, however, be restored to some extent by stretching, marked changes in the physical properties of the fibre being produced.[1] The micelle is rectangular or rhombic in shape, and may contain 1,500–2,000 glucose units.

The micellar concept implies a discontinuous structure for cellulose. Modern opinion tends to the view that, whilst fitting in well with X-ray data, this concept is not necessary to explain the features of swelling, dissolution, the influence of axial tension in mercerising, and certain reactions of nitration, methylation etc. The continuous theory of cellulose structure is of greater service. It assumes that cellulose is composed of long chains which have crystallised, leaving, however, in between irregular regions of material which, not being so perfectly crystalline, appear amorphous towards X-rays and dispersing agents.

THE MOLECULAR WEIGHT OF CELLULOSE

The molecular weight of cellulose has been determined (*a*) by end group estimations, (*b*) by osmotic pressure, (*c*) by viscosity

[1] Cf. "The Development of Nylon," E. K. Bolton, *Chem. and Ind.*, 1942.

measurements, and (*d*) by ultra-centrifuge methods. A useful review has been given by Davidson.[1] Since any cellulose or cellulose derivative is a mixture of units of varying length, the results given by these different processes will not be the same. End group and osmotic pressure methods give a "number average," while viscosity gives a "weight average," and both can be derived from sedimentation data.[2] It is probable that in dilute solution polymers of high molecular weight exist as single chain molecules. If, however, aggregation takes place, the values derived from osmotic pressure and sedimentation analysis (which give particle size) will not be the weight of the molecule defined as the largest unit in which the atoms are connected by primary valencies. This molecule is recorded by the chemical (end group) methods. Results obtained by viscosity determinations, which depend upon the value assigned to Staudinger's constant K_m, formerly differed considerably from those given by other physical methods, but revised figures [3] show that they now fall into line with ultra-centrifuge results,[4] as shown in the table below. The molecular weight is obtained by multiplying the numbers by 162.

DEGREE OF POLYMERISATION

	By Viscosity (Staudinger).	By Ultra-centrifuge (Kraemer).
Native Cellulose	2–3,000	3,500
Cotton Linters (purified)	—	1,000–3,000
Wood Pulp	900–1,500	600–1,000
Rayons	250–500	200–600
Cellulose Nitrate (lacquers)	300–600	500–600
Cellulose Acetate	200–350	175–360

A. Determination of the Iodine Number

The iodine number is the number of millilitres of $N/10$ iodine required to oxidise 1 g. of substance. Originally devised [5] for use with acetylated carbohydrates it can be used for cellulose provided the material is ground in a ball mill and grinding continued during titration.

[1] G. F. Davidson, *J. Text. Inst.*, 1936, **27**, 144.
[2] E. O. Kraemer and W. D. Lansing, *J. Amer. Chem. Soc.*, 1935, **57**, 1369.
[3] H. Staudinger, *Papier Fabrik.*, 1938, **36**, 474.
[4] E. O. Kraemer, *Ind. Eng. Chem.*, 1938, **30**, 1,200.
[5] M. Bergmann and H. Machemer, *Ber.*, 1930, **63**, 316, 2304; see also p. 1922.

The air-dry material (about 1 g.) is ground with 200 ml. of $N/4$ NaOH, using hard porcelain balls for a short time, then 50 ml. of $N/10$ iodine is added and, after 4 hours grinding with the mill still running, 10 ml. of chloroform and 10 ml. of $5N$-H_2SO_4 are added and the excess iodine titrated in the usual way. Grinding for 1·5 hours is nearly as efficient as 4 hours, and results may be corrected to 4 hours by the addition of 10 per cent. for large values and 20 per cent. for small, *e.g.* iodine numbers determined at 1·5 and 4 hours, respectively, for cotton were 0·6 and 0·76; for cellulose acetate 1·14 and 1·24.

The assumption is made that one atom of oxygen is required per molecule so that the molecular weight = 20,000/iodine number.

B. The End Group Estimation of Chain-Length

In this method,[1] cellulose is acetylated to the triacetate, which is hydrolysed and methylated under conditions which the authors claim involve no alteration in the original chain-length. The trimethyl cellulose is hydrolysed, the sugars isolated, converted to glucosides, and these separated by distillation. From the methoxyl content and refractive index of the fractions the amount of tetramethyl glucose can be calculated. A later review [2] shows that the procedure (*loc. cit.*) is sound, and may be followed completely when the acetate (as with degradation products) is soluble in acetone.[3] With cellulose itself the observation that cellulose triacetate swells in dioxan, or a mixture of acetone and dioxan, to give a highly viscous solution very suitable for methylation, greatly improves the process and avoids the need for deacetylation.

The original use of fuming hydrochloric acid for hydrolysis of the methylated derivatives leads to the production of methyl laevulate. The amount of this is greatly reduced by employing a mixture of equal volumes of glacial acetic acid and 8 per cent. hydrochloric acid.

The experimental procedure is illustrated by its application to a sample of linters of copper number 0·08 and iodine number 0·2.

Preparation of Fully Acetylated Cellulose.—Linters (50 g.) were steeped in glacial acetic acid (500 ml.) containing a little chlorine and 250 ml. of acetic anhydride, containing SO_2 equivalent to the chlorine, added. The mixture was left at 0°, and then at 15° till homogeneous (24 hours), diluted with an equal volume of glacial

[1] W. N. Haworth and H. Machemer, *Chem. Soc. Trans.*, 1932, 2,270.
[2] W. N. Haworth, E. N. Hirst, *et al.*, *ibid.*, 1939, 1887.
[3] *Cf. ibid.*, 1939, 1902. See also Hydrocellulose, p. 172.

acetic acid and poured with stirring into cold water. The precipitate was washed and dried (vacuum), 400 g. of linters giving 632 g. of acetate. A portion purified from acetone-alcohol-chloroform solution by precipitation with light petroleum had copper number, 0·05; iodine number, 0·2; $[\alpha]_D^{20°}$ — 21° (*c*, 2·5 in chloroform). M. Wt. (osmometric) gave a chain-length of 230 glucose units.

Methylation of Triacetyl Cellulose in Air at 55°.—The finely powdered triacetate (10 g.) was added to dioxan (200 ml.), and kept for 12 hours. The mass, diluted with acetone (500 ml.), gave a clear solution. This was treated in two parts to each of which, at 55°, methyl sulphate (250 ml.) and sodium hydroxide (30 per cent., 750 ml.) were added with vigorous stirring (essential) in tenth portions every 10 minutes, the acetone lost being replaced at intervals. Boiling water (1·5 l.) was poured in and the mixture kept at 95–100° for 30 minutes. The solid was washed with hot water and dried (vacuum): OMe content, 41 per cent.

270 G. of this product were methylated in the same way in units of 10 g., and then in units of 15 g., giving in all six further methylations. The final product, washed with acetone and ether, was white. Yield 165 g. (85 per cent.). It was purified by fractionation from a mixture of chloroform (1·6 l.) and ether (0·6 l.) by addition of light petroleum (8 l.). Head and tail fractions (5 g. and 3 g.) were discarded, leaving 150 g., m.p. 225°; $[\alpha]_D^{20°}$ — 5° (*c*, 3·0, chloroform); OMe, 45·6 per cent.; M. Wt. (osmometric) gave a chain-length of 100 glucose units. Product appeared homogeneous.

Variations of the above, in which (*a*) the methylation was carried out in nitrogen, (*b*) in which three treatments only were given as in the original technique, and (*c*) in which a lower temperature, 40°, was used, all gave products which by precipitation could be resolved into fractions with different properties, (*a*) for example, giving 90 per cent. with $\eta_{sp.}/c$, 0·38 and 10 per cent. with the value 0·23. Hess *et al.*,[1] consider that methylation in the absence of oxygen is essential.

Determination of Chain-Length.—The purified methyl cellulose (147 g.) was dissolved in glacial acetic acid (1·5 l.) at 90°. Hydrochloric acid (10 per cent., 1·5 l.) was added, and the whole kept at 90–95° till polarimetric readings showed that hydrolysis was complete. The liquid was treated with charcoal, neutralised with barium carbonate (470 g.), and the filtrate evaporated at 50°. The residue was extracted 10 times with chloroform and the extract (10 l.) concentrated to a syrup (vacuum). Yield 155 g. (98 per cent.), partly crystalline.

[1] K. Hess, *et al.*, *Ber.*, 1940, **73**, 505.

A preliminary separation of the sugars was made by dissolving the 155 g. in water (1 litre), and extracting 15 times with chloroform. The extract (1·5 l.) taken to dryness gave syrup A_1 (16·5 g.). The aqueous residue concentrated to 250 ml. and again extracted with chloroform (300 ml.) gave a syrup which at once crystallised. This product, taken up with ether, gave 2 : 3 : 6-trimethyl glucose (12 g.). The ethereal mother liquors and washings gave syrup A_2. The aqueous residue taken to dryness and the residue dissolved in ether gave crystalline 2 : 3 : 6-trimethyl glucose (82 g.). The ethereal mother liquors and washings gave syrup B (24 g.). Total yield of 2 : 3 : 6-trimethyl glucose 94 g.

Fractions A_1, A_2 and B were converted to glucosides by heating under reflux 7 to 10 hours with dry methyl alcohol containing 2 per cent. HCl. After neutralisation with silver carbonate and evaporation 16·0, 6·1 and 24·2 g. of glucosides, respectively, were obtained. These were repeatedly fractionated at 0·01 to 0·10 mm. in a Widmer flask with a vacuum jacketed column. Fraction A ($A_1 + A_2$) gave, finally, the following :—

Fraction.	1*a*.	2*a*.	3*a*.	4*a*.	5*a*.	6*a*.
Temp. of bath .	75–90°	95–100°	100–105°	110–120°	115°	125°
Weight (g.)	0·180	0·220	0·612	0·832	1·138	3·524
$n^{17°}$ . .	1·4246	1·4499	1·4452	1·4525	1·4560	1·4562
OMe % .	24·2	55·6	62·6	54·1	52·0	—

and fraction B was separated into four portions with n_D varying between 1·45 and 1·47.

Fraction 1*a* was methyl lævulate, and some was present in 1*b*. The refractive indices and methoxyl contents show that only 2*a*, 3*a*, and 4*a* contain tetramethyl methylglucoside, and calculation gives the amounts as 0·123, 0·612 and 0·270 g., respectively, or 1·0 g. in all from 147 g. of methylated cellulose. This yield gives a chain-length of 180 units (which, after the correction of 10 per cent. for experimental loss, becomes 158 units) calculated as follows :—

(*a*) Tetramethyl methylglucoside, $C_{11}H_{22}O_6$; M. Wt. 250.
(*b*) Trimethyl cellulose unit, $C_9H_{16}O_5$; M. Wt. 204.

Since

1 g. of (*a*) is derived from 147 g. or 147/204 mol. of (*b*) 250 g. (1 mol.) of (*a*) is derived from 250 × 147/204 unit mols. of (*b*) *i.e.* 180·0 units.

Notes on the Method.—(*a*) *Correction for Experimental Error.*—Averill and Peat [1] showed that the loss during conversion to glucosides and subsequent fractional distillation as above varied with the proportion of tetramethyl glucose in the mixture compared with trimethyl glucose. Thus, for example,

Per cent. tetramethyl glucose in the mixture .	1·05	0·216	0·132	0·106
Per cent. tetramethyl glucose found . .	0·93	0·142	0·082	0·056
Per cent. recovery	89	66	62	53

A curve can be drawn from these values and used in any special case. With cellulose the amount of tetra-derivative is of the order of 0·5 per cent., and the correction is taken as 10 per cent.

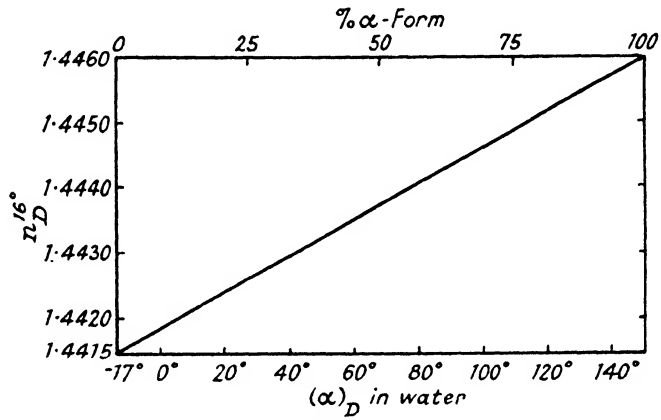


FIG. 47.—Mixtures of tetramethyl α- and β-methylglucosides.

(*b*) *Control of the Distillation Process.*—In the original method (1932) the whole of the tetramethyl methylglucoside was isolated by fractional distillation, and observations on mixtures of the "tri" and "tetra" containing 1 to 10 per cent. of the latter have shown that 95 per cent. of the total "tetra" can be obtained in this way. Under the standard conditions the mixed glucosides are allowed to reach equilibrium with respect to their α- and β-forms during preparation. In this case the same degree of accuracy may be obtained by refractive index measurements alone. But if equilibrium has not been reached such measurements would give inaccurate results. The solution of this difficulty has given a helpful control method for general use. It is found [2] that if the specific rotation and $[n]_D$ of the fractions are measured during the distillation, the $[n]_D$ values

[1] F. J. Averill and S. Peat, *J. Chem. Soc.*, 1938, 1344.
[2] E. L. Hirst and G. T. Young, *J. Chem. Soc.*, 1938, 1248.

for the successive fractions, when pure " tetra " is being collected, fall on the line in Fig. 47, and when the distillate is pure " tri " they fall on the line of Fig. 48. When a mixture of the two is present the values fall on neither line. This makes it possible to determine with accuracy the point (A) at which the collection of pure tetramethyl methylglucoside ceases and the point (B) at which the collection of pure " tri " commences. Point B is found with ease, and when all the fractions are strongly dextrorotatory (equilibrium mixtures as in most chain-length determinations) the $[n]_D^{16°}$ value for the $\alpha\beta$-mixture of tetramethyl methylglucosides present in the intermediate fractions is always very close to 1·4445, and that of the mixed trimethyl methylglucosides distilling at point

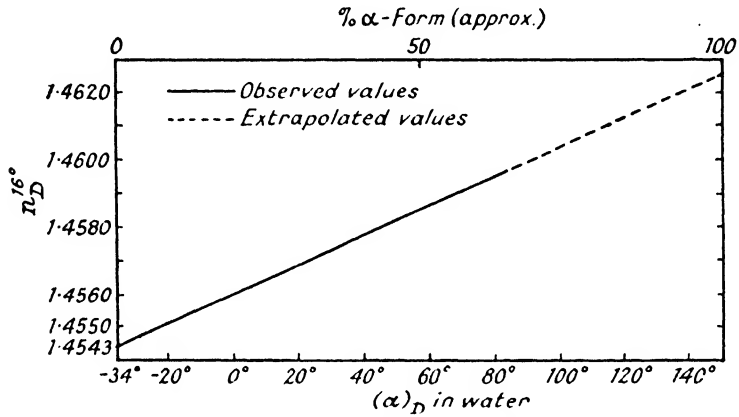


FIG. 48.—Mixtures of 2 : 3 : 6-trimethyl α- and β-methylglucosides.

B very close to 1·4580, and it is known that there can be little variation in the latter figure when the two glucosides are distilling together.

The choice of an $[n]_D$ value for the tetra- and tri-methyl methyl glucosides in calculating the proportion of the former in any fraction is, however, important as a small variation in that of the " tetra " will make a great difference. Thus, in an extreme case, when " tetra " was taken as 1·4440 and " tri " as 1·4572, the content of " tetra " was 30 per cent., whereas taking rotation and other factors into consideration, which gave the corrected values 1·4440 and 1·4548, the amount was only 14 per cent. Since the β-forms are the more volatile, the glucoside fractions become richer in the α-form as distillation proceeds and the $[n]_D$ to be taken for pure " tetra " must rise from about 1·4430 to about 1·4450 in the last drop. The " tri " must also rise from about 1·4550 to a higher value given by the $[n]_D$ at which pure " tri " begins to distil. The degree of fractionation and the size of each fraction, especially if

coupled with the rotation and methoxyl content, enable a value correct to 0·0005 to be chosen.

Maximum accuracy in "end group" determination is, however, obtained when the bulk of the "tetra" is isolated in the pure condition, and only traces are estimated by refractive index.

The refractive index values of the mixed tetramethyl methylglucosides diminish by 0·0004 per 1° rise in temperature, and those of the mixed trimethyl methylglucosides by 0·00035.

(*c*) *Deduction of a Graphical Method for the Estimation of Tetramethyl Methylglucoside in Admixture with Trimethyl Methylglucoside.*—A useful development of the above observations has been suggested.[1] If the lines of Figs. 47 and 48 are plotted on one diagram to the same scale, it will be seen that they are approximately parallel and finite. A mixed fraction collected beyond the point A at which pure tetramethyl methylglucoside ceases to distil, and before the point B at which the pure tri-glucoside commences to distil, will give $[n]_D$, $[\alpha]_D$ values represented by a point, say P, lying between the graphs. If a straight line is drawn through P cutting the lower graph in E and the upper in F, then EP/PF gives the ratio of tri- and tetra-methyl methylglucosides present. As the weight of the fraction is known, the weight of each component can be calculated.

(*d*) *Control of the Purity of the Fractions obtained by Distillation.*—(i) *Isolation of* 2 : 3 : 4 : 6-*Tetramethyl Glucose.*—A first fraction, b.p. 117–120° (0·5 mm.), $[n]_D^{19°}$, 1·4460; OMe 61·2 per cent., for example, was hydrolysed by boiling 0·5 g. with 5 per cent. HCl (30 ml.) for 3 hours. After neutralising with silver carbonate and taking to dryness (reduced pressure) at 50°, the product was extracted with ether and gave 0·4 g. of "tetra" which from light petroleum had m.p. 88°.

Alternatively, 6 per cent. sulphuric acid is used, followed by barium carbonate. The alcohol extract crystallises: $[\alpha]_D^{20°}$ + 83° (equilibrium in water).

(ii) *Isolation of* 2 : 3 : 6-*Trimethyl Glucose.*—38 g. of distillate, b.p. 130–140°/0·5 mm., $[n]_D^{16°}$ 1·4578 were boiled with 5 per cent. HCl (500 ml.) for 5 hours. After neutralisation (barium carbonate) the filtrate was taken to dryness. The chloroform extract gave trimethyl glucose (27 g.); m.p. 120°; $[\alpha]_D^{20°}$ + 69° (equilibrium in water).

(iii) *Isolation of Dimethyl Methylglucoside.*—The distillation is continued beyond the point at which the rotation (Fig. 48) shows that pure trimethyl methylglucoside ceases to distil. Its estimation

[1] D. J. Bell, *Biochem. J.*, 1944, **38**, 199.

in the distillate, on the assumption that $[n]_D^{15°}$ is 1·4570, follows the usual method (*J. Chem. Soc.*, 1939, pp. 1918, 1920).

(iv) *Presence of Furfural and Methyl Lævulate.*—Furfural may occur in earlier fractions, and as its $[n]_D^{16°}$ is 1·52 causes error. It is removed by adding cold *N*/25 permanganate to the mixed glucosides till the aniline acetate test is negative. Its presence is best avoided by control during glucoside formation. The sugars should be boiled 10 hours with 1 per cent. methyl alcoholic hydrogen chloride, the acid completely neutralised before removal of the solvent and the glucosides dried at 90°/12 mm. before distillation. A routine test for furfural should be made, using the band λ 2,750 A, ϵ 20,000.

Methyl lævulate appears in certain fractions causing low OMe and b.p., with irregularities in the n_D/α_D values. It gives an absorption band at 2,630 A. It is eliminated by careful fractionation (Averill and Peat, *loc. cit.*).

Partition and Adsorption Methods for the Estimation of the Methylated Sugars and their Glucosides derived from Polysaccharides.—Several methods of this type have been described and promise to be useful in the "end-group" analysis of methylated celluloses. They are especially applicable to derivatives from hemicellulose and pectin substances as they can be adapted to the separation of dimethyl glucose from higher methylated glucoses and even to the separation, for example, of the glucosides of trimethyl *l*-arabinose and trimethyl *d*-xylose from one another.

(A) A method[1] for the separation of 2 : 3 : 4 : 6-tetramethyl glucose from 2 : 3 : 6-trimethyl glucose is recommended, because it avoids errors caused by the tendency of partly methylated sugars to undergo autocondensation and demethylation during glucoside formation. It consists in partitioning the sugars between chloroform and water held in a rigid column of silica gel and quantities of 50 to 200 mg. of 2 : 3 : 4 : 6-tetramethyl glucose can be separated from 2 : 3 : 6-trimethyl glucose when present in the ratio of 1 up to 200 molecules. The separation is quantitative and the sugars analytically pure. Trimethyl- may be separated from dimethyl-glucoses by using a silica-water column and a mixture of chloroform with *n*-butanol (10 : 1 by vol.)—a solvent which extracts 12 times as much 2 : 3 : 6-trimethyl glucose from water as does chloroform alone.

The preparation of the silica, which is very important, and the general procedure follows on the lines described by Gordon, Martin

[1] D. J. Bell, *J. Chem. Soc.*, 1944, 473.

and Synge.[1] A special flask is used for the evaporation of the extracts.

Procedure.—(*a*) The silica, in columns each of 2·5 g. in tubes A and B of 10 mm. diameter, is first tested for adsorptive quality. One mg. of each sugar in 1 ml. of chloroform is pipetted on to the top of the column and allowed to sink in. One column-length of chloroform is passed through A and four through B. The gels are pushed out on to a plate and dried at 110°. They are then spotted at regular intervals with drops of alcoholic α-naphthol, followed by sulphuric acid. Both columns should show a marked band of mauve-coloured spots at the top (trimethyl sugar) and A will probably show a second band (tetramethyl sugar) at the bottom. If the silica is "good" (low absorption) B will show only the top band, all the tetramethyl glucose being eluted.

(*b*) Hydrolysis of the glucosides must be complete otherwise oligosaccharides will load the tetramethyl fraction. The substance, dissolved in glacial acetic acid (5 pts.) with 5 per cent. (*w*/*v*) HCl (10 pts.), is heated for 5 hours on the water-bath.

(*c*) The hydrolysate, containing 100 to 200 mg. of tetramethyl sugar in 10 to 15 pts. of water, is filtered (charcoal) and adjusted to about 5 per cent. solution. This is shaken nine times with its own volume of chloroform and the latter evaporated (moist) in air. The residue contains all the tetramethyl sugar and about 10 per cent. of the trimethyl sugar.

(*d*) This residue in chloroform is transferred to a column made from 25 g. of silica in a tube 4 cm. in diameter. The "tetra" is eluted by passing column-lengths of chloroform as found necessary under (*a*) with two additional ones—usually seven in all for "good" and eleven for "poor" silica-gel.

(*e*) The solution of "tetra" from (*d*) is evaporated to dryness in the presence of a little $BaCO_3$ (always necessary with chloroform solutions to avoid autocondensation), dried (vacuum desiccator), redissolved in light petroleum-dry ether (3 : 1) and dried to constant weight.

(*f*) The aqueous phase from (*c*) is shaken with its own volume of chloroform-butanol (9 : 1) removing about 15 per cent. of the trimethyl sugar. Extraction is continued till less than 0·5 g. of sugar remains in the water, which is then taken to dryness (low pr.). The residue, dissolved in the above solvent (9 : 1), is pipetted on to the same column and the trimethyl sugar eluted by more of the above solvent, using the same number of column-lengths as before.

[1] *Biochem J.*, 1941, **35**, 1388; 1943, **37**, 79. Cf. *ibid.*, 1942, **36**, xxii.

(*g*) The chloroform-butanol solutions from (*f*) are taken to dryness (low pr.) with the addition of water to remove butanol. The trimethyl glucose left is dissolved in ether-acetone (2 : 1) and an aliquot containing about 1 g. of sugar is concentrated and then dried to constant weight in a high vacuum.

(*h*) To isolate any dimethyl sugar remaining the column is removed and the gel extracted five times each with 100 ml. of acetone.

As an example of working, a mixture of 58·6 mg. (1 mol.) of tetramethyl- and 11·2 g. (200 mols.) of trimethyl-methylglucoside was submitted to the above hydrolytic and partition treatment. Recovery was 50 mg. (86 per cent.) and 10·55 g. (94 per cent.) respectively, *i.e.* 1 : 224 mols., but with a higher proportion of " tetra " as in glycogen or rice-starch recovery was of the order of 95 per cent.

(B) *Separation of Tetramethyl Methylglucoside from Trimethyl Methylglucoside by Adsorption on Alumina.*—This process [1] is accurate and quick in working. Quantities of 150 mg. of the " tetra " glucoside may be recovered in 94 per cent. yield from admixture with twenty times the amount of " tri " glucoside. It is thus most useful for the determination of chain lengths of the order of 15 to 50 units.

Procedure.—Activated alumina (Peter Spence and Sons Ltd., Widnes ; Grade 100/200 Birlec type) is used. All solvents should be stirred with this before distillation. As an example of method a mixture of trimethyl methylglucoside (3 g.) and tetramethyl methylglucoside (150 mg., $n_D^{16°}$, 1·4430) in 50 ml. of ether-light petroleum (1 : 1) was filtered through a column of the alumina and the chromatogram developed with ether-light petroleum (2 : 1). The filtrate collected in 20 ml. portions gave in order (i) 3 mg. impurity, (ii) 142 mg. or 94 per cent. of " tetra " ($n_D^{16°}$, 1·4426), (iii) solvent only, (iv) 174 mg. of " tri." The remainder of the " tri " was eluted with methyl alcohol.

On applying the method to a rice-starch, separation was not so sharp. The first fraction contained all the " tetra " mixed with some of the " tri " and required a repetition of the adsorption process for complete separation.

C. Viscosity Methods

These are based on the empirical relation of Staudinger [2]

$$\frac{\eta_r - 1}{C} = \frac{\eta_{sp.}}{C} = K_m M,$$

[1] J. K. Jones, *J. Chem. Soc.*, 1944, 333. [2] *Ber.*, 1930, **63**, 222, 230.

where η_r is the viscosity of a solution of the linear polymer divided by that of the solvent, C is the molar concentration with regard to the structural unit of the chains, K_m a constant, and M the molecular weight. The concentrations in which specific viscosity $\eta_{sp.}$ is determined should be in a range over which η_r is proportional to C. This is not possible in many cases, and the value of $\eta_{sp.}/C$ obtained by extrapolation to zero concentration is employed.

The constant K_m was determined with comparatively small polymers, the molecular weight of which could be found by other means. The values agreed fairly well with those found by osmotic pressure measurement, even with polymers of much higher molecular weight, but led to many anomalies. Thus the original value of K_m, 10×10^{-4} gave the degree of polymerisation of nitrates and acetates as greater than that of the cellulose regenerated from them by methods which were expected to produce no shortening of the chains.[1]

This was overcome in the case of the acetates [2] by reducing the value to 5×10^{-4}, and a later list of constants for use in viscosity calculations for cellulose and its derivatives was given.[3] When these are used the values given by viscosity measurement fall into line with the ultra-centrifuge determinations, as will be seen from the table on p. 182.

Viscosities are determined usually in an Ostwald viscometer in, for example, 1/200 molar solution in *m*-cresol at 20° for acetates,[4] followed by 1/400 and 1/800 molar solutions, $\eta_{sp.}/C$ being plotted against C in grams.

D. The Ultra-Centrifuge Method

The determination of the sedimentation equilibrium by the ultra-centrifuge not only gives the molecular weight of high polymers, but also evidence of heterogeneity. The apparatus is specialised, and at present not often available. Reference, therefore, may be made to the work of T. Svedberg and K. O. Petersen, "The Ultra-centrifuge", Clarendon Press, Oxford, 1940, and to the papers of Kraemer, *Ind. Eng. Chem.*, 1938, **30**, 1,200; *J. phys. Chem.*, 1935, **39**, 153.

[1] H. Staudinger, *et al.*, *Cellulosechem.*, 1934, **15**, 67; *Ber.*, 1935, **68**, 1611.
[2] H. Staudinger and G. Daumiller, *Ann.*, 1937, **529**, 219.
[3] H. Staudinger, *Papier Fabrik.*, 1938, **36**, 381.
[4] H. Staudinger, *Ber.*, 1930, **63**, 222; E. Elöd *et al.*, *Z. physik. Chem.*, 1934 (13), **25**, 45.

E. Osmometric Methods

Osmometers designed for use with solutions of cellulose derivatives in organic solvents have frequently been described.[1] An improved instrument which has been extensively used in polysaccharide investigation is perhaps preferable. With it particle weights varying between 3×10^3 and $3{\cdot}5 \times 10^6$ have been determined.

A full account of its setting-up and working has been given,[2] together with an examination of the equations involved.

The osmometer works on the counter pressure principle. Two strong glass bells of 5 ml. capacity are separated by a membrane of " Viscacelle 600 ". This material swells in water to a certain maximum (double thickness), and is then permeable to ordinary solutions. Alcohol has no swelling effect, so that any degree of swelling can be reached by soaking the dry film in alcohol-water mixtures and transferring to absolute alcohol. The permeability is defined by stating the volume per cent. of the mixture employed, *e.g.* 70/30 (alcohol-water).

The film is supported by a perforated curved brass disk (radius 7·5 cm.). The upper bell contains the solution under test, and is connected to an air reservoir and a manometer. Water (up to 100 cm.), and mercury (to 1 at.) are used to give pressure.

The bells are sealed with a mercury seal, and special care is needed to eliminate air bubbles. Temperature regulation to $\pm$ 0·001° is maintained in a 30 litre thermostat. The level in the capillary connected with the lower bell is read with a microscope to 0·01 mm.

Chloroform is the most generally useful solvent. The concentration of the solution must be carefully determined, a Pregl drier and micro-balance being used. It is obtained in g. per 100 g. of solution, and is converted to g./100 ml. by a density measurement.

In making an observation homogeneity of the solution (secured by an electro-magnetic stirring device) is of great importance.

The results obtained by the authors were best expressed by the equation of Wo. Ostwald, *viz.*, $\pi = ac + bc^n$, where a, b and n are constants to be determined in each case.[3] The total pressure π is thus the sum of the true van't Hoff pressure $\pi_v = ac$, and the " swelling pressure " $\pi_Q = bc^n$. π is given in atmospheres, and c in g./100 ml. The value of n in all cases was a little over 2.

[1] E. H. Büchner and P. Samwel, *Trans. Faraday Soc.*, 1933, **29**, 32; A. Dobry, *J. Chim. physique*, 1935, **32**, 46.

[2] S. R. Carter and B. R. Record, *J. Chem. Soc.*, 1939, 661, 664.

[3] Wo. Ostwald, *Kolloid-Z.*, 1929, **49**, 60.

Owing to the deviations from the ideal van't Hoff relationship shown by substances of high molecular weight, the particle size calculated from the equation $\pi = RTc/M$ will depend on concentration. Measurements are therefore made at various concentrations, and the curve extrapolated to zero concentration. The π/c ratio, or specific osmotic pressure, is best obtained by plotting curves with π/c as ordinate and c as abscissa. The intercept on the axis gives $(\pi/c)_0$ directly from which the particle size may be calculated from the above equation, *viz.*, $M = 2{\cdot}48 \times 10^5 c/\pi$ at 20°, π being in cm. of water.

Thus a methylated lichenin gave results calculated as follows :—

$$(\pi/c)_0 = \text{limit } (c \to 0)\pi/c = 17{\cdot}8 \text{ cm. water ;}$$

$$M(\text{at } 20°) = \frac{RT}{(\pi/c)_0} = 248{,}000\ c/\pi = 13{,}900.$$

Speed in working is claimed for the apparatus of Buchner and Samwel (*loc. cit.*), measurements being made after 1 hour. External pressure is applied so that the velocity of movement of the meniscus is proportional to the difference between the applied and the osmotic pressures. Extrapolation to zero velocity gives the value of the osmotic pressure. Membranes of partially denitrated collodion are used for 1 per cent. solutions of cellulose in acetone.

CHAPTER IX

THE DEGRADATION PRODUCTS OF CELLULOSE

It will be apparent from the discussion in Chapter VIII that the degradation products of cellulose will be either glucose or poly-saccharides based on anhydro-glucose units. The hydrolysis of cellulose by mineral acids may be considered an almost continuous process of change. The series passes from hydrocelluloses of copper number below 5, which retain the fibrous form, to those of increasing copper number which are powders ; thence to the cellulose-dextrins and oligo-saccharides composed of units such as $(C_6)_{25}$, downwards, finally, to cellobiose and glucose. The modification of hydrolysis in which acetylation simultaneously takes place—acetolysis—leads similarly to acetylated derivatives based on glucose, and from the hydrolysis of methylated cellulose also, the simpler methylated sugars are obtained. Thermal decomposition gives β-glucosan directly.

It was by studies of these reactions that the chain-molecule theory was evolved, and some of the investigations which were carried out are described as examples of method in this field.

THE CELLULOSE GLUCOSE RELATIONSHIP

The lines of investigation into the cellulose glucose relationship may be summarised thus :

I. Cellulose : heated in a vacuum → β-glucosan (50 per cent.).

II. Cellulose : 72 per cent. H_2SO_4 → glucose (*ca.* 95 per cent. of theoretical).

III. Cellulose : acetolysis (*a*) → Biosan (90 per cent.) → Cellobiose (50 per cent.).

(*b*) → Anhydrotrisaccharide (35 per cent.) → Cellobiose.

IV. Cellulose, methyl- and acetyl-cellulose on hydrolysis or acetolysis as follows :—

(*a*)	(*b*)	(*c*)
Triacetyl cellulose	Trimethyl cellulose	Cellobiose
↓	↓	↓
Methyl glucoside	Trimethyl methyl glucoside	Octamethyl cellobiose
↓	↓	↓
Glucose	2 : 3 : 6-Trimethylglucose	2 : 3 : 6-Trimethylglucose

In view of the importance of 2 : 3 : 6-trimethyl glucose as a key substance, a summary of its properties is first given.

Properties of 2 : 3 : 6-Trimethyl Glucose.—This sugar does not form definitely crystalline derivatives, so that identification depends upon the isolation of the sugar itself in a crystalline condition. Its ability to separate in the solid form is, however, seriously inhibited by impurities and even by drying, or heating above its melting-point. Once it has solidified it can easily be purified by crystallisation from ether. The melting-point usually obtained is about 114–115°—lower than that reached with larger quantities.

Normally, it forms needles, but a second and more soluble variety comes out in short-pointed prisms, m.p. 92–93°. These are not the β-form, as they show mutarotation in the downward sense.

The mutarotation in methyl alcohol is very slow ; if accelerated by the addition of HCl, the value of + 70° is reached in half an hour. The final value given in aqueous solution is the more trustworthy constant.

The change in rotation consequent upon the formation of 2 : 3 : 6-trimethyl methylglucoside is characteristic. A 1 per cent. solution in methyl alcohol containing 0·25 per cent. HCl undergoes condensation in the cold, and the specific rotation, calculated on the weight of sugar originally present, is after 0 minute, + 77° ; 3 to 90 minutes, + 64·3° ; 200 minutes, + 62° ; 1 day, + 36·2 ; 50 hours, + 4·1° ; 64 hours, − 5·1° ; 100 hours, − 27° ; 200 hours, − 36°.

The sugar, 2 : 3 : 6-trimethyl glucose :—

1. Forms fine needles or short prisms, m.p. 122–123° or 92–93° ; $[\alpha]_D$, + 90·2° → + 70·5° (in water) ; n_D, 1·4743.

2. Gives no phenylosazone, and on oxidation with nitric acid forms a dimethyl saccharic acid.[1]

3. Gives 2 : 3 : 6-trimethyl methylglucoside, m.p., 57·5° ; $[\alpha]_D$ (methyl alcohol) − 29·3° (from cellulose or trimethyl starch).[2]

NOTE.—2 : 3 : 4-trimethylglucose [3] is a syrup $[\alpha]_D^{20°}$ + 42·7°. →66·8° ; n_D, 1·4780. The methyl glucoside formed from it [2] (or from trimethyl glucosan) has m.p. 93–94° ; $[\alpha]_D$ (methyl alcohol) − 23·1°.

The Preparation of β-Glucosan.—This substance is best prepared in quantity from starch as the low thermal conductivity of all forms of cellulose prevents uniform heating of the mass. Details are given by Irvine and Oldham.[4]

Trimethyl β-Glucosan.—This is obtained after two treatments with methyl iodide (in methyl alcohol) and silver oxide. After extraction with boiling ether the syrup is fractionated at 18 mm.

[1] J. C. Irvine and E. L. Hirst, *Chem. Soc. Trans.*, 1922, **121**, 1222.
[2] J. C. Irvine and J. Macdonald, *ibid.*, 1926, 1506 ; see also Fig. 48.
[3] J. C. Irvine and J. W. Oldham, *ibid.*, 1921, **119**, 1756.
[4] J. C. Irvine and J. W. Oldham, *ibid.*, 1921, **119**, 1754.

into two fractions—(*a*) b.p. 145–150°, and (*b*) b.p. 165–169°. Product (*a*) is recrystallised from ether, giving 2 : 3 : 4-trimethyl β-glucosan, m.p. 62–66°. On hydrolysis with dilute hydrochloric acid this gives 2 : 3 : 4-trimethylglucose, b.p. 160–164°/0·2 mm., $[\alpha]_D^{20°}$ (methyl alcohol) + 55–69°.

PROPERTIES OF β-GLUCOSAN AND ITS DERIVATIVES

	Melting-point.	Boiling-point.	$[\alpha]_D$.
β-glucosan . . .	179–180°	Boils undecomp. (9 mm.)	−66·17° *
β-glucosan-hydrate .	108°	—	—
Triacetyl-β-glucosan .	110°	—	−45·5° †
Tribenzoyl-β-glucosan .	199–200°	—	—
Trimethyl-β-glucosan .	62–65°	135·5° (12 mm.)	−63·5° *

* Water. † Alcohol.

Conversion into 2 : 3 : 4-*Trimethyl* β-*Methylglucoside.*—A 4·4 per cent. solution of 2 : 3 : 4-trimethyl glucosan in methyl alcohol containing 0·5 per cent. of HCl is heated at 110°. Samples withdrawn after about 80, 160, and 200 hours, respectively, all contain the α- and β-isomeric forms of 2 : 3 : 4-trimethyl methylglucoside.

Conversion of Cellulose to Glucose by the Action of Mineral Acids.—Hydrochloric acid of concentrations greater than 40 per cent. HCl dissolves cellulose in a few seconds and by dilution after a short time the cellulose is recovered in a modified form, though it does not reduce Fehling's solution. If a 1 per cent. solution is kept at room temperature the optical rotation, at first zero, rises slowly until in 1 to 2 days it reaches a constant value [1] which corresponds to a yield of glucose of about 97 per cent. of theoretical. Later observations [2] showed that wood celluloses reached the same $[\alpha]_D^{20°}$ (of about 100°) as cotton cellulose.

The action of dilute sulphuric acid in producing glucose from cellulose has been very much investigated. The satisfactory technique of Monier-Williams is given below, as in this case the glucose is isolated in the crystalline form, the yield being about 95 per cent. of the theoretical.

Preparation of Glucose from Cellulose (G. W. Monier-Williams [3]).—10 g. of cotton wool are dissolved in 50 ml. of 72 per cent. sulphuric acid, and the dark-coloured solution left for 1 week at room

[1] R. Willstätter and L. Zechmeister, *Ber.*, 1913, **46**, 2401.
[2] E. C. Sherrard and A. W. Froehlke, *J. Amer. Chem. Soc.*, 1923, **45**, 1729.
[3] *Chem. Soc. Trans.*, 1921, **119**, 803.

temperature, after which it is diluted to 5 litres with water, and boiled under reflux for 15 hours. The liquid, after filtering, is almost colourless. It is neutralised to litmus paper with barium carbonate, filtered, and evaporated to dryness (40 mm.). Since alkalinity develops during concentration, a few drops of methyl red are added to the distilling flask, and the liquid is kept neutral to this indicator during concentration, by addition of $N/10$ sulphuric acid. The residue from the distillation is extracted under reflux with methyl alcohol, free from acetone. After being filtered and decolorised by boiling with a little charcoal, the solution is evaporated in a current of dry air at a low temperature. Crystals form, and the residue, after evaporation of the alcohol, is completely crystalline. Yield obtained, 9·718 g. containing per cent :—

Moisture, 3·28 ; ash, 1·53 ; glucose (by polarimeter, 94·73 ; by copper reduction, 94·41) in mean 94·57—total, 99·38 per cent.

On recrystallisation from absolute alcohol the residue gave white crystals, m.p. 144–145° (uncorr.), with a phenylosazone, m.p. 204-205° (uncorr.). Allowing for moisture and ash in the original cellulose, and for the small quantity (0·162 g.) which was not dissolved by the acid, the yield of crystalline glucose, calculated from the crude product, amounted to 90·67 per cent. of the theoretical quantity. No other product of hydrolysis could be detected.

Quantitative Study of the Conversion of Cotton Cellulose into α- and β-Methylglucosides.[1]—In this investigation the cellulose was converted into the triacetate, and this was simultaneously hydrolysed and condensed with methyl alcohol. The transformations involved and the average yields obtained are as follows :—

	Parts.	
Cotton cellulose (anhydrous)	100	Yield, 99·5 per cent.
↓		
Cellulose triacetate	177	
↓		
α- and β-Methylglucosides	114·1	Yield, 95·5 per cent.
↓		
Equivalent of glucose	106·0	

The overall yield from the polysaccharide to the hexose is thus 95·1 per cent. of the theoretical amount.

(*a*) *Preparation of Cellulose Triacetate.*—This was prepared by the method of Barnett (p. 280). 10 g. of air-dry cotton are soaked in 50 ml. of glacial acetic acid through which dry chlorine has been passed for 30 seconds. After half an hour 60 ml. of acetic anhydride are added, and sulphur dioxide gas passed for 1 minute.

[1] J. C. Irvine and E. L. Hirst, *Chem. Soc. Trans.*, 1922, **122**, 1585.

The mass is stirred for 1 hour, the temperature raised to 65° and maintained there until the cellulose dissolves. After cooling to 30° an equal volume of chloroform is added, and then excess of cold water. The chloroform is evaporated, with stirring, when the acetate separates in granular particles. Yield, 99·5 per cent. Acetyl 44·2; $C_6H_7O_5(CH_3 . CO)_3$ requires 44·8 per cent.

(*b*) *Hydrolysis of Cellulose Triacetate and Condensation with Methyl Alcohol.*—This useful method requires exact control. Treatment of the triacetate with cold methyl alcohol saturated with HCl does not give a quantitative yield of methylglucoside. For small scale quantitative work sealed tubes are best. The acetate, 3·99 g., is heated at 125° for 50 to 60 hours with pure methyl alcohol, 60 ml. containing 0·75 per cent. of HCl. The liquid is neutralised with silver carbonate, the filtrate decolourised with charcoal and evaporated at low pressure. Traces of solvent are removed at 100°/10 mm. in a current of dry air. The syrup crystallises and is dissolved in a little hot alcohol, which is removed after several hours, the alcohol giving a crystalline residue, m.p. 125–150°, in agreement with that of the equilibrium mixture of α- and β-methylglucosides.[1] Permanent $[\alpha]_D$ + 108°. Yield, 95·6 per cent. On recrystallisation from absolute ethyl alcohol crystals of α-methylglucoside are obtained, m.p. 165°, $[\alpha]_D$ (water) + 157·5 (*c*, 0·6). The mother liquors contain excess of the β-form, giving $[\alpha]_D$ + 77·5.

A similar process of hydrolysis was applied to trimethyl cellulose.[2]

(*c*) *Hydrolysis of Trimethyl Cellulose and Conversion to* 2 : 3 : 6-*Trimethyl Methylglucoside.*—The methylated cellulose was heated at 100° with methyl alcohol containing 1 per cent. of HCl. The charge for a sealed tube is 4·5 g. of the solid and 60 ml. of the acid reagent. Heating was continued for 100 hours at 130°, after which only a trace remained undissolved. The solution was neutralised with silver carbonate, filtered, and evaporated. The colourless syrup, after drying at 100°/10 mm., represented 95 per cent. of the theoretical yield. The syrup was fractionated (0·5 mm.), and at 115–118°, 84 per cent. came over as 2 : 3 : 6-trimethyl methylglucoside, OMe, 52·6 per cent.; n_D, 1·4583; $[\alpha]_D^{20°}$ (methyl alcohol) + 72·0°; in chloroform + 66·0° (mixed isomerides).

For other methods of hydrolysis see pp. 173, 184 and 440.

(*d*) *Hydrolysis of Trimethyl Methylglucoside to* 2 : 3 : 6-*Trimethyl Glucose.*—Method given on p. 188.

[1] J. C. Irvine and C. W. Soutar, *Chem. Soc. Trans.*, 1920, **117**, 1489.
[2] J. C. Irvine and E. L. Hirst, *Chem. Soc. Trans.*, 1923, **123**, 528.

THE ACETOLYSIS OF CELLULOSE AND THE OLIGOSACCHARIDES

The discovery (1901) that cellulose, when treated with a mixture of sulphuric and acetic acids and acetic anhydride, gave the acetates of cellobiose and glucose was of primary importance. The conditions originally used led to these final products of acetolysis, but with modified conditions a series of products lying between cellulose and cellobiose can be obtained, all of which are constituted on the same structural plan. These are the oligosaccharides, or cello- or cellulose dextrins, and units of chain-length from $(C_6)_{25}$ to $(C_6)_{10}$ down to the reducing sugar units $(C)_6$, $(C_6)_4$ and $(C_6)_3$ have been isolated.

Hess and Friese [1] were the first to use modified conditions. They claimed that by their process the following chemical individuals were always obtained, *viz.* acetyl cellulose, acetyl biosan (see below) and the acetates of cellobiose and *iso*-cellobiose. The biosan has since been shown [2] to be a mixture of oligosaccharides of high molecular weight and the *iso*-cellobiose is a trisaccharide [3] falling naturally into the degradation series.

The Biosan of Hess and Friese.—This product affords a useful material for the preparation of the oligosaccharides. The methods of acetolysis and fractionation are briefly given. It was originally thought to be a single substance of formula $C_{24}H_{32}O_{16}$.

(*a*) *Preparation of Acetylbiosan.*—Into a mixture of 150 ml. each of acetic anhydride and of glacial acetic acid with 4 ml. of concentrated sulphuric acid at — 18°, 40 g. of cotton wool, air-dry, are introduced gradually, the temperature being kept below — 5°. The mixture is left at 30° for $2\frac{1}{2}$ days, the yellow solution filtered and poured into cold water. The precipitate is washed with water until neutral, dried in air, and then at 50–60°. Yield, 67·9 g.

For putification the solid is boiled up twice in portions of 20 g. with 1 litre of absolute methyl alcohol. About one-third goes into solution, 2 g. of which comes out on cooling. The soluble portions are probably acetylcellobiose. The snow-white powder left, insoluble in methyl alcohol, has m.p. 247–248°.

The biosan acetate is insoluble in ether, soluble with difficulty in hot methyl alcohol and benzene, and moderately soluble in hot nitrobenzene and amyl acetate.

(*b*) *The Biosan.*—The acetate is saponified with a 10 per cent. excess of 2*N*-methyl alcoholic NaOH. After 12 hours at ordinary

[1] K. Hess and H. Friese, *Ann.*, 1926, **450**, 40 ; *Ber.*, 1930, **63**, [B], 518.
[2] W. N. Haworth, E. L. Hirst *et al.*, *J. Chem. Soc.*, 1932, 2369.
[3] J. C. Irvine and G. J. Robertson, *ibid.*, 1926, 1488.

temperature the biosan is isolated as a white powder. On heating it begins to decompose at 270°.

It is insoluble in water and all organic solvents, but dissolves easily in 2*N*-NaOH to a colourless solution, which, on warming, becomes yellow. It is precipitated from the solution by acids or 25 per cent. ammonia. The biosan slightly reduces Fehling's solution; $[\alpha]_D^{20°}$ — 6·31° (in 2*N*-NaOH).

Acetolysis to Cellobiose and Iso-cellobiose.—These derivatives result from acetolysis mixtures worked up after 4 or 5 weeks, instead of after the 2½ day period at which the production of biosan reaches a maximum.

Methylbiosan.—This was originally prepared by repeated methylation of the biosan with dimethyl sulphate. It is, however, more conveniently prepared [1] directly from the acetate by treating 10 g. in acetone (250 ml.) with dimethyl sulphate (60 ml.) and 30 per cent. NaOH (160 ml.) at 50–55° in the usual way (p. 315).

On treating the product with cold benzene and pouring off quickly the yellow portion is removed. The residue is dissolved in 100 ml. of a cold mixture of benzene and alcohol, the liquid centrifuged, and evaporated in a vacuum to half volume. About 3 g. separate, and a further portion is obtained by mixing with light petroleum. M.p. 210–215°; $[\alpha]_D^{20°}$ — 10·2° (water). It dissolves in cold water, but is precipitated on warming. Soluble with difficulty in alcohol and acetone. On treatment with methyl alcoholic hydrochloric acid, it yields 2 : 3 : 6-trimethylglucose (α, β)-methylglucoside.

PROPERTIES OF BIOSAN DERIVATIVES COMPARED WITH THOSE OF CELLULOSE

	Cellulose Triacetate.	Biosan hexa-acetate.	Cellulose Trimethyl Ether.	Biosan hexamethyl Ether.
Melting-point (in tube)	295° sinters 295° decomp.	247/248° clear yellow liquid.	230° sinters 239° melts	210/215° clear liquid.
$[\alpha]_D^{20°}$ in				
Chloroform	— 22·4°	— 15·4°	— 4·3°	—
Glacial acetic acid	+ 4·8°	+ 5·4°	— 9·8°	—
Pyridine acetone (4 : 1)	— 28·3°	— 22·1°	— 5·1°	—
Benzene	—	—	— 18·5° (at 0°)	— 4·5° (at 20°)
Water	—	—	— 18·4°	— 10·2°

Fractionation of the Biosan.—This was carried out by Haworth and Machemer,[2] who found that after repeated solution and

[1] W. N. Haworth and H. Machemer, *J. Chem. Soc.*, 1932, 2372.

[2] *J. Chem. Soc.*, 1932, 2372; *cf.* also M. Bergmann and H. Machemer, *Ber.*, 1930, **63**, 316, 2304.

fractional precipitation, the biosan acetate could be separated into five main groups, consisting of compounds, each of approximately the same chain-length (*cf.* p. 173).

The acetolysis was carried out as given above. The product was dissolved in chloroform and precipitated by alcohol. The more insoluble parts were collected and each was hydrolysed (KOH + MeOH) and the insoluble part reacetylated (Ac_2O + NaOAc at 130° for 1 hour). These acetates were again fractionated. The final results are shown in the table, the chain-lengths being calculated from the iodine numbers.

FRACTIONS OF CELLODEXTRIN ACETATES

No.	Yield per cent.	$[\alpha]_D$ in $CHCl_3$.	Sinter and Decomp. at	AcOH yield per cent.	No. of Glucose Units.
I . .	14	− 18·1°	274–280°	62·6	21
II . .	17	− 17·9	265–272	63·2	19
III, IV .	37	− 16·6	252–258	63·0	14
V . .	9	− 15·6	227–235	64·3	12
VI . .	13	− 14·9	210–215	64·5	12
X . .	<10	− 19·5	290–295	62·5	(Cellulose-acetate)

Each acetate fraction was then methylated by the standard method (p. 315), giving yields up to 90 per cent. in one operation. The derivatives were purified from chloroform solution by the addition of ether. The properties of the more important fractions are given in the next table, the fraction numbers corresponding to those of the acetate fractions above. The chain-lengths were determined by end group estimation. Each fraction had OMe 44 to 45 per cent.

FRACTIONATION OF METHYLATED CELLODEXTRINS

Fraction.	Wt. g.	$[\alpha]_D$.	Sinter and Decomp.	Tetra-methyl Derivative Per cent.	Avg. Chain-Length Glucose Units.
I*a* . .	22·2	− 12·6°	230–235°	5·7	21
II*a* . .	27·5	− 12·1	229–232	4·6	26
III*a* .	23·5	− 12·5	220–235	5·0	24
IV*a* . .	27·0	− 11·7	222–225	5·1	24
IV*b* . .	4·0	− 9·3	205–210	9·0	13
V*a* . .	9·1	− 9·6	186–190	8·5	14
V*b* . .	8·4	− 4·4	160–163	10·4	11

Isolation of Cellohexaose, Cellotetraose and Cellotriose.—These sugars were obtained by Zechmeister and his co-workers [1] from the hydrolysis products of cellulose with concentrated hydrochloric acid by elaborate fractionation from alcohol-water mixtures. The work was assisted by the observation that the solubility and the specific rotation increase as the chain-length diminishes, the value of $[\alpha]_D$, for example, for the sugars $(C_6)_6$, $(C_6)_4$, $(C_6)_3$, $(C_6)_2$, and glucose being 13°, 18°, 23°, 32·5° and 52·5° respectively. The following is an example of small-scale working :—

Dried cotton (112 g.) was stirred into 1,100 g. of HCl, *d*, 1·21, a clear liquid resulting after 8 minutes. After 3 hours at 20° as much as possible of the acid gas was removed in 10 minutes by the pump and the liquid then mixed with ice (3 kg.). The acid was neutralised with silver carbonate, the precipitate washed three times, each with 1 litre of water, and traces of silver removed from the filtrate by HCl. The liquid was concentrated to 1·25 l., and the precipitated dextrins separated. Lead carbonate may replace silver carbonate, excess being removed by sulphuretted hydrogen.

Fractional precipitation by alcohol gave 20–30 fractions, the most difficultly soluble of which contained water-swelling dextrins ; the easiest soluble cellotriose, and the mother liquors glucose. The middle fractions were therefore required. The 1·25 l. of hydrolysate were mixed with 2·5 l. of alcohol, the precipitate removed, and the filtrate treated with 5 l. of alcohol. The combined solids (*ca.* 10 g.) gave on fractional precipitation from water by alcohol, 1·75 g., easily soluble, *i.e.* the tetraose fraction. The mother liquors from the original 10 g. were concentrated to 200 ml., and by addition of 8·5 l. of alcohol gave 10 g. of solid which, after purification from water by alcohol, gave as the most soluble part the triose fraction.

Cellotriose is insoluble in alcohol. It dissolves in pyridine in the cold (difference from cellobiose). It forms prisms, m.p. 210° (decomp.), not sharp. M. wt. found 456–513 ; $C_{18}H_{32}O_{16}$ requires 504. Acetate m.p. 200° ; $[\alpha]_D^{20°}$ + 7·2°.

Cellotetraose, when quickly crystallised, forms white clusters soluble slowly in water, easily in pyridine and hot acetic acid. It sinters at 205°, m.p. 240°, not sharp. M. wt. found 662–706 ; $C_{24}H_{42}O_{21}$ requires 666 . $[\alpha]_D^{20°}$ + 21°. Acetate m.p. 225° ; $[\alpha]_D^{20°}$ — 15·6° (chloroform).

Cellohexaose forms star-shaped clusters of needles. M. wt. found 918–957 . $C_{36}H_{62}O_{31}$, requires 990. It is obtained from the difficultly soluble fractions.

[1] L. Zechmeister and G. Toth, *Ber.*, 1931, **64**, 854 ; R. Willstätter and L. Zechmeister, *ibid.*, 1929, **62**, 722.

Cellobiose and its Derivatives

This sugar, which results from the acetolysis of cellulose, was first isolated by Franchimont (1879), and was later studied by Skraup and Koenig [1] and by Maquenne and Goodwin.[2] Numerous variations of the acetolysis conditions are recorded by investigators seeking to obtain a maximum yield of cellobiose on which constitutional formulae could be founded. In practice yields rarely exceed 35 per cent., but maxima of 50–60 per cent. have been claimed.

Preparation of Cellobiose Octa-acetate.—1. *Method of Hess and Friese.*[3]—A series of experiments on the yield of cellobiose obtained from celluloses of different origin and pre-treatment, showed that in each case the yield was the same, *viz.* about 50 per cent. of the theoretical. In general 19 g. of dry cellulose gave 20–20·5 g. of cellobiose octa-acetate.

Preparation from Cotton Wool.—A cooled mixture of 75 ml. glacial acetic acid and 75 ml. of acetic anhydride to which, at — 15°, 8 ml. of concentrated sulphuric acid has been added, is prepared. 20 g. of cotton wool are added in portions, the temperature being kept below + 5°. After 2 hours at room temperature, and then in a thermostat at 30°, solution takes place in 8 hours ; the first crystals form after 5 to 6 days, and after 10 to 13 days are filtered off ; yield, 10 g. ; m.p. 222°. The filtrate is poured into 1·5 l. of water, neutralised with sodium acetate (Congo red), and after a day the solid is removed, washed and dried. Yield, 16·9 g. (crude). This product is shaken twice for 2 hours with 80 ml. of alcohol-ether (1 : 3), and the residue crystallised from 350 ml. of alcohol. Yield, 7·7 g. of the acetate. $[\alpha]_D^{20°}$ + 41·8 (chloroform) ; m.p., 221°.

The ether-alcohol extract and mother liquors are evaporated and taken up with 100 ml. benzene and precipitated twice with 75 ml., and once with 200 ml., of petrol ether. A further 2·9 g. are obtained, making the total yield 20·5 g., or 50·5 per cent.

Preparation from Wood Pulp.—10 g., air dry, are brought into a mixture of 40 ml. glacial acetic acid, 40 ml. acetic anhydride, 4·1 ml. sulphuric acid, and left 13 days at 30°. Pure crystals, separated, 3·8 g. Filtrate precipitated by water gives 8·8 g. of crude product. After shaking this with methanol-ether (1 : 1) and solution in absolute alcohol, 3·9 g. of pure crystals are obtained. The residues, after evaporation and extraction with ether, are digested with alcohol-ether (2 : 1) and crystallised from alcohol, giving 2·2 g. more. Total 9·9 g., or 49 per cent. of theory.

[1] H. Skraup and J. Koenig, *Monatsh.*, 1901, **22**, 1016.
[2] L. Maquenne and W. Goodwin, *Bull. Soc. Chim.*, 1904, [iii.], **31**, 854.
[3] K. Hess and H. Friese, *Annalen*, 1927, **456**, 49.

2. *Method of Haworth and Hirst.*[1]—This process is quick and convenient, but for success the filter paper used must have the right water content, as if too moist heating takes place, and if too dry it does not become impregnated with the reagents.

Filter paper in layers of four sheets is kept in a dry atmosphere at 20° for 3 days, and is then cut into pieces of about 1 square cm. 20 g. are stirred into a mixture of 80 ml. of acetic anhydride, containing 11 ml. of sulphuric acid. The whole is cooled in water so as to keep the temperature of the mixture just below 20°. After stirring for 5 minutes a viscid paste should be obtained.

A bath of calcium chloride and water, previously heated to 120°, is then employed to heat the paste, which must be thoroughly stirred. It rapidly darkens in colour, and at about 112° a red mobile liquid is formed which begins to boil. Immediately the red solution appears to be changing to black, it is poured into 1½ l. of water. A yellow precipitate of crude octa-acetate separates in 10 minutes. The success of the experiment can be tested as follows : a sample of the precipitate should dissolve in boiling alcohol, but not in cold ; from the hot solution white powdery crystals are deposited which under the microscope show characteristic rosettes of needles.

The precipitate is left in water for 6 hours, filtered, washed and dried at 40°, and then boiled under reflux for half an hour with 300 ml. of 90 per cent. ethyl alcohol. The solution is filtered hot and the minute crystals, after 12 hours, are washed with dilute alcohol, and dried. Yield, 25–35 per cent. of the cellulose ; m.p. 224–227° (uncorrected) ; $[\alpha]_D$ + 41·5 (chloroform).

Removal of Acetyl Groups.—10 g. cellobiose octa-acetate are moistened with a little absolute alcohol and mixed, during constant stirring, with a solution of 12 g. of KOH in 50 ml. of absolute alcohol. After 2 hours the potassium cellobiosate is collected on a filter, washed with alcohol, and dried in a vacuum. Yield, 6 g. The free disaccharide is isolated by the method of Maquenne (p. 206).

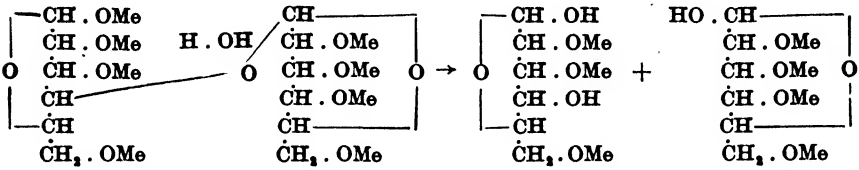
Heptamethyl Methylcellobioside.—The potassium cellobiosate may be used. 11 g. in a little water are methylated with 38 ml. of methyl sulphate and 36 g. of NaOH in 70 ml. of water. A liquid distilling just below 200°/0·2 mm. with n_D, 1·4687 is obtained, having the composition of hexamethyl methylcellobioside.

To introduce the remaining methyl group this product is digested on three occasions with methyl iodide and silver oxide. After this practically the whole will distil at 190–200°/0·02 mm. as a faintly yellow syrup, n_D, 1·4620, which rapidly becomes crystalline. After

[1] W. N. Haworth and E. L. Hirst, *Chem. Soc. Trans.*, 1921, **119**, 197.

grinding with light petroleum colourless crystals are obtained, m.p. 76–78°; n_D, 1·4643; $[\alpha]_D$ + 9·0° (water); OMe, 53·2 per cent. [$C_{12}H_{14}O_3(OMe)_8$] requires OMe, 54·6 per cent.

On hydrolysis a mixture of tetramethyl- and trimethyl-glucose is obtained thus:—



Heptamethyl methylcellobioside. 2 : 3 : 6-Trimethyl-glucose. 2 : 3 : 4 : 6-Tetramethyl-glucose.

This is effected by heating 10 g. with 500 ml. of 5 per cent. HCl for 5 hours at 80–95°. The acid is neutralised (barium carbonate), and the solution taken to dryness under diminished pressure. The residue is extracted several times with boiling ether. Yield, 7·7 g. of syrup, which partly crystallises on treatment with a specimen of the above tetramethyl glucose. The tetramethyl glucose is isolated by repeated digestion with boiling light petroleum, from which it crystallises. M.p. 88–89°, $[\alpha]_D$ + 83·3°, in equilibrium in water. Trimethyl glucose is obtained from the residual syrup, dissolved in boiling ether; m.p. 115–116°.

Cellobiose from Cellobiose Octacetate.—1. *Method of Maquenne and Goodwin.*[1]—A solution of 12 g. of KOH in 40 ml. of alcohol is made, at 90° if necessary. 10 g. of finely powdered octacetate are added with shaking, temperature not above 35–40°. The potassium salt of cellobiose separates as a viscous mass. After a time the liquid is decanted and the mass washed twice with absolute alcohol, the residue is dissolved in the minimum of warm water, and the solution exactly neutralised with perchloric acid. The potassium perchlorate is filtered off and the filtrate concentrated until a thin film begins to form, when it is cooled and again filtered. The liquid is concentrated to incipient crystallisation, decanted, 3 to 4 volumes of methyl alcohol added, and the mixture allowed to stand 24 hours. The cellobiose is washed cautiously with methyl alcohol. Yield, 3 g.

2. *Method of Peterson and Spencer.*[2]—The authors state that the following method reduces the time and the expense of preparation besides giving usually a better yield—for example, 85 per cent. of the theoretical.

[1] L. Maquenne and W. Goodwin, *Bull. Soc. Chim.*, 1904, **31**, [3], 855.
[2] F .C. Peterson and C. C. Spencer, *J. Amer. Chem. Soc.*, 1927, **49**, 2822.

A 10 per cent. solution of sodium ethylate is prepared in 95 per cent. alcohol. 10 g. of finely pulverised cellobiose octa-acetate are brought into 85 ml. of this solution during 1 hour with constant stirring. The reaction is complete in less than an hour. The sodium salt is collected, washed with alcohol and dissolved in a minimum of ice water and again filtered. Glacial acetic acid is added until a precipitate begins to form. Complete crystallisation takes place 15 minutes after the addition of sufficient acetic acid.

The crude cellobiose is washed with ether and dried at 65°. It is purified by dissolving in a minimum of water and adding acetone until reprecipitation is complete. A product of sufficient purity is obtained after two recrystallisations from acetone; m.p. 225° (uncorr.) rotation (in water) 24·4° in 15 minutes and 35·2° in 27 hours.

PROPERTIES OF CELLOBIOSE AND ITS DERIVATIVES

Cellobiose Derivative.	Melting-point.	$[\alpha]_D$.
β-Cellobiose	225° *	+ 34·6° †
Cellobiosazone	198°	− 18° ‡
Cellobiosephenylhydrazone	90°	—
β-Methyl-cellobioside	193°	− 18·7° †
α-Octa-acetyl-cellobiose	228°	+ 41·41° §
β-Octa-acetyl-cellobiose	202°	− 14·63° §
Hepta-acetyl-cellobiose	204°	+ 22·6° §
Hepta-acetyl-β-methylcellobioside	187°	− 25·4° §

* With decomposition. † In water.
‡ In pyridine-alcohol. § In chloroform.

DERIVATIVES OF METHYL FURFURALDEHYDE

On treatment with dilute aqueous acids cellulose gives ω-hydroxymethyl furfuraldehyde in small amounts, but larger quantities are obtained from modified cellulose.[1] Thus by the action of a 5 per cent. solution of oxalic acid at 180° for 30 minutes cotton gave 0·8, viscose cellulose 5·2, and hydrocellulose (Knoevenagel) 10·8 per cent.

Similar quantities are formed during the distillation of cellulose materials with dilute hydrochloric acid, as in the standard method for the estimation of pentosan—*e.g.* a cotton wool gave 0·3, the same mercerised 1·0, a viscose cellulose 2·4, and an oxycellulose 0·7 per cent.[2] (p. 380). The small amount isolated is due probably to decomposition of the aldehyde into lævulinic acid during the distillation.

[1] E. Heuser and W. Schott, *Cellulosechem.*, 1923, **4**, 85.
[2] M. Cunningham and C. Dorée, *Biochem. J.*, 1914, **8**, 438.

Halogen acids in non-aqueous media give ω-substituted derivatives.

ω-Bromomethyl Furfuraldehyde.[1]—This is obtained as follows: 10 g. of the cellulosic material are covered with 250 ml. of chloroform, which has been saturated at 0° with hydrogen bromide. The mixture is placed in a stoppered bottle and heated in a water bath for 2 hours. After some hours the mixture is treated, first with solid sodium carbonate, and then with a few drops of concentrated solution, filtered, and the solution dried over calcium chloride. The bulk of the solvent is distilled off and the residue allowed to evaporate to a thick syrup. It may be seeded with a crystal of ω-bromomethyl furfuraldehyde.

Hibbert and Hill, who obtained higher yields, find it best to let the mixture stand for 12 hours before heating to 100°.

The following table shows the yields obtained by these methods from 10 g. of the materials named :—

Material (10 grams).	ω-Bromomethyl Furfuraldehyde in grams.	
	Fenton and Gostling.	Hibbert and Hill.
Cotton	3·3	5·6
Viscose Cellulose . .	—	5·5
Glucose	0·33	1·2
Cane sugar	0·85	3·5
Cellobiose	—	2·7

The bromine in this compound is so reactive that it may be estimated by titration with silver nitrate by Volhard's process, the crystals being dissolved in dilute alcohol—*e.g.*,

0·1970 g. required 10·5 ml. *N*/10 $AgNO_3$. Br, 42·63 per cent.; calculated 42·32 per cent.

[1] H. J. H. Fenton and M. Gostling, *Chem. Soc. Trans.*, 1901, **79**, 362; H. Hibbert and H. S. Hill, *J. Amer. Chem. Soc.*, 1923, **45**, 176.

CHAPTER X

THE DETECTION AND ESTIMATION OF ACIDS IN CELLULOSIC MATERIALS

THE tendering produced by minute quantities of acids when dried into cellulose makes their detection a matter of importance. Lester [1] described the tendering produced when 0·01 per cent. of HCl was dried into fabric which was subsequently ironed.

Coward, Wood and Barrett [2] carried out some experiments in which solutions containing 0·005, 0·015, 0·05, 0·15, 0·50 per cent. of HCl on the dry weight of the cotton were allowed to dry on the fabric, which was subsequently heated at 100° or 120°. The results showed that 0·05 per cent. of acid produced a serious tendering (over 40 per cent. loss in strength), while even 0·01 per cent. produced a loss of some 10 per cent.

Cotton, when steeped in solutions of various acids, also becomes tendered. Fort and Pickles [3] concluded " that the tendering action (hydrolysis) of acids on cotton, like the inversion (hydrolysis) of cane sugar, is dependent on the strength or electro-conductivity of the acids ". Coward and his co-workers confirmed this, and their results show, also, the importance of the time factor. They found definite tendering with solutions of the stronger acids at 100° in concentrations as low as 0·01*N*- in one hour. Some of their results are given below.

PERCENTAGE TENDERING AT 100°

	2*N*-Acid.			*N*-Acid.			*N*/10 Acid.		
Time in Minutes:	1	15	60	1	15	60	1	15	60
Acid.									
Hydrochloric . .	100	100	100	100	100	100	9	54	100
Sulphuric . .	22	100	100	34	100	100	12	32	32
Hydrofluoric . .	11	100	100	7	28	51	0	11	31
Acetic . . .	0	15	15	4	9	18	—	5	14
Monochloracetic .	3	35	100	17	23	39	0	0	16
Trichloracetic .	—	—	—	5	84	100	—	—	11
HCl + NaCl . .	100	100	100	100	100	100	12	34	100

[1] J. H. Lester, *Jour. Soc. Chem. Ind.*, 1915, **34**, 934.
[2] *J. Text. Inst.*, 1917, **14**, No. 12.
[3] *J. Soc. Dyers and Col.*, 1915, **31**, 255.

Detection and Estimation of Acid and Alkali in Cotton Fabrics.[1]—The investigations of these authors comprised—

(*a*) The preparation of a neutral cloth. Two samples of good bleached calico were treated with dilute NaOH and HCl respectively. The fabrics were extracted repeatedly with boiling neutral distilled water *—the acid fabric in a quartz vessel, the alkaline one in a silver beaker. After drying it was found that methyl red was the only indicator which showed any difference between them. The fabric originally alkaline showed a neutral tint; the other gave a purer red, free from yellow. The originally alkaline fabric was allowed to absorb a weight of solution which contained 0·005 per cent. of acid calculated on the weight of cloth. After drying the colour given by methyl red was indistinguishable from that given by the cloth originally acid. This latter when similarly allowed to absorb 0·005 per cent. of alkali gave an alkaline test with methyl red. Therefore neither cloth was nearer neutrality than 0·005 per cent. respectively. It follows that if a cloth gives no reaction when spotted with methyl red *it is neutral within* 0·005 *per cent. HCl or equivalent acid or alkali.*

(*b*) Approximate estimation of acidity or alkalinity by "spotting" an indicator on the fabric. The following table contains the results observed with various indicators. They apply to sulphuric and hydrochloric acids only :—

Indicator.	Colour.	Indication. Acid or Alkali per cent. on Weight of Cloth.
1. KI . KIO_3 . starch	Blue, increasing .	0·01 per cent. H_2SO_4 upwards.
2. Lacmoid . .	Blue . . .	0·02 per cent. H_2SO_4 and less.
,, . .	Blue centre, red ring	0·03–0·06 per cent. H_2SO_4.
,, . .	Red . . .	0·06 per cent. upwards.
3. Methyl orange .	Yellow-red . .	0·10–0·16 per cent. H_2SO_4.
4. Thymol blue .	Purple . . .	0·16 per cent. upwards.
5. Methyl red .	Red . . .	0·005 p.c. H_2SO_4 upwards.
,, ,, .	Yellow . . .	0·005 p.c. NaOH upwards.
6. Brom-thymol blue	Green . . .	0·02 per cent. NaOH (present as Na_2CO_3).
,, ,, ,,	Blue . . .	0·04 per cent. NaOH upwards.
7. Phenolphthalein	Pink, increasing .	0·12 per cent. NaOH upwards.

The indicators are prepared as follows :—

No. 1. Iodide-iodate starch reagent. 2 g. of KI and 1 g. of KIO_3 boiled with 100 ml. of water till a drop cooled and diluted

[1] H. F. Coward and G. M. Wigley, *J. Text. Inst.*, 1922, **13**, 121.

* A quicker method of preparation of the neutral cloth is to boil out with a dilute solution of common salt, which removes the acid more rapidly than water.

gives no colour with starch solution. It is made up to 100 ml. with neutral water and mixed with a solution of 1 g. of starch in 100 ml. water made at boiling-point. This reagent keeps if CO_2 is excluded.

No. 2. Lacmoid. A 0·5 per cent. solution in alcohol.

No. 3. Methyl orange. A 0·01 per cent. solution in water.

Nos. 4 and 6. Thymol blue and brom-thymol blue. A 0·04 per cent. neutralised solution in water.

No. 5. Methyl red. A saturated aqueous solution.

(*c*) Quantitative estimation of acid and alkali in cotton by titration. The method of estimating acid in cloth by extracting with boiling water and titrating the extract in the absence of the cloth was shown to be unreliable, and with concentrations of acid of the order of 0·1 to 0·2 per cent. little more than half may be extracted; *e.g.* added 0·1, 0·2; found 0·05, 0·16 per cent., respectively.

Coward and Wigley found, on the other hand, that titration in the presence of the cloth gave results the error of which did not exceed 0·005 to 0·008 per cent. of acid per 100 g. of cloth; *e.g.* added H_2SO_4 0·2, found 0·192 g. The following process is therefore recommended.

Procedure.—100 ml. of distilled water, in a conical flask of hard glass, are brought to the boiling-point and 1 ml. of 0·5 per cent. phenolphthalein (in alcohol) added, and the whole titrated with $N/50$ NaOH solution till a faint colour, just visible against a white background, and permanent for 10 minutes, is obtained. The flask is loosely stoppered during standing. If the cloth is acid—

3 g. of the cloth are put in and the liquid boiled for a few minutes. It is then titrated with $N/50$ NaOH until the colour remains permanent in the closed flask for 10 minutes. A neutral cloth requires no more than 0·1 ml. of $N/50$ alkali. Until experience is gained it is advisable to make a standard with cobalt nitrate and copper sulphate solutions as recommended by McBain,[1] who emphasises the precautions necessary with this reagent. A solution slightly alkaline to phenolphthalein, for example, may be decolorised by the CO_2 introduced with a piece of cloth.

If the cloth is alkaline, or neutralises acid through the presence of calcium carbonate, etc., the colour of the indicator will not be discharged in the above procedure. In that case an excess of $N/50$ sulphuric acid is added, the whole is boiled for 10 minutes, and titrated back with the alkali to the standard pink.

The determination of alkali by this method is correct to 0·02 of 1 per cent., *e.g.* added 0·287 g. NaOH to 100 g. of cloth; found, 0·274 g.

[1] J. W. McBain, *Chem. Soc. Trans.*, 1912, **101**, 814.

The Estimation of Minute Quantities of Acid in Cellulose Material.—Cellulose, as has been seen, tenaciously retains traces of mineral acids with which it has been treated or modified. With cellulose containing combined sulphuric acid it was found that boiling for 6 hours with 1 per cent. NaOH did not effect a complete removal of the acid. It can, however, largely be removed by boiling for 8 hours with $N/20$ hydrochloric acid.[1]

For the estimation of combined sulphuric, hydrochloric and phosphoric acids the following methods by D. A. Clibbens and A. Geake,[2] are recommended :—

(*a*) *Estimation of Sulphuric Acid.*—About 2 g. of cotton in pastille form, previously washed with water and air-dried, is weighed after drying at 110°, moistened with 2 ml. of 0·05N-sodium carbonate in a porcelain or silica crucible, and again dried at 110°. It is then burnt carefully in front of an electric muffle, and ignition completed by heating in the muffle for an hour at 550–600°. Three or four drops of water followed by 0·7 ml. of 2N-nitric acid are added to the ash ; the excess acid is removed on a water bath, and the residue gently ignited over a micro-burner to complete the oxidation of unburnt particles. The residue is dissolved in 0·7 ml. of N-HCl, filtered through a micro-filter of fritted glass 1 cm. in diameter, and washed. The filtrate and washings, of volume about 5 ml., are collected in a hard-glass beaker of 7 ml. capacity, heated to about 100° in a vessel jacketed with the vapour of boiling toluene, and 0·7 ml. of a hot, filtered, 0·1N-barium chloride solution added. After digesting for an hour the solution is separated from the precipitate by drawing it under suction through a micro-filter immersed in the liquid. The bulk of the precipitate is left in the beaker, and is then washed four times by inverse filtration with about 2 ml. of hot water. The filter plate is of the finest grade fritted glass 8 mm. in diameter, and the glass walls of the filter are ground down flush with the plate. The arrangement is shown in Fig. 49. After washing, the filter is detached and dried in the beaker in a vessel jacketed with boiling aniline. The filter and beaker containing the barium sulphate are weighed together to 0·01 mg., having been weighed clean before beginning the analysis. The results are about 3 per cent. too low. For example, 0·5 g. of 0·1N-sulphuric acid was dried into 1 g. of cotton : H_2SO_4 added, 2·70 mg. ; found, 2·62 mg.

(*b*) *Estimation of Hydrochloric Acid.*—The procedure is similar, but to avoid loss of acid a large excess of alkali is added during the ashing process.

[1] A. Caille, *Chim. et Ind.*, 1925, **13**, 901.
[2] *J. Text. Inst.*, 1927, **18**, 168T.

About 2 g. of cotton, previously washed with water and air-dried to a known moisture content, are moistened with 2 ml. of 0·5*N*-sodium carbonate solution, dried at 110°, and reduced to ash as before, but owing to the large quantity of sodium carbonate, a residue of unburnt carbon usually remains. The ash is dissolved in 0·7 ml. of water, filtered and washed as above, the filtrate made acid with dilute nitric acid, a slight excess of 0·1*N*-silver nitrate added, and the solution digested for an hour in a vessel jacketed with the vapour of boiling toluene. After cooling it is filtered through the inverted filter, the beaker and filter washed four times with about 2 ml. of cold water, dried at the temperature of boiling aniline, and weighed

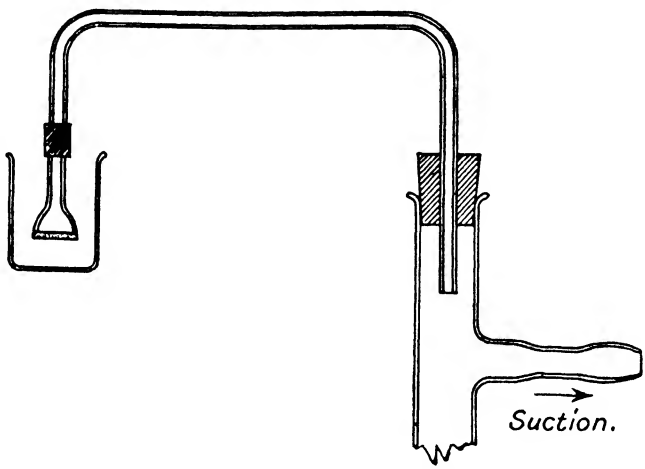


FIG. 49.—Micro-filter for barium sulphate.

to 0·01 mg. The precipitate is kept from light except during filtration and weighing. The results are about 0·7 per cent. too low.

(c) *Estimation of Phosphoric Acid.*—Accurate micro-chemical methods for this estimation devised by Kleinmann,[1] Hamburger [2] and others were adapted to cotton by A. Geake,[3] whose method is described below. It is very rapid, and is preferable to the usual processes even when the phosphorus content is high.

The principle consists in the precipitation of phosphoric acid as strychnine phosphomolybdate; the volume of the precipitate which, under the prescribed conditions, is about thirty times that of the equivalent amount of ammonium phosphomolybdate, is measured in the graduated stem of a centrifuge tube. The procedure is as follows :—

[1] *Biochem. Z.*, 1919, **99**, 19, 150.
[2] See Abderhalden, "Handbuch Biol. Arbeitsmeth.", Abt. **1**, p. 868.
[3] *J. Text. Inst.*, 1924, **15**, 81T.

1. **The Reagents.**—Solution A. 50 g. ammonium molybdate in 150 ml. water.

Solution B. Nitric acid (*d*, 1·350) *i.e.* 753 g. HNO_3 per litre.

Solution C. 15 g. of strychnine nitrate dissolved in hot water and diluted to 1 litre.

The Reagent. 90 ml. of A are poured into 270 ml. of B and 120 ml. of C are added. The mixed reagent is left for a week before use, and it keeps indefinitely. It may be filtered from time to time.

Solution D. A standard phosphate solution may be made of 0·0575 g. of pure anhydrous potassium dihydrogen phosphate in 1 litre of water, 2 ml. of this being equivalent to 0·06 mg. of P_2O_5.

2. **The Apparatus.**—The upper part of the centrifuge tube A, Fig. 50, is about 2 cm. in diameter and 3 cm. in length. The lower portion is a capillary 5·5 cm. long and 1 mm. internal diameter. The conical part connecting the two is about 4 cm. in length with uniform slope and without a shoulder upon which precipitate might settle. The capillary is of uniform bore over the lower 5 cm. of its length, and this is etched with a scale of 100 divisions starting from zero at the bottom. Each division is thus 0·5 mm. long and the tubes used by the author have a mean volume per scale division of 0·518 c.mm. determined by mercury calibration. A mark corresponding to 6 ml. is convenient. The equivalent of 0·06 mg. of P_2O_5 yields about 25 c.mm. of precipitate, corresponding to about fifty divisions. The tubes must be absolutely clean, and when not in use should be filled with chromic acid solution.

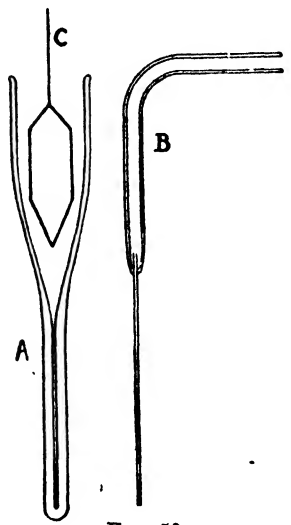


FIG. 50.

The suction tube B is made of thin-walled platinum, 0·75 mm. diameter outside and 7 cm. long, sealed into glass as shown. If a glass tube is used it should be coloured, so that any fragment breaking off may be detected. Mechanical stirring shown at C is preferable to the use of a glass rod, which may scratch the tube.

3. **The Process.**—A weight of cotton containing phosphorus equivalent to about 0·06 mg. of P_2O_5 (*e.g.* 0·12 g. of American or 0·06 g. of Egyptian cotton) is burnt in a porcelain crucible, before the muffle furnace, and the ashing completed inside the muffle at dull red heat. The ash is dissolved in 1 ml. of *N*-sulphuric acid, and the solution transferred to the tube shown at A, Fig. 50. To

avoid air in the capillary it should be filled first, and this is easily done by adding a few drops of water and inserting a fine tube, shown at B, to the bottom of the capillary, and removing air from beneath the water by the filter pump.

The solution of the ash is diluted with water to 6 ml. and centrifuged for 5 minutes to throw out insoluble matter; 2 ml. of the strychnine molybdate reagent are then added from a pipette at the rate of 1 to 2 drops per second, the solution being stirred, either by hand, or mechanically with a stout platinum wire of the shape shown at C. After 30 minutes the tube is centrifuged for about 15 minutes at a speed of 2,500 to 3,000 r.p.m. with a radius of 18 cm. to the bottom of the tube. The height of the precipitate is read, the tube is centrifuged for 5 minutes, and this repeated until a constant reading is obtained. The insoluble matter is easily distinguished from the yellow precipitate, and its volume must be subtracted. The correction is generally less than 1 per cent. of the whole.

To avoid errors due to variation in conditions, check measurements are made simultaneously on a standard phosphate solution. For the latter 2 ml. of solution D are diluted to 6 ml. with 1 ml. of *N*-sulphuric acid and water. If the check solution contains the equivalent of 0·06 mg. of P_2O_5, a proportionality can be assumed to exist between the volume of precipitate and the weight of P_2O_5 within the limits 0·05 to 0·08 mg. of P_2O_5 in the test solution.

These details must be followed closely to obtain concordant results. The errors do not exceed 5 per cent., and the results agree closely with those of the gravimetric method of Embden [1] and the colorimetric method of Tisdall.[2] The colorimetric method of Zinzadze,[3] coupled with a photo-electric colorimeter, has also been used in connection with cellulose.

[1] G. Embden, " Abderhalden's Handbuch d. Biol. Arbeitsmeth. ", Abt. 1, Teil 3, Heft 5, p. 913.

[2] F. F. Tisdall, *J. Biol. Chem.*, 1922, **50**, 329.

[3] *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 227.

CHAPTER XI

THE INVESTIGATION OF CASES OF DAMAGE IN COTTON AND LINEN CELLULOSE

MECHANICAL damage may or may not be accompanied by a change in chemical or physical properties. Great pressure applied locally to a fabric will alter its dyeing properties, whilst rubbing and powdering may alter the state of dispersion of the cellulose, causing increase in alkali solubility and decrease in viscosity. Effects attributed to mechanical causes may sometimes be due to the action of heat developed during mechanical treatment.

The action of heat is partly destructive and partly due to oxidation effects. It has been found (author's laboratory), that cotton when heated in air under conditions devised to exclude local overheating, is not measurably affected up to a temperature of 140° after 4 hours. Above that temperature the copper number increases and the viscosity falls. The rate at which these changes take place is greatly lessened, if the heating is carried out in an inert atmosphere. The initial action of heat, therefore, is probably one of oxidation; in the later stages decomposition also takes place.

The destructive action of moulds and other micro-organisms is frequently due to prolonged storage under moist conditions (mildew, (etc.). When damage occurs in the case of cotton stored in bulk at least 9 per cent. of moisture must have been present. Below this limit bacterial growth does not take place to any extent.[1]

Immersion in sea-water for a few weeks causes the break-down of almost all textile fibres. This is due largely to the action of micro-organisms.[2] The damage caused by the growth of micro-organisms is partly disruptive or mechanical, and partly chemical, due to a slow localised hydrolysis of the cellulose at the point of attack.

It is often necessary, not only to discover the cause of damage, but to assign the responsibility respectively between the manufacturer, the user, and the launderer or dyer. The diagnosis therefore requires a combination of observational skill and deduction, coupled with the application of microscopical and chemical tests, and consequently no more than general lines of action can be indicated.

[1] A. C. Thaysen and N. Fleming, *Biochem. J.*, 1921, **15**, 407.
[2] C. Dorée, *Biochem. J.*, 1920, **14**, 709.

I. Examination of Fabrics

1. A fabric should be examined as a whole, and then the warp and weft threads studied separately. The appearance and strength of a damaged area and of individual warp and weft threads will afford an indication of whether the damage is mechanical or not.

2. A microscopical examination gives useful information, especially under low powers and correct illumination. Suitable staining and swelling agents will bring out greater detail. Methylene blue and Congo red are useful stains. Sodium hydroxide solutions and the viscose reaction (p. 224) may be used for swelling the fibres. A number of publications dealing with the use of the microscope in textile work are available, for example :—

" Textile Microscopy ", L. G. Lawrie, Benn, Ltd., London, 1928.

" Notes on the Use of the Microscope in the Textile Laboratory ", L. G. Lawrie, *J. Soc. Dyers and Col.*, 1926, **42**, 73.

" Modern Textile Microscopy ", J. M. Preston, Emmott and Co., London, 1933.

3. The following tests enable the damage to be located, and throw some light on its nature :—

(*a*) The fabric is heated in dilute methylene blue solution, when affected areas will be coloured more deeply. Calcium soaps and silicates, and other adventitious substances, may also fix the dyestuff. The test carried out with buffered solutions of the dye can be made to give a rough distinction between the action of bleaching agents and that of acids (pp. 24, 218).

(*b*) The fabric, after heating in Fehling's solution and washing, may show red patches of copper oxide on the affected areas. The procedure of the Schwalbe-Braidy method often reveals damage which is not shown by a short treatment with Fehling's solution.

(*c*) The dyeing test with Indanthrene Yellow (p. 121) will reveal damage represented by copper values greater than 0·5 (Schwalbe-Braidy). The reduction of silver nitrate is about equally sensitive.

(*d*) The Benzopurpurine test for mercerisation (p. 100) may indicate areas affected by alkaline treatment.

4. To ascertain whether the damage is due to acid or oxidation attack the following tests may be employed. More elaborate quantitative methods are mentioned on p. 172.

(*a*) The reaction (*p*H) of the damaged area may be ascertained by spotting with a Universal or other indicator.

The acid or alkali may sometimes be extracted and its nature ascertained. Usually, however, subsequent treatment will have removed it.

(*b*) In certain cases the following methylene blue test will differentiate between acid and oxidation change. Acid and neutral buffered methylene blue solution as p. 19; Fehling's solutions A and B; three test tubes with the fabric, one containing the acid, one the neutral methylene blue, and the third Fehling's solution made by mixing equal volumes of A, B and water are required.

The fabric is introduced, the tubes immersed in a boiling-water bath, and after 1 minute the two containing the methylene blue are removed, the fabric rinsed and placed on blotting paper. The tube containing Fehling's solution is heated for 5 minutes, the fabric rinsed several times with water, once with dilute acetic acid and again with water.

If the damage revealed by the reduction of Fehling's solution has been caused by the drying in of acid at moderate temperature, the material will dye considerably less deeply in the acid methylene blue than in the neutral solution. The same difference, however, is observed with undamaged fabric. Unless, therefore, the Fehling solution shows reduction, no importance can be attached to any difference between the dyeings.

(*c*) Test with gold chloride.[1] This is stated to differentiate between oxy- and hydro-cellulose, and, moreover, to operate even in cases where the fabric has been treated with alkaline solutions subsequently to acid or oxidising attack.

The material is freed from loading or dressing (p. 5) and is then soaked for 2 hours, with occasional shaking, in a 1 per cent. solution of stannous chloride (the turbidity of the solution is of no importance). It is then thoroughly washed in running water and soaked in a solution of gold chloride so dilute as to be only faintly yellow.

With oxycellulose a purple colour is rapidly developed, whereas with hydrocellulose little colour appears.

(*d*) The measurement of the strength and the fluidity of the yarn or hair before and after boiling in alkali may be considered. The results detailed on p. 161 show that cotton modified with acid or with alkaline hypochlorite shows little additional loss in strength after a boil in 1 per cent. sodium hydroxide for a few hours. Neutral hypochlorite and most other oxidising agents (but not peroxides and perborates) cause a greatly increased loss in strength after alkaline treatment.

The fluidity follows the same course: little increase after boiling with alkali in the case of damage caused by acids or alkaline hypochlorite, but a great increase in the case of neutral hypochlorite,

[1] R. Haller, *Textilberichte*, 1931, **12**, 257.

acidified dichromate, etc. The test is of no value if the fabric has been scoured or laundered subsequently to attack.

The fluidity test (p. 52) may be carried out with small quantities of material, as in the case of the copper number, with results that are sufficiently good for diagnosis. Using small capillary viscometers we have been able to work with quantities of the order of 0·03 g. of cotton. The rolling sphere viscometer (p. 52) is also suitable for such determinations as it requires less than 0·01 g. of material.

5. The period at which over-bleaching may have occurred can sometmes be ascertained by the use of the micro-copper number or micro-fluidity measurements. A cotton pillow-slip, for example, fails in laundering. It is usually possible to obtain sufficient of the sewing cotton from it to determine the copper number or fluidity. If the values found are normal, whilst those for the fabric are high, the over-bleaching must have occurred in manufacture; if both are high and of the same order, the over-bleaching has occurred in laundering.

6. Mechanical damage is revealed by characteristic microscopical appearance, and particularly by the Congo red test (see p. 221). The absence of chemical damage is shown by the general soundness of the cloth as revealed by its strength, fluidity, and copper number.

7. The recognition of damage due to micro-organisms and its distinction from that due to mechanical or chemical means has been greatly facilitated by the tests which are described in the following section.

II. Examination of Tendered Fibres

Several useful methods of investigating the cause of tendering in cotton and other fibres have been described. They are—

1. **The Segmentation Test.**—"The Microscopic Study of 'Tendered' Flax and Cotton Fibres." [1]

2. **The Congo Red Test.**—"The Microscopical Examination of Damaged Cotton Hairs by the Congo Red Test and by the Swelling Test of Fleming and Thaysen." [2]

3. **Swelling Test with Sodium Zincate.** [3]

4. **The Swelling Test.**—"The Swelling Test and the Bacterial Damage of Cellulose, etc." [4]

[1] G. O. Searle, *J. Text. Inst.*, 1924, **15**, 371T.
[2] T. W. Bright, *ibid.*, 1926, **17**, 397T; G. G. Clegg, *ibid.*, 1940, **31**, 49T.
[3] J. W. Lewis, *ibid.*, 1932, **24**, 122T.
[4] A. C. Thaysen and N. Fleming, *Biochem. J.*, 1920, **14**, 25; 1921, **15**, 407; A. C. Thaysen and H. J. Bunker, *ibid.*, 1924, **18**, 141; *J. Roy. Microscopical Soc.*, 1923, **21**, 303.

5. **The Heat Test.**—" A Fluidity Method." [1]

The first paper develops what may be called the Segmentation Test, which distinguishes clearly between chemical damage, including that due to heat and light, and damage due to micro-organisms. The Congo red test differentiates mechanical damage very sharply from bacterial damage. The Swelling Test detects damage to the cuticle, and is specially applicable to that due to micro-organisms.

1. **The Segmentation Test** (G. O. Searle).—The technique described relates chiefly to flax, but may be applied to cotton. When mounted in a non-swelling medium (water, paraffin-wax) a tendered flax fibre generally shows breaks transverse to the fibre length, with jagged edges, giving the fibre the appearance of having cracked at different levels. No tendency to break up in a longitudinal direction is observed. The dislocation marks are very distinct, especially in polarised light, giving a gnarled appearance. The marks are generally more reactive than the rest of the structure, and may be due to depolymerised cellulose.

The fibres are mounted in a non-swelling medium and submitted to slight pressure through the cover glass. A normal fibre at once reveals its spiral structure,[2] and no amount of increased pressure will cause the spiral markings to disappear, and there is no tendency to break transversely. If the normal fibre is treated in this way, in a swelling medium, the appearance is somewhat different, the spiral complex being resolved into a number of spiral bands (Fig. 51).* A tendered fibre, in a non-swelling medium, shows a number of fissures transverse and oblique to the fibre axis (Fig. 52),* the fissures separating what appear to be bundles of short, thick rods piled one on top of the other. The rods are straight if the tendering is severe ; otherwise they may be more or less curved, and examination shows that the fissuring takes place parallel to the spiral components of the normal fibre. Increased pressure may cause separation into rod-like fragments resembling bacilli. These fragments (unlike the cellulose powder of Fort[3]) are still doubly refracting in polarised light.

Some normal fibres, when swollen in 15 per cent. sodium hydroxide, may show an appearance of transverse segmentation. To distinguish a normal fibre showing such markings from a tendered one, the fibres are fastened at each end to a slide by means of a drop of Canada balsam so that they remain just straight. A drop of 15 per cent. sodium hydroxide will then cause the tendered fibres to break at the planes of segmentation, whilst the undamaged fibres will not.

* Figs. 51 and 52, facing p. 224.

[1] D. A. Clibbens and A. H. Little, *J. Text. Inst.*, 1936, **27**, 294T.

[2] C. R. Nodder, *J. Text. Inst.*, 1922, **13**, 161T.

[3] C. F. Cross and E. J. Bevan, *J. Soc. Dyers and Col.*, 1918, **34**, 215.

The immersion in alkali causes a very regular development of narrow parallelogram-shaped units whose angles are approximately 60° and 120° (Fig. 53).* Further pressure resolves them into a series of rectangular blocks (Fig. 54).*

These tests were applied to the following cases of damage :—

Samples tendered by Acid.—Dilute acid dried into the cloth produced the above effects. A cloth moistened with dilute sulphuric acid, and kept for 6 weeks at room temperature, showed all stages from the normal, with continuous spirals, to complete segmentation.

Samples tendered by Heat.—A cloth heated at 160° for 2 hours showed, in the alkaline solution, nearly a normal appearance, but after 8 hours' heating at 160° the appearance shown by the test was similar to that of the acid-treated specimens. When maintained at 96° segmentation was observed after 330 hours' heating. A cotton cloth tendered by 5 years' exposure to light in England also showed segmentation.

Samples tendered by Oxidation.—The action of acid oxidants produced the same effects as those due to acids.

Tendering by Damp (Action of Micro-organisms).—The application of the above tests shows that tendering by bacterial attack is not attended by segmentation in the case of cotton and linen. The appearance of a tendered swollen cotton hair shows the spiral markings very clearly, but no signs of fissure.

It would appear that chemical damage, whether due to acid, oxidation, or heat and light, is clearly revealed by segmentation, the development of which enables such damage to be differentiated from that due to bacterial action. The Congo red test, on the other hand, enables a clear distinction to be drawn between the effects of mechanical and bacterial action.

2. **The Congo Red Test.**—This very useful test is based on the observation that the cuticle of cotton hairs, which have been swollen in sodium hydroxide, stains faintly red when immersed in a solution of the dyestuff. If, however, the cuticle has been damaged or removed the exposed secondary cellulose becomes a bright red.

It has been found (Clegg, *loc. cit.*) that when cotton fibres are treated with alkaline solutions there is a change in the shape of the cross-section, but no swelling of the wall, with concentrations up to 7 per cent. NaOH. Between 7 and 11 per cent. the wall thickness increases, and the swelling proceeds inwards. At 9 per cent. there is just no pressure on the cuticle, but at 11 per cent. pressure develops,

* Figs. 53 and 54 between pp. 224–225.

and at 13·5 per cent. the outward pressure and the fibre width reach a maximum which does not increase further up to a concentration of 37 per cent. NaOH.

The normal cuticle has a spiral line of weakness and at 18 per cent. NaOH considerable splitting is seen with staining of the exposed cellulose, whilst 11 per cent. NaOH has little effect. If the fibre has been tendered by heat, bleach, etc., such treatment reveals a gradual breakdown of the cuticle which splits into spirals, coarse with mild damage, but finer as the damage increases until with severe damage no spiral structure is seen and the fibres stain uniformly (Figs. 59, 60, 61).* These are the "slow" or cuticle spirals, but in addition there are "quick" spirals caused by heat, chemical or fungal action, which appear to follow the fibrillae of the secondary cellulose. They are revealed by staining after swelling the fibre in 9 per cent. NaOH, which is of insufficient strength to cause the slow spirals to develop.

Procedure.—The cotton sample is (*a*) immersed for 3 minutes in caustic soda of requisite strength (see below); (*b*) washed very thoroughly and the surplus water removed by squeezing and filter paper; (*c*) immersed in a saturated solution of Congo red; (*d*) washed as in (*b*) and at once immersed in caustic soda of 18 per cent. concentration. This gives a final swelling and improves contrast in the staining. The fibres are removed and mounted in the alkaline solution for microscopic examination. To prevent escape of the alkali the cover glass is sealed with a suitable cement. A $\frac{2}{3}$-in. objective and a × 10 eyepiece are used, and the iris diaphram is left wide open to fill the back lens of the object glass with light.

The strength of the caustic soda solution † under (*a*) is of the utmost importance. In searching for mechanical damage a 9 per cent. solution is sufficient because the damage, if present, will have already broken the cuticle and exposed the secondary cellulose. For weakening of the cuticle caused by heat, light, chemical action and mildew-attack 11 per cent. NaOH is used. With this strength there is sufficient outward pressure to cause spiral splitting in the case of the already weakened cuticle. If damage to the cuticle is likely to be slight, as in processing, and also in cases where considerable pressure is required to open up the cuticle, as in abnormally thickened fibres, a solution of 18 per cent. NaOH can be used.

A normal hair swells strongly in the 11 per cent. alkali, but the cuticle does not burst. The 18 per cent. solution causes further swelling which ruptures the cuticle, exposing a strip of white cellulose which contrasts with the slightly pink tint of the cuticle. A

* Between pages 224–225.

† Given in grams per 100 g. of solution.

difficulty arises with lint and fuzzy hairs, which often show an abnormal cellulose thickening. With such the 11 per cent sodium hydroxide will frequently rupture the cuticle in a spiral course (Fig. 56),* revealing the cellulose, which stains deeply. This, therefore, does not necessarily indicate damage, and, with such hairs, an initial treatment with sodium hydroxide of 9 per cent. can be given.

Cotton Free from Damage.—The hairs show pink, with no deep red except where the hairs have been torn from the seed. The damage done by teasing out on the microscope slide is easily recognised by the absence of staining. Commercially undamaged cottons may show occasional patches of colour (bruises) and the effects due to immature and thick-walled hairs (spirals). (See Figs. 55, 56, 62.)*

Mechanically Damaged Cotton.—Damage represented by gentle tapping with the pestle in a mortar gives an appearance of bruising (Fig. 57). When grinding is employed the whole surface may be stained and the outline ragged (Fig. 58).* The test is usefully employed to detect localised damage in processing, and it is possible to distinguish normal breaks, clean-cut ends, broken ends, singed fibre ends, ends damaged by chemicals and ends tendered by mildew, etc.

Heat Damaged Cotton.—Heated at 110° in a closed dish, hardly any effect is produced in 6 days, but if the cotton is suspended in the oven, spiral bands, simple or multiple, are seen in about 20 per cent. of the hairs. Four hours at 150° produced many spiral bands, the points of reversal (Fig. 60)* being clearly visible (*cf.* Figs. 59, 61). Some hairs also spirally marked had, however, not swollen, but remained in ribbons with a corrugated outline. Steam heat, 15 lb. per square inch for 15 minutes, had no effect.

Damage due to the Attack of a Fungus.—With a strain of *Aspergillus niger* the hairs after attack showed a deep uniform staining in some cases (Fig. 62), while others with considerable tendering showed multiple spirals (*cf.* Fig. 61). Cracks and abrasions were entirely absent. Another fungus which was known to penetrate the lumen caused the hairs to break into short lengths under the test, which revealed uneven staining and many cracks and abrasions.

Damage due to Sulphuric Acid.—Cotton was steeped at ordinary temperature for 48 hours and dried in the air. Concentrations of acid up to 30 g./100 ml. produced no effects visible in the test, but with 40 g./100 ml. the hairs remained unswollen and were covered with streaks and patches quite different from those produced by heat or mechanical means.

* Between pp. 224–225.

SUMMARY OF THE EFFECTS OBSERVED WITH THE CONGO RED TEST IN COTTON HAIRS IN VARIOUS STAGES OF DEGRADATION

Extent of Damage.	Cause of the Damage.			
	Mechanical.	Heat.	Fungus.	Sulphuric Acid.
None.	Pink.	Pink.	Pink.	Pink.
Slight.	Surface "bruises."	Broad simple red spiral bands.	Narrow multiple red spiral bands.	—
Moderate.	Deep cuts.	Narrow multiple red spiral bands.	Stained an even red.	Irregular red patches.
Severe.	—	Stained red and cuticle singed.	Stained red and cracked.	—

3. **Swelling Test with Sodium Zincate.**—A valuable test for mechanical damage. The fibres are treated with the reagent under a cover-slip and washed. Perfect fibres, or those damaged, *e g.* by cutting, but with the cuticle mainly intact, show a clear dumbell-shaped swelling at the ends. With slight chemical damage, as with normal bleaching, a few fibres are swollen, their outline less definite, and the swelling at the ends not so clear. When the damage is extensive the fibres are greatly swollen, the ends and edges blurred with some, even, passing into solution.

4. **The Swelling Test of Fleming and Thaysen.**—This test makes use of the swelling of cellulose induced by the xanthate reaction (W. L. Balls, 1918). It is employed to examine qualitatively the damage caused by micro-organisms.

The cotton, 0·1 to 0·3 g., is purified if necessary in 1 per cent. NaOH and then steeped in 1·5 ml. of 15 per cent. NaOH, followed by addition of 1·5 ml. of carbon disulphide freshly distilled. After 15 to 45 minutes a test portion is placed on a glass slide, covered with a slip, and a drop of water is allowed to diffuse underneath.

The first effect, which takes place 2 or 3 minutes after the disulphide has been added, consists of a swelling of the hair to the elastic limit of the cuticle. Then, after 15 to 45 minutes, the stress caused by the expanding cellulose ruptures the cuticle. The breakdown occurs along a spiral, so that the cuticle rolls back to form a tightly stretched cord which moulds the cellulose into a shape resembling either a chain of beads or bulbs, or a corkscrew (Fig. 63). After a time the edges of the cellulose begin to dissolve. The above applies to a normal hair. If the cuticle is mechanically split or opened the cellulose at this point bulges out and very soon dissolves, so much so that after a time the hair will separate at this point. The bulging of the cellulose prevents the formation of beads in the undamaged

FIG. 51.—Normal flax fibre swollen in sodium hydroxide solution and compressed.

THE SEGMENTATION TEST.

FIG. 52.—Segmentation of tendered linen fibre, showing spiral fibrillae breaking down to rod-like components.

After G. O. Searle.

[*Between pages* 224–225.

FIG. 53.—Segmentation of fully tendered fibre showing parallelogram-shaped units with angles of 60° and 120°.

THE SEGMENTATION TEST.

FIG. 54.—The tendered fibre of Fig. 53 resolved by increased pressure into rectangular blocks.

After G. O. Searle.

Fig. 55.

Fig. 56.

Fig. 57.

Fig. 58.

Fig. 59.

Fig. 60.

The Congo Red Test.

Fig. 55.—Normal hair, undamaged.
Fig. 56.—Thick-walled hair, undamaged.
Fig. 57.—Slight mechanical damage.
Fig. 58.—Severe mechanical damage.
Fig. 59.—Tendered by bleaching.
Fig. 60.—Damaged by heat.

After T. B. Bright and G. G. Clegg.

FIG. 61.—Spiral splitting due to bleaching (Congo Red Test).

FIG. 62.—Damage due to *Aspergillus niger*. Attacked fibres with no secondary thickening stain with Congo red. Unattacked fibre does not.

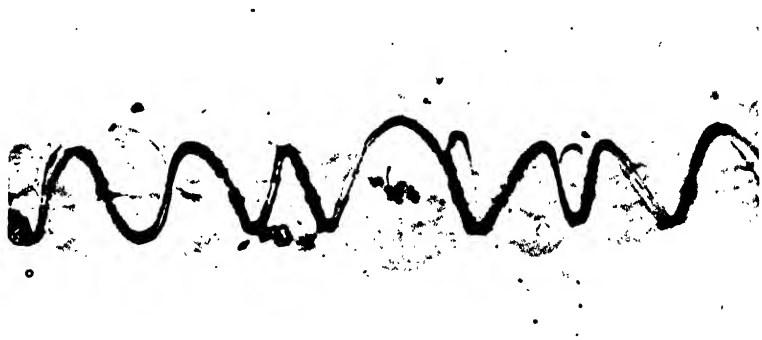


FIG. 63.—Swelling Test showing the ruptured cuticle with the appearance of a corkscrew.

After G. G. Clegg and T. B. Bright.

[*Between pages* 224–225.

portion of the hair. Very similar effects are observed on hairs damaged by *Aspergillus niger* and other micro-organisms. Damage to the cuticle prevents in all cases the formation of the bulb-like swellings, the hair merely swelling uniformly before passing into solution.

For its use as a quantitative measure of the degree to which a given sample of cotton is damaged by micro-organisms reference should be made to the original paper.[1]

5. **The Heat Test.**—Contracts for cotton material often specify the absence of " injurious chemicals " which might produce tendering during storage, especially at temperatures above the normal. Acidity, actual or potential, is the most likely cause of such tendering, but its detection is not easy.

A satisfactory standard test has been devised, which consists in heating the sample and measuring the increase in fluidity produced. One gram, or less, is heated for 18 hours at 110° in a closed stoppered bottle. Since loom-state cloth is difficult to get into solution in cuprammonium a standard purification is given by boiling for 1 hour with 1 per cent. NaOH. The fluidity is then compared: (*a*) of the cloth purified only, (*b*) of the cloth after heating and purifying as above.

Cotton in the raw state, or when properly bleached and washed, shows a rise in fluidity of 1 or 2 units only. Material is considered satisfactory if the rise does not exceed 3 units, since experiment shows that cotton, into which its own weight of $N/1000$ H_2SO_4 or HCl has been dried, gives an increase of 5 or 11 units respectively.

Acetic acid of $N/10$ strength caused a rise of 4 units, but other organic acids in common use have a greater effect, in proportion to their dissociation constants.

One per cent. of the sulphates of Na, Mg, Am and Al, when present in the cloth, caused rises of 0·6, 3·2, 7 and 45, respectively, under the conditions of the test, cloth containing 1 to 2 per cent. of the chlorides of Zn, Mg or Ca after storage, at ordinary temperature, for 8 years was found to be unaffected. Under the heat test, however, increases in fluidity of 6 to 18 units were observed, showing that, under abnormal conditions of heat, damage might be caused.

[1] N. Fleming and A. C. Thaysen, *Biochem. J.*, 1921, **15**, 407.

PART II

SYNTHETIC DERIVATIVES OF CELLULOSE

CHAPTER XII

CELLULOSE ESTERS AND ETHERS. SOME GENERAL METHODS AND CONSIDERATIONS

CELLULOSE tri-esters of the type $C_6H_7O_2(OR)_3$ are generally insoluble and deficient in the physical properties needed for industrial application. By restricted esterification, or by following complete esterification with a process of hydrolysis, products can be obtained which, on the older molecular concept, were described as mono- and di-esters of cellulose. It is doubtful, however, whether either of these has been obtained in a homogeneous condition, since the factors involved in their formation are exceedingly complex. Thus of the three hydroxyl groupings in cellulose (p. 178), one (position 6) is primary and two are secondary. It was at one time supposed that the primary hydroxyl was more reactive, and was preferentially esterified, but, in all probability, there is little to choose between them in this respect.[1] The other view that the reactivity of the primary group in the polysaccharides was restricted by engagement in internal linkage[2] is not fully confirmed, and the conclusion of Lieser that the xanthate reaction (mono-ester) always involved the hydroxyl at position 2 is no longer maintained.[3] It is most probable that reaction between the three hydroxyl groupings and the acidic radical is largely a matter of chance.[4]

Accepting the comparatively equal reaction-capacity of the hydroxyl groupings, many workers consider that the tri-ester is always formed and that the "lower" esters are mixtures, or dispersions, of the tri-ester with cellulose or with less highly esterified cellulose. In the special case of the nitrate, however, it is found that although preparations of any particular nitrogen content can be separated by solubility into fractions, these fractions do not differ in degree of nitration, but only in the length of the cellulose chain.

[1] G. B. Hatch and H. Adkins, *J. Amer. Chem. Soc.*, 1937, **59**, 1694.
[2] W. J. Heddle and E. G. Percival, *J. Chem. Soc.*, 1938, 1690.
[3] T. Lieser, *Papier Fabrik.*, 1938, **36**, 272.
[4] H. M. Spurlin, *J. Amer. Chem. Soc.*, 1939, **61**, 2224.

The actual mechanism of esterification (or etherification) is obviously complex. The structure of the natural fibre due to growth-conditions as well as the fine (micellar) structure of the cellulose are dominant factors, since the reagents have to penetrate these structures by diffusion processes before reacting—the so-called heterogeneous-micellar reaction. The penetration may take place in two ways. The reagents, if not of the type which cause swelling, attack the outside of the micellar units, gradually diffusing inwards so that there is always present an unchanged inner section retaining the original cellulose structure. The reagents become exhausted by reaction at one face, and the action may pause till more of the reagent reaches the new surface. Further, the constituents of a mixed reagent may not diffuse at the same speed. The result is the formation of layers or bands of material which has been observed [1] in the case of cellulose acetylated to the triacetate in the presence of benzene. The process has also been made evident [2] by X-ray cinematography during the nitration of cellulose with nitrogen pentoxide, the regular arrangement in the direction of the fibre axis gradually changing to the new fibre-period (25·1, A) of the tri-nitrate.

Lorand [3] has been able to follow the reaction between alkali-cellulose and benzyl chloride under the microscope. This reaction is greatly affected by the existence of two immiscible liquid phases—water and benzyl chloride—which hinders progressive diffusion. As the action proceeds the hydrophilic system becomes hydrophobic, expelling aqueous lye and forming a dispersion. The reaction is shown to pass from layer to layer, and its progress depends upon the ratio of the velocity of reaction and the velocity of diffusion. These are equal at about 60° and an even product results.

At higher temperatures the reaction velocity increases more rapidly than the diffusion rate, and differences are found in the degree of benzylation of the layers. The outer layers finally form an insulating jelly around the unreacted region, which by preventing diffusion brings the action to an end.

These considerations are sufficient to indicate that with reagents which do not cause swelling or partial solvation of the fibres the chances of obtaining a homogeneous mono- or di-ester are small, even though the reaction-product may give analytical figures which point to their formation (*cf.* p. 297).

If the reagent-system produces swelling, penetration of the

[1] K. Kanamaru, *Helv. Chim. Act.*, 1934, **17**, 1429.
[2] M. Matthieu, *Compt. rend.*, 1936, **202**, 46.
[3] E. J. Lorand and E. A. Georgi, *J. Amer. Chem. Soc.*, 1937, **59**, 1166.

micelles takes place in "spots," or regions, in the micelles.[1] The chain bundles open out at these points, the hydroxyl groups reacting along part of the chain-length so that, for example, a given chain bundle may be opened out, swollen and fully esterified at the top while the lower part retains its normal cellulose structure. In between are zones of intermediate swelling and esterification. The unreacted portion of the bundle holds the new structure together, and assuming this remains insoluble, any hydroxyl groupings which initially escaped reaction are unlikely, in later stages, to be approached by the reagents.

Greater uniformity of reaction is obtained when the derivative formed is soluble in the reagent mixture. Thus the acetic anhydride-acetic acid mixture used in the preparation of cellulose acetate has a swelling action on the fibre and the reaction proceeds smoothly, the triacetate passing into solution. Still more complete uniformity is seen if all the reactants are in the liquid phase. Cellulose can be dissolved in various organic bases (p. 251), and in this condition an even esterification takes place. The hydrolysis of primary cellulose acetate to the secondary (p. 273) and the chlorination of cellulose acetate to form the trichloracetate are other examples of reaction in solution.

The course of the reaction and the properties of the derivatives also depend on the condition of the original cellulose. This may have been modified, for example, by hydrolysis, giving a cellulose of shorter average chain-length (hydrocellulose); or by oxidation, which produces both shorter chain-length and new chemical properties. Reactivity may also be increased, without chemical change, by swelling (hydration, mercerisation). Regenerated cellulose, *e.g.* from viscose in which both activation and degradation from normal have taken place, can be usefully employed in the laboratory preparation of esters and ethers

Many reagents, *e.g.* acid chlorides, tend to "degrade" the cellulose during the reaction, and the extent to which this takes place affects the character of the final product.

The factors which mainly influence the course of any particular reaction of esterification or etherification have been summarised by Spurlin (*loc. cit.*) thus :—

(*a*) The condition of the cellulose—whether dissolved, no swelling, swelling (intramicellar, intermicellar).

(*b*) The solubility or otherwise of the product in the reaction system.

[1] H. M. Spurlin (*loc. cit.*).

(*c*) The number of reagents which must reach any one point before reaction can take place (*e.g.* two phase reagents of etherification, etc.).

General Properties of Cellulose Esters.—Certain general relationships between the physical properties of cellulose esters have been deduced, especially the influence of increase in length of the substituent carbon chain.

The possibilities of variation, outlined above, make it necessary in such investigations to standardise the cellulose and to select conditions of reaction and treatment which will reduce to a minimum any changes in its degree of polymerisation. The older experiments of Hagedorn and Möller [1] afford an example. To secure uniformity they aimed at the production of the tri-ester by a method giving little structural change (acid chloride, pyridine and an indifferent solvent). A series of fatty acid esters, including the valerate (C, 5), the caproate (C, 6), the laurate (C, 12) and the stearate (C, 18) was examined. It was found that with esters of the lower fatty acids the solubility was dominated by the cellulose-component and the range of solvents was limited, but that with esters of the higher fatty acids the acidic radical had a progressive influence. Thus the number of available solvents for each ester increases up to the valerate (C, 5). All the esters were insoluble in water, but the lower ones were sensitive to it, as shown by the deformation of their films on wetting. This effect gradually decreases up to the laurate (C, 12), which with the higher esters is indifferent to water. All the esters examined (except the formate) were soluble in chlorinated hydrocarbons. Aliphatic hydrocarbons act as solvents from the laurate and above, whilst aromatic hydrocarbons dissolve the butyrate and above. Acetone has a special position, acting as a solvent for esters from the propionate (C, 3) to the pelargonate (C, 9) but not above this.

Measurements of the strength and extension of films showed that with increasing length of the substituent carbon chains, the strength decreased and the extension increased almost in the same proportion.

Similar observations on fully substituted esters of homologous fatty acids have been recorded by Sheppard and Newsome,[2] some of whose results are given in the table on page 230.

When these measurements are plotted the curves representing melting-point and moisture-regain run almost parallel. The melting-point reaches a minimum at C, 9 and C, 10, and then slowly rises.

[1] M. Hagedorn and P. Möller, *Cellulosechem.*, 1931, **12**, 29.

[2] S. E. Sheppard and P. T. Newsome, *J. phys. Chem.*, 1932, **36**, 819; 1935, **39**, 143.

The regain falls rapidly till a minimum value is reached at C, 6 to C, 8, followed by a very slow rise to C, 14. From the contact angle recorded in the last column the work of adhesion is calculated.

PROPERTIES OF CELLULOSE TRIESTERS AT 25°

	C Atoms in Chain.	Density.	Melting-point.	Per cent. Moisture Regain at 100 per cent. R.H.	Contact Angle in Water.
Cellulose .	0	1·618	—	18·8	—
Acetate .	2	1·377	245*	10·0	50°
Propionate	3	1·268	239	4·4	78
Butyrate .	4	1·178	183	3·5	84
Valerate .	5	1·178	160	1·7	90
Caproate .	6	1·110	87	0·9	93
Heptoate .	7	1·081	97	0·8	100
Caprylate .	8	1·058	85	0·9	99
Pelargonate	9	1·032	66	1·0	100
Caprate .	10	1·026	64	1·5	100
Laurate .	12	1·004	80	1·4	101
Myristate .	14	0·991	87	1·5	104

* With decomposition.

A method of recording the properties of mixed esters is given on p. 302.

The solubility required in a cellulose derivative is usually obtained by empirical methods. A comprehensive study by Coltof,[1] however, has brought to light some general factors upon which solubility depends. These are mainly two, one associated with the solvent, the other with the solute. The capacity of the liquid to bring about solution depends upon the atomic groupings present in it. Some of these groups induce swelling of the polymer, some dispersion, and some both, whilst others are inactive. The inactive groupings the author refers to as " ballast," and their presence tends to counteract the working of the dispersion processes.

If solution is to take place, both swelling and dispersion must be induced, but the atomic groupings required for this purpose need not be in the same molecule, so that mixtures of solvents, carrying between them the necessary atomic groupings, will bring about solution.

The factor in the cellulose complex which influences its solubility is the possession of major and minor groupings. Thus ordinary cellulose esters and ethers contain, *e.g.* acetyl and methyl as major

[1] W. Coltof, *J. Soc. Chem. Ind.*, 1937, **56**, 363.

groupings, with a minor proportion of hydroxyl groupings. The former are referred to as the A group and the latter as the B group. It is found that the A set respond to the swelling groupings in the solvent, while the B set respond to those causing dispersion. The tri-acetate of cellulose, with no hydroxyl groupings, is generally insoluble, but the secondary acetates containing a proportion of hydroxyl are readily soluble in solvents carrying the necessary swelling and dispersing groupings. When the proportion of hydroxyl (B grouping), however, becomes too large, solvation is again restricted.

From an examination of the action of some 120 liquids on cellulose acetate (Coltof, *loc. cit.*), the following results may be quoted: Pyridine of all known solvents has the smallest ballast coupled with powerful swelling and dispersive action, so that it is able to dissolve all forms of cellulose acetate, even when the acetic acid content is as low as 30 per cent. Hydroxyl is one of the strongest dispersing groups with very little swelling capacity. The double bond, generally, and the —C—C— linkage in hydroaromatic compounds act as swelling groups only, and require the presence of a dispersing group to enable them to act as solvents. The benzene ring, being cyclic and unsaturated, has a strong swelling action.

The carbonyl group produces both swelling and dispersion, so that the lower aldehydes and ketones act as solvents. The higher ones are affected by the mass, or ballast, of the groups attached to the carbonyl which reduces the dispersing action below the minimum necessary for solution to take place. The carboxyl (COOH) grouping contains both carbonyl and hydroxyl, and should favour solvent action, but while the acids of low carbon number act as solvents, the higher members do not, owing to the ballast action of the rest of the molecule. Esters behave like ketones and acid anhydrides also are good solvents.

The nitro-group gives both swelling and dispersion, but nitrobenzene is not a good solvent, owing to the ballast (anti-dispersing) effect of the C_6H_5 grouping. The addition of a little alcohol, however, supplies the necessary dispersive power to enable solution to take place.

Cellulose esters, such as the nitrates and the triacetate, which will not dissolve in a particular solvent or solvent mixture at ordinary temperature, frequently do so at lower temperatures, *e.g.* —50°. This may be due to the formation of soluble molecular compounds which dissociate at moderate temperatures, and to the exothermic character of the reaction.[1]

[1] E. Berl, *J. Amer. Chem. Soc.*, 1939, **61**, 154.

Solubility and other qualities can also be modified by heat treatment. An X-ray study of the effects of quenching and annealing on cellulose triacetate, tributyrate and acetate-butyrate have shown [1] that various molecular states from crystalline to disordered can be produced.

[1] W. B. Baker, *J. Amer. Chem. Soc.*, 1942, **64**, 776.

CHAPTER XIII

CELLULOSE NITRATE

THE following table shows the formulae and nitrogen content of the cellulose nitrates theoretically possible, assuming a C_{24} unit formula for cellulose :—

Cellulose.	Formula.	Nitrogen, per cent.
Dodecanitrate . . .	$C_{24}H_{28}O_{20}(NO_2)_{12}$	14·16
Endecanitrate . . .	$C_{24}H_{29}O_{20}(NO_2)_{11}$	13·50
Decanitrate . . .	$C_{24}H_{30}O_{20}(NO_2)_{10}$	12·78
Enneanitrate . . .	$C_{24}H_{31}O_{20}(NO_2)_9$	11·98
Octanitrate . . .	$C_{24}H_{32}O_{20}(NO_2)_8$	11·13
Heptanitrate . . .	$C_{24}H_{33}O_{20}(NO_2)_7$	10·19
Hexanitrate . . .	$C_{24}H_{34}O_{20}(NO_2)_6$	9·17
Pentanitrate . . .	$C_{24}H_{35}O_{20}(NO_2)_5$	8·04
Tetranitrate . . .	$C_{24}H_{36}O_{20}(NO_2)_4$	6·77

A mononitrate of a $C_6H_{10}O_5$ unit, therefore, should contain 6·77, a dinitrate 11·13, and a trinitrate 14·16 per cent. of nitrogen. Since, however, the nitration of cellulose is a heterogeneous reaction (p. 227) involving the irregular esterification of some or all of the three hydroxyl groupings present in each C_6 unit,[1] it is only in the case of the trinitrate that a homogeneous product is likely to be formed and the attribution of definite formulae to products of a lower degree of nitration is not valid. If for theoretical purposes the average number (n) of nitrate groupings per C_6 unit is required, it can be calculated from the relation

$$n = \frac{162N}{1400-45N},$$

where N is the percentage of nitrogen found on analysis. Thus a product containing on the average one nitrate grouping per C_6 will contain 6·77 per cent. of nitrogen, but in support of the above reservation evidence given by X-ray analysis seems to show that the "mono-ester," at least, is a mixture of unchanged cellulose with higher esters.

The nitrogen content of any particular nitrate largely defines its solubility and other properties, and consequently its technical

[1] *Cf.* M. Matthieu, *Bull. Soc. Chim.*, 1936, **3**, 346 ; "La Nitration de la Cellulose", Paris, 1936.

application, as may be seen from the following summary of the types of cellulose nitrate used in industry :—

Nitrogen, per cent.	
10·7–11·2.	Soluble in alcohol. Used with camphor, triphenyl phosphate dibutyl phthalate, etc., to produce celluloid plastics.
11·2–11·7.	Soluble in methyl alcohol, ether-alcohol, ethyl acetate, acetone and other solvents. Used for photographic films, lacquers and nitrate rayon.
11·8–12·3.	Soluble in the usual ester solvents—*e.g.* ethyl, butyl and amyl acetates, ether-alcohol and acetone, but practically insoluble in ethyl alcohol. Used for the manufacture of lacquers, artificial leather and gelatinous explosives.
12·4–13·0.	Partially soluble in the usual solvents but completely soluble in acetone. Used for explosives such as smokeless powders.

The proportion of combined nitrogen is conveniently indicated by the volume of nitric oxide obtained per gram when the ester is treated as in the nitrometer method.[1] Although cellulose can be nitrated with nitric acid alone (*d*, 1·5), nitration is, in practice, always effected by the use of a mixture of nitric and sulphuric acids. The nitrogen content of the products depends upon the amount of water present. The highest nitration is obtained with systems represented by $HNO_3 + n(H_2SO_4 . H_2O)$ and the lowest when the nitric acid is present as the hydrate $HNO_3 . H_2O$.[2] The sulphuric acid appears, therefore, to act by dehydrating the nitric acid. The increased proportion of water required for the lower degrees of nitration favours dissociation of the acids with consequent hydrolysis of the cellulose which, again, may be irregular. The resulting degradation influences considerably the solubility and viscosity of lower nitrated products, so that an adjustment of the nitrating conditions to offset this effect may be necessary.

Nitration can, however, be carried out without degradation of the cellulose. This has been explained[3] by the rapidity of the initial reaction which converts cellulose into a product remarkably indifferent to the action of acids. When phosphoric acid is substituted for sulphuric acid swelling of the fibre takes place with even penetration of the nitrating acid.[4] X-ray analysis shows that the lattice changes from that of natural cellulose to that of hydrate cellulose, an effect which is not observed when sulphuric acid is used. If nitration (with phosphoric acid) and washing are carried

[1] G. Lunge and E. Berl, " Chemisch-Technische Untersuchungsmethoden " (J. Springer, Berlin, 1910), vol. i, p. 156, vol. iii, p. 120.
[2] K. Kullgren, *Z. Schiess- u. Sprengstoffw.*, 1908, **3**, 146.
[3] H. Staudinger, *Ber.*, 1937, **70**, 2296.
[4] E. Berl and G. Ruff, *Ber.*, 1930, **63**, 3212.

out under tension, the point diagram of cellulose trinitrate is obtained. Nitrates with nitrogen contents of 14–13·7 per cent. are formed under these anhydrous conditions (p. 63), but fibrous products of 11–11·5 per cent. cannot be prepared.

The influence of the water content is well shown in the table below, although these experimental mixings are not employed for the manufacture of nitrates of the corresponding nitrogen contents. Equal weights of nitric acid (*d*, 1·50), and sulphuric acid (*d*, 1·83) were taken in each experiment; temperature 16° to 18°; time 24 hours, and the ratio of nitric acid to cellulose (cotton wool) was constant. The bulk of the acid was pressed out, the mass brought into a large excess of cold water, filtered and washed during 2 days with boiling water.

INFLUENCE OF WATER CONTENT OF THE NITRATING MIXTURE ON THE DEGREE OF ESTERIFICATION OF CELLULOSE NITRATES [1]

Nitration Mixture in per cent.			C.c. NO / 1 g. ester	NO_2-groups / $C_6H_{10}O_5$	Per cent. Nitrogen.	Solubility in Ether-Alcohol, per cent.
H_2SO_4.	HNO_3.	H_2O.				
45·31	49·07	5·62	217·73	2·8	**13·65**	1·50
42·61	46·01	11·38	210·68	2·7	**13·21**	5·40
41·03	44·45	14·52	203·49	2·5	**12·76**	22·00
40·66	43·85	15·49	198·00	2·4	**12·58**	60·00
40·14	43·25	16·61	196·35	2·4	**12·31**	99·14
39·45	42·73	17·82	192·15	2·3	**12·05**	99·84
38·95	42·15	18·90	184·78	2·2	**11·59**	100·00
38·43	41·31	20·26	174·29	2·0	**10·93**	99·82
37·20	40·30	22·50	155·73	1·7	**9·76**	74·22
36·72	39·78	23·50	148·51	1·5	**9·31**	1·15
35·87	38·83	25·30	133·94	1·3	**8·40**	0·61
34·41	37·17	28·42	103·69	1·0	**6·50**	1·73

For some purposes more useful information is obtained from an analysis of the spent acids remaining in approximate equilibrium with the cellulose nitrate at the end of the reaction. An example is given in the table on p. 236. In these experiments the initial ratio $H_2SO_4 : HNO_3$ was constant. It will be noticed that in each group there is a range over which the degree of nitration is little influenced by the water content, but beyond this region any further increase is accompanied by a marked decline in the nitrogen-value attained. The water content obviously has a critical influence on the production of the industrially useful products containing less

[1] G. Lunge and J. Bebié, *Z. angew. Chem.*, 1901, **14**, 486.

than 13 per cent. of nitrogen. The first four products in each series, for example, were insoluble in ether-alcohol, the others fully soluble.[1]

EQUILIBRIUM AT THE END OF NITRATION

Nitrating Mixture at end of Reaction in per cent.			Per cent. Nitrogen in the Product.
H_2SO_4.	HNO_3.	H_2O.	
79·4	17·7	2·9	11·9
77·7	17·0	5·3	13·3
76·0	16·4	7·6	13·7
72·6	15·0	12·4	13·6
69·1	14·6	16·3	12·7
65·0	14·25	20·75	11·6
70·5	26·5	3·0	13·85
68·8	25·55	5·65	13·75
67·3	24·9	7·8	13·8
64·0	23·3	12·8	13·6
61·0	22·7	16·3	12·8
57·4	22·2	20·4	12·1
51·0	45·2	3·8	13·8
48·85	43·9	7·25	13·8
47·0	42·9	10·1	13·85
45·75	42·15	12·1	13·8
42·8	40·5	16·7	12·1

A useful range of products can be made taking three parts by weight of sulphuric acid (*d*, 1·84) to one part of nitric acid (*d*, 1·5). By varying the water content from 7 to 20 per cent., cellulose nitrates with nitrogen content from 13·1 down to about 11·0 per cent. can be obtained.

The dry cotton fibre (about 1 per cent. moisture) is immersed as quickly as possible in forty to fifty times its weight of acid at ordinary temperatures and left for 2 or 3 hours. It is then removed and immersed in a large volume of cold water to remove the bulk of the acid. This crude nitrate may be contaminated with sulphuric esters of the cellulose and nitro-compounds from impurities in the fibre employed. These impurities render the product (especially with the higher nitrated types) liable to spontaneous decomposition. Their removal is effected by prolonged boiling in water, maintained just alkaline, followed by bleaching.

[1] Private communication. See also G. Schiemann and S. Kühne, *Cellulosechem.*, 1934, **15**, 78; M. Sendo, *J. Cellulose Inst.*, Tokyo, 1932, **8**, 210, 290.

The breaking up of the sulphuric ester is most rapid when the boiling is carried out under slightly acid conditions, but as this also attacks the cellulose nitrate, "stabilisation," as this purification is usually termed, must be carefully controlled. For gun-cotton prolonged boilings in weakly acid solution are followed by shorter boilings in which the water is kept neutral by the addition of chalk, unless the water supply is naturally hard. In his classical paper on the "Purifying and Stabilising of Gun Cotton",[1] Robertson states that when the wash water has an acid concentration equivalent to H_2SO_4, 1 per cent., acidity is about right for the acid boil.

With the lower nitrated products required for plastics, films, etc., the thorough elimination of impurities is not so essential, but degradation of the cellulose nitrate complex, as shown by viscosity, must be avoided as much as possible. In these cases purification is best effected by short initial acid boiling followed by more prolonged neutral boiling.

By variations in the concentration of the nitrating mixture stable nitrates can be made with any nitrogen content up to about 13·2 per cent., and, if chemical stability is not required, nearly up to the theoretical 14·14 per cent. The process seems to be continuous, and does not show any tendency to produce definite compounds corresponding to the theoretical nitrates for which formulæ have been given. It has been stated, however, that each chain molecule in the cellulose complex is nitrated to the same extent, and that although a given nitrate can be fractionated from solution the fractions differ only in chain length and not in degree of nitration.[2] The degree of nitration required must be regulated, therefore, by close adherence to the experimental conditions which are found, in practice, to be necessary.

The cellulosic raw materials used in manufacture include cotton linters purified by keiring with caustic soda and bleaching; waste cotton from textile processes, such as spinner's sweeps and card waste, degreased and similarly purified; and chemical wood pulp, sulphate or sulphite, purified according to the purpose for which the nitrate is required. The cotton celluloses are generally nitrated in the "bulky" condition: wood celluloses, either in the form of paper, or broken up into a loose mass resembling linters. The nitration of pulp in sheets is of limited application.

A large amount of nitrating acid, *e.g.* 30 to 50 times the weight of the cellulose, is employed. This high ratio is necessary owing to the bulk of the cellulose, but it has the advantage of securing

[1] R. Robertson, *J. Soc. Chem. Ind.*, 1906, **25**, 624.
[2] F. D. Miles, *Trans. Faraday Soc.*, 1933, **29**, 110.

uniformity in nitration, since rise of temperature is moderated and there is less relative change in the composition of the acid mixture as the reaction proceeds.

Two methods are employed for separating the product. In the displacement process advantage is taken of the high density (1·7) of the mixed acid to float water on it while the acid is gradually run off from the bottom of the stoneware nitrating pan. A fairly sharp acid-water interface thus passes slowly through the nitrocellulose which is almost entirely freed from surplus acid without causing excessive dilution. With the centrifugal process nitration is carried out either in the centrifuge or in a vessel placed above it, the spent acid being separated centrifugally and the product rapidly freed from adherent acid by " drowning " in a large volume of water. Stabilisation by boiling in slightly acid, followed by weak alkaline, solutions, follows as mentioned above.

In the case of nitrated paper and cotton waste, and normally with other forms of nitrocellulose, the product is reduced to small fibre particles by " pulping " in hollander beaters or similar machines, either during or after stabilisation. It is then centrifuged to about 50 per cent. moisture content for storage and transport. If the nitrate is to be dissolved in subsequent operations, the water is often displaced from it by forcing a suitable liquid, *e.g.* ethyl or butyl alcohol, under hydraulic pressure through the cake of nitrocellulose in a " dehydrating press " ; the liquid selected is a component of the solvent mixture employed in the subsequent processing, but is not, by itself, a solvent for the nitrate.

1. **The solubility of cellulose nitrates** varies considerably, as will be seen in the following table [1] :—

SOLUBILITY OF CELLULOSE NITRATES

N per cent.	Solubility per cent. in—		
	Acetone, Ethyl acetate Amyl acetate	Ether-alcohol 2 : 1	Absolute Alcohol
13·1 –13·4	95–100	Insoluble	Insoluble
12·75–13·1	95–100	<30	Insoluble
12·5 –12·75	95–100	50–100	<10
12·0 –12·5	95–100	95–100	<50
11–12	95–100	90–100	50–100
10–11	95–100	80–100	<50
9–10	30–90	30–90	Insoluble
7–9	<30	<30	Insoluble
3–7	Insoluble	Insoluble	Insoluble

[1] Ullmann " Enzyk.," 1917, **5**, 96.

Cellulose nitrates are soluble in cuprammonium.[1]

2. **Viscosity.**—Cellulose nitrates are prepared with a wide range of viscosities. One factor of control in manufacture is given by pre-treatment of the cellulose employed, since the high or low viscosity of the cellulose (in cuprammonium) is reproduced in the ester made from it. Nitrates of low viscosity, therefore, are obtained from cellulose which has been modified, *e.g.* by mercerisation, oxidation, the action of acids or of heat. A table showing the viscosity range supplied by a particular manufacturer is given on p. 242. Nos. 6 and 6A are typical low viscosity "cottons," used for the preparation of cellulose brushing and spraying lacquers. While high viscosity enables thinner and more pliable films to be made, low viscosity cottons produce a thick film with a minimum number of coats. Products 8A and 8 are used for metal lacquers and give a tough and elastic film. Their solutions can be diluted with benzol, toluol, or methylated spirit. High viscosity cellulose must be used for the preparation of cellulose nitrate suitable for the manufacture of gelatinous explosives.

A. Laboratory Preparation of Cellulose Nitrates

1. **Trial Nitration prior to Large-scale Preparation.**—The suitability of a cellulosic raw material for the production of a particular grade of nitrate is best examined by means of a laboratory-scale nitration in which manufacturing conditions are imitated as far as possible, except that the use of a centrifuge for laboratory nitration is not advisable. The dry cellulose (cotton, shredded paper or pulp) is introduced into the nitrating mixture in a wide mouthed, glass-stoppered jar and worked with a glass rod or spatula. After standing the requisite time, with temperature control if necessary, the contents are quickly transferred to a small centrifuge and the liquid spun off. The nitrocellulose is then drowned out, either by pouring a large volume of ice cold water into the basket, or by transferring it to a large volume of cold water. For quantities up to 50 g., however, a suction filter is quite suitable, and if well pressed the mass will not retain much more acid than with the centrifugal method. It is important to avoid air streaming through the acid-wet material.

The displacement process can be imitated, though not very successfully, by using a Buchner funnel (to the stem of which a glass tap is fitted with acid-resisting cement) in which to carry out

[1] E. Knecht and A. Lipschitz, *J. Soc. Chem. Ind.*, 1914, **33**, 122.

the nitration and washing. Stabilisation is done by three boilings, each of 12 hours, with 50 parts of water containing small lumps of calcite. If alcohol is used higher nitrogen contents are obtained.

2. Preparation of highly nitrated Cellulose Nitrates.[1]—(*a*) *From Filter Paper.*—An acid mixture containing 71·03 H_2SO_4, 28·11 HNO_3, and 0·86 per cent. H_2O was prepared and 100 g. used to each gram of dry paper. After three quarters of an hour at 25°, the excess of acid was squeezed out, and the mass gradually brought into glacial acetic acid with cooling and shaking. The acid was removed, the product transferred to 50 per cent. acetic acid and washed with rapid stirring. It was then boiled for 1 hour with 50 per cent. acetic acid, washed with the same acid, and finally with water until neutral.

For analysis it was dried 1 hour at 70°, reduced to powder and dried for 2 hours at 95 to 100°, and finally in a vacuum over phosphorus pentoxide at 100°. The estimation of nitrogen can be done by Dumas' method if the fine powder is mixed with copper oxide so that it occupies 10 to 15 cm. in the tube. On analysis, 0·1078 g. gave 13·2 ml. N_2 at 15° and 738 mm.; N = 13·94 per cent.

The preparation contained a trace of sulphuric acid, so that the treatment with acetic acid was repeated several times. It was then free from acid, but gave N, 13·6 per cent.

(*b*) *Preparation from Linters.*—These were purified and dried to below 1 per cent. moisture. Acid mixture, H_2SO_4, 73; HNO_3, 25·77, and H_2O, 1·23 per cent.; cellulose-acid ratio 1 : 150; temperature 15 to 18°; time 7 hours; the linters introduced in portions. The mixture was cooled to 0°, the acid squeezed out, and the mass introduced into cold 50 per cent. acetic acid with shaking as before, the temperature not rising above 10°. After pressing, the nitrocellulose was boiled for 1 hour in fresh 50 per cent. acetic acid, and then for 7 hours in alcohol to remove traces of sulphuric acid. This preparation contained N, 13·72 per cent.

(*c*) *Preparation from Viscose Cellulose.*—Viscose rayon was treated as under (*a*), above. Temperature 22°; time, 7 hours; ratio cellulose to acid, 1 : 200. After pressing, the mass was introduced into cold water with stirring, boiled for 1 hour with 50 per cent. acetic acid in which it turns yellow, and after washing heated for some hours in alcohol. Decomposition temperature, 189°; N, 13·77 per cent.

Details of experiments on the nitration of various types of wood pulp are given by Schrimpff.[2]

[1] K. Hess, "Chemie der Zellulose," Leipzig, 1928, p. 381.

[2] A. Schrimpff, "Nitrocellulose aus Baumwolle und Holzzellstoffen," München (1919), p. 158.

3. Denitration of Cellulose Nitrate.—This is best done by treatment with ammonium sulphide solution. Complete removal of nitrogen is difficult. After the usual denitration the fibres still contain 1 to 2 per cent. and give the diphenylamine test. For complete removal of nitrogen the nitrate must be very finely divided before treatment.

The reagent may be prepared as follows [1]: 400 ml. of 27 per cent. ammonia are mixed with 600 ml. 96 per cent. alcohol and a rapid stream of sulphuretted hydrogen passed for 2 hours. The cellulose nitrate is treated with this solution for 5 to 6 hours at 18 to 20°.

B. Analysis and Examination of Cellulose Nitrates and their Solutions

(*a*) **Dry Weight of Damped Collodion Cotton.**—An average sample is drawn and 10 g. spread out on a tin, aluminium or porcelain tray, which is placed in an oven maintained at 45 to 50°. The door should be closed, but not fastened. The first weighing is taken after 6 to 8 hours. Small quantities may be dried at 100 to 105°. Aluminium boxes with close-fitting cap lids make suitable containers.

Material of unknown origin should be tested for acidity before drying, by moistening 0·5 g. with a saturated solution of Congo red in acetone-alcohol (1 : 1 by volume). If a bluish tinge appears the sample should not be dried much above room temperature, or it may be stabilised, *e.g.* by hot alcohol extraction, and then dried. If the Congo red solution gives a bluish colour after drying the drying conditions should be made less severe.

With larger quantities rapid drying may be effected by exposure to a current of warm air at 60°, the material being suspended in a muslin cage. For nitrogen estimation drying should be completed at 100 to 105° for 10 to 15 minutes.

(*b*) **Percentage of Solid Ester in Collodion Solutions.**—10 g. of the solution are dried off in a flat dish at 70 to 80°. It is very difficult to remove the last traces of solvent.

The solid may, also, first be thrown out by addition of a miscible non-solvent. If high-boiling plasticisers are present special treatment, *e.g.* ether extraction, of the recovered solid may be necessary (p. 249).

(*c*) **Viscosity of Cellulose Nitrate Solutions.**—The Ostwald viscometer, as described for cellulose acetate, is used, but the falling-sphere method is more general, viscosities being given as time of

[1] B. Rassow and E. Dörr, *J. Prakt. Chem.*, 1924, **108**, 169. *Cf.* P. Karrer and P. Schubert, *Helv. Chem. Act.*, 1926, **9**, 894.

fall, in seconds, observed under definite conditions. A simple adaptation for technical purposes consists in the measurement of the viscosity as time of fall of a steel ball 2 mm. in diameter through 25 cm. of a solution of cellulose nitrate (5 to 25 g per 100 g. of solution) in 99 to 100 per cent. butyl acetate at 18°. Some results with the special types of nitrate manufactured by a particular firm are given below :—

Type of Cellulose Nitrate.	Dry Cellulose Nitrate in Solution, per cent.	Solvent.	Time Limits in Seconds.		Viscosity according to the American method, seconds.
			Minimum.	Maximum.	
5	25	Butyl Acetate.	35	60	½
6	25		90	120	⅓
6A	22		90	120	¼
7	15		75	120	2
8	13		60	100	4
120	11		80	100	
8A normal.	9		80	100	20–30
8A extra thick.	7		80	100	60–80
17	5		80	120	250–400

The estimation is carried out by mixing, for example, 25 g. (dry weight) of the sample with 75 g. of butyl acetate and shaking to complete solution. The liquid (adjusted to 18°) is poured into a cylinder not less than 3 cm. wide, filling it to the top mark, which may be 1 to 2 cm. from the top. A second mark is made about 5 cm. lower and a third exactly 25 cm. lower still and about 5 cm. from the bottom of the cylinder. The 2 mm. steel ball (a ball bearing usually weighing 0·0320 g.) is held in tongs very near the surface and exactly in the centre of the cylinder. It is then allowed to fall and the time taken for it to pass between the second and third marks observed.

In the method of the American Society for Testing Materials (Method D 301–33) the solvent is a mixture of ethyl acetate (85–88 per cent.), denatured alcohol and toluene in the ratio of 4 : 5 : 11 parts, respectively, by weight. Solutions of nitrocellulose (lacquer-type) are made up at concentrations of 12, 20 or 25 per cent. by weight, according to viscosity, and the time taken for a steel ball 0·312/3 inch in diameter (2·035 ± 0·01 g.) to fall through a distance of 10 inches of a solution at 25° contained in a glass cylinder of 1 inch internal diameter, is observed.

The dependence of viscosity on nitrogen content under constant

conditions was examined by Krüger.[1] The following figures give an example. Nitration details: H_2SO_4, 42·9; HNO_3, 47·8; H_2O, 9·1 per cent.; acid to cotton, 55 : 1; 24 hours at 13°. Ostwald viscometer, using 8 per cent. solution in acetone.

Nitrogen per cent.	12·54	11·96	11·05	10·87	9·95
Viscosity, seconds	246·2	202·8	27·0	22·4	11·7

The influence on the viscosity produced by the use of phosphoric acid in place of sulphuric acid has also been studied.[2]

(*d*) **Solubility Tests.**—Examination is made (i) for clarity of solution in a given solvent or solvent mixture, comparison being made, if necessary, with a standard sample.

(ii) For the presence of under-nitrated material. A solution of about 2 g. of the sample in 100 ml. of acetone is centrifuged, or allowed to stand, until insoluble matter has settled. This is filtered off, washed with acetone, dried and weighed, after which it is transferred to a platinum crucible, moistened with paraffin, ignited, and the residue weighed. The difference between these weights is taken as organic matter insoluble in acetone.

(iii) For the amount of low-nitrated material in samples containing 11–12 per cent. of nitrogen. The sample is extracted with alcohol in a Soxhlet apparatus and the weight of product in the extract determined. A similar test can be applied to products of the gun-cotton type by extracting with ether-alcohol (2 : 1, vol.) the loss in weight of the sample being determined.

These tests sometimes give useful indications of departure from normal manufacturing conditions.

(iv) Compatibility, or the Dilution-ratio (*cf.* p. 289) is found by adding a diluent such as toluene slowly from a burette to a solution of the nitrate, *e.g.*, in an aliphatic acetate till a permanent turbidity appears.

(*e*) **Ash Content.**—A suitable sample (say 5 g.) is weighed into a platinum dish and moistened with liquid paraffin or molten paraffin wax. It is then warmed and lighted with a flame. When only a charred mass is left the whole is ignited, preferably in an electric muffle furnace, at about 900°. Addition of a few drops of ammonium nitrate solution before the final heating assists the oxidation and collects the ash into a compact mass. The ash is usually treated either with ammonium carbonate solution (10 per cent.), followed by drying to constant weight at 200°, or with sulphuric acid (10 per cent.), followed by ignition in the furnace. The ash-content is accordingly returned as "carbonated" or

[1] D. Krüger, *Cellulosechem.*, 1934, **15**, 85.
[2] E. Berl and G. Ruff, *Cellulosechem.*, 1933, **14**, 115.

"sulphated"—the former probably corresponding more nearly to the mineral matter present in the sample.

An alternative to burning down with paraffin consists in treating the sample with excess of nitric acid (*d*, 1·42) and "fuming off" on a hot plate.

Determination of the Nitrogen Content of Cellulose Nitrates

Three methods are given below. The nitrometer method is generally applicable. A modification for rapid and continuous testing is described in which the correction for temperature and pressure of the gas obtained is automatic. The Schultz-Tiemann method is useful in all cases, and particularly when solution in sulphuric acid does not readily take place. A third method involves the use of the Devarda alloy.

The Nitrometer Method.—When the nitro-cellulose is in a fine state of division it will usually dissolve easily in 94 per cent. sulphuric acid and the Lunge nitrometer is well adapted for the estimation. A few samples may be resistant to acid of this concentration, requiring stronger acid or a longer time for solution. In these cases the results tend to be somewhat too low. The material is broken up by sieving, dried at 55–60°, and about 0·55 g. weighed out into a stoppered weighing bottle in which it is mixed with 10 ml. of 94–95 per cent. sulphuric acid, known to be free from nitric acid. The nitrocellulose is allowed to dissolve at room temperature, the process being assisted by occasional rotation of the bottle. About half an hour is usually sufficient.

The most suitable type of nitrometer should have a bulb of 100 ml. capacity between the cup and stopcock, and the graduated tube. This enables a convenient amount of substance to be handled. The nitrometer, having been filled with clean mercury, the acid solution is poured into the cup and drawn into the bulb. The weighing vessel and cup are washed with a further 5 ml. of acid in two or three additions, and the washings drawn into the nitrometer.*

The apparatus is then vigorously, but carefully, shaken. The aim is to break up the mercury into very fine droplets so as to give a large reaction surface, and it will be found that considerable practice is necessary in order to liberate the whole of the nitric oxide. It is advisable to make preliminary trials with pure potassium nitrate. The decomposition proceeds according to the equation

$$3H_2SO_4 + 2HNO_3 + 3Hg = 3HgSO_4 + 4H_2O + 2NO.$$

* Some workers use 5 ml. of acid for solution and 10 ml. for washing. Others weigh the sample by difference into the nitrometer bulb and dissolve it in the acid by stirring with a glass rod.

By keeping the side reservoir well up, the reaction is completed while the mixture is entirely in the bulb during 3 or 4 minutes shaking. When all the gas has been liberated the nitrometer is clamped with the mercury-level, in the levelling tube, higher than in the reaction tube by about one-sixth of the column of sulphuric acid, and allowed to stand half an hour to take the temperature of the room. A drop of acid is always held in contact with the bore of the stopcock by capillary attraction. By opening the cock very slightly it can be seen by the tendency of the drop to enter or leave the nitrometer, whether the gas in the bulb is below or above atmospheric pressure. The levelling tube is then adjusted until the opening of the stopcock does not displace the drop of acid. The gas is then at atmospheric temperature and pressure. Its volume is measured and calculated to the percentage of nitrogen in the original nitrocellulose.

To avoid delay the nitrometer may be water-cooled during the operation. A conical rubber Gooch crucible-seating is fixed loosely with wire so that the base rests on the shoulder of the bulb below the tap. By adjustment this can be made to distribute a stream of water evenly over the bulb and tube. Waste is run off into a hemispherical rubber cup (or one made from a rubber disk shaped into a cone), fixed round the lower part of the measuring tube.

Note.—When large numbers of tests have to be made a device is sometimes employed for eliminating the correction for temperature and pressure. The decomposition is carried out as before, but the tube need not be graduated, as the gas is transferred for measurement to the apparatus shown in Fig. 64, which is similar to the ordinary nitrometer, with the addition of an extra bulb B connected to the common levelling tube. This bulb contains a volume of air so adjusted that at normal temperature and pressure the mercury stands at the mark D. Once a suitable quantity of air has been introduced, B is permanently sealed off. The air in B must be sufficiently dry to prevent condensation of moisture under any temperature or pressure variations likely to be found. The gas to be measured is drawn into the measuring vessel and the levels adjusted so that the mercury in B stands at the fixed mark. The gas volume is then read and no correction for temperature or pressure is required.

The Schultz-Tiemann Method for the Estimation of Nitrogen.—When the material to be tested is in such a physical condition that solution in sulphuric acid does not readily take place, the method of Schultz-Tiemann is more suitable. It may, however, be usefully employed in all cases.

A strong, wide-necked, round-bottomed flask A (Fig. 65), of 200

ml. capacity, is fitted with a rubber stopper and two bent glass tubes B and C, of which B projects about 1 cm. below C. Rubber connections and pinch cocks at D and E connect *via* glass tubes to a beaker F and the pneumatic trough G.

The reducing agent employed is a saturated solution of ferrous chloride made by the action of hydrochloric acid on iron, the iron being kept in excess. The reaction is

$$HNO_3 + 3FeCl_2 + 3HCl = 3FeCl_3 + 2H_2O + NO.$$

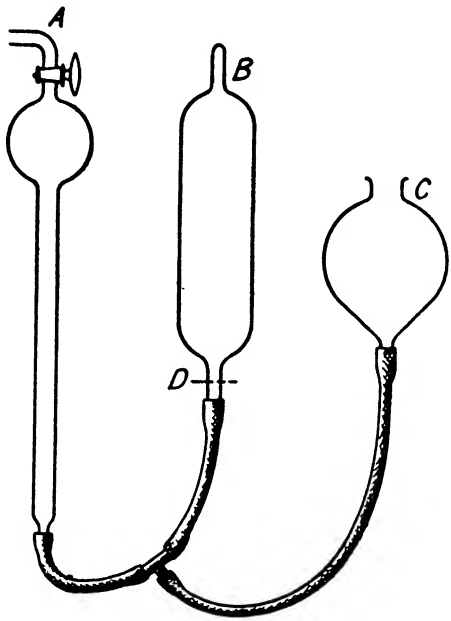


FIG. 64.—Apparatus for eliminating correction for temperature and pressure.

The nitrocellulose (0·5 g.) is placed in the flask A with 50 ml. of water, and 20 ml. each of ferrous chloride and concentrated HCl are placed in F. D and E are both opened and the delivery tube removed from the trough G. The flask is then boiled until about 40 ml. have evaporated. All the air will then have been driven out of the apparatus and the liquid in F will be boiling. D is closed, G is filled with 20 per cent. sodium hydroxide solution, the delivery tube inserted, clip E closed, and the flame removed. The measuring tube H, also filled with sodium hydroxide solution, is placed in position, and by cautiously opening D the liquid in F is drawn into the reaction flask, which is now under partial vacuum, and is followed by boiling water to clear the tube D of acid. Care must be taken not to admit any air during the operation.

The flask is then cautiously heated and the rubber connections D and E (now collapsed under vacuum) are watched. When the rising pressure in the flask causes them to expand to normal shape, E is opened and the liberated gas collected in H. When evolution ceases the flame is removed and E closed. It will be found that a small amount of gas has been absorbed by the liquor remaining in the tube B, as indicated by the " brown ring," visible in the tube. To collect this a little more water is admitted from F and transferred to H by reboiling as before. The measuring cylinder is placed in a jar of water to cool, the pressure adjusted to atmospheric, and the volume of gas measured. The calculation for nitrogen is made as before, but in this case it must be remembered that the gas is saturated with water vapour.

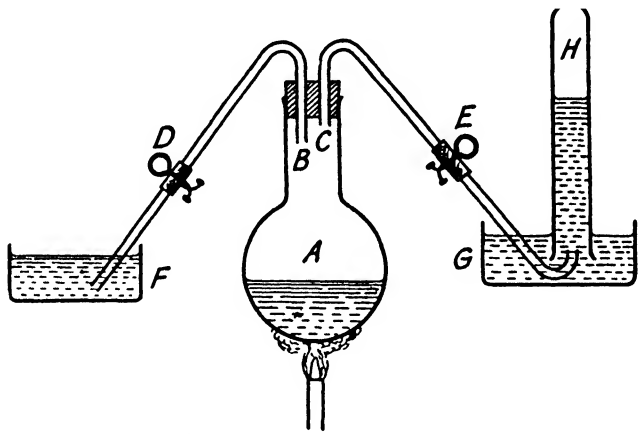


FIG. 65.—The Schultz-Tiemann method.

Modified Devarda Method for Estimation of Nitrogen in Cellulose Nitrate.—Working conditions must ensure (*a*) that loss of nitrogen by side reactions at the solution stage is avoided and (*b*) that the " caustic spray," formed during reduction and distillation, is retained. A small, long-necked flask, containing about 10 ml. of water which is kept at boiling-point by a small flame, is therefore interposed as a scrubber between the still-head of the reaction flask and the usual Kjeldahl ammonia-collecting trap. The ammonia is absorbed in a 2 per cent. solution of boric acid aud titrated with *N*-10 HCl, using as an indicator a mixture of 5 vols. of 0·1 per cent. bromcresol green and 1 vol. of 0·1 per cent. methyl red, both in absolute alcohol. This gives a green colour with ammonia, pink-mauve with boric acid, and pink with mineral acid.

About 0·3 g. of the dry sample is weighed by difference into a round-bulb flask with a long neck, and washed down with 2 to 3 ml.

of alcohol. Then water (60 ml.), 25 to 30 per cent. H_2O_2 (15 ml.) and NaOH solution, 40 per cent. (10 ml.) are added. The flask is covered and warmed gently (steam bath) till the nitro-compound has dissolved. The liquid should be light yellow in colour—if brown, treatment has been too severe and the result will be low. The excess of hydrogen peroxide is destroyed by heating on the steam bath till effervescence ceases, when the flask is cooled and 40 ml. of 40 per cent. NaOH solution are added with cooling. Powdered Devarda alloy (2·5 g.) is put in and the flask at once connected with the distillation train. After standing, with occasional shaking till hydrogen-evolution has practically stopped (20 mins.) the contents are heated, a slow current of pure air being drawn through the apparatus. To complete the distillation the liquid is kept boiling for 20 to 30 minutes. The ammonia evolved is titrated as above.

A similar, but less rigid, procedure is as follows: 0·5 to 2 g., according to the nitrogen content (moisture on duplicate) are placed in a 750 ml. Erlenmeyer flask. 2 to 3 ml. of ethyl alcohol, 30 ml. of 12 per cent. hydrogen peroxide, 50 ml. of sodium hydroxide solution (*d*, 1·31), and about 50 ml. of water are added and the whole heated on the water bath for 45 minutes. After standing for 1 to 2 hours, the flask is heated over the open flame to decompose the hydrogen peroxide.

The contents are cooled and the flask fitted with a still head and a condenser leading into a known volume of $N/10$ hydrochloric acid. 5 ml. of alcohol and 2·5 g. of Devarda alloy are added quickly, and when the vigorous reaction has subsided the liquid is distilled until most has passed over. The excess of acid is titrated with standard alkali.

Stability of Cellulose Nitrates

Under the Explosives Act of 1875 nitrocellulose, like other explosives, is required to comply with certain standards of safety before it can be sold and used.

The official test in Great Britain is known as the "Heat Test". In this a quantity of the material is placed in a test tube, in the upper part of which is suspended a starch iodide test paper half of which is moistened with glycerine and water. The tube is placed in a water bath at 170° F. and the time which elapses before a brown line appears at the junction of the wet and dry portions of the test paper, of intensity equal to that of an official standard, is taken.

The test is empirical, and its utility depends upon close adherence to the specifications laid down. Details will be found in the Report

of the Departmental Committee on the Heat Test published by the Home Office.

The actual quantity of nitrogen oxides evolved is extremely minute, and the test is usually supplemented by others in which the heat treatment is more drastic, so that the amount of nitrogen oxides evolved is quantitatively measurable.

These tests can be divided into two classes, according as the products of decomposition remain in contact with the nitro-cellulose during the whole period of heating, and are thus able to react catalytically and hasten the decomposition, or whether they are removed as soon as formed, in a stream of inert gas such as carbon dioxide.

In the former class may be mentioned the Bergmann and Junk Test, in which decomposition takes place at 132° for 2 hours; in the latter class the chief is the Will Test, which is carried out for 4 hours at 135°.

With these also it is essential that standard conditions are strictly followed, and, in addition, the apparatus must be so enclosed that the operator is protected in case of accidental explosion.

Analysis of Mixtures containing Nitro-Cellulose

The possible number of ingredients which may be found in a commercial explosive or pyrotechnic mixture is so great that it is impossible to lay down a definite scheme for analysis. Experience alone can tell how to proceed in individual cases, but the following notes may help and at the same time minimise the risk of accident.

The sample should first be extracted with ether in a Soxhlet apparatus. This will remove all organic nitro-compounds and nitrates, with the exception of nitrocellulose. The ether extract will also contain non-volatile solvents, such as camphor and organic plasticisers.

The residue, after drying gently to remove ether, should be extracted with hot water, which will remove nitrates, chlorates, etc., added as oxygen-carriers, and any other salts. The nitrocellulose is next extracted from the residue by means of acetone. The residue, if any, will be free from dangerous material, and can be examined by ordinary methods. Charcoal pigments and cellulosic materials are the most likely ingredients to be met with at this stage.

Nitrocellulose is used for explosives both in its natural fibrous condition and in a gelatinised form produced by the action either of volatile solvents, or of non-volatile ones, generally known as plasticisers. The effect of the gelatinisation is to moderate the explosive action of the compound, so that whereas fibrous gun-cotton detonates

with enormous velocity, the gelatinised product burns rapidly, but progressively, and is used in gunnery as a propellant.

Nitrocellulose as applied in industry is almost always required in the gelatinous form, as in celluloid, a solid solution in camphor, and in various lacquers where other solvents are employed. The inflammability of the material has led to its replacement by cellulose acetate in some processes where it was once supreme.

The cellulose can, however, be regenerated in the form of a continuous colloid by denitration of the nitrocellulose, giving a product which, though combustible, is not highly inflammable. This is effected by the reduction of the nitrate radicle with a hydrosulphide. Ammonium hydrosulphide was originally used, but is now replaced by the cheaper compounds of sodium and calcium.

The reaction, as carried out industrially, always leaves sufficient of the nitrate to give the characteristic reaction with diphenylamine in 80 per cent. sulphuric acid. The deep blue colour produced when a denitrated cellulose is immersed in this reagent, affords a means of distinguishing it from cellulose regenerated from viscose or cuprammonium.

CHAPTER XIV

CELLULOSE SODIUM XANTHATE

CELLULOSE xanthate was discovered by Cross and Bevan in 1892.[1] It results from the interaction of carbon disulphide and alkali cellulose, *i.e.* cellulose impregnated with sodium hydroxide of mercerising strength. Theoretically cellulose sodium xanthate is formed according to the equations given by the discoverers :

$$(C_6H_{10}O_5)_n + n\text{NaOH} = (C_6H_9O_4.\text{ONa})_n + nH_2O$$

$$C_6H_9O_4.\text{ONa} + CS_2 = CS\begin{matrix}\text{SNa}\\ \text{O.}C_6H_9O_4\end{matrix}$$

The dilute alkaline solution of the product constitutes viscose, which probably contains units of this nature loosely combined with sodium hydroxide and dispersed in the solution.

T. Lieser,[2] whose work has done much to throw light on the viscose reaction, has prepared a sodium di-cellulose thiocarbonate of the formula $CS\begin{matrix}\text{O.}C_6H_9O_4\text{ . }C_6H_{10}O_5,\\ \text{SNa}\end{matrix}$ indicating the possibility of the presence of more complex compounds in viscose. The view that the hydroxyl group of the cellulose unit in position 2 alone takes part in the formation of the xanthate [3] is no longer maintained (*cf.* p. 226), but only one of the three hydroxyls is xanthated in the viscose process, which is essentially a reaction between swollen cellulose and carbon disulphide. Lieser [4] has shown that if cellulose is dispersed in an organic base all the hydroxyls react and a trixanthate is formed, *e.g.*

$$C_6H_7O_2(OH)_3 + 3\text{NEt}_4\text{OH} + 3CS_2 = C_6H_7O_2(\text{O.CS.SNEt}_4)_3 + 3H_2O.$$

The solutions required for dispersion vary from 2·3 to 4*N*- for the tetraethyl-, and 1·7–2·4*N*- for the ethyl-tributyl ammonium hydroxide. Tetramethyl ammonium hydroxide, which only swells cellulose, does not give the trixanthate.

Lieser [5] considers that, in xanthate formation (and dispersion in

[1] C. F. Cross, E. J. Bevan and C. Beadle, E.P. 8700 (1892) ; *Ber.*, 1893, **26**, 1090.
[2] T. Lieser, *Cellulosechem.*, 1929, **10**, 156 ; *Ann.*, 1928, **464**, 43.
[3] T. Lieser, *Ann.*, 1929, **470**, 104 ; *Papier Fabrik.*, 1938, **36**, 272.
[4] T. Lieser, *Chem. Zeit.*, 1936, **40**, 387 ; *Ann.*, 1936, **522**, 56.
[5] T. Lieser *et al.*, *Papier Fabrik.*, 1938, **36**, 272.

cuprammonium) interior units of the micelle remain unchanged, and only the outer units take part, the most favourably placed hydroxyl grouping entering into reaction. The xanthate is represented by the formulation

$$(C_6H_{10}O_5)\left[C_6H_9O_5 \cdot C\begin{matrix}S\\ SNa\end{matrix}\right]$$

where the curved brackets include all interior units and the square ones all those reacting outside.

The equation of Cross and Bevan involves a theoretical mass ratio $C_6H_{10}O_5 : NaOH : CS_2$ of 162 : 40 : 76, or 4 : 1 : 2. The ratio of cellulose to sodium hydroxide necessary in practice is, however, of the order of 2 : 1, or $C_6H_{10}O_5 : 2NaOH$. This fact led the discoverers to assume that the alkali, carbon disulphide and cellulose interact to form a compound $C_6H_8O_3.(ONa).O.CS.SNa$, the existence of which in freshly prepared viscose was apparently confirmed by Ost.[1]

The ratio of carbon disulphide to cellulose necessary for the preparation of viscose on a laboratory scale is rather greater than that of $CS_2 : C_6H_{10}O_5$, but on the technical scale the proportion of carbon disulphide can be very greatly reduced, quantities down to 60 to 75 per cent. of the theoretical value, only, being required for satisfactory working. In consequence, considerable discussion has taken place as to whether the equation of Cross and Bevan in any way represents the main reaction.[2] The physico-chemical changes taking place in viscose solutions, and the anomalous mass reactions observed, are best explained with the aid of the micellar concept of cellulose, somewhat on the following lines.

The electrolytes most effective in swelling and dispersing cellulose are those which have the most heavily hydrated ions. In absorbing ions cellulose also imbibes the water they carry, and in consequence swells. The imbibed water may, in the end, set up such tensions that the cohesion forces holding together the cellulose fibrils are overcome and dispersion (solvation) follows. Sodium hydroxide of 17·5 per cent. concentration swells (mercerises) cellulose, but does not cause solvation. If, however, the soda cellulose is xanthated, the cellulose sodium xanthate imbibes a higher proportion of water and solvation ensues, giving viscose. The viscosity of the newly formed viscose is very high, probably due to the fact that much of the water is present as envelope-water of the internal disperse phase, with less in the external aqueous disperse medium. If sodium hydroxide

[1] H. Ost, F. Westhoff and L. Gessner, *Ann.*, 1911, **382**, 349.
[2] *Cf.* E. Berl and J. Bitter, *Cellulosechem.*, 1926, **7**, 47.

is added to the viscose, by raising the osmotic pressure of the external phase it attracts water from the envelope of the disperse phase into the external phase, thus reducing the viscosity. During the ripening period the cellulose sodium xanthate gradually decomposes and its envelope-water passes into the external phase : the viscosity falls and becomes low enough for spinning. The regenerated cellulose, and any alkali cellulose not at first xanthated, remain emulsified in the presence of the undecomposed xanthate, which acts as a protective colloid.

After a time the amount of xanthate present becomes insufficient to afford protection and the cellulose begins to coagulate. Spinning is begun just before this point is reached, and it is evident that a very little electrolyte will then cause coagulation—*i.e.* the salt figure (p. 268) is low. These changes may be represented [1] after the notation of McBain devised for soap solutions :

$$\text{Na Cell.} + CS_2 \rightarrow \text{Na Cell. Xan.} \rightarrow \text{Na} + \left\{\begin{matrix}\text{Cell. Xan.}\\ \text{Na Cell. Xan.}\\ \text{Water imbibed}\\ \text{Cell. reverted}\end{matrix}\right\} \text{[Micelle ion]}$$

$$\rightarrow \text{Cellulose} + \text{NaOH} + H_2O \text{ Aq.} + \text{etc.}$$

It will be seen that increase in the content of sodium hydroxide in the external phase will diminish the rate of decomposition by its mass action, and will also withdraw further water from the envelope of the micelle by osmotic pressure. The maximum effect in this direction with solutions containing 7 per cent. of cellulose, is obtained with a total concentration of sodium hydroxide of 8 per cent. In practice, however, a concentration of 5 per cent. is used.

A cellulose solution prepared for spinning contains crystallites which are rod-shaped particles dispersed without order. The particles are probably not free-floating, but form a network. In the filament parallel arrangement of micelles would ensure maximum cohesion through secondary valency forces. X-ray observation shows that in actual rayon filaments the particles are far from parallel. The irregular arrangement, however, confers the essential property of elasticity.[2]

The existence of a " skin " or outer layer, differing in properties from the inner layers, has been suspected in normal viscose-rayon fibres ; but in certain cases, notably in connection with the fault known as " milky " or " streaky " yarn, its presence has been

[1] J. J. Fox, *J. Soc. Chem. Ind.*, 1930, **49**, 85T.
[2] A. W. Schorger, *J. Soc. Chem. Ind.*, 1930, **49**, 157T.

demonstrated.[1] It appears to be due to the fact that the friction of the orifice tends to orient and parallel the micelles on the surface which is first coagulated, whilst the micelles in the interior of the fibre remain unoriented. The draft applied has an additional influence in causing surface orientation.

Reactions of Cellulose Sodium Xanthate.—Cellulose sodium xanthate is decomposed by mineral acids with the formation of cellulose and carbon disulphide according to the following equations, where X represents the cellulose residue :

$$CS\begin{matrix}OX\\SNa\end{matrix} + H_2SO_4 = XOH + NaHSO_4 + CS\begin{matrix}OH\\SH\end{matrix}$$

and the dithiocarbonic acid further decomposes as follows :

$$CS\begin{matrix}OH\\SH\end{matrix} = H_2O + CS_2.$$

The acid is, however, " stronger " than organic acids such as acetic acid, and its salts are only slightly decomposed on treatment with them. The amount of sodium (as NaOH) combined as xanthate in a viscose solution was formerly estimated by titrating successively with *N*-acetic acid and *N*-hydrochloric acid. As, however, some decomposition takes place even with acetic acid, the end-point is badly defined, and the method is not now used.

Cellulose sodium xanthate in reaction with iodine undergoes a condensation similar to that resulting in the formation of sodium tetrathionate from sodium thiosulphate, thus :

$$2CS\begin{matrix}OX\\SNa\end{matrix} + I_2 = 2NaI + \begin{matrix}OX & XO\\ CS & SC\\ S\text{——}S\end{matrix}$$

The compound is precipitated as a flocculent mass, which is redissolved by alkaline solutions in the presence of reducing agents to form the original compound.

The reaction can be used for the estimation of the cellulose xanthate present in viscose solutions.[2] The solutions must be acidified with acetic acid in very slight excess. An excess of standard iodine solution is added and allowed to act for half an hour, after which the excess of iodine is titrated with thiosulphate solution.

[1] J. M. Preston, *J. Soc. Chem. Ind.*, 1931, **50**, 199T.

[2] H. Jentgen, " Laboratoriumsbuch für die Kunstseide-u. Ersatz-faserstoffindustrie " (W. Knapp, Halle, 1923), *Kunststoffe*, 1911, **1**, 165; E. Heuser and M. Schuster, *Celluosechem.*, 1926, **7**, 27; *ibid.*, 165.

The values found for hydroxide-free (precipitated) xanthates agreed very well with those found by direct titration with mineral acid—*e.g.* Na by *N*/10 HCl, (i) 0·586, (ii) 0·268 ; by iodine titration, (i) 0·531, (ii) 0·270 (E. Heuser). The method of working is given on p. 264.

The most important by-product formed in the viscose reaction is sodium thiocarbonate, to which the yellow colour of the solutions is probably due. This substance is slowly attacked by water in alkaline solution according to the equation

$$Na_2CS_3 + 3H_2O = Na_2CO_3 + 3H_2S$$

causing the odour which is observed on keeping viscose solutions. The addition of sodium sulphite prevents this change. Sodium thiocarbonate is decomposed rapidly by organic and mineral acids, *e.g.*

$$Na_2CS_3 + H_2SO_4 = Na_2SO_4 + CS_2 + H_2S.$$

Cellulose xanthate also gives carbon disulphide when decomposed by mineral acid, but the estimation of the total carbon disulphide formed on acidification of a viscose sample cannot, therefore, give an accurate measure of the cellulose xanthate present. G. de Wyss [1] accordingly acidifies with acetic acid till thiocarbonate is destroyed, extracts any carbon disulphide with ether, and then estimates the disulphide formed from xanthate on acidification with mineral acid. This procedure (p. 266) also eliminates carbon disulphide which may be formed during the ripening of viscose, thus—

$$\left(CS\begin{matrix}OC_6H_9O_4\\SNa\end{matrix}\right)_4 \rightarrow CS\begin{matrix}OC_{24}H_{39}O_{19}\\SNa\end{matrix} + 3CS_2 + 3NaOH.$$

Cellulose xanthate can also be separated as a white (usually slightly green) coagulum, by the cautious addition of brine. The product, however, is not very pure as it always adsorbs and retains alkaline by-products. The impurities can be decomposed by treatment with organic acids, which generally results in the production of sulphuretted hydrogen ; or by the action of sulphurous acid or sodium bisulphite, in which cases sodium thiosulphate is produced with bleaching of the solution. The xanthate is not seriously affected by these reagents.

Ripening and Coagulation of Viscose Solutions.—The changes taking place in a viscose solution were explained by Cross and Bevan as follows : The formula $CS\begin{matrix}OX\\SNa\end{matrix}$ having been

[1] G. de Wyss, *Ind. Eng. Chem.*, 1925, **17**, 1043.

established, the maximum degree of reaction may give $CS\begin{matrix}OC_6H_9O_4,\\SNa\end{matrix}$, but in reality, with a freshly prepared solution, X lies between a C_6 and a C_{12} unit cellulose and the compound cannot be precipitated by dehydrating agents. After one day X approaches a C_{12} unit, and at this point the compound can be precipitated by such reagents as alcohol or brine, and can be re-dissolved in water. After 6 to 12 days in alkaline solutions, X has become of C_{24} dimensions and the compound can be completely precipitated by acetic acid so that it has now become insoluble in water. "The cellulose when re-aggregated to these dimensions is not soluble as a sodium xanthate, but requires the further combination of its hydroxyl groups with the alkaline hydrate to produce a stable compound" ("Cellulose", London, 1916, p. 318). Finally aggregation increases until spontaneous coagulation takes place.

The more probable explanation is that the unripe viscose contains xanthate compounds which gradually decompose into cellulose. This remains suspended in the xanthate solutions. As ripening proceeds the proportion of cellulose to suspending agent increases, making coagulation less difficult until in the end spontaneous coagulation takes place.

The cellulose comes out as a stiff coagulum which takes the shape of the containing vessel. The clot on keeping shrinks away from the walls, until finally a tough mass of gelatinised cellulose containing 10 per cent. of cellulose and 90 per cent. of water is obtained.[1] If, however, the original solution was stronger than 10 per cent. the coagulum takes up water and expands.

The rate of coagulation is retarded by the presence of alkali in excess. Thus a viscose solution made to 7·8 per cent. NaOH could be kept for 19 days at 20°.

Coagulation is also retarded by low temperature. At 10° and under, coagulation may take 14 days, while between 10° and 20° it will take 6 to 10 days (C. F. Cross). C. Beadle observed the following with a viscose solution :—

Temperature	1·7°	8·3°	18·3°
Time before coagulation (days) .	40	25	6

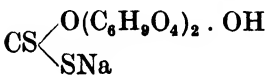
It is generally recognised that a rise of 5° doubles the speed at which viscose will ripen. A thin film on a glass plate coagulates in a few minutes if heated to 120°.

Apart from this spontaneous change there are three ways of effecting coagulation: (1) by the addition of salt solutions;

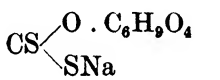
[1] C. Beadle, *J. Franklin Inst.*, 1894, **143**, 3.

(2) by changing the cellulose sodium xanthate into a less soluble compound such as the zinc or ammonium salt ; (3) by decomposition of the xanthate into cellulose by the action of mineral acid. The last is the only one employed for spinning purposes, but unless the viscose is sufficiently ripe (p. 268) the rate of coagulation, owing to the dispersed condition of freshly prepared xanthate, is too slow. Usual conditions for rayon manufacture are a ripening period of 96 hours at 17–20°, and coagulation by acid of concentration between 10 and 20 per cent. H_2SO_4.

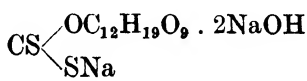
The complex changes taking place during ripening have been exhaustively studied. A typical systematic examination of them will be found in the work of Heuser and Schuster (*loc. cit.*). They concluded that the compound between cellulose and alkali metal hydroxides is of the type $(C_6H_{10}O_5)_2 . MOH$, so that the xanthate present at the beginning of the ripening process should be (I).



(I.)



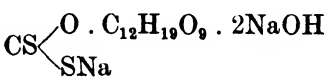
(II.)



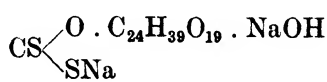
(III.)

They were not able to isolate the theoretical xanthate (II). Alkali cellulose when treated with excess of carbon disulphide for 7 hours gave a product (precipitated by 80 per cent. alcohol), which, on analysis, showed, Cellulose, 61·7 ; Na, 12·85 ; S, 12·17 per cent., giving a ratio $2C_6H_{10}O_5 : 3Na : 2S$, as in formula (III).

In another series the cellulose sodium xanthate was precipitated from viscose by alcohol. Determinations made at intervals up to the coagulation point showed that the ratio $Na : S : C_6H_{10}O_5$ varied between 3 : 2 : 2 and 2 : 2 : 4, corresponding to such formulæ as



3 : 2 : 2



2 : 2 : 4

Hours after Solution (at 4°) before Precipitation.	Cellulose per cent.	Na per cent.	S per cent.	Na : S : $C_6H_{10}O_5$.
12	81·9	4·3	11·4	1·05 : 1·95 : 3
26	83·5	3·3	9·2	0·84 : 1·65 : 3
36	90·9	3·0	—	0·94 : — : 4
50	91·5	3·0	8·9	0·92 : 1·96 : 4
61	92·1	3·1	8·2	0·96 : 1·80 : 4
106	94·6	2·32	5·6	1·08 : 1·80 : 6
112	96·1	1·19	4·22	0·80 : 2·20 : 10

A further series dealt with the "pure" alkali-free xanthate prepared by acidifying the viscose, during ripening, with dilute acetic acid and then precipitating with brine. Xanthates of the type $CS\langle^{O.Cellulose}_{SNa}$ were obtained and analysed. The results are given in the table on page 257.

Theoretical formulæ corresponding to these values are :—

$CS\langle^{O\,.\,C_{18}H_{29}O_{14}}_{SNa}$ 1 : 2 : 3 (Na, 4 ; S, 11 ; Cell. 83 per cent.)

$CS\langle^{O\,.\,C_{24}H_{39}O_{19}}_{SNa}$ 1 : 2 : 4 (Na, 3 ; S, 8·6 ; Cell. 87 per cent.)

$CS\langle^{O\,.\,C_{36}H_{59}O_{29}}_{SNa}$ 1 : 2 : 6 (Na, 2 ; S, 6 ; Cell., 91 per cent.)

$CS\langle^{O\,.\,C_{60}H_{99}O_{49}}_{SNa}$ 1 : 2 : 10 (Na, 1·3 ; S, 3·7 ; Cell., 94 per cent.)

The methods used in the analyses are given on p. 270.

Viscosity Changes during the Ripening of Viscose Solutions.—The changes taking place in the viscosity of a particular solution on standing are shown in Fig. 66.[1] The measurements were taken in a 2 per cent. solution. The viscosity at first falls rapidly, reaching a minimum in about 2 days. Then follows a steady increase from the third to the fifteenth day, after which a rapid increase takes place up to the coagulation point. The finer points of the viscosity-time curves are, however, best examined in a 7 per cent. solution.

The initial sharp decrease and the final increase are probably accounted for by particle size. The initial fall is due to the slowness with which the primary xanthate disperses. Long after the solution appears homogeneous this diminution in particle size continues. When the minimum is reached hydrolysis of the xanthate in the direction of cellulose, causes the viscosity slowly to increase. Finally, particle aggregation begins, with rapid rise in viscosity.

The actual viscosity of a particular viscose solution depends upon a number of factors :—

(*a*) The origin and pre-treatment of the cellulose employed. Generally speaking, cotton or pulp, after any treatment which causes a fall in its viscosity produces a viscose of a correspondingly lower viscosity.

(*b*) The age and treatment of the alkali cellulose. Viscose

[1] E. Heuser and M. Schuster, *Cellulosechem.*, 1926, 7, 45.

solutions which are formed by the addition of the carbon disulphide during, or immediately after, mercerisation have maximum viscosity. The viscosity falls markedly with the age of the alkali cellulose—*e.g.* a sample of viscose prepared from a one-day-old alkali-cellulose showed a minimum viscosity of 17, while a comparable viscose, prepared from the alkali cellulose after 6 days' storage, showed a minimum viscosity of 7·5. The same effect is obtained by gentle oxidation of the alkali cellulose—*e.g.* with air in the presence of catalysts, or with sodium peroxide.[1]

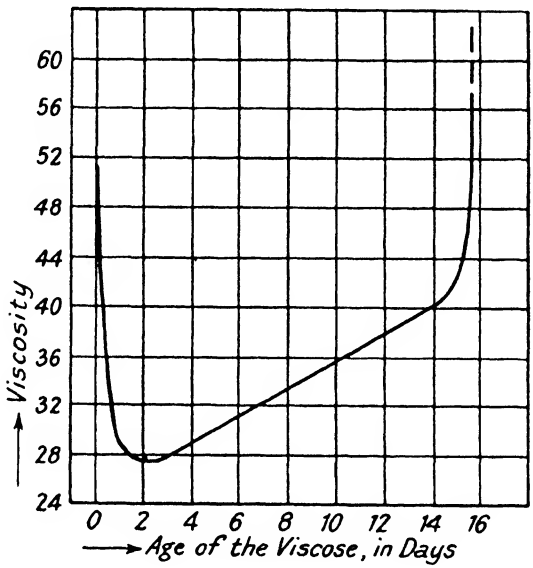


FIG. 66.—Viscosity changes during the ripening of viscose.
(*Heuser and Schuster.*)

(*c*) The age of the viscose solution. The change in viscosity on keeping viscose solutions has been mentioned. The rate of change is retarded by low temperature and by the presence of excess of alkali.

Experimental studies of the influence of these factors will be found in the papers of Ost, Westhoff and Gessner,[2] and Heuser and Schuster, from which quotations have been given. A study of the influence of variations in the method of preparation on the nature of the rayon fibres produced[3] shows that the mean degree of polymerisation decreases with increased time of ripening. Swelling of

[1] L. P. Wilson, *J. Soc. Chem. Ind.*, 1920, **39**, 177T.
[2] *Ann.*, 1911, **382**, 349.
[3] H. Schwarz and H. A. Wannow, *Kolloid-Z.*, 1942, **99**, 190.

the fibre is affected only by time of ripening, initially increasing and then decreasing with it. Ripening also is the factor dominating the orientation of the crystallites and the shape of the fibre cross-section.

EXPERIMENTAL

Examination of Sulphite Pulp for the Manufacture of Viscose.—This is fully described on pp. 479–483. As will be seen, information as to the suitability of a sample of pulp can be obtained by conversion to viscose under defined conditions and measurement of xanthate viscosity. A standard German method [1] was the following :—

5 g. of pulp are macerated with 25 ml. of 17·5 (vol. per cent.) NaOH at 20° and left for 1 hour. It is then removed to a special filter disk of the Buchner type with fine holes. The filter-funnel is fitted, with a bung, into the top of a measuring cylinder which has a side tube entering just above the topmost graduation. The cellulose mass is broken up without pressing and the alkali removed by suction, the filtrate being passed through a second time. The cake is pressed lightly at first and finally with strong pressure during 10 minutes. The volume of the filtrate which should be 11·5 to 12·5 ml. is noted. The cake is broken up, placed in the sulphiding flask and left closed for 22 hours at 30° and then at ordinary temperature for 5 minutes. After this 3·6 ml. (4·6 g.) of carbon disulphide are added over 4¾ hours at 15° with frequent shaking.

The excess of disulphide is then removed by suction through the side tube and a volume of 17·5 per cent. NaOH equal to that removed by filtration (with an additional 2 ml.) is added to the mass. The volume is brought to 120 ml. with water, and the flask shaken on the machine at 20–22° to complete solution.

The liquid is diluted to 500 ml. with cold water, making the solution 1 per cent. calculated on the cellulose present. Its viscosity is measured in an Ost-Ostwald viscometer at 15°.

$$\text{Xanthate viscosity} = \frac{\text{Exit-time of viscose (secs.)}}{\text{Exit-time of water (secs.)}}.$$

Examination of Alkali Cellulose *.—1. *Alkali as NaOH and* Na_2CO_3.—5 g. are digested with 50 ml. of water and the solution titrated with *N*-acid, first to phenolphthalein and then to methyl

[1] Faserstoff-Analysenkomm. des Vereins der Zellstoff und Papier-Chemiker u.s.w., *Papier Fabrik.*, 1936, **34**, 57.

* These methods are based partly on the work of E. Wheeler, " The Manufacture of Artificial Silk ", London, 1931.

orange. The usual works method is to add excess of standard sulphuric acid and to titrate back with alkali.

2. *The α-Cellulose.*—The residual cellulose from the above estimation is filtered off on a tared filter and washed with boiling water till free from sulphate, then dried at 105° to constant weight.

This is really α- and β-cellulose, and with most silk pulps if the total cellulose in the crumbs is 27·0 per cent. about 1·3 per cent. of this will be β-cellulose and 25·7 per cent. α-cellulose. The alkali cellulose " crumbs " ready for the sulphiding treatment should not weigh more than 225–235 g./litre and should contain—α-cellulose, 26–27 per cent.; NaOH, 15–16 per cent.; Na_2CO_3, 0·3–1 per cent.

Manufacture of Viscose.—The proportions employed on the works scale are somewhat as follows: Sulphite pulp 100 kg. + 1,600 litres NaOH (17–18 per cent.) pressed down to 325 kg. of alkali cellulose. This treated with 33 kg. of CS_2 gives 355 kg. of xanthate, which is dissolved in 720 kg. of NaOH (3 per cent.), giving 1,075 kg. of viscose solution containing 8 per cent. cellulose.

1. *Alkali Cellulose.*—The 100 kg. of pulp are steeped in the alkaline solution at ordinary temperature for 2 to 4 hours.

The soda cellulose is next pressed to 3 to 3·5 times the original weight of cellulose, *e.g.* to 300–350 kg., and kneaded in a water-jacketed machine which converts it into a crumb-like mass. This takes 2 to 3 hours at 18–22°. The crumbs are placed in covered bins and matured at 20–25° for 2 to 3 days.

2. *Formation of Cellulose Xanthate.*—325 kg. of alkali cellulose are placed in a water-cooled sulphide drum (Barratte) of about 1,200 litres capacity, which can be rotated two or three times per minute. Between 30 and 32 kg. of carbon disulphite (*i.e.* 1 mol. of CS_2 to 1·2 to 1·5 mol. of cellulose) are allowed to run in slowly. The reaction, which is exothermic, takes 2 to 4 hours, varying with the temperature, which should be kept below 30°. Churning must stop before the product commences to cake together in large masses.

3. *Mixing.*—The xanthate is now mixed with sufficient alkali and water to produce a viscose containing cellulose 7 to 8 per cent., NaOH 6·5 to 7 per cent. The process lasts 3 to 6 hours at room temperature.

4. *Ripening.*—The viscose is kept at 15–20° until ready for spinning.

Laboratory preparation of Viscose.—We have found the following method [1] very suitable: 37 g. of cotton wool with 558 ml. of 17·5 per cent. sodium hydroxide (*d*, 1·2) are kept at 20° for 1·5

[1] F. D. Snell, *Ind. Eng. Chem.*, 1925, **17**, 198; E. H. Morse, *ibid.*, 1926, **18**, 398.

hours in a stoppered bottle. The product is drained and pressed to weigh 160 g. It is then picked apart and kept in a stoppered bottle at 18° for 96 hours, after which it is placed in a closed rotating vessel and 30 ml. of carbon disulphide added over 2 hours. The colour should then be a deep orange yellow.

The product is brought into solution by the gradual addition of a mixture of 120 ml. of 4 per cent. NaOH with 25 ml. of 10 per cent. sodium sulphite, with mechanical stirring. More sodium hydroxide is added, if necessary, until the viscosity by the falling-sphere method gives a reading of 20 mm. in 30 seconds. The solution is then filtered through a fine filter cloth under 40 lb. per square inch, and left in a vacuum of 20 mm. for 3 to 4 hours to remove bubbles. It is kept in a closed bottle at 18° for 90 to 150 hours to age.

Marsh and Wood [1] recommend the following process: Air dry disintegrated sulphite pulp (30 g.) is treated, in a wide mouth 32 oz. bottle, with 450 ml. NaOH solution (*d*, 1·2). The mixture is shaken and left for 1·5 hours after which it is put into a cloth bag and centrifuged down to 105 g. Xanthation is done in the bottle, which is set on revolving rubber rollers, by adding 26 ml. of CS_2, about 5 ml. at a time, over 1 hour. After some 3 hours the orange crumbly mass begins to stick together. Excess disulphide is removed by suction, and the mass dissolved in dilute alkali and left to ripen.

The viscose thus prepared is spun, or made into film, at an ammonium chloride number of 8 to 10. For spinning 140 g. of the viscose solution, 6 ml. of NaOH solution (*d*, 1·315) and 50 ml. of water are mixed. The day before spinning when the ripening number is, say 15, the viscose is filtered through a pad made of a thin section of cotton wool between muslin. A pressure of 3 to 4 atmospheres is necessary. The liquid is received in glass bottles which are then evacuated to remove bubbles.

Spinning bath: 200 g. glucose in 600 ml. water with 280 g. sodium sulphate mixed with 200 g. sulphuric acid in 700 ml. water at 40–50°. Rate 100 ft. per min. at 30/40 lb./sq. inch. Thread collected on perforated bobbin from which it is twisted off after desulphurising with 50 g. sodium sulphide in 1·7 l. of water at 50–60°, washed, bleached and scoured in weak HCl.

U.S.P. 2,126,975/6, 1938, claims that by using a volatile organic liquid, *e.g.* acetone, which is miscible with CS_2 and aqueous NaOH, one-solution xanthation is achieved. Cellulose (100 pts. dry) is treated with alkali as usual and the CS_2 (35–40 pts.) mixed with acetone (5–20 per cent. of the weight of CS_2), added. After 4

[1] " Introduction to Cellulose Chemistry ", 1942.

hours at 15–20° the reaction is complete and the solution may be used for the preparation of rayon.

The following are examples of spinning baths for viscose rayon :—

1. Courtaulds and Wilson (E.P. 5595/1908). Sulphuric acid 8, ammonium sulphate 17·5, glucose 7·5, water and sodium sulphate 67 per cent.

2. Courtaulds and Napper (E.P. 406/1911). Sulphuric acid 8, glucose 10, sodium sulphate 12, zinc sulphate 1, water 69 per cent.

Lilienfeld rayon, which has a high tenacity, is formed by spinning viscose into a strongly acid bath, containing 50–85 per cent. of sulphuric acid alone, or at least 40 per cent. of sulphuric acid, together with the usual additions—metallic sulphates, glucose, glycerine, lactic acid, etc.

To prepare a film the viscose is spread uniformly on a glass plate and exposed for 2 minutes to a coagulant made up of glucose 10, sulphuric acid 10, zinc sulphate 1, sodium sulphate (anhyd.) 14, and water 65 per cent. Setting by means of salt or sal-ammoniac solutions, or by heat, followed in each case by acid treatment also gives good films with little precipitation of sulphur. Sulphur is removed by digesting with 1 per cent. sodium sulphide at 48–50°. The sheet is washed, bleached with dilute permanganate followed by sulphurous acid, washed and dried under tension.

Examination of Viscose for Rayon Manufacture

1. **Alkali as NaOH.**—3 g. are treated with 30 ml. of water and 10 ml. of N-H_2SO_4 slowly added. The mixture is warmed for 15 minutes with constant shaking, and the excess of acid neutralised with N-NaOH to methyl orange. The alkalinity is calculated as NaOH.

2. **Cellulose.**—4 g. of viscose are weighed on to a clean, flat glass plate and dried on the water bath. The viscose decomposes and forms a film, which is removed by soaking in saturated brine. The film is then steeped in dilute HCl to remove sulphur compounds, and, after washing, is dried at 100° and weighed as cellulose.

3. **Total Sulphur.**—The sulphur compounds in the viscose are oxidised to sulphate by digestion with sodium hypochlorite, hypobromite (p. 271), or permanganate and the sulphate estimated as barium sulphate. The benzidine method has also been used.

25 g. of viscose are diluted to 250 ml. and 25 ml. used for estimation. This volume is treated on the water bath for 2 or 3 hours with an excess of hypochlorite (about 7 per cent. available

chlorine) or hypobromite ; then acidified with HCl, the excess of chlorine (or bromine) boiled off and the sulphate precipitated as usual.

4. **Xanthate Soda.**—The percentage of sulphur existing in the viscose as xanthate may vary from 1·6 to 1·8 per cent. in a new viscose to 1·1 to 0·9 per cent. in a ripened viscose ready for spinning, while the total sulphur may be 2·2 to 2·5 per cent. C. F. Cross has proposed to express the sulphur in terms of cellulose-xanthate soda —*i.e.* the weight of sodium (calculated as NaOH) combined as xanthate with 100 g. of cellulose ; *e.g.* an analysis showed :—

Cellulose xanthate sulphur . . . 1·7 per cent.
Cellulose . . . . . 7·5 ,,

$$\text{Cellulose xanthate soda} = \frac{1{\cdot}7 \times 40 \times 100}{64 \times 7{\cdot}5} = 14{\cdot}5 \text{ per cent.}$$

As already mentioned, the reaction with iodine requires careful attention if accurate results are to be obtained. The following method suggested by Wheeler, gives satisfactory results : 50 g. of viscose are diluted to 500 ml. and 100 ml. of the solution are cooled to 0°. Purified carbon dioxide gas is passed through until the odour of sulphuretted hydrogen disappears (about 1 hour). The solution is then diluted to 200 ml., and to 100 ml. of this, in a stoppered bottle, are added 15 to 20 ml. of $N/10$ iodine and 25 ml. of 10 per cent. acetic acid and the mixture allowed to stand for 15 minutes. The excess of iodine is estimated by titration with thiosulphate. Vigorous shaking is necessary as the end-point approaches.

The second 100 ml. are treated with 150 ml. of saturated solution of sodium chloride, the precipitated xanthate filtered off and an aliquot portion of the filtrate treated with 5 ml. of $N/10$ iodine and 25 ml. of 10 per cent. acetic acid, and the excess of iodine estimated as before. The difference between the iodine used in the second process and that used in the first (calculated to equivalent volumes of solution), gives the amount of iodine reacting with cellulose xanthate to form the dithiocarbonate, from which the sulphur combined as xanthate can be found. This may be expressed as xanthate soda per 100 g. of cellulose as above.

Example.—The amount of $N/10$ iodine combining in the first stage was 16·56 ml. In the second stage the filtrate and washings were made to 500 ml., of which 100 ml. reacted with 1·27 ml. $N/10$ iodine. The total original volume therefore requires 6·35 ml. Hence iodine equivalent to xanthate is 16·56 — 6·35 = 10·21 ml. This represents 10·21 × 0·0032 × 2, or 0·06534 g. of combined

sulphur, since I_2 is equivalent to 2 molecules of xanthate containing 4 atoms of sulphur. This weight, allowing for dilutions, is contained in 5 g. of viscose, giving 1·307 per cent. of combined sulphur. The cellulose content was 7·1 per cent.

$$\text{The cellulose xanthate soda} = \frac{1{\cdot}307 \times 40 \times 100}{64 \times 7{\cdot}1}$$
$$= 11{\cdot}26 \text{ per cent.}$$

D'Ans and Jäger [1] have studied the different methods of carrying out the xanthate soda test in connection with ripening. They found that comparable results can be obtained with all of them provided certain modifications are employed. They compared especially the " Film " method of Cross and the " Flask " method of Jentgen. In the former the viscose is made into a film which is coagulated in brine containing acetic acid. The product is dissolved in alkali, acidified and titrated with iodine. In the latter one-half of a dilute viscose solution is treated in a closed bottle with acetic acid, so that the titration with iodine includes the sulphuretted hydrogen liberated. The other half is treated with mineral acid and titrated with iodine under the same conditions. The difference represents iodine consumed by the xanthate. The solution of viscose must be very dilute (1 g. in 6 l.) and acidification with acetic acid must not be greater than 0·02 to 0·05 per cent. free acid.

D'Ans and Jäger give the following instructions for the Film method of working : Viscose (2–3 g.) is weighed from a small flask on to a glass plate 9 × 12 cm. which is then covered with a second plate, using gentle pressure so as not to get too thin a film. The plates are separated slowly giving two films, which should be similar and free from defects. They are put into a dish with saturated salt solution at not above 15°. After 15 minutes the coagulated, nearly colourless films are lifted with the finger nail. No trace should remain. They are steeped in fresh salt solution, 4 or 5 times over 30 minutes, draining each time and pressing with the fingers. All yellow colour should have gone. They are then dissolved in 9 to 10 per cent. NaOH and the solution made up to 0·5 l. with water. This is neutralised to phenolphthalein by the addition of glacial acetic acid, with cooling, and 1 to 2 ml. of acid added in excess before titration with 0·1-*N* iodine.

Films of new viscose are difficult to remove from the glass. In that case acetic acid may be added to the first salt solution, but not more than sufficient to give 0·5 per cent. acetic acid.

[1] J. D'Ans and A. Jäger, *Cellulosechem.*, 1935, **16**, 22.

The Index Number is given by the relations

$$I = \frac{6 \times \text{per cent. Cell.}}{162{\cdot}1} \times \frac{\text{g. Viscose} \times 10^3}{100 \times \text{ml. Iodine}}$$

$$= 3{\cdot}702 \times \text{per cent. Cell.} \times \frac{\text{g. Viscose}}{\text{ml. Iodine}},$$

and the usual uncorrected percentage of xanthate alkali by

$$X = \frac{\text{ml. Iodine} \times 40{\cdot}01}{\text{g. Viscose} \times 100} \text{ and } I = 1{\cdot}481 \times \frac{\text{per cent. Cell.}}{X}.$$

The table below gives some results obtained by these modified methods. The viscose was prepared by sulphiding with 35 per cent. CS_2; cellulose 7 per cent.; NaOH, 7·1 per cent.

COMPARISON OF RIPENESS TESTS ON VISCOSE

Age of Viscose. Days.	Ripeness by		Index Figures.		
			Film.		Flask.
	AmCl.	NaCl.	Iodine.	Gravimetric.	
2	10·8	3·0	16·8	16·5	16·5
4	8·8	1·7	20·4	20·0	20·8
6	7·7	0·8	24·0	24·4	24·4

The xanthate may also be determined by estimating the carbon disulphide formed from it on acidification.[1] The methods, although somewhat laborious, have an interest for the research worker.

Procedure.—(*a*) *Removal of CS_2 arising from Thiocarbonate, etc.*—100 ml. of viscose solution diluted to about 1 per cent. cellulose are placed in a separating funnel, acidified (to litmus) with 10 per cent. acetic acid, and gently shaken. As soon as it is colourless the solution is shaken with 100 ml. of ether, the aqueous layer removed, and a further extraction given.

The aqueous layer is put into a 200 ml. flask, the ether solution being washed with 25 ml. of water and the wash water also added.

(*b*) *Estimation of CS_2 from the Cellulose Xanthate.*—The flask is connected through a ground-glass joint with an ascending condenser and a drop funnel. At the upper end of the condenser is a U-tube filled with pumice which has been saturated with copper sulphate solution and dried at 120°. During an experiment it is maintained at 75°, by heating in a water bath, to avoid retention of carbon

[1] G. de Wyss, *Ind. Eng. Chem.*, 1925, 17, 1043.

disulphide. This tube is connected with two U-tubes half filled with 5 per cent. alcoholic KOH, the last tube being connected to suction. 10 to 15 ml. of sulphuric acid (1 : 5) are added through the drop funnel and a slow current of air drawn through the apparatus.

After half an hour the contents of the flask are raised to boiling-point and maintained there for 1 hour to expel all the carbon disulphide set free. This is drawn over the copper sulphate (which retains sulphuretted hydrogen) into the potassium hydroxide. It is absorbed as potassium ethyl xanthate.

The contents of the U-tubes containing the potassium ethyl xanthate are washed out, neutralised with acetic acid, a little ice being used for cooling, after which the xanthate is precipitated as copper xanthate by addition of a 10 per cent. solution of copper sulphate. After 5 minutes the precipitate is filtered off on a Gooch crucible and washed with water. It is then decomposed, without removal, by treatment with 10 ml. of concentrated nitric acid, the filter washed with hot water, and the copper nitrate solution taken to dryness. The residue is dissolved in a little hot water, neutralised with sodium carbonate, and made slightly acid with acetic acid. After adding 1–2 g. of KI the copper is estimated as usual with 0·1*N*- thiosulphate solution. 1 ml. of thiosulphate represents 0·01283 g. of sulphur.

(*c*) *Estimation of the Sulphur present in the Forms of Xanthate, Thiocarbonate and Sulphide.*—By decomposing the viscose solution with mineral acid without previously treating it with acetic acid and ether, the total carbon disulphide sulphur is obtained. The difference between this and the xanthate carbon disulphide sulphur gives the thiocarbonate value. The sulphide sulphur can be determined by adding 25 ml. of the dilute viscose solution to an excess of 0·1*N*- potassium iodide-iodate solution previously acidified with sulphuric acid, and titrating the excess of iodine with thiosulphate solution. This sulphide sulphur represents the sulphur present as sulphide plus the amount of thiocarbonate sulphur set free as hydrogen sulphide :

$$Na_2CS_3 + H_2SO_4 = Na_2SO_4 + CS_2 + H_2S.$$

H. Jentgen determines the sulphide sulphur after diluting the viscose tenfold. 25 ml. of this are diluted with 2 l. of water in a large flask closed with a rubber stopper carrying a separating funnel. Through this 25 ml. of *N*- sulphuric acid are forced by excess pressure into the flask. The contents are shaken, and after 15 minutes an excess of *N*/10 iodine solution is added similarly through the funnel, and after thorough agitation the excess iodine is estimated as usual.

The results obtained by de Wyss showed that with viscose prepared with a sulphur-cellulose ratio approximately $S_2 : C_6H_{10}O_5$ the fall in xanthate sulphur was very rapid during the first 40 hours of ripening, being about half the total fall. With other samples made in the ratio 1 : 1 or 0·9 : 1 the fall was slower, reaching half value after 60 hours. The curves for xanthate sulphur closely followed those of the salt number determined by Hottenroth's method (below), which is known to give a good indication of the progress of ripening (*cf.* p. 266).

The rate of fall in xanthate sulphur was much reduced by keeping the samples at lower temperatures.

5. **Degree of Ripening.**—This is measured either by the determination of the "salt point", or by titration with ammonium chloride (Hottenroth), or with acetic acid. The ammonium chloride method is perhaps the more usual and effective. Complete experimental reviews of all these methods and their modifications have been given.[1]

(*a*) *The Salt Point.*—This is the percentage concentration of a sodium chloride solution which is just sufficient to coagulate 1 drop of viscose. A strong solution of sodium chloride may be made and gradually diluted down. 0·1 ml. of viscose is dropped into 20 ml. of the solution. The drop is rapidly mixed with the solution, after which examination is made to see whether the viscose has disappeared or has coagulated.

A new viscose has a salt point of about 13 and a ripened one, ready for spinning, of 6 to 3.

(*b*) *Degree of Ripening by Titration with Ammonium Chloride Solution.*—20 g. of viscose solution diluted with 30 ml. of water are titrated with 10 per cent. ammonium chloride solution, with shaking, until coagulation sets in. The following are results obtained by this method compared with those obtained by titrating with 5 per cent. acetic acid :—

After Days.	State.	Acetic Acid. ml.	Amm. Chloride. ml.
1	Unripe	26·5	13·1
3	Nearly ripe	22·8	11·2
5	Ripe	18·2	9·6 (optimum)
7	Ripe	11·5	7·8
9	Over-ripe	8·5	5·2
12	Coagulated	—	—

[1] J. D'Ans and A. Jäger, *Cellulosechem.*, 1935, **16**, 22 ; *Kunstseide*, 1926, **8**, 17, 57, 110.

A viscose ready for spinning should take 6 to 8 ml. of ammonium chloride (Wheeler).

6. **The Viscosity of Viscose.**—This may conveniently be determined by the falling-sphere viscometer.

For technical control the viscosity is taken, first of a sample after mixing, and again of one from the spinning tank at an age of about 72 hours. Two methods are in use : (*a*) A ball-bearing $\frac{1}{8}$ in. in diameter is allowed to fall through a column of viscose 20 to 25 cm. deep and the time of fall observed. This will be, at the time of spinning—say, 18 to 33 seconds, according to the type of viscose

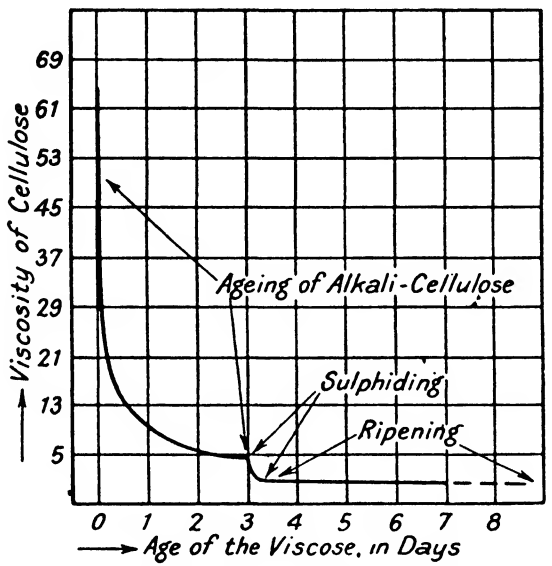


FIG. 67.—Changes in the viscosity of the cellulose during the stages of the viscose process. (*Heuser and Schuster, Cellulosechem*, 1926, 7, 45.)

prepared. (*b*) The time taken for the viscose to flow out through a standard orifice is compared with the time taken by an equal volume of pure glycerin at the same temperature. The viscosity of the viscose at spinning will be between 1·7 and 3·3 times that of the glycerin, dependent on whether low or high viscosity viscose is being spun. With Lilienfeld viscose the value may be twelve times that of the glycerin.

The experimental study of the ripening of viscose would include :

The effect of variations in preparation and pre-treatment on the properties of the solution.

Determination of alkali (NaOH) free and combined, sulphur as xanthate, as thiocarbonate, and other sulphur ; variations taking place in the content of these compounds during ripening.

Examination of the cellulose obtained by precipitation at various times during preparation and ripening, its α-cellulose content and viscosity.

Measurement of viscosity of the viscose and its coagulation point, etc., at different times.

The influence of various changes in the preparation and ageing of the viscose on such measurable characters. Pre-treatment of cellulose measured by copper number or viscosity ; influence of the concentration of the alkali and its ratio to cellulose ; temperature of formation of alkali cellulose, its age, etc. The proportion of carbon disulphide required, etc.

The work of Heuser and Schuster (1926), de Wyss (1925), and Ost (1911) involved a number of these determinations, and the

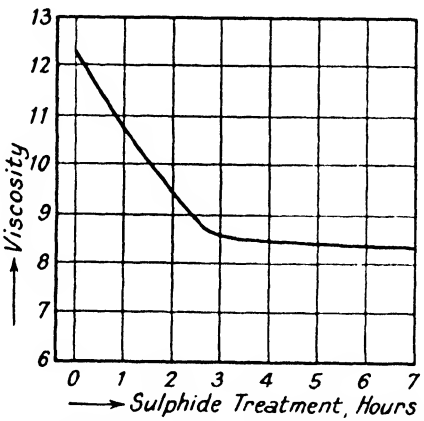


FIG. 68.—Changes in the viscosity of the cellulose during the 7-hour sulphiding treatment.
(*Heuser and Schuster, loc. cit.*)

general results are given in the introduction to this chapter. As a further example, Fig. 67 shows the general course of the degradation of the cellulose, as measured by its viscosity in cuprammonium, during the ripening of the alkali cellulose (3 days), during reaction with carbon disulphide (7 hours), and during subsequent ripening of the viscose up to the eighth day. Fig. 68 shows on an enlarged scale the 7-hour sulphiding period.

Experimental Study of the Ripening Process.—The methods used by Heuser and Schuster (1926) in their investigations on the ripening of viscose were as follows :—

1. *Isolation of Anhydrous Sodium Cellulose Xanthate.*—20 g. of cotton linters were treated with 200 ml. of 17·8 per cent. NaOH, and after 1 hour pressed to weigh 60 g. The mass was kept in a closed flask for 3 days, after which 10 ml. of carbon disulphide

were added. After 7 hours the mass was dissolved in 250 ml. of *N*-NaOH. The solution was clear and free from fibre. It was kept in a thermostat at 15°, and samples of 40 g. were precipitated at intervals by running them, in a thin stream, into alcohol. The product was reduced to powder and ground repeatedly with alcohol, washed with ether, and dried in a vacuum.

The alkali-free cellulose sodium xanthate was isolated by acidifying slightly with acetic acid and precipitating by saturated salt solution.

2. *Estimation of Cellulose.*—0·5 g. in 150 ml. of water or dilute alkali was acidified with HCl and warmed. The washed cellulose precipitate was dried with alcohol and at 105°.

3. *Estimation of Sodium.*—0·2 to 0·3 g. was ashed, the residue treated with sulphuric acid and weighed as sodium sulphate.

4. *Estimation of Sulphur.*—The following method was found as accurate as the Carius method: 0·3 to 0·5 g. was dissolved in 100 ml. of 4 per cent. NaOH free from sulphate, excess of bromine water added, and the mixture warmed. On acidifying with dilute HCl oxidation sets in and the liquid boils. The boiling was maintained until all bromine was removed. The sulphuric acid was precipitated, as usual, with barium chloride.

A recent method [1] employs a mixture of aqua regia and perchloric acid as the oxidising agent for semi-micro-quantities (2–6 mg. of sulphur). The sulphate ion is titrated with barium chloride solution, using tetrahydroxybenzoquinone as indicator.

5. The viscosity of the cellulose was measured in 2 per cent. solution in cuprammonium. That of the viscose in 2 per cent. solution, using the Ostwald viscometer.

[1] J. H. Jones, *J. Assoc. Off. Agric. Chem.*, 1943, **26**, 182.

CHAPTER XV

CELLULOSE ACETATE

PART I

Methods of Preparation

THE action of acetic anhydride on cellulose should theoretically yield a triacetate $C_6H_7O_2(O.COCH_3)_3$. On this basis 100 parts of air-dry cellulose would react with 188 parts of acetic anhydride : in practice, 250 to 400 parts are employed. The products frequently show the theoretical composition of mono- or di-acetates of cellulose, or of mixtures of these with the triacetate, but, in all probability, the triacetate is first formed, and this is subsequently hydrolysed to products of lower acetyl content (secondary acetates). A characteristic property of the secondary acetates is their solubility in acetone. The optical rotation of the acetone-soluble products is of the order of $[\alpha]_D$ —21°, whilst acetates soluble only in chloroform or tetrachloroethane have $[\alpha]_D$ about —20° in these solvents, and —50° in pyridine. The acetic acid content of the acetone-soluble products is not definite. Those prepared by Miles' process (below) give acetic acid varying between 51 and 58 per cent. A diacetate of cellulose would give 48·8 and a triacetate 62·5 per cent. After purification by repeated solution in benzene-alcohol (1 : 1), in which the products are easily soluble at 60°, their acetic acid content becomes 51 to 54. This might represent a mixture of 80 parts of diacetate with 20 parts of triacetate, but explanations based on such molecular conceptions are no longer tenable.

The results of X-ray analysis seem to require that only the triacetate actually exists. The acetone-soluble or dispersible product used for the production of acetate rayon (acetic acid 55–58 per cent.) would, on that basis, consist of a mixture of 88 to 92·5 per cent. of triacetate with 12 to 7·5 per cent. of cellulose.[1] There is a good deal of concurrent evidence in support of this possibility in connection with the dispersion of cellulose in xanthate-water and cuprammonium solutions.

The presence of acetic acid and water has a great deal to do with the property of dispersion in acetone. The triacetate disperses in chloroform, and merely swells in acetone, but the partially hydrolysed

[1] *Cf.* I. Sakurada, *J. Soc. Chem. Ind.*, Japan, 1938, **41**, 383B.

product (secondary acetate), which contains water, acetic acid and, on the above hypothesis, cellulose, disperses readily in acetone, but only swells in chloroform. The gradual addition of water to the acetone dispersion causes a decrease, and then an increase, in viscosity up to the point where coagulation takes place.

It appears, then, that the triacetate can adsorb acetone only to the extent of causing swelling, but in the presence of some 10 per cent. of reverted cellulose, water and acetic acid, the adsorption for acetone increases, so that dispersion takes place. With chloroform the effect is the opposite. The water may increase the viscosity by increasing the envelope water content.

As a general rule, solubility in chloroform begins when about two-thirds of the hydroxyl groupings have been acetylated and it increases rapidly. Many attempts have been made to modify the solubility of cellulose acetate by after treatment. Thus solutions of salts, such as $CaCl_2$, which cause swelling, have been used (U.S.P. 1,998,267). Solubility in methylene chloride (but not in acetone) has been achieved by heating with various alcohols (B.P. 443,564) and, by digesting the triacetate with nitric or perchloric acid at 30°, acetates of 58·5 per cent. acetic acid content can be obtained, which are soluble in acetone and nearly so in chloroform.[1]

I. Industrial Preparation of Cellulose Acetate

The first stage in the acetylation process results in the production of an acetate soluble in chloroform, but insoluble in acetone (primary acetate). Following a "ripening" period, secondary acetates, soluble in acetone and similar solvents, are obtained. Catalysts are invariably employed, chiefly dehydrating agents, such as sulphuric acid, phosphoric acid, zinc chloride, the chlorides and oxychlorides of sulphur and phosphorus, dimethyl sulphate, chloracetic acid and others. Sulphuric acid, owing to its action in degrading the cellulose and in forming sulpho-acetates which are difficult to remove, sometimes gives rise to inferior products. These form dark solutions and brittle films which do not last well. The others frequently give acetates whose solutions are either coloured, or not brilliantly clear. Sulphuryl chloride, however,[2] is satisfactory in these respects, and even better results are claimed by the use, separately, of small quantities of chlorine and sulphur dioxide roughly in molecular ratio.[3] A variety of colourless esters can be

[1] I. Sakurada, *J. Soc. Chem. Ind.*, Japan, 1938, **41**, 381.
[2] Chem. Fabrik. von Heyden, Eng. Pat. 24,382 of 1910.
[3] W. L. Barnett, *J. Soc. Chem. Ind.*, 1921, **40**, 8T.

prepared with valuable properties of strength, film flexibility and solubility (see below). The acetic acid content required for plastics is usually 50–53; for acetate rayon 53–55, and for acetate films 55–58 per cent.

The preparation involves five stages:

(*a*) Acetylation of air-dry cellulose by acetic anhydride and acetic acid in the presence of sulphuric acid or other catalyst.

(*b*) Addition of water and acetic acid to produce hydrolysis, precipitation of the acetate being avoided.

(*c*) A ripening period at a fixed temperature. This conditions the physical properties of the final product.

(*d*) The addition of a large excess of cold water, which precipitates the product in white flakes.

(*e*) Washing, centrifuging and drying at 20–30°.

The following are typical examples of technical patented methods of preparation, purified cotton linters or wood pulp cellulose being employed:—

1. **G. W. Miles' Patent** (B.P. 19,330, 1905).—(i)—*The Acetylation.*—100 g. of dry cellulose, moisture about 5 per cent., are treated (below 40°) with a mixture of 270–310 g. acetic anhydride; 390–410 g. glacial acetic acid; 3–9 ml. concentrated sulphuric acid, the temperature (controlled by cooling) being allowed to rise to 50°. The cellulose is converted into an opaque, pasty mass. When the temperature begins to fall (end of the exothermic reaction), the mass is warmed to 50–55° and kept there for 36 to 40 hours, or until the mass is more or less transparent and less viscous, the colour being light brown. A test portion, precipitated by water, washed to neutrality and dried, should be insoluble in absolute acetone, but completely soluble in alcohol-free chloroform.

(ii) *The Ripening Process.*—60 ml. of glacial acetic acid are diluted with 60 ml. of water and the mixture added slowly to the cellulose acetate with vigorous stirring to avoid precipitation. The whole is kept at 40–50° for 12 to 16 hours, or until a test precipitate, after washing and drying, is entirely soluble in acetone, but only plastic in warm chloroform. The bulk is then poured into cold water, the precipitate washed to neutrality and dried at 35–40°, yielding 130 to 145 g. of partially hydrated cellulose acetate.

The white fibrous mass is insoluble in water, ethyl and amyl alcohol, amyl acetate, carbon tetrachloride, benzene and petroleum ether, but becomes plastic in hot chloroform, and in glycerol at 125°. It is readily soluble in acetone, tetrachloroethane, and chloroform containing alcohols, less soluble in pyridine, ethyl acetate and

nitrobenzene ; soluble with difficulty in formic and acetic acids. It dissolves in hot 70 per cent. aqueous ethyl alcohol, gelatinising on cooling. It is soluble also on heating in a mixture of ethyl alcohol and benzene, coming out on cooling.

2. **H. Dreyfus's Patent** (Fr. Pat. 478,023, 1914).—100 g. cellulose (cotton or paper), air-dry, are stirred into a bath composed of glacial acetic acid, 300–400 g. ; acetic anhydride, 250 g. ; sulphuric acid, 10–15 g., cooled to 0°. The temperature rises to 5–15° and later falls to 5–10°. The cooling is then stopped and the temperature allowed to rise to 15–20°, after which the cooling is continued, the mass being stirred as the temperature falls. The product is kept standing till all fibres have disappeared and water is added to promote hydrolysis. The product should have a high viscosity.

These methods of acetylation still remain substantially unchanged. Developments include the pre-treatment of the cellulose material to change its reactivity and viscosity, and improved methods of purification, stabilisation, etc., including the use of liquid ammonia. The trend of these advances may be seen from the following abstracts :—

Cellulose, Pre-treatment of (H. Dreyfus, B.P. 312,098).—The reactivity of cellulosic materials is increased by pre-treatment with the halogen acids, or mixtures thereof, or with these acids in combination with organic acids such as acetic acid.

Cellulose Esters of Higher Fatty Acids, Manufacture of (H. Dreyfus, B.P. 311,790).—Cellulose acetates and cellulose esters of higher homologues, or mixed cellulose esters thereof, are prepared by subjecting cellulosic materials to a pre-treatment with organic acids, particularly lower fatty acids, such as formic or acetic acids, and then to esterification by means of fatty acid anhydrides, particularly acetic anhydride in presence of one or more chlorides or other halides of antimony, arsenic, or phosphorus, or mixtures thereof, with or without halogen acids, or mixtures thereof.

Acetylation of Cellulose (S. A. Ogden, B.P. 310,563).—Cellulosic material is partly acetylated by treating it (either dry or while wet with a trace of sulphuric acid), with acetic acid and then heating the product until dry. The partly acetylated product can be treated in known manner with acetic anhydride, until it is completely acetylated, or until the desired degree is obtained.

Cellulose Acetate, Manufacture of (H. Dreyfus, U.S. P. 1,711,111). —The cellulosic materials are first penetrated by acetic vapours and then acetylated in the presence of under 3 per cent. (on the cellulose) of condensing agent, and in the presence of six times its weight of acetic acid, the acetylation being effected in benzene suspension.

Cellulose Esters of Higher Fatty Acids (H. Dreyfus, B.P. 312,095), —Cellulose acetates and esters of higher homologues of acetic acid or mixed esters thereof, are prepared by subjecting cellulosic materials to a pre-treatment with organic acids, particularly formic or acetic acids, and then to esterification by means of acid anhydrides, e.g. acetic anhydride, in presence of ferric chloride or bromide or a mixture thereof, the ferric halide being preferably in proportions of 10–30 per cent. of the weight of cellulose. Also zinc chloride or zinc halide in association with halide acid, each in amount not less than 2 per cent. on the weight of cellulose, and preferably 5 to 20 per cent. is used (B.P. 308,322).

Preparation of Cellulose Acetate (H. L. Barthelemy, B.P. 305,096, 1929).—Cellulosic material is first submitted to direct oxidation, *e.g.* by alkali or hydrogen peroxides, persalts in the presence of moderating agents, *e.g.* alkali carbonates, silicates, soaps, or sulphoricinates, and afterwards to a softening treatment with at least 50 per cent. of its weight of hot vapours of acetic acid containing a small amount of halogen. The acetylation is then carried out in four stages, and finally the ester is partly saponified and the sulphuric esters decomposed by adding aqueous formic or acetic acid. The esters have low viscosity, high plasticity and tensile strength, with good elasticity and keeping properties.

Treatment of Cellulosic Materials for the Production of Cellulose Esters (B.P. 332,607–8, 1929).—Purified cellulose is more easily esterified if treated first with acetic anhydride, either alone or mixed with a liquid hydrocarbon, or with the same mixture in the vapour form, and secondly with an organic acid with or without anhydride, *e.g.* acetic acid and acetic anhydride; alternatively cellulose is treated first with one or more organic acids (*e.g.* formic or acetic), alone, or mixed with inert diluents, and then with one or more organic anhydrides, without or with organic acids, with a condensing agent if required.

Velocity of Acetylation with different Forms of Cellulose.—Using acetic anhydride with toluene and 0·5 per cent. perchloric acid as catalyst, the velocity of acetylation diminishes with the material used in the order viscose rayon, cotton, sulphite pulp, cuprammonium rayon. Soaking in acetic acid modifies the surface layer of viscose rayon and makes it more reactive than the others.[1]

Use of Liquid Ammonia in the Preparation of Cellulose Esters and Ethers.—This reagent is used both to prepare a reactive dry alkali cellulose and to ensure " stabilisation " of the product by removing traces of the acid catalyst employed. U.S.P. 2,123,806 claims that

[1] Z. Rogvin, *J. Appl. Chem. Russ.*, 1939, **12**, 1870.

an alkali cellulose with the alkali dispersed almost in molecular form can be obtained by soaking linters in 20 to 40 per cent. NaOH for 1 hour, squeezing down till the mass is 4·7 times the weight of the linters and treating with liquid ammonia and sodium till all water is removed. The mass is then covered with toluol and warmed to remove ammonia. It esterifies with great smoothness, *e.g.* by action at 20° of an organic halide or anhydride, the temperature, finally, being raised to below 120° (see also U.S.P. 2,232,926-7 ; 25/2/41).

Cellulose triacetate containing diacetate is stabilised by adding it to liquid ammonia at not higher than —33°. After 2 hours the diacetate is dissolved and the insoluble triacetate contains less than 0·02 per cent. of H_2SO_4 and does not discolour at 200°. Cellulose acetate-butyrate, stearate and saturated fatty acid esters are mainly insoluble in liquid ammonia, and can be treated in the same way (U.S.P. 2,139,661–4).

Use of diminished Pressure as a Control in Esterification (U.S.P. 2,136,030 ; 8/11/38).—Cellulose is treated with sufficient liquid, *e.g.* acetic acid, to dissolve the ester produced and enough fatty anhydride (*e.g.* Ac_2O) for complete esterification. Temperature required is controlled by reducing pressure to correspond with the vapour pressure of the constituent of lowest b.p. at that temperature, *e.g.* for acetate 38° is used and maintained by keeping the pressure at about 35 mm. A reflux is inserted between reaction vessel and pump.

3. **Use of Liquid Sulphur Dioxide** (B.P. 301,036, 306,531).—The acetylation is performed in liquid sulphur dioxide, temperature being controlled by manipulation of the pressure. The sulphur dioxide is allowed to boil away and its recovery, together with that of the acetic acid, is easy.

4. **Keten,** CH_2:CO has been used for the preparation of cellulose acetate. Cellulose, preferably activated, is either moistened with an inert solvent, *e.g.* toluene, containing a trace of catalyst, *e.g.* $ZnCl_2$, H_2SO_4, or with acetic acid, or anhydride. The mass is then exposed to keten gas, which may be under pressure (B.P. 237,573 ; 237,591). Substituted ketens, especially of high molecular weight, have been used to give a waterproof finish to yarns and rayon. The material is steeped in a benzene solution of the keten and heated to 110° (B.P. 522,033 ; 522,204).

5. **Refining of Cellulose Derivatives.**—Coloration can be removed by treating the powdered or fibrous ester with dilute hydrogen peroxide and drying without washing (U.S.P. 2,135,980). Ethers are dissolved in alcohol or alkyl esters and treated with

NaOCl to remove colour and improve stability (U.S.P. 2,138,757 ; 29/11/38). To bleach with a minimum of degradation to produce haze-free films, the ether, in a slurry of 1–7·5 per cent., is treated at 40–80° with hypochlorite (1–5 per cent. available chlorine on the ether) at *p*H 9–11·8 for 30–50 minutes. At this *p*H chlorination is not likely and bleaching is rapid (U.S.P. 2,238,912 ; 22/4/41).

II. Laboratory Methods of Preparation

A series of examples illustrative of different methods of working will be found in the following pages. Some of the authors claim the production of acetates of definite composition corresponding to di- and tri-acetates. To retain the fibrous structure a non-solvent such as benzene must be present. The use of perchloric acid as a catalyst will be found convenient (No. 5).

1. **Preparation of Triacetyl Cellulose with Acetic Anhydride in the presence of Sulphuric Acid.**[1]—(*a*) *With the Fibrous Structure Retained* (Ger. Pat. 184,201).—Bleached ramie fibres are suitable. 10 g. are moistened with water to a content of about 30 per cent. The moist fibre is mixed with a solution of 60 g. of acetic anhydride in 180 g. of benzene to which 1·5 g. of H_2SO_4 is added, and the whole warmed at 75° until, after about 8 hours, a chloroform-soluble product is obtained. The fibres are pressed, washed with benzene and with alcohol, and dried. Yield, 17·6 g. The fibres are white and strong.

The product yields 62·5 per cent. acetic acid. $[\alpha]_D$ in chloroform, −22° ; in pyridine-acetone (4:1), −29·6°. M. wt. in glacial acetic acid, 280.

(*b*) *With Loss of Fibrous Structure, similar to Miles' Patent* (Ger. Pat. 252,706, 1905).—20 g. of cotton wool are warmed at 30° for 6 to 7 hours in a mixture of 75 ml. of glacial acetic acid, 2 ml. concentrated sulphuric acid, and 75 ml. of acetic anhydride, when complete solution should take place. The liquid is centrifuged after diluting, if necessary, with acetic acid and allowed to flow into ice-water, which is vigorously stirred. After 24 hours the solid is removed, washed free from acid and dried.

2. **Preparation of Triacetyl Cellulose with Acetic Anhydride in the Presence of Zinc Chloride.**[2]—10 g. of cellulose are mixed with a hot solution of 20 g. of zinc chloride in 40 ml. of glacial

[1] Examples (1) to (4) are by K. Hess *et al.*, "Die Zellulose," Leipzig, 1928.

[2] H. Ost, *Zeit. angew. Chem.*, 1919, **32**, 68 ; K. Hess and G. Schultze, *Ann.*, 1927, **455**, 91.

acetic acid and thoroughly kneaded. 40 ml. of acetic anhydride are added and the temperature kept at 30°. After 36 hours the commencement of acetylation is recognisable by swelling, and after 2 days structure disappears and the mixture forms a stiff paste. It is allowed to stand 10 to 12 days to complete the reaction.

The mass is taken up in 200 ml. of glacial acetic acid, the solution warmed to 30°, and well shaken. The acetyl cellulose is precipitated by water, washed and dried. Yield, 16·8 g.

3. **Preparation of Triacetyl Cellulose by Means of Acetic Anhydride in the Presence of Chlorine and Sulphur Dioxide.**—This method, due to Barnett, is described on p. 280. The product was obtained in quantitative yield. Its properties are given in the table below.

PROPERTIES OF TRIACETYL CELLULOSE PREPARED BY THE FOREGOING METHODS[1]

Mode of Preparation.	$[\alpha]_D$ Chloroform.	$[\alpha]_D$ Pyridine-Acetone (4 : 1).	Nature of Solution in Chloroform 2 per cent.	Films formed.
1. Fibre structure retained —use of benzene . .	−22·06	−29·61	viscous	Good elasticity
2. With $ZnCl_2$ . .	−22·62	−28·32	viscous	,, ,,
3. With chlorine and sulphur dioxide . .	−22·6	−28·3	viscous	,, ,,
4. With acetyl chloride. (Cellulose acetate A, p. 283) . . .	−19·5	−28·38	Fluid	Brittle

4. **Preparation of Tri-acetyl Cellulose by Means of Acetic Anhydride in the Presence of Pyridine.**[2]—Methods employing acidic and similar catalysts involve the possibility of hydrolysis of the cellulose during acetylation. With the following technique this possibility is reduced to a minimum, and a triacetate is obtained which differs from others in its insolubility in the usual solvents.

One part of cellulose is steeped in sodium hydroxide solution. In the case of viscose or cuprammonium rayons in 2*N*-NaOH for 30 minutes; in that of linters or pulp in 4*N*-NaOH for 1 hour. The material is then washed free from alkali and the water displaced by steeping in pyridine, the pyridine being changed from time to time. The mass is pressed and treated with 10 parts of acetic anhydride

[1] K. Hess *et al.*, *Ann.*, 1927, **455**, 91.
[2] K. Hess and N. Ljubitsch, *Ber.*, 1928, **61**, 1460.

and 16 parts of pyridine. The whole is shaken for a day, and then heated at 40–45° for a number of days which varies with the nature of the original cellulose. The products obtained after treatment for 5 days contained 40 to 50 per cent. of acetic acid. The theoretical value of 62·5 was reached with the products obtained from viscose rayon after 30 days. Linters required 43 and pulp 52 days.

The products are insoluble, but swell, in chloroform and pyridine.

5. **Preparation of Cellulose Acetates with Perchloric Acid as Catalyst.**[1]—This acid has advantages over sulphuric acid in that very small quantities are needed and it is not retained by the product. A triacetate is formed in 1 day by treating linters (5 g.) with a mixture of acetic acid (20 ml.) and anhydride (20 ml.) containing 15 mg. of $HClO_4$. A fibrous triacetate is formed (Boehringer, B.P. 387,533) by steeping linters (10 parts) in glacial acetic acid (100 parts) for 4 hours, squeezing and then treating with a mixture of acetic anhydride, 38 parts; SO_2, 38 parts; $HClO_4$ 0·05 part, and toluene 54 parts for 10 hours.

Acetates prepared with perchloric acid, however, give very brittle films. Flexibility is improved by pre-treatment of the cellulose with 15 per cent. H_2SO_4 in 60 per cent. acetic acid for 4 hours at 20°. By using a mixed catalyst (5 per cent. H_2SO_4 + 0·1 per cent. $HClO_4$) for 4 hours at 35° with 30 per cent. acetic anhydride in toluene the flexibility of the films is as good as when the catalyst consists of H_2SO_4 (13 per cent.) alone.[2]

Perchloric acid gives acetates of high clarity if added to the esterification product (H_2SO_4 catalyst) shortly before completion of the reaction or during hydrolysis (B.P. 521,884; 1938).

6. **Preparation of Cellulose Diacetate and Triacetate by the use of Chlorine and Sulphur Dioxide as the Catalytic Agent** (W. L. Barnett).[3]—The nature of the product can be varied according to the conditions of acetylation. With temperature below 65° and only a trace of sulphur dioxide, the composition of the product is that of a diacetate. If the ratio of Cl_2/SO_2 is approximately unity (the best condition), a triacetate results.

1. *Preparation of a Diacetate.*—200 g. of acetic acid just coloured with chlorine gas are added to 50 g. of filter paper, and, after some time, 250 g. of acetic anhydride are poured on, followed by the passage of a few bubbles of sulphur dioxide. The temperature is kept down to a maximum of 65° by cooling. In 1 hour a clear solu-

[1] Kreuger and Tschirch, *Ber.*, 1931, **64**, 1874.
[2] Z. Rogovin *et al.*, *J. Appl. Chem. Russ.*, 1940, **13**, 255.
[3] W. L. Barnett, *J. Soc. Chem. Ind.*, 1921, **40**, 8; also J. C. Irvine and E. L. Hirst, *Chem. Soc. Trans.*, 1922, **121**, 1585.

tion results. After standing overnight the jelly is diluted with acetic acid; chloroform is added, and the mixture treated with excess of water. When the volatile solvent is distilled off the acetate is gradually precipitated by the rising of the globules of chloroform through the water. Each globule becomes coated with a film of precipitated acetate. On stirring these are disintegrated, and the ester obtained as a fine powder which is washed free from acid. It can be dried at 100° for several days without change of colour.

The acetate is a white powder soluble in acetone, chloroform, pyridine, nitro-benzene (hot), aniline and benzene-alcohol mixture (slightly). Acetic acid yield, 48·8 per cent.

2. *Preparation of a Triacetate.*—5 g. of cellulose are immersed in 20 ml. of glacial acetic acid and 20 ml. of acetic anhydride containing 0·32 g. of chlorine are added, followed by 2 ml. of acetic anhydride containing 0·26 g. of sulphur dioxide. Solution is complete in less than 5 minutes. After stirring further for 5 minutes 20 ml. of chloroform are added and the ester separated as above. Acetic acid yield, 62·4 per cent. Yield quantitative, 178 per cent. (see also pp. 198, 279).

One-fifth of the above weights of catalysts can be used, giving solution in 10 to 20 minutes.

7. **Preparation of Acetone Soluble Primary Acetates** (V. E. Yarsley).—This author, in a study of the acetylation reaction,[1] made the following observations :—

1. Primary acetates soluble in acetone and capable of being filtered, can be prepared if the following conditions are observed :—

(*a*) The temperature during the first hour should not exceed 25°, after which it is kept at 25–30° until the process is finished.

(*b*) Between 10 and 15 per cent. of concentrated sulphuric acid must be used. The author found that this did not cause degradation of the cellulose, but it readily combined if the initial temperature was too high. It is necessary to use 3 parts of acetic anhydride to 1 part of cellulose. The anhydride does not influence the reaction as a diluent, the progress of the reaction depending rather on the efficiency of the mixing.

2. The viscosity of the primary acetate is high, but not uniform. On standing coagulation takes place, the time varying from 1 to 200 days.

3. The primary acetates are useless for the preparation of rayon, but they give clear, tough films.

[1] V. E. Yarsley, "Über die Herstellung und physikalishen Eigenschaften der Celluloseacetate": Berlin, J. Springer, 1927.

4. Solutions of primary acetates, taken to dryness, give in many cases a residue no longer completely soluble in acetone.

5. Secondary acetates are obtained by hydrolysis of the primaries with 95 per cent. acetic acid at 70°, or, if done immediately after acetylation, temperatures of 40–50° suffice.

6. Secondary acetates of acetic acid content 55 to 58 per cent. are miscible with acetone in all proportions. Their viscosity is lower than that of the primary acetates.

7. The most satisfactory secondary products are obtained from primary products which are difficultly soluble in acetone.

The details of these preparations are as follows :—

1. *Preparation of Primary Acetate.*—The proportions found best are given in Table I, catalyst sulphuric acid viz. 1 part cellulose, 5 parts acetic acid, and 3 parts acetic anhydride. In general, the mixture was cooled below 5° and the cotton gradually introduced, after which the temperature was kept below 20–25°. Stirring was continued until the cotton dissolved, when the mixture was allowed to stand. The acetate was precipitated by pouring into water. It was washed and dried in the air, but not completely, otherwise it becomes difficult to dissolve in acetone. These acetates are more readily soluble in moist acetone than in the pure solvent. They are soluble in warm glacial acetic acid, but hardly soluble in chloroform. Table I shows results in which the reaction conditions were varied.

The secondary acetates were prepared from the primary by hydrolysis, usually by adding a mixture of 65 ml. of water and 60 ml. of acetic acid to the mixture at the end of the acetylation, and maintaining at 40–50° (see table II). Complete acetone solubility was obtained after 8 to 10 hours, and after 12 hours the acetic acid content became constant. Combined H_2SO_4 was very low.

I. Preparation of Primary Acetates

10 g. Cellulose with			Temperature °C.		Reaction Time in Hours.	Acetic Acid Content.	Yield per cent.
Acetic Acid.	Anhydride.	Catalyst.	Min.	Max.			
50	30	1·5	10	40	24	63·0	94·0
50	30	1·5	10	30	96	62·8	89·0
50	30	1·5	10	25	96	61·0	91·0
50	30	1·5	10	45	48	61·9	93·0
50	30	1·5	5	30	56	60·9	89·6
50	30	1·0	5	30	16	63·4	—
50	30	1·7	3	30	48	60·3	—

Combined H_2SO_4 from 1 to 2·5 per cent.

II. Hydrolysis of Primary Acetate

Time in hours	1	3	5	7	11	13
Acetic A. per cent.	60·3	59·8	58·9	57·5	54·4	53·2

On a larger scale 200 g. of cotton, air-dry, were treated at 5° with 600 g. acetic anhydride, 500–1,000 g. glacial acetic acid, and 10–35 g. sulphuric acid. The initial temperature was between 18° and 25° and reaction time between 5 and 24 hours. The acetic acid content was rather lower, varying between 62 and 58. The combined sulphuric acid was low, generally only 0·2 per cent.

The secondary acetates were prepared in two ways :—

(i) By diluting the mixture immediately with water and keeping at 40–50° until a test was completely soluble in acetone.

(ii) If the primary product was isolated by pouring into water, etc., it was hydrolysed by warming with 95 per cent. acetic acid at 70°, using sufficient to give 3 parts acetic acid to 1 of acetate. In some cases a temperature of 50° was employed until solution had taken place, after which it was slowly raised to 70°. A rapid rise must be avoided. Heating was continued until a test, precipitated by water, was white and opaque. The acetic acid content varied between 57 per cent. found after treatment for 7 hours at 50–60°, and 54 per cent. after 12 hours at 60–70°.

8. **Preparation of Cellulose Acetate A** (Hess, Weltzien and Messmer [1]).—54 g. of air-dry cotton with 600 g. of acetyl chloride are shaken strongly in a pressure flask at 17–20°. After 3 to 4 hours disintegration begins, and after 4 to 8 days practically all the cotton dissolves to a solution of great viscosity. The material is worked up at once, otherwise decomposition products are formed. The flask is opened after cooling to 0° and the gas allowed to escape during warming up to room temperature. The solution should be grey-brown, a dark brown indicates decomposition. The liquid is mixed with a little chloroform and evaporated in a vacuum. To remove hydrochloric acid the treatment with chloroform, and evaporation to dryness, is repeated many times. The residue forms a brittle mass, which is powdered in a mill and freed from traces of acid in a vacuum at 80° over potash. The residue after extraction with ether to remove acetyl chloride, etc., still contains about 1 per cent. of halogen. Yield, 88 g. (92 per cent.).

For purification 5 g. are dissolved in 100 ml. of warm glacial

[1] K. Hess, W. Weltzien and E. Messmer, *Ann.*, 1923, **435**, 48 ; *ibid.*, 1924, **435**, 44.

acetic acid and the solution filtered. A hardened paper, placed on a large suction filter and covered with a thick layer of kieselguhr, exhausted with glacial acetic acid, is used. When filtration becomes slow it is promoted by scraping off the top layer of kieselguhr. The filtrate shows colloidal turbidity. It is warmed slightly and mixed with a volume of ether about twice that of the acetic acid used. The white precipitate is granular, the mother liquor light yellow. After filtering the precipitate is rubbed up with a mixture of 3 volumes of ether and 1 of glacial acetic acid, and again filtered. The treatment is repeated till the filtrate is colourless. The residue is then washed with ether to remove acetic acid, and extracted in a Soxhlet apparatus with ether giving cellulose acetate A as a faintly yellow, often white powder. Yield, 58 g. (60 per cent. of theory).

Properties.—M.p. 270–275°, with decomposition. Soluble in chloroform and glacial acetic acid easily, acetone and acetic ester partially. Insoluble in alcohol and in ether. Analysis gave C, 49·45; H, 5·75; Cl, 0·50; ash, 0·25; CH_3COOH, 60·5 per cent.

The $[\alpha]_D^{18°}$ (chloroform) is $-14·5°$ independent of concentration. In glacial acetic acid it varies between $+ 4·8°$ at 6 per cent. to $+ 7·5°$ at minimal concentrations (0·2 per cent.).

Saponification of Cellulose Acetate A to Cellulose A.—40 g. are mixed with 500 ml. of normal methyl alcoholic NaOH and allowed to stand 2 days. After filtering, the residue is treated with water and dilute sulphuric acid till acid, and the mixture warmed to decompose the NaOH compound formed. The product is then separated and dried. The crude cellulose A is purified by solution in 2*N*-NaOH. Precipitation with acid does not remove coloured impurities, but the passage of a stream of gaseous ammonia, at 0°, to saturation throws out a white powder, the impurities remaining in the mother liquor. The powder is centrifuged while still ice-cold, washed with dilute ammonia and with water. A part again goes into solution so that the wash water is allowed to stand separately. In this dilute solution the cellulose A gradually separates as a gel, which on the addition of an electrolyte (a few drops of acetic acid), is easily separated by the centrifuge. The products are washed free from alkali and dried.

Cellulose A is a white powder, insoluble in organic solvents, but easily soluble in 2*N*-sodium hydroxide and in concentrated acids—*e.g.* hydrochloric acid. It gradually turns brown above 120°. Found on analysis C, 44·23, 44·65; H, 6·22, 6·33. Ash zero.

Another alkali-soluble form of cellulose is prepared [1] by washing

[1] T. Lieser, *Cellulosechem.*, 1926, 7, 85.

cellulose with highly concentrated hydrochloric acid below 0°. The bulk of the product is soluble in alkali, but the change is not accompanied by any increase in the copper number.

9. **Cellulose Sulpho-acetate** $(C_6H_7O_2)_4.SO_4.(C_2H_3O_2)_{10}$.—This is said to be formed by immersing cotton in a mixture of 50 parts each of acetic acid and acetic anhydride with 4 to 6 parts of sulphuric acid at 30–40°. The cotton rapidly dissolves.

Part II

Analytical Methods

A. The Estimation of the Acetic Acid Content of Cellulose Acetate

1. **Saponification Methods.**—Cellulose acetates are very little affected by cold dilute aqueous alkalis; dilute ammonia, for example, having hardly any action. Rapid saponification takes place if the ester is previously swollen by the action of aqueous acetic acid, alcohol, acetone, or a mixture of acetic acid and alcohol. The reagent is washed out and the swollen product saponified with $N/2$ aqueous alkali hydroxide at 25°—*e.g.* 0·5 g. of the acetate, powdered and quite dry, is moistened with 2 ml. of absolute alcohol. It is then mixed with 10 ml. of $N/1$ NaOH, and allowed to stand 1¼ hours at room temperature, with occasional shaking. The mixture is then diluted with 100 ml. of water and titrated with vigorous shaking, first with $N/1$ and finally with $N/10$ sulphuric acid, using phenolphthalein. The process requires care to obtain satisfactory results, but it is one of the best and quickest methods * of estimation.[1]

By the use of N- to $2N$-methyl alcoholic NaOH saponification may be effected without previous swelling—*e.g.* 40 g. of cellulose acetate are treated with 500 ml. of the reagent for one day at ordinary temperature (K. Hess).[2]

The standard processes given below have been critically examined by Genung and Mallatt [3] and modified in minor points. These authors consider the Eberstadt the best of the alcohol-swelling methods (accuracy ± 0·1 per cent.), and the distillation method of

* For a rapid method, using pyridine, see *Ind. Eng. Chem. Anal.*, July, 1931.

[1] O. Eberstadt, *Diss. Heidelberg*, 1909; O. Torü, *J. Chem. Ind. Japan*, 1932, **25**, 118; E. Knoevenagel and K. König, *Z. angew. Chem.*, 1914, **27**, 507.

[2] K. Hess, "Chemie der Zellulose," p. 415.

[3] L. B. Genung and R. C. Mallatt, *Ind. Eng. Chem. Anal.*, 1941, **13**, 369; see also *ibid.*, 1944, **16**, 501.

Ost and Katayama (as modified) the quickest. The changes suggested by Genung and Mallatt are given in brackets.

(*a*) *Method of O. Eberstadt.*[1]—This method is convenient and useful. The principle consists in swelling the ester with alcohol and saponifying with *N*/2 sodium hydroxide.

1 g. of acetate is warmed for 30 minutes at 50–60° in 20 ml. (40 ml.) of 75 per cent. alcohol. The acetate is then swollen and in some cases dissolved. 50 ml. (40 ml.) of *N*/2 NaOH are added and the whole warmed to 50°, allowed to cool, and with frequent shaking, left for 24 (to 48) hours. The excess of alkali is then estimated by adding *N*/2 sulphuric (or hydrochloric) acid in slight excess, phenolphthalein being used as indicator, and then, after gentle warming on the water bath (or leaving for several hours, adding more acid if required), titrated to neutrality with *N*/2 alkali.

(*b*) *Use of Sodium Ethylate.*[2]—This reagent is necessary when saponification is difficult : 0·5 g. of substance is added to 40 ml. of an *N*/4 solution of NaOH in 95 per cent. alcohol and left for 16 to 24 hours, temperature not exceeding 30°. Titration with *N*/4 HCl is carried out as above. Accuracy ± 0·2 per cent. acetyl.

Blanks should be run especially with fresh materials.

(*c*) *Method of W. L. Barnett*[3] *for Acetone-soluble Acetates.*—The following method is convenient and indicates differences of the order of 1 per cent. in acetic acid content.

About 0·3 g. of ester is dissolved in 25 ml. of acetone, shaken with excess (4·5–5·0 ml.) of *N*/1 NaOH in the cold in a stoppered flask, and left for 1 day. The liquid is diluted with water and titrated with *N*/10 sulphuric acid, using phenolphthalein. Under these conditions the correction for regenerated cellulose is very small and for comparative work may be neglected. For especial accuracy two blank experiments are made, (*a*) using a known weight of cellulose in the form of filter paper ; (*b*) using the volume of acetone only, as in the following example :—

	Weight g.	Acetone ml.	*N*/10 NaOH ml.	*N*/10 H_2SO_4 ml.	Acetic Acid per cent.
Ester . .	0·3167	30	47	18·85	48·98
Ester . .	0·3387	30	47	17·05	48·81
Cellulose blank .	0·3000	30	47	44·20	—
Acetone „ .	—	30	47	45·90	—

[1] O. Eberstadt, *Diss. Heidelberg*, 1909.
[2] L. B. Genung, *et. al., loc. cit.*
[3] *J. Soc. Chem. Ind.*, 1921, **40**, 9T.

The ester is approximately a diacetate, so that the regenerated cellulose will be about two-thirds of its weight. Hence the number of millilitres of alkali neutralised by the regenerated cellulose in the first example must be

$$2/3 \times (0{\cdot}3167/0{\cdot}3) \times 1{\cdot}7 = 1{\cdot}2 \text{ ml.}$$

The alkali equivalent to acetic acid = 45·9—18·85—1·2 ml.

2. **Distillation Methods.**—These are to be preferred in certain cases, *e.g.* estimation of acetyl in acetate-nitrate, acetate-phthalate, etc. (*a*) *Method of H. Ost and T. Katayama.*[1]—These authors first introduced the method of acid hydrolysis, with subsequent distillation and estimation of the volatile acid. The original process specified standing with sulphuric acid for a day, but L. Genung (*loc. cit.*) finds that 1 hour is sufficient, thus greatly shortening the estimation. His procedure is as follows :—

The finely powdered ester (0·3 g.) is treated with 10 ml. of 50 (vol.) per cent. sulphuric acid, shaken and allowed to stand for 1 hour at ordinary temperature, and the liquid then diluted with 50 ml. of CO_2-free water. The solution is distilled in steam so that 600 ml. distils per hour, the volume in the flask being kept constant. The water used for steam production should be boiled out and mixed with sodium hydroxide to retain carbon dioxide. After 1·5 to 1·6 litres have passed over, the distillate is titrated with $N/10$ sodium or barium hydroxide. It should give no precipitate with barium chloride.

(*b*) *Method of A. G. Green and A. G. Perkin.*[2]—These authors used alcohol for the distillation, acetic ester being formed. 0·4 g. of acetate is allowed to swell in a mixture of 30 ml. alcohol and 2 ml. concentrated sulphuric acid which is then slowly distilled. When the liquid in the flask has decreased one half, fresh alcohol is added. This is repeated three times, the distillation being continuous. The acetic ester formed is condensed and allowed to run into an excess of standard alkali, the excess being titrated back with acid.

(*c*) *Standard Method for the Estimation of the Acetic Acid Content of Cellulose Acetate* (K. Hess [3]).—This aims at an accuracy within 0·2 per cent., and was used successfully in several hundred analyses. The principle consists in hydrolysis of the ester with 50 per cent. sulphuric acid. After treating the excess of acid with sodium

[1] H. Ost and T. Katayama, *Z. angew Chem.*, 1912, **29**, 1467.

[2] A. G. Green and A. G. Perkin, *J. Chem. Soc.*, 1906, **89**, 811 ; 1904, **85**, 1462 ; 1905, **87**, 107 ; 1907, **91**, 1230.

[3] K. Hess, W. Weltzien and E. Messmer. *Ann.*, 1923, **435**, 65 ; *cf.* also W. Weltzien and R. Singer, *ibid.*, 1925, **443**, 110.

phosphate the acetic acid is distilled off in a vacuum at a low temperature with complete exclusion of carbon dioxide. The apparatus is shown in Fig. 69. It consists of a steam flask A connected with the short-necked distillation flask B (300 ml.), in which the hydrolysis takes place. The steam purifier D is connected to the flask F (2 litres).

The steam purifier is shown separately in section. It is kept hot during the estimation by filling the outer jacket with water heated to 100°.

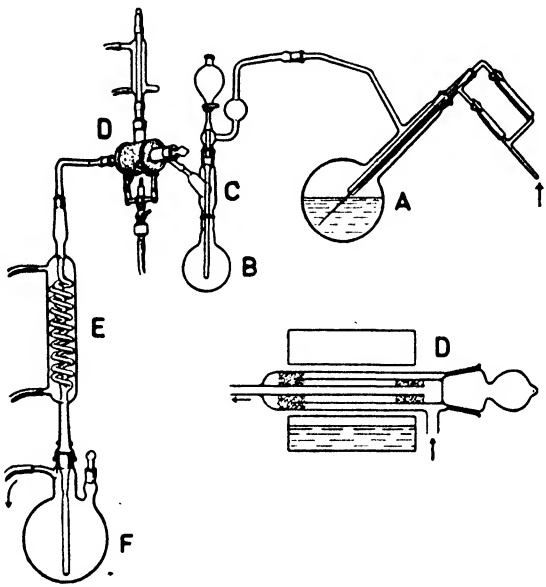


FIG. 69.—Apparatus for the estimation of the acetic acid content of cellulose acetate. (*From K. Hess*, "Die Chemie der Zellulose," Leipzig, 1928.)

Procedure.—0·2 to 0·3 g. of acetate is put into B and mixed with about 2 ml. of 50 per cent. sulphuric acid. The flask is closed and allowed to stand until a clear solution is obtained, which may take 2 to 24 hours at 15 to 35°. The flask is then connected with C, and F is filled with water (previously boiled out in a current of air free from CO_2) so that the condenser dips into it. The flask B is put into a boiling water bath and a current of hydrogen passed. Saponification is complete in 10 minutes. The contents are cooled, and 13 ml. of sodium phosphate solution are run in through the tap funnel. This is prepared by mixing 1,170 g. of di-sodium hydrogen phosphate with 150 g. of 84 per cent. phosphoric acid, and diluting to 900 ml. The apparatus is now evacuated while A is kept at 40° to 50° on a water bath.

The distillation from B to F begins at a speed adjusted by the working of the condenser E. The liquid in the flask is taken to dryness, so much water run in that the contents are re-dissolved, and the water again distilled off. The process is repeated for a third time. Care must be taken to displace moisture in the tubes between B and E.

The apparatus is again filled with hydrogen and, through the tubulure in F, a burette with a long jet is inserted and the contents titrated with $N/20$ baryta water, using phenolphthalein. The formation of acid products by decomposition of carbohydrates does not take place under the conditions employed. The results are accurate to 0·1 to 0·3 per cent.

If the substance contains halogen, a small quantity of silver sulphate is added to the flask.

B. Estimation of Combined Sulphuric Acid

The methods in use for this estimation involve the destruction of the organic matter and the liberation of the sulphur combined in the form of sulphuric acid. This is accomplished either in the wet way, by the use of nitric acid, aqua regia or nitric acid-chlorate mixture, or in the dry way, by fusion with alkaline oxidants. For example:

(*a*) 5 g. of acetate are heated for 2 hours with 20 ml. of nitric acid of *d*, 1·38. The liquid is diluted to 200 ml., filtered, and the acid precipitated as barium sulphate.

(*b*) 5 to 10 g. are oxidised with aqua regia or a mixture of nitric acid and potassium chlorate (*cf.* p. 271).

(*c*) 1 g. of acetate is mixed with 1·5 g. of nitrate of potassium and 5 g. of anhydrous carbonate of soda. The mass is gently ignited to fusion.

C. The Solvent Power Number

For factory routine and for research purposes it is often necessary to determine the best solvent, whether a single liquid or a mixture of liquids, for cellulose acetate, nitrate or other esters. An indirect method of doing this is to find the solvent which is capable of yielding solutions that will bear the greatest dilution with an indifferent, miscible non-solvent, such as petroleum ether, before the cellulose ester is precipitated (F. Sproxton "Third Report on Colloid Chemistry", p. 84). This principle has been embodied in the standard method of E. W. Mardles,[1] "The Determination of the Solvent Power Number".

[1] E. W. J. Mardles, *J. Soc. Chem. Ind.*, 1923, **52**, 127; *Chem. Soc. Trans.*, 1924, **125**, 2244; *Kolloid-Z.*, 1929, **49**, 4, 11.

Definition.—The solvent power number is the number of millilitres of a miscible non-solvent required to start precipitation of a cellulose ester from 1 g. of a 5 per cent. solution at 20°.

Method.—5 g. of bone-dry acetate are placed in a 150 ml. stoppered bottle, with 100 ml. of the solvent and the mixture shaken in a reciprocating shaker for 1 hour, when complete solution should occur. Petroleum spirit (b.p. 90–100°, for example), is then run slowly from a burette into the cellulose acetate solution (contained in a thermostat at 20°), with vigorous shaking, until an incipient cloudiness is noticed. The end-point is rather difficult to observe accurately, and in all cases the sample should be compared with a " blank ", using a standard acetate. The cloudiness of the samples can be better matched if the solutions are observed in long narrow cylinders of about 1 cm. diameter. From the volume of spirit added the solvent power number is calculated.

As little as 5 ml. of the solution may be employed. Several minutes of shaking are needed after each addition of non-solvent. At the end 1 drop of non-solvent will cause a turbidity to spread through the sol, and if this persists for 2 or 3 minutes the volume added may be read. If the precipitate is gelatinous (often with liquids like benzyl alcohol or nitrobenzene), the end-point is shown by opalescence. If the refractive index of the precipitate happens to be the same as that of the medium, the non-solvent must be changed.

SOLVENT POWER NUMBERS FOR ACETONE SOLUTIONS

Non-solvent.	Cellulose Acetate.	Cellulose Nitrate.	Cellulose Chloroacetate.
Benzene	0·66	4·6	3·75
Toluene	0·36	3·0	2·1
Xylenes	0·26	2·0	—
Pentane	0·13	0·67	—
Petroleum spirit (b.p. 90–100°)	0·09	0·45	0·35
Amylenes	0·20	—	0·9
Heptylenes	0·18	—	0·64
Octylenes	0·13	—	0·6
Ethyl alcohol	0·65	3·5	0·6
Water	0·33	0·14	0·07

The determination of viscosity is considered in Ch. III. The strength and qualities of films and threads are measured by the usual apparatus common to the industries of paper and indiarubber.

D. Example of the Specification Requirements for Cellulose Acetate. Specification by the British Standards Institution.[1]

1. *Water Content.*—2 g. heated in a boiling water oven for 2 hours must not lose more than 5·5 per cent. in weight.

2. *Insoluble Matter.*—7·5 g. are placed in a 200 ml. wide-mouthed stoppered bottle and 19 ml. each of alcohol (B.S., 3D.9) and benzol (B.S., 3D.10) are added and the mixture allowed to stand until the acetate is thoroughly moistened. 60 ml. of acetone (B.S., 3D.22) and 3 ml. of benzyl alcohol (B.S., 3D.7) are added slowly with shaking. The mixture is further shaken for such a time that the whole operation of preparing the solution takes 1 hour.

Within 3 hours of the commencement of this operation the resulting dope shall be shaken and then centrifuged in a machine so that the product $D \times R^2 \times T$ is not less than 20,000 (D, distance in centimetres from surface of liquid to centre of axle of the centrifuge when in motion; R, revolutions per second; T, time in hours). Suitable limits for R are 30 to 100.

The volume of the insoluble matter collecting at the bottom of the tube shall not exceed 0·1 per cent. of the volume taken.

3. *Viscosity.*—The viscosity at 25° of the solution prepared under (2), determined in the Ostwald viscometer described on p. 65, shall be not less than 30 per cent. and not more than 45 per cent. of the viscosity at 25° of a pure glycerine of d, 1·2526 at 25°/4°.

4. *Film Test.*—Not less than 10 ml. of the solution used for viscosity are allowed to evaporate in still air on a horizontal glass plate at a temperature not greater than 15° and R.H. not less than 70 per cent., the area occupied by the solution being about 50 sq. cm. A film free from whiteness must result, which is removed from the plate, rapidly bent double, and the crease pressed with the fingers. No cracking should result.

5. *Acidity.*—Free acid, calculated as acetic acid, shall not exceed 0·01 per cent. by weight on the material as received, when determined as follows:—

6 g. are shaken with 100 ml. of acetone till dissolved, the solution poured slowly with stirring into 100 ml. of neutral, recently boiled, cold distilled water. The solution, and an exactly similar "blank" solution, are shaken for 30 minutes and a large aliquot portion of the clear liquid of each is titrated with $N/100$ caustic alkali, using phenolphthalein. The bottles should not yield alkali to distilled water overnight when tested by phenolphthalein.

[1] Abstract by permission from B.S.I. publication, 2D, 50, October, 1929.

6. *Ash.*—This must not exceed 0·2 per cent.

7. *Stability.*—The amount of acetic acid liberated when the material is treated as below shall not exceed 0·5 per cent. by weight.

Stability Test.—2 g. are placed in a test tube 7 by $\frac{3}{4}$ in.* so that no particles adhere to the upper part of the tube. 2 ml. of distilled water are added and the tube sealed off.

The tube is totally immersed in boiling water for 7 hours, after which it is cooled and washed with distilled water. It is then crushed under 50 ml. of water and the mixture titrated with an $N/20$ caustic alkali solution to phenolphthalein.

A blank is carried out with 2 ml. of water, and if the alkali dissolved from the glass is more than the equivalent of 1 ml. of $N/50$ caustic soda the tubes should be rejected.

8. *Charring Point.*—This, both with material in its original state and after washing with neutral distilled water and drying, shall be not lower than 200° when determined as follows :—

Tubes 7 by $\frac{1}{2}$ in.,* are filled with the acetate (both original and washed) to a depth of 1 inch. They are then placed in a bath previously heated to 180°, the temperature of which is raised about 2° per minute. The bath temperature at which distinct discoloration occurs is taken as the charring point.

An account of similar methods in use in France will be found in an article by M. Deschiens.[1]

* The tubes must be cleaned with boiling dilute acid and steamed for two hours.

[1] M. Deschiens, *Chim. et Ind.*, 1929, **21**, 1131.

CHAPTER XVI

CELLULOSE ESTERS OF OTHER ACIDS AND THE MIXED ESTERS OF CELLULOSE

PART I

Simple Cellulose Esters

THE simple esters are prepared and their properties determined by processes similar to those used in the case of the acetate. An important general method suitable for the preparation of esters of all types, simple and mixed, is also available. This is based on the discovery (B.P. 313,408) that substituted organic acid anhydrides, *e.g.* monochloracetic anhydride, in conjunction with an organic acid, act as "impellers", bringing about esterification between the cellulose and the acid without themselves taking part. Monocarboxylic acids and the half-esters of dicarboxylic acids can be used, *e.g.*,

$$C_6H_7O_2(OH)_3 + 3\,X\begin{<}COOR\\COOH\end{>} + 3\begin{<}ClCH_2.CO\\ClCH_2.CO\end{>}O$$
$$= C_6H_7O_2(O.CO.X.COOR)_3 + 6ClCH_2.COOH.$$

It is thus possible to prepare esters of weak and sensitive acids (*e.g.* unsaturated or halogenated acids) which cannot be treated by the usual methods.

The reaction conditions will be seen from the examples in the table given on the following page. A catalyst, usually magnesium perchlorate, is employed with a temperature of 50–80°. The fibrous cellulose gradually dissolves in the reaction mixture.

The following are examples of the application of this method: (*a*) A cellulose formate soluble in acetone is prepared (U.S.P. 1,880,420) by digesting normal cellulose for a long time with a mixture of chloracetic anhydride (40 parts) and formic acid, 85 per cent. (20 parts) at 35–40°. The product contained 1·75 formyl groups per C_6.

(*b*) The method does not succeed with halogen substituted fatty acids containing 5 carbon atoms or less, owing to the inhibiting effect of the halogen, but with the higher members it works satisfactorily so that esters, for example, of α-bromocaproic acid,

9 : 10-dibromostearic acid, etc., can be prepared. They form non-inflammable films (B.P. 304,279).

(*c*) With alkyl hydrogen esters of dibasic acids, such as propyl hydrogen succinate, ethyl hydrogen phthalate, etc., the acidic hydrogen reacts with the cellulose hydroxyls and the product still contains the alkyl grouping as shown in the equation above (*cf.* p. 299).

USE OF CHLORACETIC ANHYDRIDE AS AN IMPELLER

Acid.	Proportions of				Time in Hours.
	Acid.	Cellulose.	Chloracetic Anhydride.	$Mg(ClO_4)_2$.	
Acetyl salicylic . . .	20	2	20	0·05	10
Benzoic	15	3	20	0·05	8
,, *o*-chloro- . .	10	2	15	0·02	5
,, *o*-methoxy- . .	10	2	15	0·02	4
Cinnamic	15	3	40	0·05	5
Crotonic	15	5	30	0·05	5
Cyclohexanecarboxylic .	10	2	15	0·02	3
Phenylacetic . . .	15	3	20	0·05	7

(*d*) Mixed esters are also obtained by the use of chloracetic anhydride (*cf.* p. 304). Thus, with a mixture of acetic acid and, *e.g.* bromostearic acid, a cellulose acetate bromostearate is formed (U.S.P. 1,698,049) and cellulose nitrate, with crotonic acid, gives cellulose nitrate crotonate (B.P. 290,570).

Cellulose Formate.—Formic acid will esterify cellulose in the presence of catalysts, mono- and di-formates being produced. Sulphuric acid, hydrochloric acid gas, zinc chloride, or phosphorus pentoxide are the catalysts usually employed. If the cellulose is made reactive by modification—*e.g.* if regenerated from solution in 70 per cent. sulphuric acid, or from viscose—or if hydrocellulose is used, esterification proceeds without a catalyst.

The products on analysis yield 18–23 per cent. formic acid, whereas one formyl group would require 24·4 per cent. A triformyl cellulose requires 56·1 per cent.

Using sulphuric acid as a catalyst [1] anhydrous formic acid acting on hydrocellulose gave a product with H.COOH, 23 per cent., while regenerated cellulose gave one yielding 50·5 per cent. HCOOH. These values vary with the time and proportion of sulphuric acid.

[1] Y. Uyeda *et al.*, *J. Cell. Inst.*, Tokyo, 1928, **4**, 1; *ibid.*, 1933, **9**, 274; *ibid.*, 1939, **15**, 212.

Thus, cellulose prepared from alkali cellulose when formylated (4 g. cellulose; 40 g. of 98·5 per cent. HCOOH; 3 g. H_2SO_4, *d*, 1·84) for 1 to 5 days at 20° gave a product with a maximum H.COOH content (39·9 per cent.) after 40 hours, but after 5 days the content was only 24 per cent. A study of the viscosity and the tensile strength of films of cellulose formate showed that the proportions given above are the best.

Formyl esters are insoluble in most organic solvents with the exception of pyridine and formic acid. They are, however, characteristically soluble in aqueous solutions of acids—*e.g.* acetic, lactic, hydrochloric; and of salts, especially calcium and other thiocyanates and zinc chloride. The formation of an acetone soluble formate (U.S.P. 1,880,420) is mentioned above.

The esterification of cellulose with 95 per cent. formic acid in the presence of a catalyst such as HCl, H_2SO_4, PCl_3 or PCl_5, or SO_2Cl_2, is greatly modified if the reaction is conducted at or below 5°. Products with a formic acid content amounting to 50 per cent. or more are obtained, suitable for making rayon with a high tensile strength when wet. The ester is dissolved in formic acid and coagulated by means of water or sodium formate solution (B.P. 260,650).

According to D.R.P. 498,157, by using a similar process at 0° a triformate is produced which is very stable even in boiling water. A novel method (U.S.P. 2,237,844; 8/4/41) consists in the action of formalin on cellulose soaked in 20 per cent. aqueous NaOH with Cu_2O or $Cu(OH)_2$ as catalyst.

Estimation of H.COOH from Cellulose Formate.—This may be done by oxidation with a sulphuric acid dichromate mixture. The dry formate (1 g.) is treated with *N*-potassium dichromate (130–150 ml.) followed by the gradual addition of H_2SO_4 (41 ml.) with stirring and cooling. After standing for 30 minutes the mixture is heated (water bath) for 8 hours and the excess of dichromate estimated either with ferrous sulphate or by the iodide method. The volume of *N*-$K_2Cr_2O_7$ solution required for the oxidation of one gram each of cellulose and of the mono-, di- and triformates is 148·14, 136·78, 128·43 and 121·95 ml. respectively.

Cellulose Chloroacetates.—Cellulose is not readily esterified by the chloracetic acids mixed with their chlorides or anhydrides. From hydrocellulose, using mono-, di- or trichloracetic anhydrides with $ZnCl_2$ or H_2SO_4, derivatives such as $C_6H_7O_5(CO.CH_2Cl)_3$ of chlorine content 26 per cent.; $C_6H_8O_5(CO.CHCl_2)_2$, chlorine content 36·6 per cent., and $C_6H_8O_5(CO.CCl_3)_2$, chlorine content 44 per cent., have been prepared.[1] To obtain $C_6H_7O_5(CO.CCl_3)_3$ of

[1] H. Rudy, *Cellulosechem.*, 1932, 13, 49.

chlorine content 53 per cent. cellulose triacetate is digested at 120° with phosphorus pentachloride in a mixture of chloroform and tetrachloroethane for 3 hours. The ester dissolves in formic acid and chloroform, and has the unusual property of resisting hydrolysis both by acids and alkalis in aqueous or alcoholic solutions.

Cellulose Propionates.—The action of propionic anhydride on cellulose in the presence of acetic acid and a catalyst proceeds smoothly, giving clear solutions, as in the case of the acetate. The tri-derivative is formed if hydrated cellulose or hydrocellulose is used. Such working conditions as cellulose (10 parts); propionic anhydride (50 parts); glacial acetic acid (45 parts) containing HCl (1 part), at 70° for 12 hours, are suitable and can be varied. The cellulose may be soaked in the acetic acid and propionic anhydride before adding H_2SO_4 as the catalyst (U.S.P. 1,824,877). The primary product undergoes hydrolysis when treated with propionic acid and H_2SO_4 giving an acetone-soluble derivative (B.P. 449,183). To retain the fibrous structure after esterification carbon tetrachloride is added to the mixture (U.S.P. 2,000,621).

Cellulose Butyrates.—These are produced by methods and modifications similar to those in use for the manufacture of the acetate. Cellulose more or less modified, catalysts such as sulphuric acid, carriers for the catalyst such as excess of butyric acid and organic diluents to restrain or modify the reaction, are all employed. A complete examination of all the variables concerned has been made.[1]

The butyrate has advantages over the acetate in that it is soluble in inexpensive solvents, such as mixtures of alcohol and benzene. The following examples of its preparation are by A. D. Little.

1. The cellulose is impregnated in a bath containing sulphuric acid, butyric acid and alcohol, and afterwards acylated as below. The alcohol prevents the separation of the mixture of sulphuric acid and butyric acid, which occurs even when traces of water are present (B.P. 161,564, 1921). The bath, mixed just before use, contains

Sulphuric acid (*d*, 1·84)	0·5–0·6 per cent.
Alcohol	5·0–7·5 ,,
Butyric acid	94·5–92 ,,

The cellulose is then removed and esterified as in (2) below with butyric acid and anhydride (B.P. 182,820, 1922).

2. Cellulose is impregnated in a bath containing sulphuric acid 1–5, water 5–8, and acetic acid 94–87 parts by weight, using about

[1] A. Nowakowski, *Cellulosechem.*, 1932, 13, 105.

15 parts of the mixture to 1 of cellulose. It is then esterified in a bath containing :

Butyric anhydride (90 per cent.) . .	465 parts.
Butyric acid	400 ,,
Cellulose	100 ,,

When the product shows satisfactory solubility in chloroform, sulphuric acid is added to accelerate transformation into products soluble in alcohol and benzene (B.P. 167,143, 1921).

The butyl content may be estimated by Zeisel's method. The material must be finely divided. The temperature of the bath is kept first at 60° for 30 minutes and then raised quickly to 130–140°. After 45 minutes the elimination of the butyl group is quantitative.

Cellulose Esters of Higher Fatty Acids.—Mono-, di- and tri-esters of cellulose with stearic, lauric and palmitic acids are stated[1] to be formed by the following processes :—

Cellulose Mono-stearate.—10 g. of dry cellulose are saturated with pyridine, 20 g. of stearyl chloride (*i.e.* 1 mol. per $C_6H_{10}O_5$), added and the mixture heated 4 hours on the water bath. The mass is boiled up with absolute alcohol, filtered, and the residue treated three times with alcohol to remove pyridine. The fibrous mass is then extracted with benzene.

Stearic acid found, 58·6 ; a monostearate requires 66·3 per cent.

Cellulose Di-stearate.—A considerable excess of acid chloride is used, some 6 mols. per $C_6H_{10}O_5$. 5 g. of cellulose are treated with 300 ml. of benzene. 60 ml. of stearyl chloride in 200 ml. of benzene are poured in, and, with shaking 50 ml. of pyridine added. The mixture is heated for 3 hours, and left 2 days, after which 15 ml. of pyridine are added and the mixture heated a further 10 hours (water bath). Purification as above. Yield, 21·5 g. Stearic acid found, 82·1 ; a di-stearate requires 81·9 per cent.

The product consists of short fibres, m.p. 220 (decomp.). It is insoluble in all usual solvents and in cuprammonium, but dissolves at 200° in fatty acids and their glycerides, *e.g.* triolein.

The laurates are similarly obtained.

Cellulose Tri-stearate, Laurate and Palmitate (G. Kita and co-workers, *loc. cit.*).—Equivalent molecules of fatty acid and phosphorus pentachloride are heated and the volatile products distilled off at 100°/20 mm. The acid chloride obtained is mixed with pyridine and benzol and dry cellulose in the form of paper added. The mixture is heated for 24 hours (water bath), the product treated with alcohol and extracted with benzene. The working details are :—

[1] A. Grün and F. Wittka, *Z. angew. Chem.*, 1921, **34**, 645. *Cf.* also G. Kita, I. Sakurada and T. Nakashima, *Cellulosechem.*, 1928, **9**, 15.

	Laurate.	Palmitate.	Stearate.
Cellulose in g.	2	2	2
Pyridine, ml.	25	25	25
Benzene, ml.	100	100	100
Acid chloride, g.	40	50	55
Product	di-ester	tri-ester	tri-ester
Per cent., sol. in benzene	20	30	25

Cellulose di- and tri-esters of the higher fatty acids soluble in benzene, have been prepared similarly from hydrocellulose and various modified celluloses.[1] An apparatus fitted with a mechanical stirrer is employed. The mixture for the preparation of di-esters is made as follows :—Hydrocellulose (Girard), 1 ; acid chloride, 5 ; pyridine, 3 ; toluene, 5 parts, heated to 110°.

Samples are removed at intervals and tested for solubility in benzene. When completely soluble alcohol is added, the precipitate dried and treated with benzene. The benzene solution is centrifuged, when 10 to 20 per cent. of insoluble " monoester " separates. The clear solution is treated with alcohol to throw out the di-ester.

The tri-esters are best prepared from the di-ester. Thus 1 part of the di-ester in a mixture of 4 parts of pyridine, 1 of toluene and 5 of acid chloride is heated to 100° for 2 hours. They may be obtained directly by using 1 g. hydrocellulose, 10 g. acid chloride, 3 ml. pyridine, 25 ml. benzene.

PROPERTIES OF THE HIGHER FATTY ACID ESTERS[1]

	Softening Point.	Form, Solubility, etc.
Mono-laurate	190–200°	Grains composed of broken fibres, insoluble in ordinary solvents, in some of which they swell.
„ palmitate	180°	
„ stearate	180–190°*	
Di-laurate	85–90°	Grains or fibre ; soluble in many organic liquids, *e.g.*, benzene, fatty acids and oils.
„ palmitate	100°	
„ stearate	85–90°†	
Tri-laurate	90°‡	Masses or pellicules ; solubility similar to that of the di-esters,
„ palmitate	80°	
„ stearate	75°	

* With decomposition. † Without decomposition. ‡ Quite liquid at 180°.

Analysis of Higher Fatty Esters of Cellulose.—About 0·5 g. is swollen with benzene by heating on the water bath. 30 ml. of

[1] H. Gault and P. Ehrmann, *Bull. Soc. Chem.*, 1926, **39**, 873 ; also B.P. 201,510, 1922.

alcoholic KOH are added and the mixture heated for 4 hours. After evaporation of the solvents the residue is heated again for 4 hours with 30 ml. of *N*-alcoholic KOH and filtered.

The alcohol is distilled from the filtrate, the soap dissolved in water, and the fatty acid precipitated with sulphuric acid and extracted with ether in the usual way. The acid is titrated in alcoholic solution with *N*/10 sodium hydroxide.

Cellulose Esters of Dibasic Organic Acids.—These may be of three types : (*a*) esters in which both carboxyl groups of the acid are combined with cellulose. These are usually insoluble, and are of little use. (*b*) Esters in which one carboxyl is combined with cellulose and the other with some other organic radicle. These show a wide range of solubility, low melting-point and a high degree of resistance to moisture. (*c*) Esters similar to type (*b*) but with the second carboxyl in the free acid form. These compounds form salts with the alkali metals which are soluble in water, whilst their heavy metal salts are insoluble—properties which suggest practical applications.

Cellulose diacetate (acetyl 35 per cent.) may be used for reaction instead of cellulose, and cellulose acetate acid phthalates, for example, form a useful group of compounds.

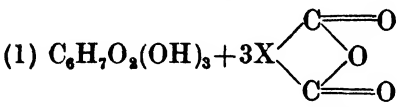
These esters have been examined by Malm and Fordyce.[1] Cellulose alkyl esters of type (*b*) were prepared by the use of chloracetic anhydride (U.S.P. 1,704,306 ; 1929). A mixture of 100 g. of cotton linters, 500 g. of chloracetic anhydride, 2·0 g. of magnesium perchlorate and rather more than the calculated quantity of the dibasic acid half ester (*e.g.* butyl acid phthalate) are heated, with stirring, at 70° for 2 to 5 hours until uniform solution is obtained. The solution is precipitated into a large volume of methyl alcohol, and the products extracted with methyl alcohol to remove uncombined acid.

Cellulose acetate alkyl dicarboxylates are similarly made. 100 g. of cellulose acetate (35 per cent. acetyl), 200 g. chloracetic acid and 100 g. of chloracetic anhydride are stirred at 60° to uniform solution. 100 g. of the dibasic acid half ester and 0·1 g. of magnesium perchlorate are added and the mixture heated to 60° with stirring for 2 hours. The derivative is isolated as before.

The above compounds of cellulose dissolve in all the usual solvents except that the methyl and ethyl esters are insoluble in butyl acetate and toluene. Those of cellulose acetate are also very generally soluble except in benzene and toluene. The m.p. falls with increase of carbon atoms in the alkyl group, e.g. methyl cellulose succinate has m.p. 195°, ethyl-, 128° and butyl-, 106°.

[1] C. J. Malm and C. R. Fordyce, *Ind. Eng. Chem.*, 1940, **32**, 405.

Cellulose Acid Dicarboxylates.—These are obtained (B.P. 410,118) by the action of dibasic acid anhydrides on cellulose in the presence of pyridine. The reaction follows the equations



$$(1)\ C_6H_7O_2(OH)_3 + 3X(CO)_2O + 3\,Py = C_6H_7O_2(O.CO.X.COOH.Py)_3$$

$$(2)\ C_6H_7O_2(O.CO.X.COOH.Py)_3 + 3HCl = C_6H_7O_2(O.CO.X.COOH)_3 + 3PyHCl$$

The compounds are insoluble in water, but many of their salts are soluble so that they dissolve in dilute alkalis. Their solubility in organic solvents is limited, but they can be used for films or coatings. The use of cellulose acetate gives a better range of solubility, and cellulose acetate acid phthalate is a useful member of this class. By varying the proportion of phthalyl, compounds with varying physical properties are obtained. The m.p. varies from 243°, with 10 per cent. phthalyl content, to 178° with 35 per cent. For details of preparation see below.

Cellulose Acetate Acid Dicarboxylates.—To 100 g. of cellulose acetate in 400 g. of pyridine are added 200 g. of the acid anhydride and the mixture heated at 100° for 12 hours as before. The solution is poured into a large volume of water containing 400 ml. of concentrated hydrochloric acid.

Cellulose Acetate Sodium Phthalate.—In 900 ml. of water 100 g. of cellulose acetate acid phthalate (35 per cent. phthalyl) are suspended and sodium bicarbonate in very small portions added, with stirring, from a weighed quantity of 20 g. After addition of about 10 g. the compound goes into solution. Further additions are made and the solution tested with bromthymol blue and adjusted to a *p*H of 7 to 7·5. The heavy metal salts are mostly insoluble in water, but those of Ca, Co and Zn are soluble.

Cellulose mono-esters of dibasic acids are prepared also by B.P. 410,125, using the anhydride of the acid and a base which satisfies one of the carboxyl groupings. Thus a mixture of cellulose (5 g.), succinic anhydride (25 g.), pyridine (75 ml.) is kept at 65° for a week. On pouring into methyl alcohol the pyridine salt of cellulose acid succinate is obtained which after drying and removal of pyridine gives a product containing succinic acid 62 per cent. A trisuccinic derivative requires 65 per cent.

Cellulose phthalates are also formed under these conditions. By varying the proportions of phthalic anhydride esters containing 72, 54 and 21 per cent. of phthalyl are obtained. Temperature should not exceed 95° (B.P. 410,118).

As an example a mixture of 100 g. of low viscosity cotton linters, 500 g. of pyridine and 400 g. of phthalic anhydride is heated for 12 hours at 100° with stirring. The solution is diluted with an equal volume of acetone and poured into a large volume of water acidified with 500 ml. of concentrated hydrochloric acid. The product contains 66 per cent. of combined phthalyl.

Cellulose esters of hydroxy-acids are obtained by using the acid anhydride in acetic acid solution at 20–30° and in any case below 50°. When the product has dissolved the liquid is poured into water (B.P. 316,160). Tri-esters can be converted to secondary products as with the triacetate. Glycollic and lactic esters are most common.

Cellulose glycollate may also be obtained from cellulose chloracetate (B.P. 320,842) by treating 100 parts with 32 parts of NaOH in alcohol added in small portions.

Cellulose esters of unsaturated acids are usually prepared from the acid chloride in pyridine or sometimes dimethylaniline (B.P. 239,726). The linolenic and cinnamic esters are examples. In some cases solubility may be improved by heat treatment. Crotonic esters are readily prepared by using the acid anhydride with a catalyst under ordinary acetylating conditions (B.P. 328,492; 329,704), and the tricrotonic ester, which is soluble in acetone and benzene, may be converted (*a*) to a di-ester insoluble in benzene, but soluble in acetone, and (*b*) to mono-ester soluble in aqueous acetone.

Cellulose Benzoates.—These are generally prepared by repeated applications of the Schotten-Baumann method.[1] The limit appears to be about two and a half benzoyl groups per $C_6H_{10}O_5$, the degree of esterification depending upon the concentration of alkali present. Products corresponding to mono- and di-benzoates are probably mixtures of cellulose with higher esters. The latter only are soluble in chloroform, and, in some cases, from the lower esters a residue of cellulose has been obtained.[2]

G. Kita and co-workers,[3] however, by the use of the Schotten-Baumann method with other acid chlorides, have obtained products which, after extraction with cuprammonium solution, have left apparently mono-esters. The action of halogen-substituted benzoyl chlorides also gives, usually, products corresponding to a mono-substituted ester.

The dependence of the benzoyl content on the alkali concentra-

[1] H. Ost and F. Klein, *Zeit. angew. Chem.*, 1913, **26**, 437; K. Atsuki and K. Shimoyama, *J. Cellulose Institute*, Tokyo, 1926, **2**, 36.

[2] R. O. Herzog and G. Londberg, *Ber.*, 1924, **57**, 329.

[3] *J. Cellulose Inst.*, Tokyo, 1926, **2**, 30.

tion observed by Cross and Bevan,[1] was confirmed by Ost and Klein (*loc. cit.*), who have given a curve showing the relation between these variables. Cross and Bevan describe a fibrous monobenzoate made, for example, by using $C_6H_{10}O_5 : 2{\cdot}5NaOH : C_6H_5.COCl$. They removed cellulose by cellulose solvents and "higher benzoates" by treatment with organic solvents. Their dibenzoate, obtained by increasing the proportion of sodium hydroxide and benzoyl chloride is structureless, and soluble in chloroform, acetic acid and pyridine. Insoluble in ether and alcohol. Hygroscopic moisture, 1·6 per cent.

For analysis Cross and Bevan state that the benzoates must be saponified by digestion with alcoholic sodium ethylate solution in the cold for 12 hours. Unsatisfactory results are obtained by the use of alcoholic sodium hydroxide solution.

Cellulose tribenzoate[2] is prepared by the action of benzoyl chloride and pyridine at 110–130° on cellulose, with the addition of nitrobenzene as a solvent for the ester produced. Excess of benzoyl chloride compared with the pyridine is used. The product is soluble in chloroform and nitrobenzene, and has $[\alpha]_D = +26°$ in chloroform.

Part II

Cellulose Mixed Esters

The introduction of more than one acidic radicle into the cellulose complex has given derivatives with a variety of useful properties which can be controlled by variations in the extent and nature of the esterification. The more important products include the acetate-nitrates; mixed esters of the simpler fatty acids, usually acetic, with propionic and butyric acids; and the C_{16}, C_{18} acids obtained from fats.

The relation between composition, and properties of technical value such as melting-point, density, moisture, sorption, solubility in solvents and in plasticisers, can be usefully recorded by the aid of the triangular diagrams[3] shown in Figs. 70(*a*) and (*b*). In these, for example, the point C represents cellulose and a point at 44·8 (per cent. acetyl) along CA represents the triacetate. Similarly, a point at 51·8 (per cent. propionyl) along CP represents the tripropionate. The properties of the fully esterified mixed product are shown by the line joining these points. Those of the practically useful, secondary (hydrolysed) products lie in the area above this line.

[1] "Researches on Cellulose," 1895–1900: London, 1901.
[2] A. Wohl, *Z. angew. Chem.*, 1903, **16**, 285.
[3] C. J. Malm, *et al.*, *Ind. Eng. Chem.*, 1942, **34**, 430.

The original paper gives diagrams for all the common properties of acetate-propionate and acetate-butyrate esters. The methods used to measure some of these may be noted.

Specific Gravity.—Films of about 0·2 mm. thick were cast from solutions in a mixture of methylene dichloride and methanol. About 0·5 to 0·8 g. was cut into strips (4·8 × 12·7 mm.), weighed in air and in a 5 ml. pyknometer which was then filled with heptane and weighed at 25°. The specific gravity of the heptane was determined in the same bottle.

Sorption of Moisture.—Dry samples were weighed in wide-mouth bottles and placed, uncovered, in desiccators charged with aqueous sulphuric acid of the dilution required to give the required

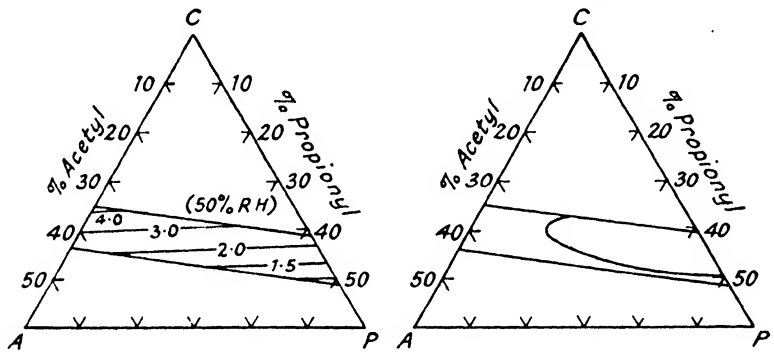


FIG. 70.—Diagrams illustrating a method of recording the properties of mixed cellulose esters (*a*) the percentage sorption of moisture at 50 per cent. R.H., and (*b*) the solubility in β-ethoxy-ethyl alcohol of cellulose acetate-propionate derivatives (*Ind. Eng. Chem.*, 1942, **34**, 430).

relative humidity.[1] The temperature was kept at 25° and the samples weighed at intervals over 7 days.

Methods for the preparation of mixed esters involve processes similar to those employed for the simple esters, with suitable modifications.

1. Cellulose may be esterified partially with one acid, A (usually acetic acid), and the esterification completed with another acid, B. As an example cellulose acetate-palmitate is obtained (B.P. 305,947) by mixing cotton (100 g.) with chlorbenzene (1·2 l.) and pyridine (235 g.) warmed to 50°, followed by about 50 ml. of acetyl chloride. After heating (steam bath) for 3 or 4 hours pyridine (70 g.) and palmityl chloride (425 g.) are added and the heating maintained for 20 hours. After heating to 120° the product becomes soluble in benzene, toluene, etc., and in aliphatic chlorinated hydrocarbons.

[1] See R. E. Wilson, *Ind. Eng. Chem.*, 1921, **13**, 326.

2. Cellulose may be treated with esterifying mixtures containing the anhydride or chloride of acid A (frequently acetic acid), and either the anhydride or chloride of a fatty acid B, or with the acid B itself. Conversely the cellulose may be treated with the acid A and with the chloride or anhydride of B.

An example of the first type is seen in the preparation of cellulose butyrate-ricinoleate (B.P. 305,947). A mixture of cellulose (100 g.), pyridine (500 g.), chlorbenzene (700 g.), butyryl chloride (200 g.) and ricinoleic acid chloride (350 g.) is kept for 12 hours at 85–90°, after which butyryl chloride (10 g.) is added and heating continued for 1 hour more at 135°. The product is thrown out with methanol.

3. Cellulose may be esterified by using a mixture of the two acids A and B in the presence of an impeller, such as chloracetic anhydride, with magnesium perchlorate as catalyst (as p. 294). Cellulose crotonate-stearate (B.P. 289,582) is obtained in this way, also cellulose acetate-oleate by using, in addition, chloracetic acid. This compound, by addition of bromine (19 per cent.), gives a dibromostearate containing 34·5 per cent. of acetyl (U.S.P. 1,698,048). For the use of the method with dibasic acids, see p. 299.

4. An interesting method of preparation consists in the partial displacement of the acid radicle in a cellulose ester by treatment with another acid of higher ionisation constant (F.P. 702,116). The ester is heated at about 100° with the acid which, preferably, should be a solvent for the ester. By this means cellulose acetate-oxalate, tartrate, maleate, pyruvate, salicylate and phenylglycollate have been obtained, and from cellulose tribenzoate a cellulose benzoate-pyruvate. As an example cellulose acetate (10 g.) in dioxan (75 ml.) containing oxalic acid (10 g.) is heated at 100° for 2 hours under reflux.

Multiple esters are prepared by variations of this process. A simple ester of cellulose, *e.g.* the acetate, is dissolved in a mixture of two (or three) organic acids, each of which has an ionisation constant greater than that of acetic acid ($1{\cdot}82 \times 10^{-5}$). With solid acids suitable solvents such as propionic acid, dioxan and ethylene dichloride are used. If a mixed cellulose ester is treated with an acid this should have an ionisation constant greater than that of either of the acids already in combination. Thus:

A cellulose acetate-lactate-pyruvate is prepared from cellulose acetate, 40 per cent. acetyl (100 g.), in a bath of 125 ml. pyruvic acid and 125 ml. of 85 per cent. lactic acid by heating at 100° for 18 hours. The product is soluble in water and is precipitated and washed with ether-acetone. M.p. 230–250°.

5. Keten (p. 277) has been used to give mixed acetate-esters.

Cellulose is steeped in the organic acid and treated with keten or, alternatively, the acyl ester, with 0·2 to 1·5 acyl groups per C_6 unit, is treated with keten (U.S.P. 1,990,843; 2,053,280).

Cellulose acetate-nitrates have received considerable attention owing to the possibility of controlling the useful qualities required in the product. They can be prepared in several ways. Cellulose is treated with a bath containing both acetic anhydride and nitric acid in which the acid is said to catalyse the acetylation and the anhydride the nitration (B.P. 341,147). Cellulose (100 g.) is added to an ice-cold mixture of fuming nitric acid (400 g.) and acetic anhydride (1,100 g.). After 1 day the excess of anhydride is hydrolysed by adding the equivalent of water. After standing another day with excess of water at 20–30°, or until suitable solubility has been acquired, the ester is precipitated. One product contained N, 13·8; acetic acid 32·3 per cent.

The action of the above mixture of reagents with the addition of glacial acetic acid was studied by D. Krüger.[1] So long as the proportion of nitric acid was considerable cellulose nitrates of varying properties were alone obtained, but as the nitric acid content was reduced acetate-nitrates were formed over a wide range of diminishing concentration.

The nitration of fibrous cellulose triacetate can be effected by nitric acid containing less than 9 per cent. of water at 0 to 30°. If the acid contains more than 15 per cent. of water the acetate is merely hydrolysed. The acetylation of higher cellulose nitrates is slow. When 2·4 g. of a sample containing N 12·5 per cent. was steeped in a bath of acetic acid and anhydride (each 9·5 ml.) with 0·3 g. H_2SO_4 for 1 hour at 30° and allowed to stand at 20° for 1 day the product contained 8·3 per cent. of nitrogen. The acetyl radicle can be detected or estimated by hydrolysing the ester with sulphuric acid followed by steam distillation. Acetic acid in the distillate is converted into sodium uranyl acetate by the addition, with a large excess of nitric acid, of a reagent made up of 1 g. each of uranyl formate, sodium formate and 50 per cent. formic acid and 3·5 g. each of 96 per cent. alcohol and of water.

The acetic acid is generally estimated by hydrolysis with dilute sulphuric acid, followed by distillation with or without a current of steam. Saponification methods cannot be used in the presence of nitrate. The Schulz-Tiemann method is said to give low results for nitrogen when acetate is present.

[1] *Cellulosechem.*, 1930, 11, 220.

The Analysis of Mixed Esters

Although formic acid can readily be detected and estimated by its reducing powers acetic, propionic, and butyric acids are difficult to determine in the presence of one another. A review of previous chemical methods has been given,[1] and they are discarded, after examination, in favour of a physical (partition coefficient) method outlined below. The colours got by extracting the copper or ferric salts with solvents have been used for qualitative purposes and a quantitative estimation has been made [2] by removing formic acid as an equivalent of mercurous chloride, measuring butyric acid colorimetrically and acetic acid by difference. Distillation of the acid mixtures under various conditions does not give good separation, and Malm therefore recommends the partition method for routine laboratory use.

Analysis of Mixed Cellulose Esters by the Partition Method.—This involves: (*a*) Estimation of the total combined acids.

(*b*) Saponification and isolation of the mixture of acids.

(*c*) Measurement of the partition coefficients, between butyl acetate and water, of both the mixture of acids and those of each acid present.

(*d*) Calculation of the molar ratios of the acids.

(*e*) Calculation of the weight per cent. of the acids (or combined acyl) from (*d*) and (*a*).

Materials Required.—A constant temperature oven or bath controlled at 40°; a vacuum distillation apparatus which may be a 500 ml. round flask with capillary leak fitted to a Kjeldahl head and a vertical spiral condenser, the leading tube going within 3 inches of the bottom of another 500 ml. side-arm distillation flask. Heating is done in a water bath and the receiver cooled to 0°.

Butyl acetate, free from water and acidity, is used, but up to 5 per cent. butyl alcohol can be allowed. The commercial product is neutralised with sodium carbonate, left over calcium chloride and distilled.

Pure samples of the acids present in the ester.

Phosphoric acid solution, 1 molar.

Procedure.—The operations listed under (*a*), (*b*), (*c*), etc., above are carried out as follows:—

(*a*) The total combined acids are determined by the modified Eberstadt method (see p. 286) or by alcoholic alkali, and calculated as acetyl.

[1] C. J. Malm *et al.*, *Ind. Eng. Chem. Anal.*, 1942, 14, 292.
[2] *J. Bact.*, 1929, 17, 79.

(*b*) They are isolated by heating (duplicate) 3 g. portions of the ester (not specially dried) with 100 ml. of 0·5*N*-NaOH in stoppered R.B. flasks at 40° for 48–72 hours. Enough of the 1*M*-H_3PO_4 is added (*ca.* 50 ml.) to give the mono-sodium salt which liberates the organic acids from their sodium salts. The mixture is distilled to dryness in the vacuum apparatus, after which 25 ml. of water are added and the residue again taken to dryness. This is repeated. No accuracy is necessary, as all that is needed is the mixed acids in the proportions in which they exist in the ester.

The distillate is diluted to 250 ml. with CO_2-free water. This usually gives a solution 0·08–0·12*N*.

(*c*) Measurement of the partition coefficients may be illustrated by the case of mixed acetic, propionic and butyric acids. The distribution ratios of the pure acids are determined first by calculating the amount of each required for a 0·1*N*-solution (1·43, 1·87, 2·30 ml. respectively, made up to 250 ml.). These (25 ml.) are titrated with 0·1*N*-NaOH (phenolphthalein) taking, say, *M* ml.

A mixture of 30 ml. of the acid solution and 15 ml. of butyl acetate are put into a small separating funnel and shaken on a routine, *e.g.* 100 per minute for 2 minutes, taking care not to heat the liquids with the hand. The lower layer is removed and a 25 ml. pipette rinsed with it, and then 25 ml. is run into 20–50 ml. of water. Titration with the same 0·1*N*-NaOH, say, M_1 ml.

This is repeated, only using 60 ml. of acid solution and 60 ml. of butyl acetate. Titration, say, M_2 ml.

For each acid is calculated M_1/M, giving k_1, k_2, k_3 respectively, and M_2/M giving k_4, k_5, k_6 respectively, so that the partition coefficient represents the fraction of the acid left in the aqueous layer.

As practice is essential to accurate working, these values of k should be checked by making a ternary mixture of the acids, of known composition, diluting 1·8–2ml. to 250 ml. for an approximate 0·1 *N*-solution and after calculating the molar composition extracting 30 ml. with 15 and 60 ml. with 60 ml. of butyl acetate as before.

The percentage partition coefficients $M_1 \times 100/M = K_1$ and $M_2 \times 100/M = K_2$ are calculated. The composition of the acid mixture is obtained from these data using equations 6, 7 and 1 (below). If the agreement is not good the partition coefficients must be checked until satisfactory results are obtained.

25 ml. portions of the distillates (*b*) are then titrated as above, giving alkali volumes M: 30 ml. portions of it are extracted with 15 ml. of butyl acetate and titrated (M_1 ml.) and then 60 ml. portions with 60 ml. of butyl acetate (M_2 ml.). K_1 and K_2 are then calculated.

Mixture of Three Acids.—Three simultaneous equations are available. If A, P and B are mole percentages of acetic, propionic and butyric acids respectively :—

$$A + P + B = 100 \quad . \quad . \quad . \quad (1)$$

$$Ak_1 + Pk_2 + Bk_3 = K_1 \quad . \quad . \quad . \quad (2)$$

$$Ak_4 + Pk_5 + Bk_6 = K_2 \quad . \quad . \quad . \quad (3)$$

Solving for P we obtain

$$P = \left(\frac{K_1 - 100k_1}{k_3 - k_1} - \frac{K_2 - 100k_4}{k_6 - k_4}\right) \Big/ \left(\frac{k_2 - k_1}{k_3 - k_1} - \frac{k_5 - k_4}{k_6 - k_4}\right) \quad (4)$$

$$B = K_2 - 100k_4 - P(k_5 - k_4)/(k_6 - k_4) \quad . \quad . \quad . \quad (5)$$

Typical values of k are

$$k_1 = 0{\cdot}852 \qquad k_2 = 0{\cdot}587 \qquad k_3 = 0{\cdot}282$$
$$k_4 = 0{\cdot}586 \qquad k_5 = 0{\cdot}261 \qquad k_6 = 0{\cdot}091.$$

Using these values, equations (4) and (5) become

$$P = 10{\cdot}5\ (58{\cdot}6 - K_2) - 9{\cdot}14\ (85{\cdot}2 - K_1) \quad . \quad . \quad (6)$$

$$B = 2{\cdot}02\ (58{\cdot}6 - K_2) - 0{\cdot}656\ P \quad . \quad . \quad . \quad (7)$$

The analyst, however, should use his own values and check them from time to time.

The mole percentages of acid are converted to weight per cent. acyl from the per cent. of apparent acyl (say W) as follows :—

$$A \times W = \text{weight per cent. acyl} \quad . \quad . \quad . \quad . \quad (8)$$

$$P \times W \times 57/43 = \text{weight per cent. propionyl} \quad . \quad (9)$$

$$B \times W \times 71/43 = \text{weight per cent. butyryl} \quad . \quad . \quad (10)$$

Mixture of Two Acids.—Here only two equations and one set of partition coefficients are needed. With a cellulose acetate-butyrate, for example :—

$$A + B = 100 \quad . \quad . \quad . \quad . \quad (11)$$

$$Ak_1 + Bk_3 = K_1 \quad . \quad . \quad . \quad . \quad (12)$$

$$\therefore\ B = (K_1 - 100k_1)/(k_3 - k_1) \quad . \quad . \quad . \quad (13)$$

Using the k values as before, we get

$$B = 1{\cdot}75\ (85{\cdot}2 - K_1) \quad . \quad . \quad . \quad . \quad (14)$$

From the other set of constants a similar equation is obtained.

Notes on the Method.—(*a*) In the case of esters having propionyl and/or butyryl content greater than about 40 per cent., alcoholic alkali must be used for saponification.[1] The alcohol must be completely removed by vacuum distillation to dryness before adding the phosphoric acid, otherwise traces of formic acid are produced.

[1] L. B. Genung *et al.*, *Ind. Eng. Chem. Anal.*, 1941, **13**, 369.

(*b*) With esters of non-volatile water-soluble acids, when alcohol is used it must be removed as above. Distilled water is added to make up the original volume, and HCl added to neutralise the alkali. The cellulose is filtered off and washed, making filtrate to 200–250 ml. The standard procedure is followed, except that as the solution now contains NaCl the coefficients of the known acids must be measured in 0·1*N*-solutions containing the same concentration of NaCl as the filtrates.

(*c*) The results are accurate. A mixture of acetic, propionic and butyric acids, for example, containing mole per cent. 62·3, 28·3 and 9·4 respectively, gave values of 62·0, 28·6 and 9·4 respectively.

(*d*) Experimental values for the partition coefficients of the more usual acids are given in the table below.

PARTITION COEFFICIENTS

	k_1.15 Ml. Bu Ac. 30 Ml. Water.	k_4.60 Ml. Bu Ac. 60 Ml. Water.
Formic . .	0·885	0·660
Acetic . .	0·851	0·589
Propionic . .	0·592	0·263
n-Butyric . .	0·288	0·093
n-Valeric . .	0·124	0·040
n-Caproic * . .	0·036	0·013
Crotonic . .	0·350	0·121
Chloracetic . .	0·532	0·233

The butyl acetate contained 0·04 per cent. water and 1·81 per cent. butyl-alcohol.

* 0·04 *N*-solution used.

Estimation of the free Hydroxyl Content of Celullose Derivatives.[1]—The free hydroxyl content is usually obtained by difference, but it can be estimated by acetylating the derivative completely with acetic anhydride in pyridine solution.

The excess is titrated, but as water must be added the cellulose is thrown out of solution. To avoid retention of the reagent * it is essential that the cellulose should be precipitated in a finely divided form. If it comes out in clots the estimation should be rejected.

The pyridine should be pure (fraction b.p. 115·5–116·5°) except for a trace of water. The reagent is made up of 50 ml. acetic anhydride + 950 ml. pyridine. An additional 5 ml. of anhydride is added for each 0·1 per cent. of water in the pyridine over 0·1. A reflux apparatus with glass joints is used.

[1] C. J. Malm *et al.*, *Ind. Eng. Chem. Anal.*, 1942, **14**, 935.

* Pyridine is difficult to wash out of cellulose. To remove it the material may be dissolved in methylene dichloride-methanol (90 : 10 by weight), poured into methanol and the precipitate boiled with water.

Procedure.—One gram of dried material with 40 ml. of the reagent (very accurately measured) is put into a 250 ml. Erlenmeyer flask and heated under reflux for 24 hours at 75–80°. Blanks are similarly treated.

To precipitate the cellulose in a finely divided condition 5 ml. of water are added down the condenser, shaking and heating for a few minutes. After cooling the condenser is removed and rinsed with about 150 ml. of water draining into a 600 ml. beaker. The contents of the flask, diluted if necessary with water, are then poured into the beaker and the liquid titrated. This is best done electrometrically to *p*H9, or phenolphthalein can be used. If N is the normality of the alkali and M ml. the difference between the blank and the sample titrations the per cent. free hydroxyl

$$(OH) = M \times N \times 1{\cdot}7/\text{wt. of sample.}$$

Triangular diagrams (*cf.* p. 303) can be made showing the relation between free hydroxyl and the composition of a mixed ester. To calculate free hydroxyl two out of three of the following must be known, *viz.*, percentages of OH ; apparent acetyl (*i.e.* whole ester calculated as acetyl) ; acetyl ; and propionyl or butyryl as the case may be.

Let a, p and b be wt. per cent. of acetyl, propionyl and butyryl and h that of the free (OH) ; N_a, N_p, N_b the number of acidic groupings and N_h that of free hydroxyl groupings, respectively. If D is used for the expression

$$162 + 42N_a + 56N_p,$$

the values for an acetate-propionate, for example, are :

Per cent. apparent acetyl $= 4{,}300\ (N_a + N_p)/D$ (i) ;

$a = 4{,}300\ N_a/D$ (ii) ; $p = 5{,}700\ N_p/D$ (iii) ;

$h = 1{,}700\ (3 - N_a - N_p)/D$, assuming 3 replaceable (OH) groups per C_6.

From (ii) and (iii) N_a and N_p are found, and

$$N_h = 3 - N_a - N_p \text{ or } N_h = hD/1{,}700.$$

When the average number of hydroxyl groups present exceeds 3 the degree of polymerisation may be calculated. Since the chains of n glucose units have for each unit 3 hydroxyls with 4 at the ends, the average number of hydroxyls per unit is $(3n + 2)/n$, whence $n = 2/(\text{average} - 3)$. Thus an acetate butyrate showed 3·111 hydroxyls per unit, giving $n = 18$. Direct estimation gave 23.

CHAPTER XVII

CELLULOSE ETHERS

For the preparation of methyl and ethyl cellulose the reagents employed are either the alkyl chloride or sulphate. Methyl chloride (b.p., — 24°) and ethyl chloride (b.p., 12·2°) are used in an autoclave. Dimethyl sulphate may be purified by distillation at 100°/40 mm. and diethyl sulphate, a colourless oil (*d*, 1·1837; b.p., 208°, decomp.), may be distilled unchanged at 118°/40 mm.

The cellulose is employed in the form of alkali cellulose, but is occasionally given the necessary reactivity by acid treatment. The more usual methods of pre-treatment will be found in the examples given. The proportion of water to alkali is of special importance. The following examples illustrate these points :—

(*a*) *Soda Cellulose for the Preparation of Ethers.*[1]—The cellulose is steeped in hot alkali of such concentration that the mass will solidify on cooling and will then contain not less than 30 per cent. NaOH or more than 35 per cent. of water—*e.g.* cotton wool is treated for a short time (up to 20 minutes) in solutions containing 55–75 per cent. NaOH at 50-90°. The mass is pressed, while still hot, till it weighs about three times as much as the original cotton. It should not be exposed to air while hot. Also p. 261.

(*b*) *Cellulose Ethers.*[2]—By using cellulose, or conversion products not soluble in alkali, so that the ratio between water and cellulose is not greater than 4, and still better if as low as 0 to 0·5, the quantities of alkali and etherifying agent may be reduced almost to the theoretical. The amount of alkali or base used must be at least equal to, or preferably three to nineteen times greater than, the amount of water present. The water is kept to this low proportion by using "water-binding" agents, such as oxides of sodium, calcium or magnesium, calcium hydride, sodamide, etc.; best in a diluent such as benzene. Example :

162 g. of cellulose impregnated with 25–36 g. of water are kneaded with 500–1,000 g. benzene and 93–124 g. of sodium oxide with cooling. The product is then kneaded with three to four molecular proportions of diethyl sulphate at temperatures not exceeding 60–80°. Etherification is complete in 1 to 4 hours. Alternatively the cellulose is impregnated with caustic soda solution, say 50 per cent.,

[1] *J. Soc. Chem. Ind.*, 1925. **44**, B, 800.
[2] H. Dreyfus, *ibid.*, 1923, **42**, A, 10; *ibid.*, 1924, **43**, B, 51.

squeezed down and well mixed in the presence of benzene with sufficient lime to remove the water wholly or in part, the mass being kept cool during the operation.

(*c*) *Cellulose Ethers* (L. Lilienfeld [1]).—One of the difficulties in the preparation of ethers of cellulose lies in the effect of variations in the proportions of alkali and water. The best results are obtained when the proportion of alkali is greater than 1 part of alkali to 1 of cellulose. If *a* represents the amount of alkali to be used to 1 part of cellulose, then the amount of water required lies between A and 1·5 A, where

$$A = \frac{a^2 - a + 2}{4}.$$

The higher limit is best, the water being added either at the beginning or during the progress of the reaction.

(*d*) *Preparation of a reactive dry Alkali-Cellulose.*—A product in which the alkali is dispersed in approximately molecular form is made by steeping cellulose (linters) in 20 to 40 per cent. NaOH for 1 hour, pressing to 4·7 times the weight of linters and adding liquid ammonia and sodium to remove all the water. The mixture is covered with toluene and warmed to remove ammonia. Ethers or esters are readily prepared by reaction at 20°, *e.g.* with halide or anhydride of an organic sulphonic acid (U.S.P. 2,123,806 ; 12/7/38).

(*e*) *Preparation of* (*A*) *Mixed, and* (*B*) *Unsaturated Cellulose Ethers.*—Approximately anhydrous cellulose (162) in a mixture of liquid ammonia (3,200 pts.) and an aromatic hydrocarbon, *e.g.* toluene (500 vols.) is treated with sodium (69) and left till the blue colour has disappeared. The mixture is distilled till 200 parts of ammonia remain and (A) etherified, *e.g.* with 250 parts of benzyl chloride + 50 parts of methyl chloride for 2 hours at — 33°. The ammonia is removed, the residue poured into water and distilled in steam, giving a product containing about 1·5 benzyl and 1·0 methyl per cellulose unit. (B) It is treated with an allyl halide for 8 to 10 hours at — 33°, the ammonia removed by raising the temperature to 25° and the product separated as before (U.S.P. 2,232,926/7, 1941 ; B.P. 509,689).

(*f*) *Preparation of Cellulose Ethers of High Viscosity* (U.S.P. 2,241,397 ; 13/5/41).—Products of η not less than 5,000 centipoises in 10 per cent. solution in toluol-alcohol mixture (2 : 1, vol.) at 25°, are obtained if conditions are such as to ensure that the ether dissolves as fast as it is formed. The following gives ethers of

[1] B.P. 200,815, 1923.

good tensile strength and flexibility and of uniform OEt content: 150 parts cellulose (η of 25 per cent. solution in cuprammonium 20–5,000) soaked in 50 per cent. NaOH solution 4 hours and squeezed to become 688 parts, are autoclaved with 1,400 parts of lower alkyl halide, *e.g.* ethyl chloride for 8 hours at 110°. The mixture after cooling is diluted with acetic acid, and the ether thrown out by water. Product has OEt 43 per cent.; η 32,000. Excess of NaOH must be maintained, as this supplies a solvent (alcohol) from the excess of ethyl chloride Using 6 parts of ethyl chloride at 100–130° for 4 to 5 hours, the η will be between 20 and 5,000.

(*g*) *Cellulose for Cellulose Ethers.*[1]—The cellulose is treated with a solution of a strong mineral acid which is removed before any marked degradation has taken place.

Laboratory Preparation of Methyl and Ethyl Cellulose

The following table gives the theoretical percentage content of alkyl substituent in the simpler cellulose ethers :—

Cellulose Ether.	OMe per cent.	OEt per cent.	OPr per cent.
Mono- . .	17·61	23·68	28·93
Di- . .	32·61	41·28	47·97
Tri- . .	45·58	54·87	61·46

The pioneer work of Denham and Woodhouse [2] on the methylation of cellulose showed that repeated treatment was necessary to obtain a high proportion of methoxyl. Treatment of cellulose with three to four times its weight of sodium hydroxide of mercerising strength and subsequently with dimethyl sulphate led to a gradual increase in methoxyl content, *e.g.* in one case the methoxyl percentage rose from an initial 5·3 to 14 after the third and 21 after the fifth repetition.

The lower products are fibrous, becoming more hornlike with increasing methylation. In the early stages they are soluble in cuprammonium, but later not so. Solubility in cuprammonium apparently requires that two hydroxyl groups per C_6 unit should be free. The following method (F. C. Wood), gives a methoxyl content up to 14 per cent. in one operation :—

100 g. of cotton are steeped in NaOH at 42° Tw. for one day and the mass centrifuged to 450 g. The soda cellulose is immersed in a mixture of 100 ml. of dimethyl sulphate (redistilled) and 700 ml. of ether, and the mixture shaken for 36 hours. The liquid is removed by centrifuge and the cellulose ether washed with warm, and

[1] *J. Soc. Chem. Ind.*, 1924, **43**, B, 784.

[2] W. S. Denham and H. Woodhouse, *J. Chem. Soc.*, 1913, **103**, 1735; 1914, **105**, 2357.

finally with boiling, water. It is then again treated with the mercerising alkali to remove degraded cellulose and washed till neutral. Average OMe content 12–14 per cent.

An example of the technique of Denham and Woodhouse will be found on p. 316. The methoxyl content falls somewhat short of that required for a trimethyl cellulose. K. Hess and his co-workers [1] have devised methods by which fully alkylated trimethyl and triethyl derivatives can be obtained. Their method of preparing trimethyl cellulose from ordinary cellulose is substantially the same as that for ethyl cellulose given on p. 318. A special modification using cellulose A and barium hydroxide at 90° gave after two treatments a product containing OMe, 38 per cent.

The repeated treatments are very tedious, and processes have been described by which cellulose can be fully methylated in one or two operations as follows :—

Preparation of Trimethyl Cellulose in One Operation.[2]— This is accomplished by simultaneous deacetylation and methylation of acetone-soluble cellulose acetate. Cellulose also, if finely divided, can be methylated completely in three operations. The product is identical with that given by the acetate, except that, in this case, it can be obtained in fibrous form.

Preparation of Acetone-soluble Cellulose Acetate.—This is done by Barnett's method (p. 280), or by the following modification.[2] Cellulose (50 g.), after exposure to moist air, is soaked (30 mins.) in 360 ml. glacial acetic acid into which chlorine had been passed for 2¾ minutes. 180 ml. of acetic anhydride into which SO_2 had been passed for 6 minutes, are added in portions, with stirring, temperature at or below 5°. A clear viscous solution results after 1 hour during which the temperature is allowed to rise to 15°, and is maintained there for 3 to 4 hours, after which, with stirring, the mixture is heated to 35° for 1½ hours. Partial deacetylation is effected by adding a mixture of acetic acid (75 ml.), water (30 ml.) and concentrated sulphuric acid (7·5 ml.), stirring and cooling so that temperature remains below 15°. After another hour, with stirring, the solution is kept at 18° for about a day. During this time portions are poured into water. When satisfactory the precipitate is asbestos-like and not in the form of hard matted fibres.

The whole is then gradually mixed with excess of ice-water. The solid dissolves in acetone to a colourless solution. It is purified

[1] K. Hess and W. Weltzien, *Ann.*, 1923, **435**, 76; 1925, **442**, 46; 1927, **455**, 209.

[2] W. N. Haworth, E. L. Hirst and H. A. Thomas, *Chem. Soc. Trans.*, 1931, 821; W. N. Haworth and H. Machemer, *ibid.*, 1932, 2273.

by adding the acetone solution to ice-water. The white precipitate, after washing, treating with alcohol-acetone and with ether, leaves 70 to 80 per cent. of acetate containing acetyl, 40 to 42 per cent.

Preparation of Trimethyl Cellulose from Cellulose Acetate.—10 g. of cellulose acetate (acetyl, 40 per cent.) is dissolved in acetone (200 ml.), in a flask fitted with a stirrer and kept at 55° during the gradual simultaneous addition of methyl sulphate (120 ml.) and 30 per cent. aqueous sodium hydroxide (320 ml.). The reagents the latter of which is filtered through asbestos, are added at the rate of one-tenth of the total every 10 minutes. A gelatinous precipitate separates, which clings to the sides of the flask. It is removed by scraping and is washed into the solution with a little acetone.

A persistent emulsion then forms. The acetone, which is maintained at a volume of about 200 ml., is distilled off, and the residue filtered hot. The solid is triturated with boiling water (1 litre) until all soluble impurities have been removed. Trimethyl cellulose remains as a white powder which, after trituration with acetone and ether, is ash-free. Yield, 85–98 per cent.

A product containing 43–44 per cent. OMe is obtained, working at 18°, by the treatment of cellulose acetate (20 g.), with methyl sulphate (160 ml.) and 30 per cent. aqueous sodium hydroxide (400 ml.), reagents added simultaneously during 5 hours. A further treatment gives complete methylation.

A variation, using acetone-insoluble triacetyl cellulose, is described under the determination of chain length (p. 183).

Methylation of finely divided Cellulose.—Filter paper is stirred in water until a thin pulp is formed. The pulp is dried, and the residue rubbed on a metal grater. The powder (4·5 g.), which is still fibrous, is stirred into acetone (350 ml.) and treated, as above, with methyl sulphate (200 ml.) and 30 per cent. sodium hydroxide solution (460 ml.), the temperature being kept at 50–55°, the addition of reagents taking 4 hours. The acetone is removed by evaporation and the temperature raised to 85°. The product (yield, 75 per cent.) is filtered off and washed with boiling water. Ash, 0·2 ; OMe, 37 per cent. Remethylation, as above, gives a trimethyl cellulose (OMe, 45 per cent.) which retains the fibrous structure.

If the dried pulp (above) is ground for a long time with sand, and the mass dried and ground again till the fibres are less than 0·2 mm. in length, the treatment gives a product with OMe content 43·4 per cent. in one operation.

Trimethyl cellulose prepared as above had m.p. 215–216° without decomposition ; higher if not fully methylated—*e.g.* 42 per cent.

OMe had m.p. 242°; $[\alpha]_D^{16}$ −10° (chloroform), −24° (benzene) and −25° (in water 0–15°). Insoluble in boiling water, acetone, lower alcohols, ether and light petroleum. Crystallised from chloroform-alcohol mixture.

Analysis agreed closely with the theoretical values for trimethyl cellulose, *viz.* C, 52·9; H, 7·8; OMe, 45·6. It gave 87 per cent. of 2 : 3 : 6-trimethyl glucopyranose on hydrolysis. Its acetolysis, carried out at 15° instead of 100° as usual for obtaining octa-acetyl cellobiose enabled a series of methylated dextrins (oligosaccharides) to be obtained.[1]

Direct Methylation of Cellulose in the form of Linters or Sliver.[2]— Cellulose in these forms when swollen in 30 per cent. sodium hydroxide solution becomes, after stirring for some hours, a gelatinous mass easily accessible to the methylating reagent (methyl sulphate in dioxan) which is added very slowly during 12 hours at various temperatures. One treatment at 18° gives a product with OMe, 41 per cent. Conditions can be varied as to (*a*) temperature, (*b*) number of treatments, (*c*) whether in air or in nitrogen. The products obtained on methylating raw cotton sliver (chemically untreated) in nitrogen at a low temperature, showed no end group when assayed for chain length.

The results obtained with these variations in procedure are shown in the table.

Substance methylated.	Temp.	No. of Treatments.	Per cent. OMe.	No. of C_6 Units.		$\eta_{sp.}/C_6$ in $CHCl_3$.
				End Group.	Os. Pr.	
Linters direct .	15°	10*	44·6	-	270	0·334
,, ,, .	40–55°c	6†	44·0	170	110	0·149
Sliver direct .	15°	5*	43·4	—	1540	1·39
,, ,, .	40–55°	8†	44·5	150	52	0·06
Linters acetone-soluble acetate	55°	2†	44·5	170	100	0·155
Linters acetone-insol. acetate .	55°	3†	44·0	240	190	0·238

* In nitrogen. † In air.

The following is a general example of the method applied to cotton linters. 15 g. were stirred with 1 l. of 30 per cent. NaOH and left overnight. Dioxan (200 ml.) was added and then methyl-sulphate (200 ml.) in tenth quantities every 20 minutes at 40°. The

[1] W. N. Haworth, E. L. Hirst and H. A. Thomas, *Chem. Soc. Trans.*, 1931, 825.

[2] W. N. Haworth, E. L. Hirst *et al.*, *J. Chem. Soc.*, 1939, 1886, 1899.

temperature was maintained whilst stirring for a further 1 hour, boiling water added and the whole kept at 95–100° for half an hour. The insoluble portion was separated and washed with hot water. It was further methylated by adding dioxan (300 ml.) and 30 per cent. NaOH (800 ml.), leaving overnight and mixing with acetone (300 ml.). The emulsion was treated with methyl sulphate as before. Four treatments were given at 40° and two more at 55°.

The methoxyl content after each of the first four methylations was 14, 36, 41·4 and 42·5, respectively, estimated on the chloroform-soluble fractions. The final product—almost entirely chloroform soluble—was precipitated fractionally by light petroleum. 180 g. yielded head and tail fractions of 30 g. and 0·2 g. and two middle fractions of 19 g. and 127 g.

As a general rule a methylated cellulose containing less than 40 per cent. of methoxyl is insoluble in chloroform, so that this property can be applied as a test of homogeneity.

Purification and Crystallisation of Trimethyl Cellulose.[1]—Trimethyl cellulose, after precipitation from aqueous solution and drying at 100°, is digested at 65° with benzene. A small insoluble residue is separated. Light petroleum is added to slight turbidity and, on centrifuging, the solid causing turbidity is removed. It consists of the nearly pure trimethyl ether, and carries with it all the colour. The solution is then mixed with about three-quarters of its volume of light petroleum and the white precipitate removed by filtration and treated with ether on the filter. If the precipitate is thoroughly moistened with ether it dries to white solid masses, otherwise to transparent grains.

This product is insoluble in acetone, ether and light petroleum, moderately in hot methyl-, ethyl-, and amyl-alcohols; $[\alpha]_D^{20}$ −18·44° (water); −5·08 (pyridine).

For crystallisation a 10 per cent. solution in alcohol-chloroform (1 : 1) is concentrated slowly in a closed vessel through which a stream of dry air is circulated. In a few days small spherical crystals form, which change into feather-like clusters. When the solvent has evaporated the whole mass will have crystallised.

Preparation of Triethyl Cellulose.[2]—The method consists in a very slow addition of ethyl sulphate to alkali-cellulose at a temperature of 50–55°. After some seven treatments * the content of OEt approaches that required for triethyl cellulose (54·87 per cent.).

[1] K. Hess and H. Pichlmayr, *Ann.*, 1926, **450**, 29.
[2] K. Hess and A. Müller, *Ann.*, 1927, **455**, 209.

* The methods of Haworth for trimethyl cellulose might be applicable to the triethyl ether.

50 g. of cellulose (preferably regenerated) are used, and the table given below shows the working of the process.

The product from each treatment I to V is poured on to a filter cloth in a hot jacketed funnel and sucked fairly dry. Hot water washing must be avoided at these stages. From No. VI the residue is washed with hot water till moderately free from alkali salts. Considerable foaming takes place in the early stages. Yield, 84 per cent. when cuprammonium rayon and 64 per cent. when viscose rayon was used.

For purification the dry product is dissolved in ten times its weight of glacial acetic acid, filtered, and the filtrate diluted with an equal volume of methanol. The solution is poured, with stirring, into ice water. The precipitate is filtered, washed and dried. If not white (from viscose rayon it is always yellowish), it is shaken for a time with methanol.

Step.	Water ml.	NaOH g.	Diethyl Sulphate ml.	Temp. °C.	Time.	OEt per cent.
I.	250	20	65	60	2 hours	
II.	—	50	—	20	20 mins.	
	—	—	25	55	1 hour	
III.	—	150	—	20	20 mins.	
	—	—	65	55	2 hours	
			Worked up for first time.			
IV.	200	200	65	55	4 hours	40·2
			Second working up.			
V.	150	250	40	50	3 ,,	47·5
			Third working up.			
VI.	150	200	40	55	6 ,,	53·7
VII.	150	200	40	55	4 ,,	55·2

Analysis agrees closely with theory which for $C_{12}H_{22}O_5$ (246·2) requires C, 58·5 ; H, 9·0 ; OEt, 54·87. The products sinter about 230° and melt at 240–245°. They are soluble in most solvents except water, methyl and ethyl alcohol, and acetone. The product from viscose rayon will not dissolve in ether, but if a solution in tetraline is thrown out by the addition of methanol, the precipitate becomes soluble in ether.

The optical rotation is remarkable in being positive. In the table on p. 319 values for the trimethyl ether are included for comparison.

Crystallisation of Ethyl Cellulose.—If a dilute solution in benzene is allowed to evaporate slowly, it deposits needle-shaped crystals in clusters or in feathery masses. Generally it comes out in flocks or evaporates to form a film.

Solvent.	Trimethylcellulose.	Triethylcellulose.
Benzene . . .	$[\alpha]_D^{20}$ −18·5	$[\alpha]_D^{20}$ + 26·1
Pyridine . . .	− 5·1	+ 49·1
Chloroform . . .	− 4·3	+ 24·4
Acetic acid . . .	− 9·8	+ 11·5
Water	$[\alpha]_D^0$ −18·4	—

Technical Preparation of Cellulose Ethers

The name of Dr. L. Lilienfeld is associated with the early development of these products.[1] His discoveries are contained in the following English patents: B.P. 12,854 of 1912; 149,318, 149,320, 163,016, 177,810, 181,391–181,395, 200,815, 200,816, 200,827, 200,834, 203,347, and 203,349. Dreyfus patents include B.P. 164,379; 176,420; 269,531 and F.P. 530,891.

Other related patents are: Leuchs-Bayer Co., G.P. 322,586 (1920); Bayer Co., G.P. 352,191 (1919); E. Tempel, G.P. 408,342 (1922), and many American patents of the Eastman Kodak and the Du Pont de Nemours Companies.

There is not much difference between the behaviour of methyl- and ethyl-cellulose, but their general properties vary markedly with the proportion of alkyl groups contained in the unit. The Lilienfeld ethers show considerable stability to water, acids and alkalis. Some of them, however, will swell, or even dissolve, in water, and this action is greater the colder the water—*e.g.* a preparation which was insoluble in water at 16° or higher, swelled considerably at 8–10° and became soluble at 4°. Such ethers when treated with agents like tannin or formalin become more or less insoluble (G.P. 406,081).

The ethers are capable of swelling, or are soluble in, a large number of organic liquids or mixtures of liquids, and are miscible with many solid organic compounds. Thus, a patent specification quotes, *inter alia*, methyl and ethyl alcohols, formic and acetic acids, methyl, ethyl, amyl, butyl acetates, acetone, carbon tetrachloride, chloroform, acetylene dichloride, trichloroethylene, tetrachloroethane, benzene, toluene, xylene, nitrobenzene, aniline, turpentine, castor, linseed and olive oil, paraffin, phenol, naphthalene, camphor, triphenylphosphate, tricresylphosphate, etc. The films or threads obtained from solutions of cellulose ethers in organic liquids are of great tenacity and flexibility, non-inflammable and of low specific gravity.

[1] Compare Reinthaler, "Artificial Silk": London, 1928.

The methods used in large-scale preparation are similar to the laboratory processes already described.

Preparation of Ethyl Cellulose Insoluble in Water at 15° upwards, using Diethyl Sulphate (Lilienfeld).—200 kg. of sulphite cellulose are converted into viscose, which is precipitated out, washed and redissolved in a solution containing 200 kg. of caustic soda so that the whole weighs about 2,400 kg. This is treated over 2 hours with 600 kg. of diethyl sulphate in separate portions, the temperature being allowed to rise to about 40°. The mixture is then warmed up to 55° for about 2 hours. A salve-like mass is formed containing an ether which is soluble in water at 16° and below. In order to convert this into an ether which is insoluble at 1–3°, 120 kg. of powdered caustic soda are added at 50°, 200–360 kg. of diethyl sulphate are stirred in, and the mass warmed to 70–90°. When at 80°, 120 kg. of caustic soda and 200–360 kg. of diethyl sulphate are stirred in, and after an interval this treatment is repeated three times, so that in all a total of 600 kg. of caustic soda and 1,000–1,800 kg. of diethyl sulphate are used. The mixture is diluted with water, filtered and the ethyl cellulose washed with water at 15°, stirred with dilute sulphuric (or sulphurous) acid, and again washed with water until free from acid. The mass is dried and forms a white powder.

Preparation of Ethyl Celluloses Insoluble in Water above 16° but Swelling or Dissolving below 10° (Lilienfeld).—These are prepared generally by using 1 part of cellulose 0·3–2·5 parts of water and 0·6–3·0 parts by weight of caustic soda, using either diethyl sulphate or ethyl chloride, preferably in the presence of salts of copper or iron as catalysts.

1. The following method gives an ether in the form of a flaky mass soluble in water at 1–5°, the solution becoming a jelly at 16°. The product is soluble in the range of organic solvents mentioned above. It forms clear flexible films which are not affected by water at 16°, but swell without disintegration in water at 8–10°, passing into solution at 4° and lower temperatures :—

200 kg. of 50 per cent. caustic soda solution and 100 kg. of powdered caustic soda are ground together and cooled ; 100 kg. of finely divided sulphite cellulose are added and the mass kneaded in a machine fitted with a cooling device. The mass absorbs 20–60 kg. of water from the air. It is placed in an autoclave, 310 kg. of ethyl chloride are added, and the whole heated at 90–150° for 8 to 12 hours with stirring. The contents are treated with water and worked up as previously described.

2. By the following variation an ether may be obtained which

is not soluble even below 10°, but which swells in water at 1–5°. The films swell in water only below 5°, but do not disintegrate :—

200 kg. of cellulose are treated with 1,800 kg. of 18 per cent. caustic soda solution and left for 12 to 28 hours at room temperature. The mass is pressed to weigh 500–720 kg., after which it is kneaded with 250 kg. of powdered caustic soda with cooling. The mass is then treated in the autoclave with 450–600 kg. of ethyl chloride and heated to 100–150° for 6 to 12 hours with stirring.

Propyl, butyl and amyl ethers are prepared usually by reaction of the alkyl chloride with soda cellulose, or with cellulose in the presence of pyridine. As the alkyl group increases in size reactivity becomes difficult and the solubility of the product decreases. See B.P. 326,865 ; F.P. 664,932.

An experimental review of the above methods has been given by E. Berl and H. Schupp,[1] and a general review by D. Traill.[2]

Solubility and General Properties.—Technical methyl ethers are of three types : (*a*) the most highly substituted which are soluble only in organic solvents and not in water, to which also they are very resistant. They are used for films, etc. ; (*b*) water-soluble products of OMe content about 22 to 26 per cent. sold under the trade names of Tylose, Colloresin, etc. ; (*c*) alkali-soluble (but not water-soluble) products of lowest methoxyl content. These can be dissolved in 5 to 12 per cent. NaOH to a concentration of about 8 per cent. Cooling is sometimes required, but, once dissolved, the solution is stable at ordinary temperatures.

Ethyl celluloses show similar characteristics. Water-solubility begins when ethylation reaches the mono-stage, about 27 per cent. OEt. The products are also soluble in acetic acid and ethyl alcohol, but for commercial purposes the (approximate) di-acetate of OEt 40 to 50 per cent. is preferred as, in addition, it dissolves in a wide range of organic liquids, giving colloidal solutions. Ethers containing as little as 5 to 10 per cent. OEt show similar alkali-solubility to the methyl esters (*c*) above.

Water-solubility thus begins when about 1·0 to 1·2 hydroxyl groups per C_6 unit have been etherified, though the solutions coagulate at moderate temperatures. B.P. 452,506 claims that by using a sodium-copper-cellulose complex, methyl ethers containing as little as 0·72 to 1·1 methoxyl groupings per C_6 can be prepared, which are soluble in water. The solutions are unaffected by heating. Ethyl ethers with 1·0 to 1·2 ethoxyl groupings per C_6, giving water solutions which are stable up to 70°, are prepared in the same way.[3]

[1] *Cellulosechem.*, 1929, **10**, 41. [2] *J. Soc. Chem. Ind.*, 1934, **53**, 337·
[3] *Cf.* W. Traube, *Ber.*, 1936, **69B**, 1483.

Cellulose ethers are stable towards alkalis and, when the alkyl content is moderately high, also towards acids. Ethers of ethoxy-content greater than 45 per cent., for example, are unchanged after treatment with accumulator acid for 6 days at 48°, but with ethoxy-contents below 42 per cent. decomposition is rapid, and even water has an appreciable effect. Methylene ethers are decomposed by acids although they resist alkali completely.

Methods for the investigation of the general properties of cellulose ethers have been given by Lorand.[1] Properties are found to depend upon the substituent group and the degree of substitution, the uniformity of etherification and the cellulose chain-length in the product. The sorption of moisture depends on the extent to which the hydroxyl groups are free and for the same degree of etherification it falls with increasing size of the alkyl group. Thus moisture sorption for methyl, ethyl and butyl ethers with about 2 alkyl groupings present was 3, 1·7 and 1 per cent. respectively. Water solubility shows a similar trend. Methyl ethers are soluble up to 1·8 methyl groupings, ethyl ethers up to 1·4, while butyl, etc., ethers are insoluble. Substitution by non-polar groups such as benzyl, butyl and higher fatty radicles, prevents solubility in water and alkaline solutions, even under cooling.

Solubility is also reduced by the lack of uniformity in ordinary preparations. Bock,[2] by ethylating cellulose in trimethylbenzyl ammonium hydroxide solution, showed that a product containing as little as 0·6 group per C_6 was soluble in water.

Cellulose Methylene Ethers.—Cellulose when treated with mixtures of sulphuric acid and paraform at 18° for times varying from 20 seconds to 5 minutes, combines with the methylene group, yielding compounds which contain from 1 to 7 per cent. of methylene oxide (CH_2O). Thus an acid mixture containing 73 per cent. of H_2SO_4 and 4·9 per cent. of formaldehyde, acting for 20 seconds, 1 minute and 5 minutes, respectively, on cotton fabric, gave products containing respectively 3·3, 5·3, and 7·35 per cent. of (CH_2O). These dye more deeply than the original and swell in water.

A Cellulose Monomethylene Ether, $C_6H_7O_2(OH)(O_2CH_2)$ containing 17·2 per cent. of methylene oxide has been obtained[3] by the use of the reactive dichlorodimethyl sulphate. It is probable that the methylene grouping is linked, through oxygen atoms, to carbon atoms 2 and 3 in the anhydro-glucose complex. Cotton is treated for 5 minutes with sulphuric acid (*d*, 1·7) containing 15 per cent. of

[1] E. J. Lorand, *Ind. Eng. Chem.*, 1938, **30**, 527.
[2] L. H. Bock, *Ind. Eng. Chem.*, 1937, **29**, 985.
[3] F. C. Wood, *J. Soc. Chem. Ind.*, 1931, **50**, 414T; *ibid.*, 1933, **52**, 33T.

paraform. The product, after removing loose formaldehyde by immersion in water and refluxing in 20 per cent. ammonia for half an hour, contains 6·3 to 7·0 per cent. of CH_2O. The ether is now soaked in NaOH (*d*, 1·2), centrifuged and immersed in dilute alkali, whilst dichlorodimethyl sulphate (three times theoretical quantity) and NaOH solution (*d*, 1·4) are run in simultaneously, under vigorous mechanical stirring which should be frequently reversed, The temperature is maintained at 60°. After one treatment the product contained 10·7 per cent., after three, 17·6, and after six, 17·4 per cent. of (CH_2O), the maximum obtainable.

Dichlorodimethyl sulphate is prepared by the method of Fuchs and Katscher.[1]

The mono-methylene ether of cellulose is fibrous, but in very short broken lengths. The usual swelling agents and solvents for cellulose are without action. The ethers are not decomposed after boiling with *N*-NaOH for 4 hours, but are quantitatively hydrolysed by *N*-H_2SO_4 with liberation of formaldehyde.

Benzyl Ethers of Cellulose.—By the use of benzyl chloride on soda- or hydro-cellulose, in the presence of alkali a fibrous product results which is insoluble in the usual solvents and in Schweizer's solution. Its composition approximates to that of a mono-benzyl ether. Repetition of the treatment leads to products with definite melting-points and solubility in organic solvents. The following methods of preparation are given by M. Gomberg and C. C. Buchler.[2]

(*a*) *A Fibrous Benzyl Ether.*—Cotton is soaked for 3 days in 15 per cent. NaOH solution and squeezed to retain three times its weight of solution. It is heated 5 hours at 100° with excess of benzyl chloride, the excess of which is removed by distillation in steam. The product is digested for two days with cuprammonium, washed, digested with dilute acid, and washed with alcohol. Found C, 58·0; H, 6·4; $C_{12}H_{19}O_{10}.C_7H_7$ requires C, 55·0; H, 6·3.

(*b*) *Structureless Benzyl Ether.*—5 g. of filter paper are digested for two days in a solution of 10 g. NaOH in 30 g. of water. The mass is treated with 30 g. of benzyl chloride and heated at 100° for 7 hours. The product is worked up as above, and the treatment repeated. The ensuing product is soluble in ethyl acetate, from which it is thrown out by alcohol. It softens at 165° and has m.p. 175–177°. Found, C, 69·7; H, 6·3; $C_{12}H_{16}O_{10}.(C_7H_7)_4$ requires C, 70·2; H, 6·4. Soluble in ethyl acetate, chloroform, and nitrobenzene; gelatinised by acetone. Both the mono- and tetra-products are very stable. They do not reduce Fehling's solution

[1] K. Fuchs and E. Katscher, *Ber.*, 1927, **60**, 2288.
[2] *J. Amer. Chem. Soc.*, 1921, **43**, 1904.

and the "tetra" benzyl ether does not give any indication of reducing sugars after heating with dilute acids for 2 hours.

The following shows the theoretical composition of the ethers possible :—

$C_6H_7O_2\langle^{(OH)_2}_{OC_7H_7}$	$C_{13}H_{16}O_5$	252	C = 61·9 ;	H = 6·35
$C_6H_7O_2\langle^{(OH)}_{(OC_7H_7)_2}$	$C_{20}H_{22}O_5$	342	C = 70·2 ;	H = 6·43
$C_6H_7O_2(OC_7H_7)_3$	$C_{27}H_{28}O_5$	432	C = 75·0 ;	H = 6·48

The present writer (1932) endeavoured to prepare a fully benzylated product, but nothing higher than a dibenzyl derivative (C_6 unit) was obtained. Alkali cellulose from cotton was found suitable for experiment, but the product from ash-free filter paper was easiest to purify. Excellent products were obtained from cellulose acetate, and from viscose cellulose.

A single treatment with alkali and benzyl chloride gave fibrous "mono"-ethers. By repetition horny soluble products were obtained.

(*a*) *Fibrous Product.*—30 g. of cotton wool were digested in 20 per cent. NaOH solution for 24 hours and pressed to weigh 90 g. The mass was heated (water bath) for 8 hours with 25 g. of benzyl chloride, removed, pressed, washed with water and alcohol, digested twice with cuprammonium, with dilute acid, and washed with water and alcohol. It was finally digested with chloroform to remove higher ethers : Found, C, 60·7 ; H, 5·86 per cent.

(*b*) *Dibenzyl Derivative.*—Filter paper 30 g., treated with alkali as above and pressed to 100 g. Benzylated with 50 g. benzyl chloride and 80 ml. of sodium hydroxide solution (25 g. NaOH in 80 ml. water), 6 hours. Benzyl alcohol removed by steam. The solid was treated with cuprammonium, etc., as above, and then heated with 50 g. benzyl chloride, etc., for 10 hours.

The product was not soluble in ethyl acetate (characteristic solvent for higher benzyl ether), but dissolved partly in chloroform and easily in pyridine.

It was again treated with 100 g. of benzyl alcohol and alkali for 12 hours and the processes repeated. The dry product was now soluble in ethyl acetate. The solution was treated with alcohol, the benzyl cellulose coming out in clots. Yield, 25 g. For purification 25 g. were dissolved in 70 ml. of pyridine and the solution poured into water. The ether came out in a thread-like form and was purified from organic solvents. On analysis it gave C, 69·0 ;

H, 6·6, approximating to the composition of a dibenzyl ether. It was optically inactive in pyridine solution.

With viscose cellulose and acetate rayon the procedure followed the same general lines. 20 g. of acetate rayon in the minimum of acetone were treated with 30 g. benzyl chloride and 200 ml. of 20 per cent. NaOH and refluxed for 5 hours. The product was given this treatment repeatedly for periods of 6 to 12 hours. Yield, 20 g. The melting-point, 221–223°, was more definite than that of any other preparation.

A complete examination of the benzylation process has been made by Mienes and also by the Japanese workers.[1] The former found that for products up to the di-ether the degree of benzylation is a function of the molar ratio of alkali to cellulose in the alkali cellulose. At higher degrees the concentration of the mercerising solution becomes important. The solubility of the products (benzene alcohol, 10 : 2) increases with the amount of pressure applied to the alkali cellulose at any particular ratio of cellulose to alkali.

The use of benzyl chloride vapour is satisfactory provided constant stirring or kneading can be employed. The addition of chlorobenzene, a solvent for the lower esters, accelerates the reaction (G.P. 555,930). The results given in the table below were obtained using benzyl chloride to cellulose 12 : 1, at 125–130° for 3 to 6 hours. The excess reagent was removed by distillation and the mass extracted with methanol and boiling water.

NaOH soln. Wt. per cent.	Pressure applied kg./cm.²	Pressed to grams of Alk.-Cellulose.	Mols. NaOH per C_6 in Alk. Cellulose.	Yield per cent.	Solubility Benzene-alcohol 10 : 2.	Carbon per cent.
20	200	57·5	1·43	125	0	—
30	200	63	2·23	135	23	65·7
35	200	69	3·00	160	73	69·0
40	200	79	3·84	175	93	70·0
25	50	90·5	2·95	160	46	—
29	50	98	3·71	172	92	68·8
20	20	104·5	2·87	150	12	—
30	20	119·5	4·86	175	96	69·8

A technical method[2] for the preparation of benzyl cellulose is as follows : 1·4 to three times the theoretical amount of benzyl chloride is added to pressed alkali cellulose at a low temperature. Solid

[1] K. Mienes, " Cellulosester u. Cellulosäther mit bensonderer Berucksichtigung der Benzylcellulose ". Chem.-technisher Verlag, Bodenbender; Berlin, Steglitz, 1934; K. Atsuki, *J. Soc. Chem. Ind.*, Japan, 1934, **37**, 128.

[2] Imp. Chem. Industries, Ltd., E. P. 360,409; 327,714.

sodium hydroxide is then added at intervals and the mass heated slowly to 80–100° and so maintained for 24 hours. The product is treated with alcohol, filtered, sodium chloride removed, the residue washed with alcohol, pressed and dried.

There are various methods for isolating benzyl cellulose on the large scale. The mixture of benzyl alcohol, benzyl cellulose, benzyl chloride, sodium chloride and water is mixed with castor oil, 2·5 litres for 500 g. of original cotton, and sufficient methyl alcohol to dissolve the oil and the benzyl alcohol. The product separates as an impalpable powder, easily washed free from salt and water. Other oils which do not dissolve benzyl cellulose and are miscible with benzyl and methyl alcohols may be used.[1]

Another process involves the treatment of the reaction mass with a mixture of aromatic and aliphatic hydrocarbons in equal parts. The former, with the by-products, cause the benzyl ether to swell to a viscous mass, while the latter control this action and enable the by-products to be removed.

The technical benzyl ethers are very stable, resisting water, alkali (up to 20 per cent. NaOH) and sulphuric acid of accumulator strength. Their viscosity is high and, for use in lacquers, processes of fairly severe acid treatment are used for reducing it (*e.g.* B.P. 342,391). An ingenious method consists in treating the crude mass, after reaction, with steam under superheat. This decomposes the excess of benzyl chloride, and the acid produced brings about the reduction in viscosity (B.P. 333,902).

Nitrobenzyl-cellulose and its Application to the Dyeing of Cotton.[2]—Cotton is convertible into a benzyl derivative by the use of Leukotrope (phenyl-benzyl-dimethyl-ammonium chloride). Nitro-leukotropes were used as follows :—

The cotton was boiled with a 1 to 2 per cent. solution of nitro-leukotrope to which slightly more than the calculated quantity of sodium carbonate had been added. The nature of the ether formed varies with the time of boiling and the proportion of cotton to the solution. Generally with 1 g. of cotton 100 ml. of 1 per cent. nitro-leukotrope solution were used and boiling continued for 10 minutes.

The treated cotton is reduced with hydrosulphite solution at 60–70° and the product diazotised at 5°. After washing it may be coupled with, *e.g.* β-naphthol (rose shade); H acid (violet); J acid (red), etc.; *m*-nitro-leukotrope, m.p. 144°, is prepared in the usual way from *m*-nitro-benzyl chloride and dimethylaniline.

[1] Pathé Cinema Co., French Pat. 615,349 (24/9/25), *J. Soc. Chem. Ind.*, 1927, **27**, 649A.

[2] D. H. Peacock, *J. Soc. Dyers and Col.*, 1926, **42**, 53.

For numerous other cellulose derivatives containing nitrogen the book of Marsh and Wood (appendix) may be consulted.

Hydroxy-alkyl and Alkoxy-alkyl Ethers

Glycol ethers and homologues are prepared (*a*) by the action of halogen derivatives of glycol and other polyhydric alcohols on soda cellulose (B.P. 166, 767), and (*b*) by reaction with ethylene oxide, propylene oxide, glycide, etc. (B.P. 343,873), as follows :—

$$\text{Cell.OH} + \underset{\backslash\text{O}/}{\text{CH}_2\text{—CH}_2} \rightarrow \text{Cell.O.CH}_2\text{.CH}_2\text{OH}.$$

The second reaction, which is of outstanding importance, affords a range of products varying with the conditions and the proportions of oxide and cellulose employed. Their composition lies between fully etherified (triglycol-) cellulose to products containing less than 0·25 glycol residue per C_6 unit. The terminal CH_2OH group may also enter into reaction.

Complete water solubility is found with glycol ethers in which 3 or more hydroxyl groupings of the cellulose are substituted ; incomplete water solubility, but solubility in dilute alkali, when 1·5 to 2·5 are substituted and solubility only in 5 to 10 per cent. alkali with substitution of 0·5 to 1 hydroxyl. These products are obtainable under the trade name of Cellofas.

Damped soda cellulose is stirred with ethylene oxide in an autoclave for 16 hours at below 30° (B.P. 359,618). The higher substituted (water-soluble) products are extracted with alcohol, the lower substituted products are dissolved in alkali and precipitated by acid.

Damask, organdie and other finishes on cotton cloth are given by soaking the cloth in mercerising alkali and treating it with the organic oxide in carbon tetrachloride solution.

Schorger [1] has examined the lower ethers containing less than one glycol group per C_6. Soda cellulose was treated, at ordinary temperature, with ethylene oxide at a rate slightly greater than it was absorbed. The reaction is quantitative and exothermic, and was continued until the necessary quantity of oxide had been added after which the temperature was raised to 45° (U.S.P. 1,941,276/8). The soda cellulose is best prepared in a lye containing 43 per cent. NaOH.

Complete solubility in dilute alkali can be obtained by freezing. Good alkali-solubility is obtained when 13 per cent. (on the dry cellulose) of oxide (or 24·8 per cent., the equivalent, of ethylene chlorhydrin) is used, and water solubility with 80 per cent. of oxide.

[1] A. W. Schorger and M. J. Shoemaker, *Ind. Eng. Chem.*, 1937, **29**, 114.

Schorger considers that with 14 to 15 per cent. of ethylene oxide one molecule has reacted with two C_6 units of cellulose. The product therefore is described as ethylene glycol dicellulose. It is fibrous and resembles cotton wool in appearance. For higher homologues see B.P. 343,873.

Ethylene oxide has b.p. 12·5°, and propylene oxide b.p. 35° (at 760 mm.); glycide, b.p. 61–65° (13 mm.).[1] Attempts to estimate the glycol radicle by Zeisel's method have not given very satisfactory results.

A useful development in the production of water-soluble alkylated hydroxymethyl ethers results from the use of trimethylbenzyl ammonium hydroxide. This dissolves cellulose and acts as a base during the reaction between it and halogen derivatives of acetals (U.S.P. 2,083,554; 2,084,125). The latter are prepared as follows, *e.g.* :—

$$\text{R.CHO} + \begin{matrix}\text{HO.CH}_3\\ \text{HO.CH}_2\text{.CH}_2\text{.Cl}\end{matrix} = \text{R.CH}\begin{matrix}\diagup\text{OCH}_3\\ \diagdown\text{O.CH}_2\text{CH}_2\text{.Cl}\end{matrix} + \text{H}_2\text{O}.$$

As an example, 165 g. of sulphite pulp was added to 1 l. of the solvent (40 per cent. solution) and stirred for 1·5 hours at about 90°. After cooling to 60°, β-chloroethylmethyl formal (186 g.) was added gradually over 2 hours. After heating for 3 hours more at 80° the excess of base was neutralised with acetic acid and the product precipitated by the addition of acetone (1·5 l.). After kneading the gelatinous mass with acetone, the ether, dried at 80°, showed 5·2 per cent. of combined formaldehyde.

A lauryl cellulose methylene ether, $C_{12}H_{25}O.CH_2.O\text{Cell.}$, was obtained in the same way from the solution of cellulose and chloromethyl lauryl ether. Reaction at ordinary temperature for 5 hours and then 2·5 hours at 45°. This product contained one lauryloxymethyl group per C_6 unit.

Celluloseglycollic Acid[2] is prepared from alkali cellulose (made with 20 per cent. NaOH), which is treated in the cold with a concentrated solution of sodium monochloracetate. The sodium salt is soluble in water, but precipitated by alcohol. The free acid is precipitated on the addition of mineral acid, and is not hydrolysed on heating with acid or alkali. Analysis and physical measurements show that only one glycollic acid residue per $C_6H_{10}O_5$ unit is combined.

[1] L. G. Lawrie *et al.*, *J. Soc. Dyers and Col.*, 1940, **56**, 6.
[2] I. Sakurada, *Brit. Chem. Abs.*, (A), 1929, 430.

Another method of preparation is to steep cellulose in aqueous monochloracetic acid and prepare a mixture containing cellulose, 17–33 ; H_2O, 27–54 ; chloracetic acid, 7–25 ; and excess of NaOH (10–30 per cent.). The mass is kept at about 20–40° (U.S.P. 2,278,612 ; 7/4/42).

Cellulose-xantho-acetic Acid.[1]—Viscose, freed from by-products by treatment with dilute acetic acid, can be brought into reaction with sodium monochloracetate to give the sodium salt of cellulose-xantho-acetic acid which is thrown out on the addition of alcohol or brine. " Xanthated " cellulose ethers are described by Lilienfeld in a number of patents (B.P. 357,154, 357,167, 357,595 ; U.S.P. 1,674,401/5, etc.).

Mixed Ethers and Ether Esters

Mixed ethers show reduced sensitivity to water below 20°, compared with methyl and (some) ethyl ethers, and this even in the case of physical admixture, *e.g.* a methyl ether mixed with a highly etherified ethyl cellulose in small proportion (B.P. 252,176). True mixed ethers are prepared either by treating cellulose first with one and then with the other alkylating agent, or by using a mixture of both agents at the same time. Thus *ethyl butyl cellulose* is prepared by treating alkali cellulose (cellulose 10 pts. ; 60 per cent. NaOH solution, 60 pts.) with about 20 parts each of ethyl chloride and butyl chloride at 120°. This product contained ethoxyl 32 per cent. and butoxyl 14 per cent., but the proportions can be varied by changes in the reacting quantities. *Ethyl benzyl cellulose*, similarly, is made from alkali cellulose (100 parts cotton in 30 per cent. NaOH solution pressed to 250 g.) which is treated with ethyl chloride (100 parts) and benzyl chloride (14 parts) for 3 hours at 110°. Alternatively the soda cellulose is ground with 2 mols. of benzyl chloride (50–100°) and then with 1 mol. of ethyl sulphate (below 50°). After a few hours powdered NaOH (6 mols.) is added, followed by 3 mols. of benzyl chloride and then 2 mols. of ethyl sulphate as before. A final treatment with 3 mols. NaOH and 3 mols. of ethyl sulphate is given.

Multiple ethers are obtained by similar means, *e.g. methylethylbenzyl cellulose* by treating methylethyl cellulose with benzyl chloride (U.S.P. 1,833,720). A *methylethylbutyl* cellulose containing the substituent radicles in equal proportion is made from alkali cellulose (cellulose, 10 ; 50 per cent. NaOH, 20, plus powdered NaOH 10 parts) etherified with a mixture of ethyl chloride 20 ; butyl chloride 30 parts

[1] T. Nakashima, *J. Soc. Chem. Ind.*, Japan, 1928, **31**, 31B.

(3 hours at 110°, 3 hours at 140°). The product is then treated in the same way with a mixture of methyl chloride 14 ; ethyl chloride 16, and butyl chloride 24 parts.

The use of ethylene oxide coupled with an alkyl chloride, usually at 50°, gives mixed hydroxyalkyl alkyl ethers, *e.g. hydroxyethylbenzyl cellulose* (B.P. 345,028 ; F.P. 686,598).

Cellulose ether esters also show good resistance to water. Mixtures of ether and ester such as methyl cellulose and cellulose nitrate have been described (G.P. 540,872) in which the water solubility of the ether component is inhibited and, in turn, the normal solubility of the ester component in organic solvents is reduced.

True ether-esters are usually made by the action of the esterifying agent on cellulose ethers. Many ethers which swell in water and are difficultly soluble in solvents become indifferent to water and soluble in acetone and other solvents after acetylation, benzoylation, etc. (G.P. 525,835). The esterification is carried out in the usual way with a catalyst, using a non-solvent diluent if a fibrous product is desired. Dimethylcellulose acetate is prepared in this way. From methyl cellulose containing between one and two OMe groupings a benzoate is obtained (39 per cent. benzoic acid) in which about 2·5 hydroxyl groups per C_6, in all, are substituted and one containing benzoic acid, 35 per cent., from monoethyl cellulose. The ether is treated with sodium hydroxide and with benzoyl chloride dissolved benzene.

Ethylcellulose stearate, laurate, oleate, linoleate, etc. (B.P. 334,897), as well as acetate, lactate, benzoate, etc. (U.S.P. 1,880,558), have been obtained from ethyl cellulose (say 40 per cent. OEt) by heating at 100–150° with the requisite fatty acid.

Improved water resistance is also given by esterification with inorganic acids. Dispersions of cellulose ethers in xylene react with inorganic acid chlorides, for example, to give products containing a small percentage of the acid radicle (G.P. 511,208). Thus a cellulose ether-silicate is prepared by adding to 20 g. of water-insoluble ethyl cellulose in 200 ml. of xylene, silicon tetrachloride (5 g.) dissolved in chloroform (10 ml.) with pyridine (5 ml.). The whole is gently heated, and forms a jelly from which the solvents are removed by the use of a current of steam. The product is extracted with benzene and contains SiO_2, 3·8 per cent.

The action of phosphoryl chloride gives products with 3 or 4 per cent. of PO_4 (B.P. 300,942), and that of diacetyl-orthonitric acid [1] acting below 10° gives cellulose ether nitrates (B.P. 347,423).

[1] D. Krüger, *Cellulosechem.*, 1930, 11, 220, refers to the explosive properties of this substance.

PART III

THE INVESTIGATION OF THE SO-CALLED COMPOUND CELLULOSES

CHAPTER XVIII

THE COMPOUND CELLULOSES

THE researches of Payen in 1838 first led to the discovery that the cellular constituents of the stem, root, leaves and seeds of plants can be resolved into cellulose, and non-cellulose, constituents. Besides cellulose itself, which gave glucose on hydrolysis, components giving other carbohydrates were recognised. Thus Muntz (1882) obtained galactose from the seeds of the leguminosæ; Reiss (1889) mannose from the ivory nut and Koch (1887) xylose from wood. These investigations were extended and developed by Schulze [1] and Tollens,[2] who showed that carbohydrates similar to cellulose were widely distributed in vegetable tissues. Their proportion in seeds, roots and tubers was found to vary with the stage of growth of the plant, and they were accordingly designated " reserve " celluloses as opposed to the normal cellulose which entered into the structure of the cell wall. This differentiation of the cellulose components was later (1891) supplemented by a chemical one, in that whilst the normal cellulose was comparatively resistant to hydrolysis by acids, and yielded only glucose, the others were much more readily hydrolysed and yielded other sugars, both hexoses and pentoses. The term " hemicellulose " was consequently applied to these easily hydrolysable products. Hemicellulose may be described or defined as a polysaccharide, which, in its natural state, is insoluble in boiling water, readily soluble in dilute caustic alkali, and is convertible into simple sugars on warming with dilute acids at normal pressure.

The recognition by Frémy [3] that vasculose (lignin) was a constant constituent of woody tissue led to the idea that the celluloses were definitely combined with various secondary constituents in the cells. Frémy, Cross and Bevan and others accordingly classified celluloses as " simple " and " compound ". Simple celluloses were typified by the cotton seed-hair, while the compound celluloses contained, in

[1] E. Schulze, *Zeit. physiol. Chem.*, 1892, **16**, 387; *ibid.*, 1909, **61**, 327.
[2] B. Tollens, *Ann.*, 1889, **254**, 304; *ibid.*, 1890, **260**, 289.
[3] E. Frémy, *Compt. rend.*, 1859, **48**, 862.

addition to cellulose and hemicellulose, other substances of the types of lignin, pectin, and cutin as their characteristic constituents.

The group of compound celluloses was therefore said to include—

1. Lignocelluloses, containing lignin as the typical constituent; woods, cereal straws, jute, esparto grass, etc.

2. Pectocelluloses, containing pectic acid and its derivatives—for example, hemp, flax, ramie.

3. Mucocelluloses, which yield mucilaginous, gummy substances —for example, algæ, fruits and tubers.

4. Adipocelluloses and Cutocelluloses, which contain waxy and fatty compounds as their typical non-cellulose constituents. Cork is the standard example of adipocellulose, and the epidermis of the leaves and twigs of the phanerogams contains cutin, which on saponification yields two main constituents—cutic acid, $C_{26}H_{50}O_6$, and cutinic acid, $C_{13}H_{22}O_6$; and two minor ones, $C_{19}H_{38}O_6$, probably identical with the phloronic acid isolated by Gilson from cork, and phellonic acid, $C_{22}H_{42}O_3$, similarly isolated by Kugler from cork.[1]

The above classification is retained for purposes of convenience, but except possibly in the case of lignocelluloses the term " compound " has very little justification. Thus the work of Cashmore [2] has thrown considerable doubt on the existence of pectocellulose in flax, although there is a certain amount of evidence in favour of the view that pectose, the insoluble pectic compound of plant tissues, exists as a pectincellulose complex. In the case of the adipo- and cuto-celluloses it is true that cork has been found to contain 2 or 3 per cent. of cellulose,[3] though its relation to the fat and wax constituents is undefined. On the other hand, the investigation of the cuticle of the agave [4] has shown that the outer layer of the cuticle (as distinct from the cutinised layer), contains no cellulose, so that the term " cutocellulose " cannot be applied in this case. There is scope for further research in connection with these relationships.

The exact nature of the association of cellulose with its " companion substances " remains, therefore, a matter for future investigation. The more important of the associated substances are classified in the following list, and their preparation and examination will be considered in the sequel.

Substances accompanying cellulose in Nature include :—

1. Pentosans—(*a*) xylan, (*b*) araban, (*c*) methylpentosan. 2. Hexosans—(*a*) galactan, (*b*) mannan. 3. Pectin. 4. Lignin. 5.

[1] V. H. Legg and R. V. Wheeler, *Chem. Soc. Trans.*, 1925, **127**, 1412.
[2] A. E. Cashmore, *Chem. Soc. Trans.*, 1927, 718, " On the Constituents of the Cell Wall of the Flax Fibre ".
[3] F. Zetsche and G. Rosenthal, *Helv. Chim. Acta*, 1927, **10**, 346.
[4] V. H. Legg and R. V. Wheeler, *loc. cit.*

Lichenin. 6. Resin, fat, wax, fatty acids, etc. 7. Miscellaneous constituents—(*a*) mineral matter, (*b*) colouring matter, (*c*) protein material.

The Nature and Composition of the Lignocelluloses.—The association of lignin with cellulose to form lignified tissue constitutes one of the most definite relationships in the plant world. The lignocelluloses may therefore be considered as typical of the compound celluloses and the problems associated with them.

Examples of typical lignocelluloses are found in the jute fibre ; Manila hemp ; esparto grass ; the cereal straws ; flax stems (shives) ; wood of forest trees : (*a*) soft woods (gymnosperms)—*e.g.* spruce wood ; (*b*) hard woods (dicotyledons)—*e.g.* beech wood.

The fibres and cereal straws are relatively simple in chemical composition, containing cellulose-α 50 to 65 per cent., and lignin about 20 per cent., with some hemicellulose and minor constituents.

Jute was selected for experiment by Cross and Bevan as a type of simple lignocellulose. It contains up to 80 per cent. of cellulose (Cross and Bevan) and 20 per cent. of lignin. Some comparative values are given in the following table :—

Lignocellulose.	Cellulose-α per cent.	Lignin per cent.	Hemicellulose per cent.
Jute . . .	*c.* 65	19–20	15
Manila hemp .	65	14	20
Esparto grass .	65	20·0	15
Rye straw (Norman)	55	19·5	32
Oat straw (Norman)	53	18·5	32

The hard and soft woods, while not differing essentially in composition, are more lignified and of greater age, so that their resolution is rendered more difficult. Examples of their analytical composition will be found in Chapter XXIII.

The celluloses isolated from lignocellulose by the usual methods are never of the order of purity of the normal cotton cellulose. When subjected to the mercerising test (p. 363) they yield 80 to 95 per cent., perhaps, of α-cellulose (pp. 479, 480). This α-cellulose, again, is not identical with cotton cellulose, as, unless repeatedly treated with alkali, it always gives a proportion of furfural corresponding to the presence of " pentosan ". An esparto cellulose, for example, obtained by the action of 3 per cent. sodium hydroxide gave 12·5 per cent. of furfural.[1] The α-cellulose content was 84 per cent., and this fraction yielded 4 per cent. of its weight of furfural. It is the custom with some workers to estimate the proportion of

[1] C. F. Cross and E. J. Bevan, *Chem. Soc. Trans.*, 1918, **113**, 182.

furfural given by a cellulose, calculate to pentosan and express the cellulose as " pentosan-free ".

The relation of the hemicelluloses (hexosans or cellulosans, and pentosans) to the cellulose and lignin in lignified tissue still remains an open question. There is little doubt that they are, in part, very closely associated with the cellulose, as is shown by the regular pentosan content of celluloses isolated by the chlorination method (*e.g.* jute cellulose), or by the soda process, as in esparto cellulose. The following figures, for example, illustrate the composition of the cellulose isolated from esparto by these two methods :—

	Esparto Cellulose isolated by	
	(*a*) Italian Chlorination Process.	(*b*) English Soda Process.
Pentosans . . .	20·04	14·57
α-Cellulose . . .	78·8	72·7
β-Cellulose . . .	13·9	21·5
γ-Cellulose . . .	7·3	5·8

The pentosan present in esparto cellulose is wholly in the form of an arabo-xylan [1] (about 20 per cent.), associated with 82 per cent. of cellulose identical chemically with cotton cellulose. Irvine and Hirst [2] favoured the view that the cellulose-xylan union was one of solid solution. The observation that, on acetolysis, esparto cellulose gave no disaccharide containing a xylose residue, was considered as evidence against the presence of a cellulose-xylan compound.

The closely associated xylan has been shown (p. 415) to be only a portion of the total xylan present. In the case of rye straw, for example, which contained 41·7 per cent. of hemicellulose, 8·34 consisted of xylan closely bound to cellulose, whilst 33·4 per cent. was " free " in the sense that it could be extracted by cold 4 per cent. alkali. For oat straw the corresponding figures were—total hemicellulose, 32·1 ; associated xylan, 9·3 ; free, 22·8 per cent. Whereas cold 4 per cent. alkali will remove 50 per cent. upwards of the xylan from straw or hardwood cellulose, the more closely associated part is tenaciously held. Thus a straw cellulose still retained 5 per cent. of xylan (22 per cent. of the original amount) after boiling with 10 per cent. alkali for 6 hours. Boiling dilute mineral acids remove up to 90 per cent. of the total xylan, but again a small proportion is firmly retained.[3] The isolated hemicelluloses show no such resistance.

[1] W. N. Haworth, E. L. Hirst *et al.*, *Chem. Soc. Trans.*, 1934, 1917.
[2] J. C. Irvine and E. L. Hirst, *ibid.*, 1924, 125, 17.
[3] A. G. Norman, *Biochem. J.*, 1936, 30, 2054.

These closely associated fractions are sometimes described as cellulosans. They may form part of the chain molecule since when, for example, the molecular orientation of a wheat cellulose was destroyed by solution in cuprammonium or by regeneration from the xanthate, 80 per cent. of the xylan was removed by water alone.[1]

Sulphite wood-pulps contain 3–6 per cent. of pentosan and soda wood-pulps 7–10 per cent. Straw pulps (soda process) will contain up to 30 per cent. of xylan.[2] By the chlorination method a straw cellulose was obtained which gave 10·3 per cent. of furfural. Six extractions with 6 per cent. sodium hydroxide were required to reduce this to 2 per cent. In the case of sulphate wood-pulp two extractions with 17 per cent. sodium hydroxide left a cellulose in which the pentosans were distributed as follows [3] :—

In the	Pentosans per cent.
α-cellulose	0·80
β-cellulose	1·26
γ-cellulose	2·16

The lignin is considered by some workers to exist in association with part of the hemicellulose and there is indirect evidence in support of this opinion. Thus lignin isolated by the Willstätter process often yields some 4 per cent. of furfural on hydrolysis. The presence of lignin, also, renders the hemicellulose resistant to alkaline extraction. Straw cellulose,[4] for example, and mesquite-wood cellulose,[5] cannot be freed from xylan until all the lignin has been removed.

Examination of the cellulose obtained from a range of lignified materials by alternate chlorination and treatment with sulphite solution has shown[6] that chlorination effects not only the removal of lignin, but also that of polyuronide hemicellulose. Thus the lignin in silver-fir wood was reduced from 29 to 1 per cent. after five chlorination-sulphite treatments, while the hemicellulose (as furfural) fell from 2·7 to 0·7 per cent. It required, however, eight such treatments to reduce both to negligible proportions. Eight sulphite extractions without chlorination had little effect, reducing the lignin to 26 and the furfural to 2·6 per cent. Further, after chlorination, the hemicellulose is easily removed by aqueous extraction. As chlorine does not act specifically on hemicellulose these

[1] A. G. Norman, *Biochem J.*, 1936, **30**, 2054.
[2] E. Heuser and A. Haug, *Zeit. angew. Chem.*, 1918, **31**, 166.
[3] E. Heuser and W. Dammel, *Cellulosechem.*, 1924, **5**, 45.
[4] E. Heuser and A. Haug, *Zeit. angew. Chem.*, 1918, **31**, 166.
[5] L. Sands and P. Nutter, *J. Biol. Chem.*, 1935, **110**, 17.
[6] A. G. Norman and J. G. Shrikhande, *Biochem. J.*, 1935, **29**, 2259.

observations could be explained by a state of combination between part of the hemicellulose and part of the lignin, the reaction of lignin with chlorine leading to a separation of the complex.

In the absence of definite information as to the exact union of these constituents, it is perhaps best to adopt as a working hypothesis the original scheme of Cross and Bevan, and to assume that a lignocellulose is made up of—

Cellulose I	⟷ Cellulose II	⟷ Lignin
	or Hemicellulose yielding furfural and some OMe.	containing OMe and $CO.CH_3$ groups.

the cellulose I being associated closely with cellulose II, part of which in turn is associated with lignin.[1]

On this view chlorination treatment disturbs the balance of the system, giving Cross and Bevan cellulose, *i.e.* cellulose I and (largely) cellulose II. The sulphite process, on the other hand, removes lignin and most of the cellulose II, leaving a cellulose I still containing closely associated hemicellulose.

Ritter [2] has illustrated these points by the following diagram, representing the composition of wood.

Holocellulose 72 per cent.

Residue	Lignin	Hemicellulose	Hemicellulose	Cellulose
6 per cent.	22 per cent.	12 per cent.	22 per cent.	38 per cent.

Lignin-Hemicellulose Compound, 34 per cent.

Cross and Bevan Cellulose, 60 per cent.

The term holocellulose is used to define the total cellulose and hemicellulose, *i.e.* total carbohydrate present in the wood. By repeated chlorination, followed by extraction with alcohol containing 3 per cent. of monoethanolamine, Ritter [2] has succeeded in isolating holocellulose quantitatively, as a white product, which changes colour on standing.

The identity with normal cellulose of the cellulose-α or pentosan-free cellulose isolated from plant products has been the subject of frequent experiment.[3] The work of Irvine, Hess and others on the chemical side, and of Herzog, Mark and others with X-ray methods tends to show that all purified celluloses are chemically identical

[1] Cf. A. G. Norman, *Biochem. J.*, 1935. **29**, 2259; 1936, **30**, 2054.
[2] G. J. Ritter, *Paper Trade J.*, 1937, **105**, T.S., 355; 1939, **108**, T.S., 65.
[3] E.g., J. Barsha and H. Hibbert, *J. Amer. Chem. Soc.*, 1936, **58**, 1006.

but differ in reactivity and physical properties. The cellulose unit—built up of a bundle of chains of anhydro-glucose residues joined end to end by principal valency forces and held together laterally by secondary valence forces—will vary in average chain-length according to conditions of growth and isolation. The shorter the average chain-length the more reactive or " degraded " the complex becomes as more " end " hydroxyl groupings become available. Since the anhydro-xylose unit in xylan differs in size and structure from anhydro-glucose only in length, wood cellulose, for example, might be regarded as having a normal cellulose chain in which a proportion of glucose residues were replaced by xylose residues. When these are removed weakening of the structure takes place with loss of strength and increase in reactivity. The discovery that the xylan chain in esparto cellulose contains an arabinose unit, however, makes this hypothesis less probable.

CHAPTER XIX

THE GENERAL QUALITATIVE AND QUANTITATIVE EXAMINATION OF PLANT TISSUES

THE qualitative recognition of lignin, pectin, and other constituents is based largely upon the use of reagents which produce a specific colour by reaction or staining. Absolute reliance can never be placed on colour tests, but they are frequently useful, both alone, and in conjunction with the use of solvents which remove a particular constituent of the tissue under examination. The actual isolation of the consitutent, or its recognition by some defined property, is obviously more exact, but requires larger quantities of material and more time.

I. THE RECOGNITION OF LIGNOCELLULOSE

The presence of lignified tissue is recognised qualitatively by the application of the " colour tests " described on p. 339, and qualitatively or quantitatively by the methods for the isolation of lignin given on p. 368. Some of the colour tests on which the botanical investigator has chiefly relied are not always specific for lignin, but are due to minute quantities of other substances which seem invariably to be associated with lignin under natural conditions. The Mäule reaction is probably due to one of these, and the red colour produced by the action of phloroglucinol is another example. This reaction is not obtained after treating the wood with small amounts of chlorine or hydroxylamine, or after gentle oxidation, although the lignin is still present apparently unaltered.

The substance responsible for the phloroglucinol reaction is probably to be identified with the " hadromal " of the botanical text-books, an aldehydic compound (related to vanillin), isolated by Czapek [1] in 1899. Although its existence has frequently been called into question, a substance agreeing in its reactions with those ascribed to hadromal has been isolated from woody tissue and its chemical nature confirmed by synthesis.

The relatively small amount of the colour-producing substance to the total amount of lignin present is shown by the earlier observations of Cross and Bevan,[2] who found that the amount of phloro-

[1] F. Czapek, *Biochemie der Pflanzen* (1913), I., 691; *Z. physiol. Chem.*, 1899, **27**, 141.

[2] C. F. Cross, E. J. Bevan and J. F. Briggs, *Ber.*, 1907, **40**, 3119.

glucinol absorbed in the production of the maximum red colour was 1 per cent., compared with a total of 6·7 per cent. which the wood sample employed was capable of absorbing.

The reaction in some cases is very sensitive. It is stated that 1 drop of a solution of phloroglucinol in a dilution of 1 part in 30,000 will produce a red spot on newsprint in one minute. There are cases, however, in which tissue undoubtedly lignified fails to give the reaction,[1] and on the other hand there are probably substances not of the nature of lignin which are capable of giving it. The method of measuring quantitatively the phloroglucinol *absorption* of lignified products which does afford an indication of the amount of lignin present is given on p. 475.

From a more definitely chemical standpoint lignified tissue is identified with exactness in two ways: First, by the yellow colour produced on treatment with chlorine, which turns to crimson on boiling with a solution of sodium sulphite. Angiosperms usually give a more intense red colour with this test than gymnosperms, but the reaction is always obtained when lignin is present.

The second method consists in the isolation of the lignin by treatment of the tissue with 72 per cent. sulphuric acid (*d*, 1·64), or with hydrochloric acid (*d*, 1·2), whereby an insoluble residue is obtained. This residue is a modified lignin, but it is still able, for example, to react with chlorine, giving the yellow colour, and to show other properties by which it can be identified.

A third test also probably specific for lignin is that with ferric-ferricyanide,[2] which depends upon the reduction of the reagent to the blue ferro-ferricyanide by the reducing groups in lignin.

The validity of some of these tests has been examined by W. M. Harlow,[3] who found that the colour given by phloroglucinol varied considerably, and suggests that too great reliance on the use of this reagent may lead to errors. Thus, with the phloroglucinol reagent, buckeye, red alder, and black ash all gave bright red; chestnut and red gum pink; basswood pale pink; and catalpa very pale pink.

In experiments on the chlorination reaction, sections of hard-woods were treated with chlorine-water for 1 minute, washed, and then dipped into a hot 3 per cent. solution of sodium sulphite until the characteristic red colour appeared (8 to 10 seconds). Temporary mounts, made immediately, when examined with the microscope, showed the colours set out overleaf.

[1] W. C. Hancock and O. W. Dahl, *Chem. News*, 1895, **72**, 16.

[2] C. F. Cross and E. J. Bevan, "Cellulose" (1903), p. 124.

[3] Bulletin of the New York State College of Forestry, 1927, **27**, 6B; *ibid.*, 1928, **1**, 3; *Paper Trade J.*, 1941, **112**, *TAPPI* Sect., 279.

Species.	Vessels.	Tracheids.	Fibre Trach.	Rays.
Basswood . .	Pink.	—	Pink.	Pink.
Red gum . .	Orange.	—	Pink.	Pink.
Yellow poplar .	Yellow.	—	Pink.	Pink.
Chestnut . .	Pink.	Pink.	Pink.	Orange.
Black ash . .	Yellow.	Pink.	Pink.	Orange.
Catalpa . .	Pink.	Pink.	Pink.	Orange.

The chlorination test in micro-chemical work, therefore, also requires care in interpretation, as the colour-producing substance seems to be present both in the secondary walls and the lignified middle lamella. This may, however, be apparent only and due to diffusion of the reagents through the tissues.

Additional reagents for lignin are : (*a*) concentrated solution of thallin sulphate in 50 per cent. alcohol, which gives an orange-red coloration (the section is first soaked in alcohol and then treated with the reagent) ; and (*b*) a 1 per cent. solution of vanillin in concentrated sulphuric acid (this is specific for aromatic substances, especially those associated with lignification, giving a bright red colour even with tissues which do not respond to phloroglucin).

H. Molisch [1] recommends five reagents—*viz.* aniline sulphate, phloroglucinol, indol, thallin, and Mäule's reagent (p. 341, No. 4).

Suberin and Cutin.—Walls which are suberised or cuticularised give the following reactions :—

(*a*) With the iodine reagents, brown or yellow.

(*b*) With concentrated potassium hydroxide solution, yellow ; on heating the colour darkens and yellow oily drops exude.

(*c*) With Schulze's macerating mixture (nitric acid containing potassium chlorate), they resist more than other tissues. On boiling oily drops of (ceric) acid form, insoluble in carbon disulphide, soluble in benzene.

(*d*) With alcoholic solutions of chlorophyll, stain green. A strong solution of chlorophyll is allowed to act for 15 minutes in the dark.

(*e*) With alcoholic solutions of alkannin, Sudan III and Scharlach R, stain red.

(*f*) With solution of cyanin in 50 per cent. alcohol, mixed with an equal volume of glycerine, stain red, after a preliminary treatment with dilute sodium hypochlorite to remove tannins.

Reactions (*d*), (*e*) and (*f*) are not given by lignified walls.

[1] " Mikrochemie der Pflanzen ", p. 344, Jena, 1923.

Pectin.—The stains, such as methylene blue, safranin, etc., recommended by earlier workers are unreliable, as they are not specific for pectic substances. Ruthenium red is satisfactory, as, although gums, mucilages and fatty acids stain with it, it is quite possible to differentiate pectin from them. Thin sections are washed with water and stained in solutions of ruthenium red (1 in 5,000 water). If the sections are warmed for a few minutes in water, the colour is removed from non-pectic bodies, making the cell walls, containing pectin, more distinct (see, further, under Pectin, p. 507), and references).

II. The Reagents used in the General Examination of Vegetable Tissues

1. Iodine-sulphuric acid reagent. This gives a blue colour with cellulose. 1 g. of KI is dissolved in 100 ml. of water, and iodine added to saturation, an excess being left in the bottle. The sulphuric acid solution is made up of two volumes of glycerol, one of water, and three volumes of concentrated sulphuric acid. The fibres are moistened first with the iodine solution and then with the acid. The suitability of the solutions may be tested on some raw flax fibres. These should not swell up and should appear pure blue. If they swell, the acid is too concentrated ; if the blue colour is not immediate or only appears violet or red, the acid is too dilute. In the former case more glycerol should be added.

The fibres are first given a short boil with 1 per cent. NaOH solution, washed, dried, and treated with the iodine solution. The excess of iodine is removed by pressing between blotting-paper, otherwise the brown colour will persist after the sulphuric acid treatment. The fibre is dried and treated with the sulphuric acid.

2. Zinc chloride-iodine. This gives a violet colour with cellulose. 1 g. of iodine and 5 g. of KI are dissolved in 14 ml. of water and 30 g. of a concentrated solution of zinc chloride added.

Calcium chloride-iodine is made by adding 0·5 g. of KI and 0·1 g. of iodine to 10 ml. of concentrated calcium chloride solution.

3. Aniline sulphate. Lignin test, yellow. A strong aqueous solution, slightly acidified with sulphuric acid.

4. Potassium permanganate (1 per cent.), followed by ammonia (Mäule's test). The tissue is treated with the permanganate, washed with hydrochloric acid and then with water, and finally treated with ammonia. Lignified tissues give a reddish colour.[1]

[1] C. Mäule, "Verhalten verholzter Membranen gegen Permanganat", Stuttgart, 1901.

5. Ferric ferricyanide reagent. Equal volumes of $N/10$ ferric chloride and $N/10$ ferricyanide solutions are mixed. The oxidisable parts of the tissue reduce the reagent to the blue ferroferricyanide (Turnbull's blue), with deep staining.

6. Phloroglucinol. 1·0 g. phloroglucinol in 100 ml. of 12 per cent. hydrochloric acid. Alternatively a 10 per cent. alcoholic solution of phloroglucinol is mixed with an equal volume of the above acid.

7. Alkannin (alcoholic). Alkanna roots are extracted with 90 per cent. alcohol sufficient to cover the roots.

8. Aniline blue picrate. 3 g. aniline blue, 2 g. picric acid dissolved in a litre of water.

9. Borax carmin (alcoholic). 3·0 g. carmin, 12 g. borax, 480 ml. water, and 480 ml. 90 per cent. alcohol.

10. Congo red (aqueous). 1 g. in 200 ml.

11. Gossypimin (aqueous). 2 g. gossypimin, 900 ml. water, and 60 ml. 90 per cent. alcohol.

12. Hæmatoxylin (Delafield). 200 ml. of a saturated solution of ammonium alum is mixed with 2 g. hæmatoxylin in 12 ml. absolute alcohol. The mixture is exposed to light and air for a week. After filtering 50 ml. of glycerol and 50 ml. of methyl alcohol are added. It is allowed to stand in sunlight until the full colour develops.

13. Ruthenium red (aqueous). 1 in 10,000.

14. Vanillin. 1·0 g. in 100 ml. of concentrated sulphuric acid.

14. Malachite green. 1 g. in 300 ml. of 92 per cent. alcohol.

16. Ferric thiocyanate (aqueous). 1·0 ml. of saturated ferric chloride to 10 ml. of 10 per cent. ammonium thiocyanate.

17. Safranine. 3 g. safranine, 500 ml. water, and 500 ml. 90 per cent. alcohol.

A full account of staining reagents will be found in C. E. Allen, " The Middle Lamella ".[1] The works of H. Molisch (" Microchemie der Pflanzen ") and Czapek (" Biochemie der Pflanzen ") summarise the various colour reactions.

The following table by M. M. Mehta [2] gives results obtained with some of these stains used as diagnostics for the different constituents of the cell wall :—

TABLE SHOWING THE PARTS STAINED BY DIFFERENT COUNTERSTAINS

STEM : Malachite green stains, phloem, xylem elements, traces to first leaf, sclerenchymatous ring, cambiform tissue, spiral vessels, primary vascular bundles, bundle sheath, annular vessels, scalariform vessels, sclerenchyma sheath, nodal diaphragm and secretion cells.

[1] *Bot. Gaz.* 1901, **32**, 1. [2] *Biochem. J.*, 1925, **19**, 987.

Borax carmin stains, primary ground tissue, cambiform tissue, pith, cortical tissue, phloem, primary medullary ray, epidermal tissue, endodermis and nucleated cortical tissue.

Hæmatoxylin stains, cortical tissue, primary ground tissue, central axis and medullary ray.

Gossypimin stains, phloem, xylem, primary medullary ray, cambiform tissue, resin canal, developing branch, thickening band of prosenchyma, starch granules and vascular bundles.

Safranine stains, xylem elements, phloem, connective tissue and pitted vessels.

Aniline blue picrate stains, cortical tissue, cambiform tissue, primary ground tissue, central ground tissue, and secreting cells of canal.

It will be seen that no stain is very specific. Ruthenium red, for example, the most definite reagent for pectic substances, also stains hemicelluloses, mannans and galactans.

III. Use of Staining Reagents in Conjunction with Solvents for the Differentiation of Plant Tissue Constituents

The following notes are taken from the paper of M. M. Mehta (*loc. cit.*) as an example of method, but it must be emphasised that considerable caution has always to be exercised in the interpretation of results obtained from colour reactions.

Sections were treated with 0·5 per cent. ammonium oxalate, 0·5 per cent. ammonium oxalate in 3 per cent. ammonia solution, 4 per cent. sodium hydroxide solution, 3 per cent. hydrochloric acid, or 95 per cent. alcohol. This was usually done by heating the sections with the respective reagents in test tubes immersed in a boiling water bath for 6 to 8 hours. To ensure complete extraction the supernatant liquid was decanted off every hour and the extraction continued with fresh reagent. The sections were then washed with hot distilled water and stained.

As an example,[1] the epidermis in the leaf of *Pinus sylvestris*, " after treatment with ammonia and ammonium oxalate, shows a slight decrease in the intensity on staining with ruthenium red and hæmatoxylin, indicating that only traces of pectic substances are present. With eosin and hæmatoxylin, after treatment with sodium hydroxide, a marked change is observed indicating the presence of hemicelluloses. The negative zinc chloride-iodine reaction indicates the absence of true celluloses."

[1] *Biochem. J.*, 1925, **19**, 987.

Xylem cells give a strong phloroglucinol reaction like true lignocelluloses, and do not give the colour tests for cellulose. Their general behaviour with different stains suggests the presence of hemicelluloses, pectic substances and oxycellulose.

Phloem does not react with phloroglucinol, but gives a strong coloration with the vanillin reagent for aromatic substances and with zinc chloride-iodine for cellulose. Its staining reactions after treatment with sodium hydroxide indicate the presence of hemicellulose, but not of pectic substances.

The use of chlorine dioxide followed by alkali sulphite solution may have value as a diagnostic for morphological work (p. 359). Sections of the seeds of *Phytelephas macrocarpa* treated as in the isolation of mannans, A and B (p. 429), and subsequently acted upon with zinc chloride-iodine, gave appearances in accordance with the quantitative chemical results.[1]

The inner membrane was coloured dark, indicating a small amount of cellulose (5 per cent. was found); the middle lamella, faintly coloured, consisted of the mixture of mannans A and B, of which mannan B was the cause of the colour. The " encrusting matter " removed by chlorine dioxide, about one-third of the weight of the seed, was from the middle lamella substance.

Ethanolamine (*cf.* p. 360) has been applied to microscopical studies in the distribution of cell-wall components.[2] In the cold it slowly removes all secondary cell-wall lignin, but not that of the middle lamella.

The use of solvents to locate cellulose, lignin, etc., has been reviewed by W. M. Harlow,[3] and the micro-structure of cellulose fibres and membranes by W. K. Farr.[4] The possibilities of the electron microscope have also been examined.[5]

IV. Colour Reactions of Vegetable Fibres

A number of the textile fibres are more or less lignified, and therefore give the reactions specific for lignin, such as that with phloroglucinol and the yellow colour with aniline sulphate.

The table on p. 345 is given by Dodge.

[1] M. Lüdtke, *Ann.* 1927, **456**, 202.

[2] L. E. Wise, F. C. Petersen and W. M. Harlow, *Ind. Eng. Chem. Anal.*, 1939, **11**, 18.

[3] *Paper Trade J.*, 1939, **109**, 38.

[4] *Nature*, 1940, **146**, 153.

[5] L. Wallner, *Textilber.*, 1942, **23**, 158, 211, 261; R. B. Barnes and C. J. Burton, *Ind. Eng. Chem.*, 1943, **35**, 120.

V. The Microscopic Examination and the Chemical Sectioning of Vegetable Fibres

The identification of vegetable fibres has hitherto depended chiefly on simple microscopic examination and on colour reactions of which the following is a summary :—

Fibre.	Iodine and Zinc Chloride.	Iodine and Sulphuric Acid.	Cupram-monium.	Aniline Sulphate.	Phloro-glucinol.
Cotton . .	Violet.	Blue.	Blue solution.	—	—
Flax . .	,,	,,	,,	—	—
Hemp . .	,,	,,	,,	Pale yellow.	Violet-red.
Jute . .	Brown-yellow.	Green-blue.	,,	Golden yellow.	Deep red.
Ramie . .	Dull violet.	Dull blue.	,,	—	—
Manila hemp .	Yellow to violet.	—	—	Yellow.	Red.
New Zealand flax	Golden yellow.	Green-blue.	Bluish.	Yellowish.	Pale red.
Aloe . .	Yellow to brown.	Yellow.	Swells ; bluish.	,,	Pink.
Coconut . .	,,	—	—	Bright yellow.	Purplish.

The works of Höhnel (" Die Mikroscopie der technisch verwendeten Faserstoffe ", 1905), Matthews (" Textile Fibres ", 1924), and Preston (see Appendix) deal fully with the microscopic characters of the various fibres.

It is suggested [1] that more use should be made of alternative methods, *e.g.* the general appearance of the fibres when tendered, when stained with Congo red, and when swollen with sodium hydroxide or by the xanthate reaction. The following six simple characteristics, which are easy to determine, would, it is stated, afford a valuable key to the identification of any vegetable fibre, *viz.* (1) The average length of the fibre strands ; (2) the average length and diameter of the ultimate fibre ; (3) the direction of the drying twist of the ultimate fibre ; (4) the appearance of the chemically formed cross-section of the fibre bundle ; (5) the appearance of acid tendered fibres mounted in alkali ; (6) a chemical test for lignification.

With regard to (3) the work of Nodder [2] has shown that this character will distinguish flax (clockwise) from hemp at all stages of

[1] M. A. el Kelaney and G. O. Searle, *Proc. Roy. Soc.* (B), 1930, **106**, 361.
[2] C. R. Nodder, *J. Text. Inst.*, 1922, **13**, 161T.

manufacture. The Linaceæ, Asclepiadaceæ, Apocyanaceæ and Urticaceæ in general show a clockwise drying twist, although it has been found[1] that *Neoglaziovia variegata* has a clockwise drying twist in contradistinction to the allied pine apple fibre (Bromeliaceæ) affording a sharp distinction between them.

The method of " chemical sectioning " mentioned under (4) is based on the observations of Searle,[1] who found that chemically tendered fibres tended to segment into thin sections perfectly transverse to the longitudinal fibre axis. The phenomenon is similar to that illustrated in Figs. 53 and 54.

To obtain sections the fibre is boiled in 10 per cent. sulphuric acid for a few minutes, roughly dried between filter paper without washing, and heated at 60–70° for about half an hour. The fibre is removed as soon as it has turned to a deep brown, almost black, and disintegrated by rubbing in a mortar or between the fingers. Portions are mounted in 10 to 15 per cent. sodium hydroxide solution, the cover-glass being pressed gently and the excess of alkali removed. The cover-glass is then repeatedly tapped with the tip of a scalpel until the fragments begin to disintegrate.

The structural details are remarkably developed, as may be seen from the illustrations accompanying the original paper. The growth rings of cotton are seen and the concentric structure of hemp, nettle and asclepias is well shown. Lignified strands become swollen and blackened in contrast to the cellulose wall and, in section, appear as lines of beads between the fibres. The sections have the great advantage of being entirely free from the artifacts caused by the use of the razor, and a preparation can be made and photographed in 10 minutes.

VI. Identification of Cellulose Fibres in Paper by Colour Tests.*

Chemical colour tests may usefully be employed for this purpose, coupled with the use of the microscope. With the latter, especially under polarised light, it is readily possible to distinguish chemical wood pulp by the bordered pits characteristic of wood vessels. It is possible also to distinguish between the different woods used in preparing the pulp—*e.g.* between spruce and poplar, and between summer and winter growth. Mechanical wood may often be identified by the polariscope, which brings into prominence parts of

[1] G. O. Searle, *J. Text Inst.*, 1924, **15**, 371T.

* See also F. W. Bentzen, *Paper Trade J.*, 1941, **112**, *TAPPI*, Sect., 47, where recent work is reviewed and a report of the Microscopy Committee is given.

the medullary rays which frequently remain after mechanical disintegration.

Chemical Staining Reagents.—No. 1. Mechanical wood may be identified by the use of the following reagents :—

Reagent.	Colours produced on Mechanical Wood-pulp.
Alpha naphthylamine hydrochloride	Bright orange.
Benzidine hydrochloride	Orange.
Aniline sulphate	Vivid yellow.
Phloroglucinol solution	Red.

The phloroglucinol solution is most characteristic. It is made by dissolving 2 g. of pure phloroglucinol in 50 ml. of alcohol to which 25 ml. of concentrated HCl have been added. A drop is spread on to the material and, after a few minutes, long, thin red markings indicate the presence of groundwood or other lignified fibres.

No. 2. Mixed fibres are satisfactorily diagnosed by the use of the following solutions, which are somewhat similar to those given under lignocellulose. Solution C gives the best results :—

A. Herzberg iodine solution :

Potassium iodide	5 g.
Distilled water	100 ml.
Iodine	2·85 g.
Glycerine	5 ml.

B. Sulphuric acid solution :
The concentrated acid (80 ml.) added to 20 ml. of water.

C. Zinc-chloride-iodine reagent (the Herzberg stain) :

(*a*)	Zinc chloride	20 g.
	Water	10 ml.
(*b*)	Potassium iodide	2·1 g.
	Iodine	0·1 g.
	Water	5·0 ml.

A little of the water is added to the mixture of iodine and KI, and when the iodine has dissolved the rest of the water is added. Gentle heat may be necessary. After cooling, solutions (*a*) and (*b*) are mixed, allowed to stand for 24 hours, and the clear liquid decanted.

These reagents are employed as follows :—

(*a*) A little of the pulped material, which may be fixed to a glass microscope slide, as described on p. 463, is treated with solution A, and after a few minutes water is run on and the excess iodine removed by filter paper. Staining should not be too deep.

Brown fibres indicate cotton, linen or bleached hemp ; yellow fibres mechanical wood, jute and straw ; grey fibres chemical wood and esparto.

(*b*) The iodine-stained fibres are now treated with the sulphuric acid solution B. The following colour reactions may be observed :—

Red and violet indicate cotton or linen fibres, and bleached jute ; blues, from blue to blue-grey, indicate chemical wood, straw and esparto ; yellows, from golden yellow to dark yellow, indicate mechanical wood, jute, Manila hemp.

(*c*) A fresh portion of the fibre is treated with the zinc-chloride-iodine reagent C. The following colours may be obtained :—

Claret colour indicates linen, cotton, and bleached Manila hemp fibres ; blue and claret will show esparto ; blue will show chemical wood pulp (sulphite or sulphate), bamboo, straw and most other chemically resolved fibres ; brownish-yellow indicates chemical wood which still contains lignin, *e.g.* certain sulphate and craft pulps ; bright yellow indicates mechanical wood pulp, unbleached jute and unbleached Manila hemp.

VII. General Quantitative Scheme for the Valuation of Cellulosic Materials after Cross and Bevan

This scheme is useful in any examination of the quality and utility of a fibrous material. The constants obtained enable conclusions to be drawn as to its resistance to attack, cellulose content, ultimate fibre length, and other characters which make it useful for cordage, paper, or other application. The constants also enable, for example, two qualities of hemp or Manila fibre to be differentiated, and damage caused by water, oxidation, and micro-organisms to be specified.

Procedure.—(*a*) *Moisture.*—This is determined by drying at 100–110°. It is to some extent an index of the susceptibility of the fibre to attack by hydrolytic agents. Textile fibres of the highest class are distinguished by relatively low moisture content.

(*b*) *Ash.*—An abnormally large ash usually indicates the presence of mineral impurities introduced during the preparation of the fibre

(*c*) *α-Hydrolysis.*—The fibre is boiled for 5 minutes (reckoned from the time at which boiling commences) with a solution of sodium hydroxide (1 per cent. NaOH) under reflux. The fibre is then washed free from alkali, soured, washed and weighed. The loss in weight indicates the amount of substance removed by the solvent action of the alkali.

(*d*) *β-Hydrolysis.*—Another portion of the fibre is boiled for 1 hour with sodium hydroxide of the same strength. In this case the loss in weight includes, not only substance removed by solvent action, but also that rendered soluble by the " degrading " action

of the alkali. The difference between the α- and β-hydrolysis values indicates the susceptibility of the fibre substance to attack by alkali.

(*e*) *Mercerisation.*—The fibre is left at the ordinary temperature with sodium hydroxide solution (33 per cent. NaOH) for 1 hour. It is thoroughly washed with cold water, soured, washed, dried, and the loss in weight determined. The visible effects are generally a shrinkage in length with a wavy and crinkled outline. The result indicates the resistance of the fibre to strong caustic alkali.

(*f*) *Nitration.*—The fibre is submitted to the action of a mixture of equal volumes of nitric acid (*d*, 1·42) and sulphuric acid (*d*, 1·84) for 1 hour at the ordinary temperature. It is then removed, allowed to drain and transferred to a beaker containing a large volume of water. After washing free from acid, it is heated with water till boiling commences and is finally dried in the water oven. The increase in weight is noted. The results recorded show that, in general, the increase in weight on nitration bears a direct relation to the other chemical constants.

(*g*) *Cellulose.*—The fibre is boiled for 5 minutes with a solution of sodium hydroxide (1 per cent. NaOH), washed free from alkali, and while still moist is exposed to the action of chlorine gas for 1 hour.* It is then washed and treated with a 2 per cent. solution of sodium sulphite, containing 0·2 per cent. NaOH, which is slowly heated until it boils ; after 2 or 3 minutes the product is collected on a calico filter, washed, treated with acetic acid (20 per cent.), washed, dried and weighed.

When the chlorinated fibre is immersed in the sulphite solution a crimson colour is produced if the fibre is a lignocellulose. With non-lignified fibres the solution remains practically colourless.

The technique of this method is detailed on p. 352.

(*h*) *Acid Purification Loss.*—The fibre is put into acetic acid (20 per cent.), which is slowly heated until it boils. The loss in weight is chiefly due to the removal of casual impurities.

(*j*) *Length and Diameter of Ultimate Fibres.*—A portion of the cellulose, obtained above, is placed in dilute acetic acid, teased out, and mounted on a glass slip. The length and diameter of a number of fibres thus separated are determined, and the maximum, minimum, and average measurements recorded.

(*k*) *Additional estimations* which may be made if desired for further information are—(i) the HCl, combining during the chlorination (p. 353) ; (ii) the α- β- and γ-cellulose in the Cross and Bevan cellulose (p. 363) ; (iii) the furfural or pentosan, in the fibre and in the Cross and Bevan cellulose (p. 381) ; (iv) the lignin (p. 369).

* Successive five-minute periods give better results.

The procedure described under (*a*) to (*j*) is that originally used by Messrs. Cross and Bevan. The following tables contain the constants of vegetable fibres obtained by this and other methods given as dry weight on dry weight of material.

RESULTS BY THE CROSS AND BEVAN METHOD ON FIBRES[1]

	Indian Jute. Extra quality.	*Hibiscus cannabinus* (Deccan Hemp).	*Ananas sativus*, Pineapple.	*Giaradinia heterophylla*, Nilgiri nettle.	*Sansevieria* Bowspring Hemp. sp.	Agave sp., Sisal Hemp.	*Musa* sp., Banana fibre.
Moisture	11·1	10·8	9·5	7·6	9·0	11·6	10·4
Ash .	1·0	1·0	1·1	2·4	0·6	1·0	2·2
α-loss .	8·5	12·2	13·7	3·2	10·0	11·7	20·1
β-loss .	12·5	19·1	19·4	5·9	12·6	13·5	24·0
Cellulose	79	74·9	81·5	93·7	74·4	77·2	74·4
Acid purification loss .	—	3–4	1·7	3·2	2·3	1·0	5·8
		Cordage fibres.					

ANALYSES BY VARIOUS METHODS

	Barley Straw (Dore).	Oat Straw (Norman).	Rye Straw (Norman).	Hemp Korean (Uyeda).	Ramie (Dore).	Manila Hemp. (Dorée).	Jute.
Moisture . .	7·23	—	—	8·83	10·50	dry.	11·4
Benzene extract	1·26	—	—	1·92	0·86	—	1·0
Alcohol extract .	12·26	—	—	1·20	0·75	—	—
Water soluble .	4·63	—	—	4·50	3·79	0·63	3·8
Soluble in NaOH	20·85	22·8	33·4	18·53	17·27	8·8	—
Cellulose . .	41·49	53·14	55·27	62·42	65·88	77·2	69·6
Lignin . .	7·40	18·54	19·5	3·32	0·66	14·5	18·8

The results given on page 351, selected from a comprehensive series,[2] are useful in that they were determined by the same methods and are therefore comparable. All fibres were ground to pass a 60-mesh sieve. Cellulose was estimated by Norman and Jenkins' method (p. 357), and lignin by the modification[3] which involves a preliminary treatment for 1 hour with 5 per cent. sulphuric acid before digestion with 72 per cent. acid.

[1] Imperial Institute Selected Reports, No. 58, Part I, "Fibres", 1909, H.M. Stationery Office.

[2] A. G. Norman, *Biochem, J.*, 1936, **30**, 831; 1937, **31**, 1575.

[3] A. G. Norman and S. H. Jenkins, *Biochem, J.*, 1934, **28**, 2147.

ANALYSES OF COMMERCIAL FIBRES (A. G. Norman).

Name and Botanical Type.*	As per cent. Oven-dry Material.			Furfuraldehyde.		
	Cellulose.	Lignin.	Xylan in Cellulose.	Total.	From the Cellulose.	From Polyuronide.
Flax (Irish) .	91·20	3·27	3·01	2·32	1·93	0·4
Ramie . .	84·12	1·26	1·30	2·39	0·78	1·6
Hemp (Italian) .	89·23	5·32	1·73	1·11	1·12	0·0
Hemp (Indian) .	77·27	7·28	1·79	2·83	1·15	1·7
Sunn Hemp, *a* .	79·27	5·24	3·1	3·18	1·96	1·2
Jute (Tossa), *a* .	78·02	11·22	11·90	10·96	7·67	3·3
Jute (soft Tossa), *a*	74·32	11·53	12·82	11·07	8·27	2·8
Manila Hemp .	74·14	8·51	14·01	9·07	9·04	0·0
Phormium tenax .	72·04	11·13	15·09	13·33	9·74	3·6
Sisal (Africa) .	74·95	6·04	18·56	13·63	11·97	1·7
Coir (good) . .	54·29	28·56	13·07	13·90	8·44	5·5
Coir (poor) . .	50·52	29·45	11·64	13·85	7·48	6·4
Mauritius hemp, *b*	79·83	4·83	15·3	13·24	9·85	4·4
† Palmyra fibre, *c*	63·50	25·01	15·7	13·80	10·16	3·6
† Pineapple fibre, *d*	79·62	5·50	11·2	10·45	7·22	3·2
Kapok, *e* . .	65·67	14·58	15·1	13·59	9·78	3·8

* Botanical type: *a*, bast fibres from dictoyledon stem; *b*, sclerenchymatous fibre bundles with residues of vascular bundles; *c*, vascular bundle with sheath of sclerenchymatous fibre; *d*, bundles of sclerenchymatous fibres accompanying vascular bundles; *e*, hairs from inner wall of fruiting capsule.

† Leaf.

An interesting point arises from the figures which show that the common fibres fall into two groups dependent on the xylan content of the cellulose present. The low-xylan group (xylan, 0–6 per cent.) includes all the high-grade fibres such as flax, ramie and Italian hemp. The high-xylan group (13–25 per cent.) contains the coarser fibres Manila hemp, sisal, etc., which are also more or less lignified. It is noteworthy that fibres with a normal xylan content of 6 to 10 per cent. in the cellulose have not been encountered.

CHAPTER XX

THE ESTIMATION OF CELLULOSE AND LIGNIN

PART I

The Estimation of Cellulose

THE older methods for the quantitative isolation of the cellulose of plant tissues are described in the work of M. Renker, "Über Bestimmungsmethoden der Cellulose" (Berlin, 1910). The chlorination method of Cross and Bevan,[1] after an enormous amount of critical work, still remains the most convenient and accurate method of determining the cellulose content of fibres and wood. The use of sodium hypochlorite, and of chlorine dioxide, has proved satisfactory, and the modification in which the cellulose is isolated as "holocellulose" (p. 360) is likely to be of value.

A. **The Chlorination Method of Cross and Bevan.**—In this process the chlorine reacts with the lignin, forming yellow compounds (chiefly di- and tetra-chloro substitution derivatives) with simultaneous production of hydrochloric acid. These compounds are removed by boiling with sodium sulphite solution. The method gives a maximum cellulose yield from fibrous materials.

Procedure.—About 5 g. of fibre (moisture on a duplicate), are (*a*) boiled for 20 to 30 minutes with a solution of sodium hydroxide (1 per cent. NaOH), which is kept at constant volume. The fibre is well washed on a cloth or gauze filter, squeezed, opened out and placed in a beaker, into which (*b*) a slow stream of washed chlorine gas is passed. Rapid reaction ensues, and the fibre changes in colour, from brown to golden yellow.* To ensure complete reaction, it is necessary to leave the fibre for some time (from 30 to 60 minutes) in the chlorine gas. (*c*) The chlorinated fibre is removed, washed once or twice with water to remove HCl, and placed in a 2 per cent. solution of sodium sulphite; the solution is gradually raised to the boiling-point, a quantity of sodium hydroxide solution is added to give 0·2 per cent. NaOH on the solution, and the boiling continued for 5 minutes. (*d*) The cellulose is thrown upon a cloth filter and washed with hot water. It should be nearly white; but to remove

[1] "Cellulose", London, 1903.

* Considerable heating takes place, and the yield of cellulose is improved by keeping the temperature as low as possible.

the last residues of non-cellulose it is bleached by immersion in a dilute solution of hypochlorite (0·1 per cent. NaOCl) for a few minutes, or treated with dilute permanganate solution (0·1 per cent.). It is well washed, treated with sulphurous acid on the filter, washed with hot water, and digested [1] for 30 minutes on the water bath with hot water to remove acidic and other bodies obstinately retained.

Determination of Hydrochloric Acid formed in the Chlorination Reaction.—This constant is useful as giving an indication of the extent of lignification and for comparative purposes—*e.g.* in comparing a sample of a genuine hemp with one of unknown origin. To determine it a separate experiment is carried out with 5 g. of substance.

Procedure.—The weighed fibre is chlorinated as above, the reaction bottle disconnected, and the chlorine blown out. A 20 per cent. neutral solution of sodium chloride is poured down the sides. A saline solution must be used, as the chlorolignin is soluble in water. The bottle is washed once or twice with the salt solution, and the united liquids titrated with *N*-NaOH in the usual way, using methyl red or orange as indicator.

The chlorine converted into hydrochloric acid, in the case of jute, is about half of the total chlorine entering into the reaction—*i.e.* 8 to 8·5 per cent. In the case of other lignocelluloses, such as wood, it is in excess of half, possibly as a result of oxidation. For the estimation of chlorine combining see p. 356.

Modifications of the chlorination process, involving variation in the specified treatments and in technique, have been devised by several workers, chiefly for the estimation of cellulose in wood.

A good deal of discussion has centred around the question of the preliminary boiling with sodium hydroxide. There is no doubt that a considerable proportion of the fibrous material dissolves under this treatment [2] (see table, p. 350), but the alkali certainly removes resins and other incrusting substances, the presence of which retards the action of chlorine. As a rule, one treatment with chlorine is sufficient, whereas without alkali treatment two or three alternate treatments with chlorine and sulphite are necessary for the complete elimination of lignin. The result is that, although there may be a certain loss of cellulose and hemicellulose in the alkali boil, the loss due to the oxidising action of chlorine on the " nascent " cellulose is so greatly reduced that the yield of " Cross and Bevan cellulose " represents, with great probability, the cellulose content of the tissue. In our

[1] G. J. Ritter, *Ind. Eng. Chem.*, 1924, **16**, 808.
[2] A. G. Norman and S. H. Jenkins, *Biochem. J.*, 1933, **27**, 818.

practice we find that a preliminary alkali boil of 5 minutes gives satisfactory results with most vegetable fibres.

In the method suggested by Dore (p. 442) for the analysis of wood (or fibres, p. 350), the material, after extraction with organic solvents, is digested with cold dilute sodium hydroxide, and several chlorinations are given if required. Schorger, in his scheme for the analysis of wood (p. 448), omits the alkali treatment, but repeated treatments with chlorine followed by sodium sulphite are necessary. An investigation [1] into the isolation of cellulose from Australian woods showed that in the particular case of the mountain ash (*Eucalyptus Regnans*) it was impossible without preliminary alkali treatment to obtain a cellulose free from lignin. A preliminary boiling with 1 per cent. NaOH solution for 1 hour, followed by a single chlorination, gave satisfactory results.

The chlorination periods originally used were long, of the order of 20, 15, 15 and 10 minutes, but Ritter and Fleck [2] have shown that better results are obtained by successive short treatments of 5 or even 3 minutes each, as degradation of the cellulose by the prolonged action of chlorine is then largely avoided. As the reaction with chlorine seems to be a surface phenomenon, the physical state of the lignocellulose influences the speed and extent of chlorination. There is little difficulty in dealing with fibres, straw, etc. Wood is treated in the form of fine shavings, raspings, sawdust, or powder of various dimensions. It has been found [3] that the largest yield of cellulose is obtained from wood powder passing an 80- but retained by a 100-mesh sieve, and this standard powder (80–100 mesh) is now generally employed.

B. **Chlorination Method of A. W. Schorger.**—2 g. of wood (80–100 mesh) in a tared alundum crucible are extracted with a mixture of 32 parts of alcohol and 68 parts of benzene for 6 hours, dried by suction and washed with hot water. The moist sample is transferred to a beaker which is placed in the chlorinating chamber and cooled by running water. Washed chlorine is introduced at the rate of forty bubbles a minute, the inlet tube reaching close to the wood. After 3 to 5 minutes the beaker is removed, a solution of sulphurous acid added to destroy the excess of chlorine, and the contents filtered. The residue is washed with water, returned to the beaker and 100 ml. of 2 per cent. sodium sulphite solution added. The beaker is heated in a boiling-water bath for half an hour, the contents filtered, washed and again chlorinated. The operations

[1] H. W. Strong, *J. Soc. Chem. Ind.*, 1928, **47**, 88T.
[2] *Ind. Eng. Chem.*, 1924, **16**, 147, 947; also *ibid.*, 1929, **21**, 40.
[3] S. A. Mahood, *ibid.*, 1920, **12**, 874.

are repeated until the residue no longer gives a pink colour on the addition of sulphite.

Coniferous wood may require four to five treatments, hard woods two or three.

The cellulose is bleached by treatment for 10 minutes with 20 ml. of 0·1 per cent. permanganate solution. It is decolorised with sulphurous acid, filtered, washed and returned to the beaker, where it is digested on the steam bath for two hours with 200 ml. of water. The cellulose is then filtered, washed with hot water, alcohol and ether, and dried at 105° for 2 hours, after which the crucible is weighed in a stoppered weighing bottle. The ash may be determined and a correction made. The author insists on the importance of the final digestion with water to remove traces of acid.

C. **The Chlorination Method of Sieber and Walter**[1] **as used by W. H. Dore.**—In this process the whole treatment is carried out in a Gooch crucible. A filter disc is obtained which fits closely at the bottom of the crucible. The disc is placed between two circles of fine muslin, the edges of which are sewn together so that when the plate is pressed down into the crucible the muslin edges form a seal. The disc is further fixed to the bottom of the crucible by passing a loop of thread up and down through the holes and tying underneath.

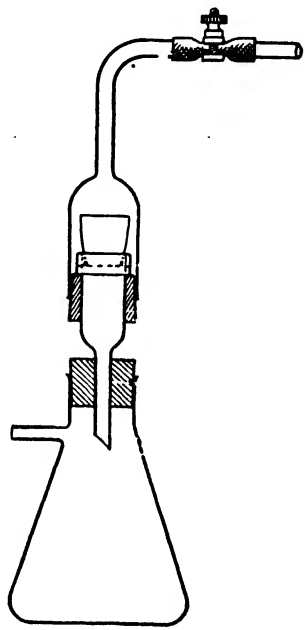


FIG. 71.—Chlorination apparatus used by W. H. Dore.

The crucible is fixed in the usual glass adapter which carries an inverted rubber plug. This enables an adapter connected with the source of chlorine to be fixed over the crucible (Fig. 71).

The crucible is prepared by boiling for 15 minutes in a 3 per cent. solution of sodium hydroxide, then washed with hot water, acetic acid, water, and again boiled with water for half an hour. It is dried and weighed in a weighing bottle, the wood sample added, and the weight again taken. The crucible is adapted to the filter flask as shown (Fig. 71) and water added to the sample with suction until the wood is saturated. It should be pressed down uniformly and gently with a glass

[1] R. Sieber and L. E. Walter, *Papier Fabrik*, 1913, 11, 1179.

rod. The adapter is then adjusted, gentle suction applied, and chlorine gas drawn through for 5 minutes. A rapid wash with sulphurous acid is given, and the crucible is then placed in a small beaker filled with sodium sulphite solution to within $\frac{1}{4}$ in. of the top of the crucible, and heated in a boiling-water bath for 45 minutes. The crucible is returned to the suction apparatus, and, after washing, the wood is again chlorinated, the procedure being repeated until the lignin has been removed. The cellulose is then bleached as usual and finally washed out into a beaker and heated with water.

S. A. Mahood (*loc. cit.*) has carried out comparative analyses between this process and that of Schorger, and finds that rather less cellulose is obtained by chlorinating in a crucible than in an open vessel, the results in the latter case being 1·5 to 3 per cent. higher—*e.g.* 51·0 (Sieber and Walter), 52·7 (Schorger).

D. **Chlorination Method for the Estimation of the Cellulose content of Pulps or Wood, together with the Estimation of the Chlorine combining (Chlorine Number):** corrected official *TAPPI* standards.—The specifications will be found in *TAPPI* standards T-201 m, 1937 (estimation of cellulose), and T-202 m, 1940 (chlorine number). The crucible method for the estimation of cellulose is used, and by coupling it with a modified Roe's apparatus (p. 468) the chlorine combining can also be determined.

The apparatus comprises (*a*) a Hempel gas-burette enclosed in a glass water-jacket and connected with a levelling tube. The top of the burette carries a two-way cock opening to an inlet and outlet for chlorine gas and to the air, (*b*) a glass crucible, 35 ml. capacity, with a fritted glass base (porosity, 5 to 7), also enclosed in a water-jacket. The crucible is fitted top and bottom with rubber stoppers carrying capillary tube connectors of which the outlet at the top carries a two-way cock connecting either with the air or with (*c*) a Hempel gas pipette. The burette and pipette are filled with a saturated solution of calcium chloride, saturated with chlorine at room temperature.

Estimation of Cellulose.—2 g. of air-dry pulp (or wood), are weighed into an alundum crucible (porosity, R.A. 98) in a weighing bottle. With wood the crucible and contents are extracted for 6 hours with alcohol-benzene (1 : 2 by vol.), dried off, and the wood washed with hot water. The extracted wood (or the pulp) is put into the water-cooled crucible, which is connected by the air inlet at the bottom with the tap of the burette and at the top with the pipette. Gentle suction applied alternately in each direction distributes water and sample evenly over the crucible.

The burette is filled with chlorine gas which is driven upwards

through the crucible into the pipette. The temperature in the jacket should be between 23·5° and 32° during chlorination. Wood requires about 230 ml. of chlorine so that the burette may need refilling. The chlorination should not exceed 4 minutes, after which the crucible is disconnected and the fibres washed with 50 ml. portions of the following reagents in order : (*a*) water, (*b*) 3 per cent. SO_2 solution, (*c*) water, (*d*) 2 per cent. Na_2SO_3 solution. The residue is then washed off into a beaker with 60 ml. of the Na_2SO_3 used in four portions. To remove the last traces the crucible is placed in a watch glass containing 10 ml. of the sulphite solution and by suction at the top the liquid is drawn through, removing any cellulose attached to the base. This is done four times, the liquid being added to that already in the beaker. The beaker and contents are heated (water bath) for 30 minutes and the cellulose collected on the crucible and washed with 250 ml. of water. If the residue still gives a pink colour with sulphite solution the chlorination is repeated twice, if necessary, for 2 or 3 minutes in each case. Final washings with 500, 50 and 50 ml. of water, followed by alcohol and ether are given. The cellulose is dried for 2·5 hours at 105°.

Determination of the Chlorine Number or Roe Value.—The same apparatus is employed, but the chlorine used is measured. If the apparatus is kept full of chlorine gas the liquid will remain saturated. Two grams of air-dry pulp are treated with about 90 ml. of chlorine gas, the volume, temperature and pressure of which are measured. After passing through the pulp the volume is again taken and the chlorination repeated until absorption ceases when the volume absorbed is noted, together with the pressure, temperature, and the tension of aqueous vapour in the tube under the conditions employed. To the weight of chlorine thus obtained a correction is applied by allowing for the chlorine combining to form HCl.

The chlorinated pulp is washed out with 100 ml. of water at 18° to 23° used in four portions, and the filtrate and washings titrated with standard alkali. The amount of chlorine contained in the HCl found is subtracted from the total weight of chlorine used, and the result expressed as weight of chlorine actually absorbed by 100 grams of the oven-dry pulp.

E. **Estimation of Cellulose in Wood, Straw, etc., by Means of Sodium Hypochlorite.**[1]—This reagent has proved convenient also for the preparation of quantities of 200–300 g. of cellulose in the laboratory, the use of a chlorinating solution making the work much easier. The process is based on a study of all the factors involved, and the product represents as closely as possible the cellulosic tissue

[1] A. G. Norman and S. H. Jenkins, *Biochem. J.*, 1933, **27**, 818.

of the plant freed from encrusting substances. The only pre-treatment is a boil with sodium sulphite solution. Two treatments are then given with " neutral " hypochlorite (*i.e.* the commercial solution) and then three or more with acidified hypochlorite, each followed by boiling with sulphite.

Procedure.—Solutions of sodium sulphite (6 per cent.), sodium hypochlorite of *ca.* 15 and 3 per cent. respectively, and sulphuric acid 20 per cent. are required.

The material should be in a fine and uniform state of division, *e.g.* woods 60–80 mesh ; straws 40–60 mesh. The woods need preliminary extraction with alcohol-benzene mixture. About 2 g. are brought to the boil in 100 ml. of 3 per cent. sulphite solution and then filtered on fine poplin stretched tightly across the top of a small Buchner funnel. This treatment opens up the material and also removes some of the lignin. The residue is then washed into a beaker, the liquid made up to 100 ml. and 5 ml. of sodium hypochlorite (*ca.* 15 per cent. available chlorine) added. After standing 10 minutes, the fibre is filtered off and returned to the beaker, the volume made up to 50 ml. with water and 50 ml. of 6 per cent. sodium sulphite added. The whole is boiled (or, better, as bumping is considerable, brought to the boil and kept in a boiling water bath) for 20 minutes. This treatment—hypochlorite followed by sulphite —is repeated. The material is then suspended in 100 ml. of water and 5 ml. of hypochlorite (3 per cent. available chlorine) added, together with 2 ml. of 20 per cent. sulphuric acid. After standing out of direct sunlight for 10 minutes, it is filtered off, made up to 50 ml. with water and sulphite added as before (50 ml.). The liquid is boiled for 10 minutes, during which the purple colour developed becomes brown. These treatments with acid hypochlorite, etc., are continued till no further indication of the presence of lignin is observed after the addition of sulphite solution. Two or three treatments with straws and four or five with woods will be necessary. The material is finally soaked in some 200 ml. of hot water, washed and transferred to a Gooch crucible containing a small circle of cloth, and dried. From the following table of results it will be seen that the amount of cellulose isolated agrees closely with that obtained by the Cross and Bevan method, if the preliminary alkaline boil is omitted. The furfural yield of the two products is identical and the apparent lignin is of the same order in both. This apparent lignin, estimated by 72 per cent. sulphuric acid, is derived largely from pentosans.

To estimate the available chlorine in commercial hypochlorite solutions, 5 ml. are diluted to 500 ml. and 10 ml. portions mixed

COMPARISON OF RESULTS OBTAINED BY THE CROSS AND BEVAN METHOD, WITHOUT PRE-TREATMENT, AND THAT OF NORMAN AND JENKINS

Material.	Cross and Bevan Method.				Norman and Jenkins.	
	No. of Chlorinations.	Cellulose per cent.	Furfural per cent.	Apparent Lignin per cent.	No. of Chlorinations.*	Cellulose per cent.
Oats . .	7	53·4	17·4	3·1	2N. 3A.	53·5
Wheat .	6	56·7	18·3	2·9	2N. 3A.	56·3
Rye . .	7	60·2	19·0	2·4	2N. 4A.	59·8
Oak . .	10	53·2	18·1	0·3	2N. 5A.	53·9
Beech .	8	58·8	15·5	1·0	2N. 5A.	59·4
Scotch Pine	8	60·2	5·2	0·8	2N. 5A.	60·8

* N., neutral hypochlorite ; A., acid hypochlorite treatment. The woods are extracted (alcohol-benzene). The furfural and lignin are calculated on the cellulose.

with 10 ml. of 5 per cent. acetic acid and 5 ml. of 10 per cent. potassium iodide. If n ml. of $N/20$ thiosulphate are required, the percentage of available chlorine is $1{\cdot}775\ n$.

F. Estimation of Cellulose by the Action of Chlorine Dioxide.[1]—This method has the advantage of removing the lignin very quickly, one or two treatments with dioxide being sufficient in cases which require four or five treatments with chlorine. Schmidt originally claimed that the method was specific, in that the carbohydrate portion of woody tissue was left intact, the loss consisting only of the lignin fraction. Since pine wood by this method showed an apparent lignin content of 36·7 and beech one of 46, instead of the usual values of 30 and 22 respectively, it is obvious that some hemicellulose must be removed. This was confirmed by Heuser,[2] who found, however, that in the cellulose fraction isolated from spruce wood a greater proportion of hemicellulose (mannan) was retained in the chlorine dioxide product than in that obtained by the chlorination method. Some results contained in the table on p. 360 show that the cellulose calculated as " pentosan-mannan free " given by each method is, nevertheless, identical.

Materials Required.—A solution of chlorine dioxide containing from 0·3 to 1·5 per cent. ClO_2. Sodium sulphite solution 2 per cent.

Preparation of the Chlorine Dioxide Solution (Heuser and Merlau). —A mixture of 240 g. of potassium chlorate and 200 g. of crystalline

[1] E. Schmidt *et al.*, *Ber.*, 1921, **54**, 1860, 3241 ; 1923, **56**, 23, 1438 ; 1924, **57**, 1834.

[2] E. Heuser and O. Merlau, *Cellulosechem.*, 1923, **4**, 101 ; E. Heuser and A. Winsfold, *Ber.*, 1923, **56**, 902.

Method.	Cellulose per cent.	Carbohydrates in the Cellulose.		
		Pentosan per cent.	Mannan per cent.	"Pure" Cellulose per cent.
Chlorine dioxide .	62·71	4·44	5·43	52·84
Chlorine . .	59·24	4·90	2·09	52·28

oxalic acid are placed in a 1·5 litre round-bottom flask and a cold solution of 120 ml. of sulphuric acid in 400 ml. of water is added. The flask is heated on a water bath between 50° and 60°. The gas evolved is washed through a little water and absorbed in water in Woulff's bottles cooled in ice. The reaction continues for about 8 hours. Although there is always danger of explosion, the carbon dioxide produced from the oxalic acid minimises this danger. The contents of the absorption bottles are mixed, and the amount of chlorine dioxide present can be determined, if necessary, by reaction with potassium iodide solution.[1]

Procedure.—0·5 g. of wood, extracted with alcohol-benzene, is placed in a glass stoppered flask and covered with 100 ml. of about 1·5 per cent. chlorine dioxide. The flask is kept in a cool place for 48 hours with occasional shaking, during which the wood acquires a red tinge. The contents are filtered and washed with warm water until the filtrate shows no reaction to potassium iodide solution. The residue is washed with hot 2 per cent. sulphite solution until the runnings are colourless, and then with hot water. A second treatment with dioxide will probably remove the lignin completely. The cellulose may be bleached by treatment with 5 ml. of 0·3 per cent. chlorine dioxide, after which it is washed, dried and weighed.

G. **Preparation and Estimation of Cellulose as Holocellulose.**[2]—This term is applied to the cellulose isolated from lignified material by chlorination, followed by treatment with an alcoholic solution of monoethanolamine. It is a Cross and Bevan cellulose still retaining the hemicellulose fraction which is lost in the sulphite boil of that process. It, perhaps, more nearly than any other product, corresponds to the "whole" cellulose as it exists in the woody tissue. A short hydrolysis of holocellulose (1·3 per cent. H_2SO_4 for 2 hours) removes the more labile hemicellulose and the

[1] E. Schmidt and E. Graumann, *Ber.*, 1921, **54**, 1862. Details are given in "The Chemistry of Cellulose and Wood", A. W. Schorger, 1926, p. 517.

[2] G. J. Ritter and E. F. Kurth, *Ind. Eng. Chem.*, 1933, **25**, 1250; W. Van Beckum and G. J. Ritter, *Paper Trade J.*, 1937, **105** (18), T.S. 277; *ibid.*, 1939, **108**, T.S. 65; *ibid.*, 1941, **113**, *TAPPI* Sect., 143.

residue, in amount and general character, is practically identical with the cellulose obtained by the Cross and Bevan method as will be seen from the table given below.

COMPARISON OF HOLOCELLULOSE WITH CROSS AND BEVAN CELLULOSE

	Yield (dry on dry).	α-Cellulose.	Pentosan.	Uronic Anhydride.	Acetyl.	Methoxyl.
ASPEN						
Holocellulose . . .	82·5	61·4	28·2	5·0	5·5	1·1
„ after acid hydrolysis .	63·7	74·3	15·9	2·6	3·1	0·7
Cross and Bevan cellulose .	64·1	76·3	19·9	2·6	1·6	0·5
WHITE SPRUCE						
Holocellulose . . .	73·3	67·5	12·2	3·6	3·2	0·96
„ after acid hydrolysis .	61·0	71·7	6·9	1·8	1·6	0·45
Cross and Bevan cellulose .	61·2	72·9	6·2	1·9	1·6	0·42

Estimation of Cellulose as Holocellulose.—Purified wood, 2·5 g., 60–80 mesh, is washed with alcohol and extracted on a boiling water-bath for 3 hours with 400 ml. of hot water. After allowing to dry in the air, 2·5 g. (moisture estimated on another sample) is moistened with cold water (10° C.), and chlorinated by suction for 3 minutes, the mass stirred and chlorinated 2 minutes more.

Alcohol, added to remove lignin chlorides, is removed by suction after 1 minute. The mass is then stirred for 2 minutes with a hot solution of the reagent—alcohol (95 per cent.) containing 3 per cent. of monoethanolamine—which is removed by suction and the treatment repeated. The mass is washed twice with ethanol and twice with water. The whole process of chlorination, etc., is repeated until the residue remains white after chlorination and does not change colour on addition of the reagent.

A somewhat similar method, in which the wood is boiled with pure monoethanolamine, has been described.[1] The residue is treated with cold chlorine water, washed with sulphurous acid, sodium sulphite, and finally boiled with 2 per cent. sodium sulphite. The cellulose isolated in this way resembles Cross and Bevan cellulose.

Ritter and Kurth originally obtained a holocellulose by alternate chlorinations and treatments with an alcohol-pyridine mixture which extracted all but a trace of lignin. This was removed by the

[1] P. Bloom *et al.*, *Paper Trade J.*, 1942, **115**, *TAPPI* Sect., 107.

action of hypochlorite at *p*H7. It has lately been shown [1] that holocellulose can be isolated from beech and pine wood by alternate chlorination and treatment with ammonia or lime water. The product contains 0·3 to 3 per cent. of lignin.

The foregoing methods are those best suited for the estimation of cellulose. Among others is the process of hydrolysis with phenol, which reacts specifically with lignin (p. 499). 2 g. of substance are heated with 16 g. of phenol for 8 hours at 220°. The product is washed with benzene and the " cellulose " bleached with permanganate. This process gave the following yields of cellulose, but the results were variable—from wood, 52 per cent. ; from sulphite pulp, 90·7 per cent. ; from jute, 79·4 per cent.

H. **Analysis of Cross and Bevan Cellulose.**—The cellulose isolated by Cross and Bevan's method is not " pure " cellulose, but represents a definite carbohydrate fraction of the wood substance which resists chlorination. It is therefore best to describe it as Cross and Bevan cellulose, as this at once gives a key to the method of isolation and to the properties of the product. Cross and Bevan cellulose contains both furfural-yielding substances (pentosans, etc.) and hexosans of the type of mannan. It retains, in the case of coniferous woods, 40–60 per cent. of the total furfural-yielding substances of the original wood, and in the case of hard woods some 55–66 per cent.

To obtain an idea of the proportion of resistant or α-cellulose in the Cross and Bevan product some authors determine the pentosan and calculate the cellulose as " pentosan-free ". The correction is not exact, but the furfural determination is always of value in an examination of isolated cellulose. The amount of mannan present is usually small, and a correction is not considered necessary.

The following determinations are therefore recommended :—

(*a*) Estimation of furfural and methyl-furfural, and calculation as pentosan.

(*b*) Estimation of α-, β-, and γ-cellulose (see below). The α-cellulose fraction still retains furfural-yielding substances, but it affords the most practical measure of the normal cellulose content of the wood. If required, the furfural yield may be determined.

(*c*) Ash. This is usually less than 0·4 per cent.

(*d*) Lignin. Lignin in small amount is often tenaciously retained. The quantity is generally estimated by the use of 72 per cent. sulphuric acid (p. 369).

For examples, see pp. 443, 444.

[1] C. Jayme *et al.*, *Papier Fabrik.*, 1939, **37**, *Tech.*, 57.

J. Estimation of α-, β- and γ-Cellulose.—These terms, introduced by Cross and Bevan (1904), and by Jentgen (1911), refer to the fractionation of a cellulose by the action of sodium hydroxide solution of mercerising strength. The fraction which remains undissolved is the α-cellulose, the β- and γ-celluloses being dissolved. Of these, the portion which is re-precipitated on acidification is called β-cellulose, while the γ-cellulose remains in solution. The α-cellulose is of somewhat the same order of resistance as normal cotton cellulose, while the β-fraction, insoluble in water, is in a less dispersed condition than the γ-fraction which remains in solution. The estimation of α-cellulose has now become a valuable diagnostic for all types of wood-pulp and other technical celluloses. The values of the β- and γ-fractions have also acquired significance, *e.g.* in the manufacture of rayon and as an indication of bleaching treatment in pulps. Their proportions are calculated for analytical purposes as cellulose, but they are not necessarily composed of cellulose at all.

The process consists of three parts : (*a*) the mercerisation ; (*b*) the dilution, and (*c*) the estimation of the amounts of the three fractions obtained.

The details given below for the *mercerisation* and *dilution* stages must be followed with scrupulous exactness, otherwise no reliance whatever can be placed on the results. For the *estimation* there are three methods in use : (1) The original *gravimetric* method of Cross and Bevan, in which the α-cellulose is washed, dried and weighed, the β- precipitated in the liquors, filtered off and weighed, and the γ- found by difference. The results are very reliable.

(2) The *volumetric* process. (3) A combination of these, which has the advantage of obviating the necessity of washing the α-cellulose free from alkali, with consequent saving in time. Alternatively the gravimetric process may be used for the α-cellulose and the volumetric for the β- and γ-cellulose.

1. The gravimetric process. Two portions of 10 g. are weighed out, one for moisture determination. The other is placed in a glass tumbler of about 200 ml. capacity and 50 ml. of NaOH solution of 17·8 per cent. strength (40° Tw.), at exactly 20°, are added. The cellulose is kneaded with a glass rod flattened at the end and allowed to stand 25 minutes at 20°. Meanwhile a litre of water is adjusted to 20°. The tumbler is filled with 150 ml. of this water and the mass stirred till homogeneous. After 5 minutes the contents are poured on to a cloth filter (mercerised muslin fabric, for example) in a Buchner funnel and the liquid drained off by the pump. The pulp is then washed, with stirring in between, using the remainder of the litre of water for 5 minutes. For treatment of the filtrate containing

β- and γ-fractions, see below. A mixture of 90 ml. of water and 10 ml. of glacial acetic acid is next poured over the pulp and allowed to percolate slowly through. The α-cellulose is finally washed with 1 litre of boiling water, pressed well, blown out into a paper tray, and dried at 105°. (Note.—The same temperature, 20°, must be employed throughout.)

The filtrate is acidified with 30 ml. of glacial acetic acid. The precipitated β-cellulose is coagulated by heating on a water bath, filtered through a fine cloth filter, and washed with boiling water till free from acid. The cloth is opened out on blotting paper, allowed to drain, and the β-cellulose scraped off and dried in a milk dish, at first at a gentle heat, and finally at 105°. If the precipitate is very small, it is better to filter through a filter paper tared against a similar one, and, if time permits, the liquid may be allowed to settle in a tall cylinder and the supernatant liquid decanted off before filtering. The γ-cellulose is obtained by difference, or it may be estimated directly by treating a fraction of the filtrate from the β-cellulose by the volumetric method.

As the γ-cellulose in most pulps largely exceeds the β-fraction, a satisfactory variation of the method consists in making the acidified liquid containing the β- and γ-fractions up to a known volume, allowing the β-fraction to settle and then pipetting off a known volume of the clear liquid. The γ-cellulose may be estimated volumetrically in this and the β-cellulose found by difference (p. 365).

The above technique, which has been used in English laboratories for a number of years, was recommended in almost identical form by the Division of Cellulose Chemistry of the American Chemical Society.[1] The *TAPPI* modification (T203 m-44, 1944) is given on p. 465.

2. The volumetric process (M. W. Bray and T. M. Andrews).[2] Cellulose is oxidised by acidified potassium dichromate to carbon dioxide and water according to the equation—

$$C_6H_{10}O_5 + 6O_2 = 6CO_2 + 5H_2O.$$

It will be seen that for the oxidation of 1 molecule of cellulose (M.Wt. 162·1) 4 molecules of $K_2Cr_2O_7$ (M.Wt. 294·5), are required, so that 1 g. of dichromate corresponds to 0·1375 g. of cellulose.

An excess of dichromate is used for oxidation, and the amount remaining is determined by titration with ferrous sulphate solution. In the complete volumetric process the α-cellulose is determined in this way on the moist residue obtained after mercerisation. The

[1] *Ind. Eng. Chem. Anal.*, 1929, **1**, 52.

[2] *Ind. Eng. Chem.*, 1923, **15**, 377; see also C. G. Schwalbe, "Die Chemische Untersuchung pflanzlicher Rohstoffe und der daraus abgeschiedenen Zellstoffe": Berlin, 1920, p. 33.

β- and γ-cellulose are then determined together in a fraction of the filtrate, and the γ- determined in the same way after removal of the β- precipitate by acidification. A satisfactory modification consists in determining the α-cellulose gravimetrically and using the volumetric process for the β- and γ- fractions.

Materials Required.—The following reagents are prepared :—

Sodium hydroxide solution, 17·5 per cent. NaOH.

Potassium dichromate solution, about 90 g. per litre.

Ferrous ammonium sulphate solution, 159·9 g. in water with 5 ml. of 10 per cent. sulphuric acid diluted to 1 litre. 50 ml. corresponds to 0·1375 g. of cellulose.

Potassium ferricyanide indicator, 1 g. in about 500 ml. water. This reagent must be free from ferrocyanide. A dilute solution of iron alum, strongly coloured by a drop of permanganate solution, should give a brown colour with the indicator, but no trace of blue or green. As an internal indicator *o*-phenanthroline can be used.

Sulphuric acid of 72 per cent. concentration.

The method of analysis of a sample of pulp is as follows : 1 g. is weighed into a 250 ml. beaker, triturated with 25 ml. of 17·5 per cent. NaOH solution until homogeneous, and allowed to stand 30 minutes. The liquid is filtered through a Gooch or alundum crucible, or, if too gelatinous, centrifuged until the α-cellulose separates. In any case, after the supernatant liquid has been filtered or poured off, the α-cellulose is washed with 50 ml. of 4 per cent. NaOH solution, followed by 300 ml. of cold water in small quantities. The insoluble residue is removed, dissolved in 30 ml. of 72 per cent. sulphuric acid, washed into a 100 ml. graduated flask with successive portions of the acid, and made up to the mark. Ten ml. of the solution are put into a beaker, 10 ml. of the dichromate solution added, with about 60 ml. of the sulphuric acid. The mixture is boiled for exactly 5 minutes, cooled in ice, and the excess of dichromate titrated with the ferrous ammonium sulphate solution. From the result the percentage of α-cellulose is calculated.

The β- and γ-cellulose are determined in the 350 ml. of filtrate by making it up to 400 ml. with water and dividing into two equal portions. One 200 ml. portion is diluted to 250 ml. and 25 ml. oxidised as above, using, however, 5 ml. instead of 10 ml. of the dichromate solution. Calculation gives the combined percentages of β- and γ-cellulose.

The other 200 ml. portion is acidified with 10 per cent. sulphuric acid, using 1 drop of methyl orange indicator, and then adding 5 ml. excess of acid. The liquid is diluted to 250 ml. The precipitate of

β-cellulose coagulates and settles on standing for some time. When settled, 25 ml. portions of the supernatant liquid are oxidised in the same way, giving the percentage of γ-cellulose.

Part II

The Estimation of Lignin

Of the various methods used for isolating lignin from lignified substances—hydrolysis by mineral acids or by alkalis ; the action of chlorine or of bisulphites—only the first is now employed to any extent for the estimation of lignin. The action of cold concentrated sulphuric or hydrochloric acid was originally assumed to remove the carbohydrate components completely, without affecting the nature or amount of the lignin isolated. It was soon found, however, that methoxyl and acetyl groupings of the " native " lignin are eliminated and that condensed carbohydrate residues, capable of yielding furfural, still remain in the product. A proportion of the acid radicle employed is also fixed and retained. The gains and losses roughly balance, for, although the product obtained is not identical with the lignin of the wood, its quantity agrees closely with the lignin content as nearly as this can be estimated. In an experiment by the present author for example, all the constituents of a spruce wood, other than lignin, were determined with the following results :—

Extract with benzene and alcohol	3·3	per cent.
,, ,, water	2·5	,,
,, ,, NaOH (5 per cent.)	3·8	,,
Cellulose	55·0	,,
Mannan	7·6	,,
Galactan	0·1	,,
		,,
Total	72·3	,,

The difference (27·7 per cent.) should be lignin, and the value of this, directly determined with hydrochloric acid (d, 1·2), was 29·1 per cent.[1] As a quantitative method, therefore, the use of mineral acid appears satisfactory. A number of modifications in the concentration and application of the acids have been suggested. The more important are indicated in the following table, which also shows the close agreement in the values for lignin obtained by each method :—

[1] C. Dorée and E. Barton Wright, *Biochem. J.*, 1927, **21**, 299.

LIGNIN IN VARIOUS WOODS [1]

Wood.	Lignin per cent. found by			
	HCl 1 per cent. (pressure).	HCl gas.	H_2SO_4 72 per cent.	HCl *d*, 1·21.
Fir	29·94	28·81	29·36	29·17
Fir	28·91	28·10	28·04	27·98
Pine	29·52	29·56	31·33	29·16
Birch	23·54	22·55	20·96	23·27
Birch	27·29	26·36	26·75	26·38
Aspen	22·14	22·36	22·06	22·45
Aspen	21·00	21·06	21·91	20·75
Beech	22·07	22·90	23·99	22·69
Ash	26·71	25·90	19·59	26·01
Willow	25·06	25·97	24·54	24·70
Alder	25·95	23·04	23·05	24·57

Some of the methoxyl groups present in lignin are removed by the action of concentrated acids. It is usually considered, for example, that spruce lignin, as it exists in the wood, contains about 17·5 per cent. of methoxyl. Heuser and Wenzel [2] found that after treatment with 43 per cent. hydrochloric acid for 1 hour, 2·65 per cent. of methoxyl were lost.

On the assumption that the whole of the methoxyl is contained in the lignin, the apparent loss of methoxyl during the sulphuric acid method of estimation is shown by the figures in the following table :—

	Lignin * in Wood (*a*). Per cent.	OMe in Wood (*b*). Per cent.	OMe in the Lignin ($b/a \times 100$). Per cent.	OMe found in Lignin isolated. Per cent.	OMe "lost" during Resolution. Per cent.
Western yellow pine	26·75	4·45	16·64	13·13	3·51
Western white pine	24·30	4·47	18·40	15·10	3·30
Tan oak	24·68	5·70	22·06	16·99	5·07
Eucalyptus	26·74	6·56	24·53	15·01	9·52
Yellow poplar (sapwood)	23·86	5·89	24·69	17·00	7·69
Yellow poplar (heartwood)	23·69	6·03	25·45	20·22	5·23

* Estimated by 72 per cent. sulphuric acid method.

The apparent loss is seen to vary from 3 to 9 per cent. It is not quite so high as it appears, since some of the methoxyl of the wood is present in the hemicellulose. Holocellulose in fact, which, as

[1] J. König and E. Becker, *Z. angew. Chem.*, 1919, **32**, 156.
[2] E. Heuser and G. W. Wenzel, *Papier Fabrik.*, 1921, **19**, 1183.

nearly as possible comprises the total cellulose, has been shown [1] to contain part of the methoxyl (as well as the whole of the acetyl) of the original wood.

Repeated treatment of white oak and yellow pine with dilute alkalis under pressure removes 63 per cent. of the methoxyl in the form of methyl alcohol. This is the same proportion as is obtained on destructive distillation.

It follows that the estimation of lignin based on the methoxyl content of wood can give only approximate values.[2]

Methods of Estimation

Modern experience has confirmed the result given in the last two columns of the table (p. 367) which show that the values obtained by concentrated hydrochloric or sulphuric acids are very much the same. On account of its convenience sulphuric acid (72 per cent.) is generally employed, and since 1930 a number of investigations have been made into its action on lignocellulose with a view to the isolation of lignin with the minimum of change and freedom from associated impurities. An account of these and of the modifications suggested by them will be given after a brief description of the older standard methods.

I. **Methods Involving the Use of Hydrochloric Acid.**—(i) *Use of Concentrated Acid of* 40 *per cent.* (*d*, 1·2) *and higher.*[3]—The reagent is prepared by passing hydrochloric acid gas into the ordinary concentrated acid, which is cooled in ice. One part of the wood is treated with 20 parts of the acid and allowed to stand, with occasional shaking, for 12 hours. The contents of the flask are then diluted with ten times their volume of water, the lignin filtered and washed until free from chlorine ions. This process is tedious, and is best done, in our experience, by allowing the solid to settle in tall cylinders and decanting off the clear liquid from time to time (compare also p. 494).

Willstätter lignin cannot be freed from chlorine by prolonged washing. It may contain 1·6 to 2·5 per cent. of chlorine.

(ii) *Use of Hydrochloric Acid Gas.*—This method avoids the preparation of concentrated hydrochloric acid. In the original process 10 g. of the wood moistened with 30 ml. of water are placed in a flask which is cooled with ice. Dry HCl gas is then passed to saturation. After 20 to 24 hours at ordinary temperature the acid is removed in

[1] G. J. Ritter and E. F. Kurth, *Ind. Eng. Chem.*, 1933, **25**, 1250.
[2] G. J. Ritter, *Ind. Eng. Chem.*, 1922, **14**, 1050; 1923, **15**, 1264.
[3] R. Willstätter and L. Zechmeister, *Ber.*, 1913, **46**, 2401; M. Phillips, *J. Assoc. Off. Agric. Chem.*, 1932, **15**, 118; *ibid.*, 1936, **19**, 341, 350.

a vacuum of about 20 mm. while the flask is slowly warmed to 70°. The residue is diluted with water and boiled for 6 to 8 hours under reflux.

A more satisfactory modification is to moisten the wood (1 g.) with ordinary concentrated hydrochloric acid (6 ml.), in which case it is only necessary to cool the absorption vessel with water. After saturation with hydrochloric acid gas and standing, the excess of acid need not be removed. The contents of the flask are diluted with water to give an acid content of 3–5 per cent. and the whole boiled up under reflux for 2 hours.[1]

(iii) *Use of Dilute Acid under Pressure* (König and Rump[2]).—The wood is heated with a 1 per cent. solution of hydrochloric acid at six atmospheres excess pressure for 6 to 7 hours.

II. **Methods Involving the Use of Sulphuric Acid.**—The reagent almost invariably employed is sulphuric acid of 72 per cent. concentration, $H_2SO_4.2H_2O$.

(i) *After Mahood and Cable.*[3]—2 g. of wood are treated with 10 g. (or better with 15 g.) of 72 per cent. acid and allowed to stand for 15 hours, after which water is added to an acid concentration of 3 per cent. and the liquid boiled for 2 hours. The boiling in dilute solution greatly increases the ease of filtration.

(ii) *After Schwalbe.*[4]—This process gives a product which filters rapidly, and the results are consistent. 2 g. are treated with 60 ml. of 72 per cent. sulphuric acid and 15 ml. of 18 per cent. hydrochloric acid, keeping cool for 24 hours. After this 500 ml. of water are added and the mixture boiled for half an hour.

(iii) *After Klason.*[5]—1 g. of wood is treated with 50 ml. of 64 per cent. sulphuric acid and allowed to stand overnight. The liquid is diluted, filtered and the solid washed with water. Treatment of residue with about 50 ml. of hot alcohol is stated to remove resin and fats, and 5 ml. of 0·1*N*-KOH is used to neutralise any free acid. The lignin, after drying, is ignited to determine the ash content, which is sometimes considerable.

(iv) *After Schorger.*[6]—This is substantially the process used for many years by the U.S. Forest Products Laboratory, The procedure is as follows :—

[1] W. H. Dore, *Ind. Eng. Chem.*, 1920, **12**, 985; also J. König and E. Becker, *Z. angew. Chem.*, 1919, **32**, 155.

[2] J. König and E. Rump, *Z. Unters. Nahr. Genussm.*, 1914, **28**, 177.

[3] S. A. Mahood and D. E. Cable, *Ind. Eng. Chem.*, 1922, **14**, 933.

[4] C. G. Schwalbe, *Papier Fabrik.*, 1925, **23**, 174.

[5] P. Klason, *Cellulosechem.*, 1923, **4**, 81.

[6] A. W. Schorger, "Chemistry of Cellulose and Wood," p. 524: London, 1926.

Into an alundum crucible previously acid extracted, 2 g. of wood are weighed and the crucible fixed in a Soxhlet extractor filled up with glass beads, in such a way that the top of the crucible projects above the syphon. The wood is extracted with an alcohol-benzene mixture for 6 hours, dried by suction, washed with hot water, and dried. The wood is transferred to a 100 ml. beaker, covered with 30 ml. of 72 per cent. sulphuric acid, and the mixture stirred thoroughly. The beaker is kept in a desiccator and the contents frequently stirred during 18 hours. A portion of the lignin is then tested for freedom from cellulose by (*a*) examination under polarised light; (*b*) staining with iodine-sulphuric acid; or (*c*) by treatment with fresh acid for 6 hours and testing the neutralised filtrate with Fehling's solution.

When the lignin is free from cellulose the contents of the beaker are washed into a large beaker and diluted to 1·2 litres. The beaker is covered with a clock glass and the contents boiled gently for 2 hours, the volume being maintained by the addition of hot water. On cooling the lignin generally settles and the bulk of the liquid may be syphoned off. The lignin is then filtered off, washed until the filtrate is neutral, dried and weighed. An ash determination is made and the necessary correction applied.

III. **Modifications of the Sulphuric Acid Method of Estimation.**—There is no doubt that the ideal method of estimation would be one which separated lignin in an unchanged state free from residues and associated products. The results of a number of investigations made with this object[1] have brought to light the following points of interest:—

1. The reactions involved during the digestion of lignocellulose with 72 per cent. sulphuric acid are very complex. They differ somewhat, as between woods and straws, for example, owing to the higher proportions of hemicellulose and protein in the latter.

2. The acid acts both by way of hydrolysis and of condensation, insoluble products being formed directly, or by hydrolysis, from pentosans (xylose and arabinose), hexosans (lævulose) as well as from proteins and from tannins, especially those of the catechol type. The yield of apparent lignin is thus higher than the true lignin.

3. Hydrolysis and demethylation of lignin set free reactive phenolic groupings. Hydrolysis of the carbohydrates produces furfural and hydroxymethylfurfural. These aldehydes readily con-

[1] A. G. Norman and S. H. Jenkins, *Biochem. J.*, 1934, **28**, 2156, 2160; *ibid.*, 1937, **31**, 1566; G. J. Ritter, R. M. Seborg and R. Mitchell, *Ind. Eng. Chem. Anal.*, 1932, **4**, 202; K. F. Bamford and W. G. Campbell, *Biochem. J.*, 1936, **30**, 419.

dense with lignin to give insoluble compounds which form part of the apparent lignin isolated. Further, both aldehydes and phenols condense with lignin, and it has been shown [1] that even when lignin has combined, *e.g.* with formaldehyde, it can still react with phenol, as illustrated by the experiments given below, which show the yield of apparent lignin from 1 g. of oat-straw treated with 15 ml. 72 per cent. H_2SO_4 for 2 hrs.; temp. $< 20°$, diluted to 600 ml. and boiled 2 hrs.

Condensation of Phenol and Formaldehyde with Lignin

Substance added.	Mg. apparent lignin.
None	176
0·1 ml. 40 per cent. formalin	225
0·2 ml. 40 per cent. formalin	225
0·1 g. phenol	194
0·2 g. phenol + 0·2 ml. formalin	280

Furfuraldehyde produces very considerable increases in the amount of apparent lignin. Thus 0·8 g. of straw treated as above gave 138 mg. " lignin ". The presence of 0·1 ml. of furfural raised this figure to 186 mg. When the digestion with sulphuric acid was prolonged to 16 hours these amounts increased to 159 and 294 mg. respectively.

4. Tannins of the catechol type also form condensation products with phenolic or aldehydic substancss. Tannic acid, for example, added during the estimation, caused an increase in the lignin figure. The apparent lignin in 0·9 g. of water-extracted straw was increased from 173 mg. to 205 mg. by the addition of 100 mg. of tannic acid under the same conditions as above.

5. Attempts to correct for the presence of protein substances on the apparent lignin content, by subtracting 6·25 × the nitrogen content of the product are unsatisfactory, and may cause more discrepancy than correction. A study [2] of the effects of the presence of some 30 nitrogenous compounds on the lignin estimation shows that the simpler compounds cause little change, *e.g.* with the same straw used under (4) the apparent lignin of 173 mg. from 0·9 g. was hardly changed by the addition of 50–100 mg. of glycine, glutamic acid, betaine, aspartic acid, etc., but rose to over 200 mg. with casein, wheat gluten, etc. The disturbance caused by proteins therefore is due to the linkage of large fission products, not necessarily through amino-groupings, and to eliminate it the treatment must be such as to resolve the proteins into smaller groupings.

[1] A. G. Norman, *Biochem. J.*, 1937, **31**, 1568.
[2] A. G. Norman and S. H. Jenkins, *loc. cit.*, 1934.

6. The influence of all these factors in raising the apparent lignin content is greatly increased when the time of exposure to the sulphuric acid is extended, *e.g.* from 2 to 16 hours (p. 373). Higher temperature also favours the condensation reactions.

7. Pre-treatment of the material with boiling water, alcohol, dilute sulphuric acid, etc., is said to remove a soluble or less polymerised lignin,[1] which thus escapes the action of the concentrated acid and tends to lower the lignin value. Thus Cohen and Harris found that, with maple wood, extractions with alcohol-benzene, alcohol ; hot and cold water followed by 50 hours' syphon extraction with water at 98°, hardly reduced the furfural content (12·8–12·1 per cent.), but lowered the apparent lignin from 23·2 to 20·2 per cent. When, in addition to the above extractions, the wood was boiled for 2 hours with 3 per cent. sulphuric acid, the furfural dropped to 3·6 and the lignin to 17·7. Longer periods of boiling up to 30 hours did not appreciably affect the lignin, but reduced the furfural to 1 per cent. Since a substance giving lignin reactions was present in the filtrates the authors recommend that all hydrolytic pre-treatments, including boiling with water, should be omitted in the case of woods. The exact opposite is maintained by Phillips and Goss,[2] who consider that results are of no value unless complete extractions, including hot water and 1 per cent. HCl, are given.

In view of these observations, changes in method have been suggested with the object (*a*) of avoiding the formation of aldehydic and other substances which condense with lignin, by removing labile carbohydrates and extractives prior to treatment with the strong acid, (*b*) of reducing the temperature and shortening the time of exposure to the strong acid, (*c*) combinations of these.

Reduction in the time of contact with the 72 per cent. sulphuric acid from 16 to 2 hours, first suggested by Ritter *et al.*, at a temperature not greater than 20°, is now generally adopted, followed by dilution to 3 per cent. concentration and boiling the solution for some hours. This basic procedure has been varied to include pre-treatment with boiling water (Ritter) or with 1 to 5 per cent. sulphuric acid (Norman) after the alcohol benzene-extraction. There is no general agreement as to the validity of these changes. Both give lower values than the older methods, and that is considered to be a step in the right direction. The preliminary hydrolysis with dilute sulphuric acid is based on an experimental study of the

[1] W. E. Cohen and E. Harris, *Ind. Eng. Chem. Anal.*, 1937, **9**, 234 ; K. F. Bamford and W. G. Campbell, *Biochem. J.*, 1936, **30**, 419 ; A. G. Norman, *ibid.*, 1937, **31**, 1571.

[2] *J. Assoc. Off. Agric. Chemists*, 1936, **19**, 341.

influence of all the factors involved, and is perhaps the most satisfactory to employ.

The following are brief details :—

(*a*) *Method of Ritter, Seborg and Mitchell.*[1]—2 g. of wood (80 mesh) are dried at 105°, extracted in a Soxhlet apparatus for 4 hours with alcohol-benzene (2 : 1 vol.) and washed with alcohol. The wood is then heated for 3 hours on a boiling water-bath with 400 ml. of water, then washed with water and alcohol and dried. It is then treated with 25 ml. of 72 per cent. sulphuric acid for 2 hours at 20°, the acid then diluted to 3 per cent. concentration and boiled for 4 hours. For pulps 20 ml. of 72 per cent. acid per gram is used.

The boiling water treatment causes a reduction in apparent lignin of 0·5 to 2 units per cent. For example, spruce, 26·06 to 25·90 ; catalpa, 18·06 to 17·30 ; mesquite, 27·71 to 24·75 (and table below).

(*b*) *Method of Norman and Jenkins.*[2]—Extraction with alcohol-benzene is followed by boiling with 3 or 5 per cent. sulphuric acid for 1 hour. Treatment with 72 per cent. sulphuric acid is for 2 hours at 20° or under (about 15 ml. to 1 g.), then dilution, etc., as above. Hydrolysis with 1 per cent. sulphuric acid is sufficient for some materials, but if 3 or 5 per cent. acid is used removal of carbohydrate is such that the time of contact with the strong acid is immaterial, the lignin values being practically the same for 2 or for 16 hours.

	Apparent Lignin without Hydrolysis, per cent.	Loss of Original Material after Hydrolysis, per cent.	Lignin after Hydrolysis, per cent.	Lignin by Ritter-Seborg Method, per cent.
Oak	28·80	34·41	20·24	—
Beech	23·30	29·43	19·50	—
Basswood	22·82	27·92	17·98	20·44
Teak	28·98	34·42	26·95	27·10
Deal	25·87	26·81	23·42	25·78
Spruce	26·18	22·10	23·46	25·38
Flax straw	24·94	30·37	21·79	23·14
Wheat straw	19·31	38·72	13·90	16·62
Bracken	30·28	54·55	23·67	—

To remove hydrolysis products as soon as possible it has been proposed [3] to give several brief treatments with the dilute acid, but a comparison (Norman, 1937) shows that little is gained by this modification. Cohen and Harris (*loc. cit.*), however, found that 10 treatments of maple wood with boiling 5 per cent. sulphuric acid (10 ml./g.) each for 4 minutes, gave lignin 19·7 compared with 17·7 when one treatment as above was given.

[1] *Ind. Eng. Chem. Anal.*, 1932, **4**, 202.
[2] *Biochem. J.*, 1934, **28**, 2147, 2160 ; 1937, **31**, 1567.
[3] K. F. Bamford and W. G. Campbell, *Biochem. J.*, 1936, **30**, 419.

A comparison of results obtained on the same materials by Norman and Jenkins' method, with and without hydrolysis pre-treatment, and by the Ritter-Seborg method, is given in the table (p. 373),[1] which shows the lignin content of various materials before and after extraction with 5 per cent. H_2SO_4 for 1 hour. Treatment 16 hours with 72 per cent. acid, temp. $< 20°$; diluted to 3 per cent. and boiled 2 hours.

Results calculated on 100 g. original material before alcohol-benzene extraction.

A method for the estimation of minute quantities of lignin is very much required, especially in connection with the analysis of pulp. The following, though not perhaps definite in respect to lignin, may be useful for comparative purposes.

IV. **Colorimetric Method for the Estimation of Minute Quantities of Lignin Isolated from Plant Tissues.**[2]—To study the distribution of lignin in woody tissues, Mehta isolated lignin as sodium lignate by digesting 0·1 to 0·2 g. with 20 ml. of 4 per cent. NaOH at 10 atmospheres for 1 hour. The liquid is made up to 100 ml., filtered, and a known volume (of 1·0 to 5·0 ml.) is measured into a 15 ml. centrifuge tube and acidified with concentrated HCl. The lignin is centrifuged, washed twice with water and dissolved in a few drops of 1 per cent. NaOH. The solution is washed into a Nessler cylinder and estimated by means of a solution of phospho-tungstic and phosphomolybdic acids in phosphoric acid. This reagent [3] gives a deep blue coloration with aromatic substances containing hydroxyl groups, in alkaline solution.

100 g. sodium tungstate, 20 g. phosphomolybdic acid, and 50 ml. of 85 per cent. phosphoric acid are dissolved in 750 ml. of water. The liquid is boiled under reflux for 2 hours, cooled and made up to 1 litre. A standard solution of lignin is prepared by dissolving 0·5 g. of lignin (isolated as above) in about 25 ml. of 4 per cent. NaOH solution and diluting to 500 ml. so that 1 ml. = 1 mg. lignin.

A series of known volumes, 1·0 to 0·1 ml. of the standard lignin solution, are measured into Nessler cylinders, 2·5 ml. of the reagent added to each, and after 5 minutes 12·5 ml. of a saturated solution of sodium carbonate. The volume is made up to 100 ml. and the colours matched with that obtained under the same conditions from the unknown amount of lignin. A fine blue colour is given, and the method is reliable so long as the depth of the colours does not differ by more than 20 per cent.

[1] A. G. Norman and S. H. Jenkins, *Biochem. J.*, 1934, **28**, 2155.
[2] M. M. Mehta, *Biochem. J.*, 1925, **19**, 966.
[3] O. Folin and W. Denis, *J. Biol. Chem.*, 1912, **12**, 239.

CHAPTER XXI

THE ESTIMATION OF FURFURAL, URONIC ACID, AND METHOXYL

PART I

The Estimation of Pentosans in Terms of Furfural

THE estimation of pentosan constituents cannot be effected directly. Their analytical determination is based on the amount of furfural which they yield on distillation with hydrolysing acids, the following reactions being assumed :—

$$\underset{\text{Pentosan}}{C_5H_8O_4} + H_2O \longrightarrow \underset{\text{Pentose}}{C_5H_{10}O_5}$$

and

$$\underset{\text{Pentose}}{C_5H_{10}O_5} - 3H_2O \longrightarrow \underset{\text{Furfural}}{C_5H_4O_2}$$

The method universally adopted as a standard consists in boiling the substance with 12 per cent. hydrochloric acid, the distillate being collected at the rate of 30 ml. every 10 minutes, until no further reaction for furfural is obtained. The furfural is precipitated as phloroglucide, and from the weight obtained the furfural, pentose, or pentosan is calculated from the tables prepared by Kröber [1] (p. 384).

These tables show the weights of phloroglucide actually obtained from the weights of pure xylose or arabinose given opposite to them, the values for xylan and araban being calculated from the relations

$$\begin{aligned} \text{Pentosan} &= 1{\cdot}363 \times \text{pentose and} \\ \text{Pentose} &= 0{\cdot}880 \times \text{pentosan.} \end{aligned}$$

The value for " pentosan " (last column), which is usually employed when the nature of the pentosan is uncertain, is the average of the figures given for xylan and araban, but results calculated as xylan, will probably more closely represent the composition of lignified materials.

The standard method has been examined by a number of investigators, notably by Pervier and Gortner,[2] by Gierisch,[3] by

[1] E. Kröber, *J. Landw.*, 1900, **48**, 357.
[2] N. C. Pervier and R. A. Gortner, *Ind. Eng. Chem.*, 1923, **15**, 1167, 1255.
[3] W. Gierisch, *Cellulosechem.*, 1925, **6**, 6, 81.

Kullgren and Tydén,[1] and by Launer and Wilson.[2] Kullgren and Tydén have modified the method by using hydrochloric acid of 13·15 per cent., saturating the acid in the flask with salt, and distilling at the rate of 25 ml. in 10 minutes. A second distillation is given to remove homologues of furfural from the distillate so that a correction for these can be obtained. The furfural is estimated by the bromate-bromide method. Launer and Wilson, after testing all the variables involved, consider the original distillation process the best, and recommend it, coupled with the bromate-bromide estimation.

Other workers have attempted to shorten the process by devising volumetric and colorimetric methods for the estimation of the furfural in the distillate. Phenylhydrazine (p. 389), potassium bisulphite and Fehling's solution have been employed, but they have never been in general use.

Investigation has shown that the distillation method gives accurate results for the estimation of pure furfural and, by the introduction of certain factors, of xylose, arabinose, and rhamnose. As a " pure " pentosan has never been obtained, the quantitative relation between furfural formed and pentosan present is necessarily less certain. It is difficult to judge how far the various changes,

$$\text{Pentosans} \longrightarrow \text{Pentoses} \longrightarrow \text{Furfural},$$

proceeding simultaneously at different velocities, influence the final yield of furfural in its relation to the original pentosan.

Another difficulty arises from the fact that the distillation of plant products with hydrochloric acid produces other substances than furfural which are capable of reacting with phloroglucin or potassium bromate-bromide. Among these are methyl furfural (from rhamnosan), hydroxymethyl furfural (from hexosans), and formaldehyde [3] (from lignin). The phloroglucin compounds of these substances are soluble in alcohol, and the actual furfural phloroglucide is often taken to be the part insoluble in alcohol, although this conclusion is not altogether satisfactory.

The old standard method of distillation can be recommended and the furfural is estimated either with phloroglucin (p. 381) or with the bromate-bromide reagent (p. 385). Kullgren's modifications are useful in special cases (*e.g.* for methyl pentosan (p. 386)), and, together with those of Launer and Wilson are described on pp. 385–388.

[1] C. Kullgren and H. Tydén, " Ingeniörsvetenskas Akad., Handlingar ", No. 94 : Stockholm, 1929.

[2] H. F. Launer and W. K. Wilson, *J. Res. Nat. Bur. Standards*, 1939, **22**, 471.

[3] K. Freudenberg and M. Harder, *Ber.*, 1927, **60**, 581.

The procedure of Kullgren has the advantage of quickness in working. It appears to eliminate satisfactorily substances other than furfural, and in the case of pure pentoses gives results in fair agreement with those of the phloroglucinol method. It does not, however, provide any distinction between pentosan and methylpentosan.

The various investigations into the distillation method have brought to light the following points :—

1. That different pentoses, on hydrolysis with hydrochloric acid, give different yields of furfural. From Kröber's tables it may be calculated that xylose gives 56·5 per cent. of furfural and arabinose 47 per cent., the theoretical yield in each case being 64 per cent. This difference has usually been ascribed to the fact that under the standard conditions the conversion of arabinose into furfural is considerably slower than that of xylose, and that the furfural produced, being exposed for a longer time to the action of the acid, is decomposed to a greater extent than in the case of xylose. Experimental work has shown that furfural is, in fact, destroyed during the distillation, but that the amount destroyed does not depend on the quantity or the concentration of the furfural or the time of action, but that there is usually a constant loss, about 3 per cent. of the furfural, both with the standard process and its modifications. The reason for the quantity of furfural actually given by the sugars being smaller than that required according to the equation above, is due, not to the varying rates of conversion into furfural, but to the fact that the equation does not adequately represent the changes taking place.

2. The concentration of the acid has only a small influence on the weight of phloroglucide obtained, as shown by the following values obtained from 0·2 g. of pentose :—

HCl *d*, . . .	1·04	1·06	1·08	1·10	1·12
HCl per cent. . .	8·2	12·0	16·15	20·0	23·8
Phloroglucide in g. from					
Xylose . .	0·2044	0·2009	0·2144	0·2177	0·2082
Arabinose . .	0·1644	0·1774	0·1826	0·1826	0·1760

3. With 12 per cent. hydrochloric acid the concentration in the flask and in the vapour must change continually during the distillation, while the boiling-point may vary from 103·5 to 108·5°. Kullgren, by using acid of 13·15 per cent. and saturating with salt, finds that the concentration of the acid in the flask and in the distillate remains at 13 per cent. throughout, and that the velocity of distillation is greatly increased as shown by the following results with pure furfural :—

Successive volumes of distillate in ml.	10	10	10	10	10	10	rest
Per cent. of total furfural obtained which distilled over :							
(*a*) Without salt . .	50·2	23·5	12·9	6·2	3·9	1·7	1·2
(*b*) With salt . . .	82·2	14·6	2·6	0·4	0·2	—	—

4. Under the condition (*b*), above, there is a constant ratio between the weight of pure pentose and the weight of phloroglucide precipitate obtained from the distillate, *viz.* :

grams xylose = 0·955 × grams phloroglucide
grams arabinose = 1·172 × grams phloroglucide.

This proportionality is not seen in Kröber's tables, owing partly to the solubility correction employed by him (0·0052 g.). Some workers consider this figure too high.

5. The estimation of furfural by means of its reaction with bromine, liberated from a bromate-bromide mixture according to the equation $5KBr + KBrO_3 + 6HCl = 6Br + 6KCl + 3H_2O$, has the merit of taking only a short time as compared with the standard method. The exact nature of the reaction between bromine and furfural has not been determined. Pervier and Gortner [1] considered that 1 molecule of furfural reacted with 2 atoms of bromine. Powell and Whittaker [2] found that in the presence of excess of bromate $2Br_2$ reacted with 1 molecule of furfural. It was shown by Gierisch (*loc. cit.*) that the consumption of bromine is not a specific reaction of furfural, and it becomes necessary to standardise the reaction conditions, of which the acidity, the temperature, and the amount of bromine in excess are obviously important.

Powell and Whittaker, using an excess of bromine, proceed with the ordinary distillate (from 12 per cent. HCl) as follows : 25 ml. of *N*/10 bromate-bromide solution are run into a bottle and treated with 200 ml. of the distillate, a blank with the acid alone being run at the same time. The bottles stand in the dark for 1 hour, after which 10 ml. of 10 per cent. KI are added and the liquid titrated. It was found that a gram-molecule of furfural reacted with 4·05 g. atoms of bromine : therefore 1 ml. *N*/10 thiosulphate solution = 0·0024 g. of furfural.

Kullgren and Tydén observed that, although the consumption of bromine in strongly acid solutions was of the order of $2Br_2$ per molecule after 1 hour, yet variations between 3·6 and 4·2 atoms were easily obtained. They found that the reaction is more rapid

[1] *Ind. Eng. Chem.*, 1923, **15**, 1167, 1255.
[2] *J. Soc. Chem. Ind.*, 1924, **43**, 35.

in proportion to the concentration of the acid, and with an excess of acid represented by no more than 3 ml. of 0·1 *N*-HCl the reaction proceeds at ordinary temperature in two stages—(*a*) a very rapid (5 minutes) absorption of Br_2 per 1 molecule of furfural accompanied by a production of hydrobromic acid rather below 2HBr to 1 of furfural; (*b*) a very slow reaction with bromine takes place after the first 5 minutes. To get rapid conditions of working, they decided to use only the initial stage. The addition of a little ammonium molybdate accelerates the reaction, a faint yellow colour developing after 0 to 4 minutes from the addition of the bromide. Exactly 4 minutes after this solid potassium iodide is introduced and the titration performed at leisure. The results are good. The working conditions are given on p. 386.

Hughes and Acree [1] confirm the initial absorption of Br_2, but in view of the variation of the second phase with " room temperature " recommend the addition of crushed ice to give a working temperature of 0° (p. 388). Their estimations of pure furfural agree within 0·3 per cent. of the weight taken.

6. Hydroxymethyl furfural (from hexosans) is of common occurrence among the distillates from the hydrolysis of plant products, but it is produced very slowly and is largely decomposed by the action of hydrochloric acid into lævulic and formic acids.

$$C_6H_6O_3 + 2H_2O = C_5H_8O_3 + H.COOH.$$

The derivatives of furfural are not very sensitive to the aniline acetate reagent, but react to a solution of aniline in alcohol. The table (p. 380) shows that the production of furfural is rapid, and is almost completed before the hydroxy-derivative begins to appear in the distillate.[2]

The colour reactions of furfural, and its methyl- and hydroxymethyl-derivatives, were observed by Cunningham and Dorée [1] in distillates obtained from the pure substances.

A correction for the errors due to these derivatives is often applied in the standard method by extracting the phloroglucides with alcohol, when the red-brown phloroglucides dissolve leaving the black furfural phloroglucide. It should be remembered, however, that the estimations on which the Kröber tables are based, do not include alcohol, extraction. In Kullgren's process a second distillation is given; this destroys 33 per cent. of the methyl furfural and the whole of the hydroxymethyl furfural. The following results were

[1] E. E. Hughes and S. F. Acree, *Ind. Eng. Chem., Anal.*, 1934, **6**, 123.
[2] M. Cunningham and C. Dorée, *Biochem. J.*, 1914, **8**, 438.

Production of Hydroxy-methyl Furfural

Substance.	Weight (anhydrous).	Distillate ml.*	Weight of Phloroglucide.	Weight soluble in Alcohol.	Furfuraldehyde per cent.	ω-Hydroxymethyl-furfuraldehyde † per cent.	Remarks.
1. Cellulose (cotton wool)	2·021	(*a*) 100	0·0073	None	0·20	—	Ppt. black.
		(*b*) 600	0·0344	0·0115	(0·67)	0·34	Ppt. red.
2. Cellulose (filter paper)	5·090	(*a*) 250	0·0296	—	0·35	—	
		(*b*) 1,080	0·0580	—	—	0·69	
3. Cellulose (No. 1 mercerised)	1·662	1,025	0·0227	all	0·00	1·0	
4. Cellulose (structureless from the xanthate)	2·142	(*a*) 200	0·0358	—	1·04	—	
		(*b*) 300	0·0317	—	—	0·9	After 180 ml. no aniline acetate reaction.
5. Cellulose (ditto) .	4·753	1,560	0·2466	0·1862	0·76	2·4	
6. Oxycellulose (from No. 3 by ozone).	2·00	660	0·0550	0·0193	1·11	0·66	After 300 ml. no aniline acetate reaction.
7. Lignocellulose (jute) .	1·869	(*a*) 210	0·3291	0·0010	9·4	— .	Part soluble was red.
		(*b*) 950	0·0357	0·0127	—	0·90	
8. Lignocellulose (beech wood).	2·600	(*a*) 400	0·6909	—	12·68	—	
		(*b*) 660	0·0148	—	—	0·50	

* (*a*) represents portion of distillate reacting to aniline acetate, (*b*) is the portion subsequently obtained active to the aniline-alcohol reagent.

† A factor of 0·6 was used to convert phloroglucide to this aldehyde.

obtained with solutions containing 2 g. of glucose to which xylose had been added :—

Weight of Xylose.	Ml. $N/20$ $KBrO_3$ used.*		Xylose per cent. calc. from bromate used in 2nd distillation.	
	1st distillate	2nd distillate.	Uncorrected.	With correction.†
0·10	12·22	9·27	98·5	101·6
0·15	17·55	13·89	98·4	101·5
0·20	22·54	18·42	97·8	100·8
0·25	28·02	22·88	97·3	100·3

* For 0·4 of the total volume.
† Correction due to loss of furfural in the distillation needing addition of 3·1 per cent. of the quantity found.

Launer and Wilson find that the addition of sodium or ammonium chloride to the acid, with or without the use of a current of steam, greatly increases the rate of production of volatile derivatives from cellulose, etc., without affecting the rate of formation of furfural from pentosans. They measured the rate at which the volatile non-furfural products are formed from cellulose and wood pulp and thus obtained a correction for the furfural figure given by their method (p. 387). The correction agrees with that obtained on redistillation as above.

Barbituric acid (and thiobarbituric acid) do not precipitate hydroxymethyl furfural if the solution is sufficiently dilute,[1] and both have been employed in the estimation of furfural (p. 389).

A. Standard Method for the Estimation of Furfural by means of Phloroglucin.

A. W. Schorger examined this method in connection with the analysis of wood, and his technique was adopted as a standard by the Cellulose Division of the American Chemical Society.[2] It will be given in some detail.

Reagents Required.—Hydrochloric acid 12 per cent. (*d*, 1·06), phloroglucin free from diresorcin ; aniline reagent prepared by adding acetic acid or hydrochloric acid drop by drop to a mixture of equal volumes of aniline and water until a clear solution is obtained.

The phloroglucin may be tested for the presence of diresorcin thus : a small quantity is dissolved in a few drops of acetic

[1] W. Gierisch, *loc. cit.*
[2] A. W. Schorger, *Ind. Eng. Chem.*, 1923, **15**, 748.

anhydride, heated nearly to boiling-point, and a few drops of concentrated sulphuric acid added; a violet colour indicates diresorcin. If more than a trace of colour appears, the sample requires purification.

The phloroglucin solution is prepared by heating 11 g. of phloroglucin with 300 ml. of 12 per cent. hydrochloric acid. When dissolved the liquid is diluted to 1·5 l. with 12 per cent. hydrochloric acid. After standing for a week any diresorcin which may be present will crystallise out.

NOTE.—It is our own custom to weigh out the phloroglucin equivalent to about twice the weight of furfural expected, dissolve it in 12 per cent. acid, and add it to the distillate.

Procedure.—(i) 1 to 2 g. of the sample (2 g. of coniferous wood or 1 g. of hard wood) is placed in a 250 ml. flask provided with a separating funnel and an outlet tube. The outlet tube is attached to a condenser. 100 ml. of 12 per cent. HCl are added, and the liquid distilled at the rate of 30 ml. in 10 minutes, the distillate being passed through a small filter before entering the receiver. As soon as 30 ml. of distillate have been collected 30 ml. of acid are added to the flask, and the distillation continued in this manner until the distillate is free from furfural. Normally all the furfural is obtained in the first 270 ml. of distillate. As long as furfural is present the distillate will give a pink colour when a drop of it is allowed to mingle with a drop of the aniline reagent placed on filter paper.

(ii) To the distillate is now added 40 ml. of filtered phloroglucin solution, and the liquid is made up to 400 ml. with the hydrochloric acid. It soon turns greenish-black and furfural-phloroglucide precipitates. After standing 16 hours a drop of the liquid may be tested with aniline, and if a pink colour is obtained more phloroglucin must be added.

(iii) The precipitate is filtered through a tared Gooch crucible with a thick asbestos mat, care being taken that the crucible is always partially filled with fluid. The precipitate is washed with exactly 150 ml. of water, dried at 100–105° for 4 hours, and weighed in a weighing bottle, as the precipitate is hygroscopic.

(iv) The crucible is then placed in a narrow beaker and 20 ml. of 95 per cent. alcohol added. The beaker and its contents are heated for 10 minutes in a water bath maintained at 60°. The alcohol is removed at the pump and the process repeated (usually four or five times) until the alcohol that runs through is practically colourless. The crucible is again weighed and the furfural phloroglucide calculated to furfural or pentosan by Kröber's tables or the formulæ

below. The pure furfural phloroglucide is not entirely insoluble in alcohol. Each extraction, as described, removes about 0·0014 g.[1] The soluble portion is, however, usually calculated to methyl pentosan. As it includes impurities the determination has little meaning, and should be omitted in the case of wood, and in most cases where Kröber's tables (p. 384) are employed.

(v) Furfural, pentose, or pentosan may be calculated from the weight, a, of furfural phloroglucide by the formulæ given below, where the factor 0·0052 represents the amount of phloroglucide remaining dissolved in the hydrochloric acid. For a weight of phloroglucide—

Under 0·03 g. :

Furfural $= (a + 0{\cdot}0052) \times 0{\cdot}5170.$
Pentoses $= (a + 0{\cdot}0052) \times 1{\cdot}0170.$
Pentosans $= (a + 0{\cdot}0052) \times 0{\cdot}8949.$

Between 0·03 and 0·30 g. :

Furfural $= (a + 0{\cdot}0052) \times 0{\cdot}5185.$
Pentoses $= (a + 0{\cdot}0052) \times 1{\cdot}0075.$
Pentosans $= (a + 0{\cdot}0052) \times 0{\cdot}8866.$

Over 0·30 g. :

Furfural $= (a + 0{\cdot}0052) \times 0{\cdot}5180.$
Pentoses $= (a + 0{\cdot}0052) \times 1{\cdot}0026.$
Pentosans $= (a + 0{\cdot}0052) \times 0{\cdot}8824.$

These equations are convenient, and give values which agree approximately with those derived from Kröber's table. Norris *et al.*, in a review of the standard method, have deduced more exact relationships which are given on p. 390.

The table given by Kröber follows on p. 384, being abridged from the original. It is assumed that the distillate is made up to 400 ml., and 150 ml. of water is employed for washing the precipitate, which is not extracted with alcohol. The tabular values include solubility corrections.

Notes on the Standard Method.—(i) An all-glass apparatus for carrying out the distillation, is shown in Fig. 72.

A metal bath may be used. Bumping in the earlier stages is often violent, making a splash head desirable. The addition of glass beads is helpful.

For convenience in introducing the acid the separating funnel may be graduated into 30 ml. portions.

[1] W. B. Ellett and B. Tollens, *J. Landw.*, 1905, **53**, 20.

TABLE FOR THE ESTIMATION OF PENTOSE AND PENTOSAN THROUGH THE PHLOROGLUCIDE AFTER KRÖBER.

Phloro-glucide.	Furfural.	Arabinose.	Araban.	Xylose.	Xylan.	Pentose.	Pentosan.
0·030	0·0182	0·0391	0·0344	0·0324	0·0285	0·0358	0·0315
0·040	0·0235	0·0501	0·0441	0·0416	0·0366	0·0459	0·0404
0·050	0·0286	0·0611	0·0538	0·0507	0·0446	0·0559	0·0492
0·060	0·0338	0·0721	0·0634	0·0598	0·5260	0·0660	0·0581
0·070	0·0390	0·0831	0·0731	0·0690	0·0607	0·0761	0·0670
0·080	0·0442	0·0941	0·0828	0·0781	0·0687	0·0861	0·0758
0·090	0·0494	0·1051	0·0925	0·0872	0·0767	0·0962	0·0847
0·100	0·0546	0·1161	0·1022	0·0964	0·0848	0·1063	0·0935
0·110	0·0598	0·1270	0·1118	0·1055	0·0928	0·1163	0·1023
0·120	0·0650	0·1380	0·1214	0·1146	0·1008	0·1263	0·1111
0·130	0·0702	0·1490	0·1311	0·1237	0·1089	0·1364	0·1201
0·140	0·0754	0·1600	0·1408	0·1328	0·1169	0·1464	0·1288
0·150	0·0805	0·1710	0·1505	0·1419	0·1249	0·1565	0·1377
0·160	0·0857	0·1820	0·1602	0·1510	0·1329	0·1665	0·1465
0·170	0·0909	0·1930	0·1698	0·1601	0·1409	0·1766	0·1554
0·180	0·0961	0·2039	0·1794	0·1692	0·1489	0·1866	0·1642
0·190	0·1013	0·2147	0·1889	0·1783	0·1569	0·1965	0·1729
0·200	0·1065	0·2255	0·1984	0·1874	0·1649	0·2065	0·1817
0·210	0·1116	0·2363	0·2079	0·1965	0·1729	0·2164	0·1904
0·220	0·1168	0·2471	0·2174	0·2057	0·1810	0·2264	0·1992
0·230	0·1220	0·2579	0·2270	0·2148	0·1890	0·2364	0·2081
0·240	0·1271	0·2687	0·2365	0·2239	0·1970	0·2463	0·2168
0·250	0·1323	0·2795	0·2460	0·2330	0·2050	0·2563	0·2256
0·260	0·1374	0·2903	0·2555	0·2420	0·2130	0·2662	0·2343
0·270	0·1426	0·3011	0·2650	0·2511	0·2210	0·2761	0·2429
0·280	0·1478	0·3119	0·2745	0·2602	0·2290	0·2861	0·2517
0·290	0·1529	0·3227	0·2840	0·2693	0·2370	0·2960	0·2605
0·300	0·1581	0·3335	0·2935	0·2784	0·2450	0·3060	0·2693

(ii) A weight of material is taken which would give a phloroglucide precipitate weighing between 0·03 and 0·3 g., assuming that the condensation takes place according to the equation—

$$\underset{96}{C_5H_4O_2} + \underset{126}{C_6H_6O_3} = C_{11}H_6O_3 + 2H_2O.$$

(iii) The first 50 to 100 ml. of distillate is rich in furfural, some of which is apt to escape unless the condensation is effective. For this reason we receive the distillate in a tall measuring cylinder sloping at 45° containing some hydrochloric acid.

(iv) The aniline acetate reagent may be prepared by shaking equal volumes of aniline and water in a test tube and adding glacial acetic acid till the solution becomes clear.

A drop of the reagent is put on a filter paper and a drop of the distillate is allowed to spread into the reagent. An arc of colour

will appear where the circles intersect. Towards the finish of the operation the red line will only show after drying the paper at a gentle heat.

Methyl furfural gives only a faint yellow colour with aniline acetate, and to test for this substance a solution of aniline in alcohol is employed. This reagent is very sensitive also to furfural and hydroxymethylfurfural, with which it gives a bright red colour.

B. Method for the Estimation of Furfural by Kullgren and Tydén.

The following reagents are required :—

(*a*) Sodium hydroxide solution 1·58 *N*. (*b*) A bromate-bromide solution containing 1·392 g. $KBrO_3$ and 10 g. KBr per litre, repre-

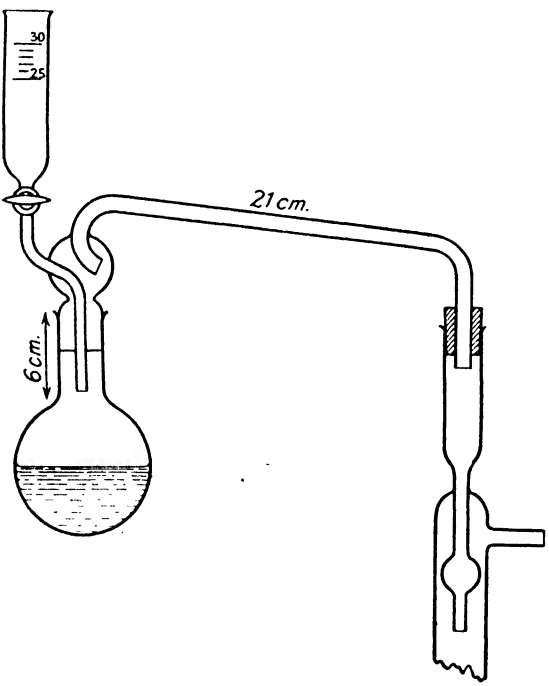


Fig. 72.—Apparatus for furfural estimation. (*Kullgren and Tydén.*)

senting 0·05 *N*-bromate solution. (*c*) A solution of sodium thiosulphate 0·05 *N*. (*d*) Ammonium molybdate solution containing 25 g. of the salt per litre. (*e*) Hydrochloric acid (*d*, 1·065), which contains 13·15 per cent. of HCl. (*f*) Common salt and solid potassium iodide.

A suitable distillation apparatus is shown in the Fig. 72. It

should preferably be made so as to avoid contact between the vapours and rubber bungs, but if this cannot be avoided, old, well-used bungs are preferable.

Procedure in the case of Pentoses or Methylpentose (Rhamnose), Pentosans, or Methylpentosan (Rhamnosan).—A quantity of the material should be taken corresponding to 0·15 to 0·2 g. of xylose or rhamnose, or 0·20 to 0·30 g. arabinose. This is placed in a distillation flask of 300 ml. capacity with 100 ml. of the 13·15 per cent. acid, to which 19 to 20 g. of common salt are added. A metal bath may be used in the case of sugars themselves, but with pentosans it is preferable to use some sort of asbestos sheet or a gauze heated with a burner, the flame of which can be controlled by a screw-clip. Care must be taken in all cases that the flask above the level of the liquid does not get overheated.

The distillation is carried on for 100 minutes (from commencement of boiling) in the case of xylose and 140 minutes in that of arabinose and rhamnose, the rate of distillation being 25 ml. in 10 minutes. When 25 ml. have distilled over, 25 ml. of fresh acid are added.

In the case of xylose about 250 ml. of distillate are obtained and in that of arabinose about 350 ml. The distillate is put into a measuring flask marked at 250 ml. or 400 ml. respectively, and made up to the mark with hydrochloric acid. Two portions of 100 ml. are withdrawn, each of which is run into a 500 ml. Erlenmeyer flask, which is closed with a cork.

While the liquid is cooling 200 ml. of 1·58 *N*-NaOH solution are added and the liquid is brought down to room temperature. At once 10 ml. of the ammonium molybdate solution are added and then 25 ml. of the bromate-bromide solution. The flask is then placed over a white surface in order to determine the moment at which a recognisable yellow coloration is seen. This is usually in 0′ to 2 minutes, frequently in 15 seconds, but an error up to half a minute does not make any great difference. It is essential that the liquid should stand 4 minutes from this time, after which about 1 g. of solid KI is added and the solution immediately shaken. It is then allowed to stand for 5 to 10 minutes and the liberated iodine titrated, as usual, with 0·05 *N*-thiosulphate.

The bromate consumed is equal to the volume of solution added minus the volume of thiosulphate required. On multiplying by 2·5 in the case of xylose and 4·0 in that of arabinose and rhamnose the total bromate consumed is obtained. If this volume be called *n* ml. of 0·05 *N*-$KBrO_3$ the quantities obtained in grams are :—

Furfural $= n \times 0{\cdot}00240$

Xylose	$= n \times 0{\cdot}00425$;	Xylan	$= n \times 0{\cdot}00374$
Arabinose	$= n \times 0{\cdot}00506$;	Araban	$= n \times 0{\cdot}00445$

Rhamnose ($C_6H_{10}O_5.H_2O$) $= n \times 0{\cdot}00346$

Rhamnosan $= n \times 0{\cdot}00278$

Pentosans (general) $= n \times 0{\cdot}00410$

This relation gives the quantity of furfural in the distillate. To obtain the quantity of furfural derived from the original substance the value obtained must be increased by 3·1 per cent.

Estimation of Pentoses or Pentosans in the presence of Hexoses and Polyoses ; Rhamnosan in the presence of Substances which belong to one of these Four Groups.—The following technique applies to most of the naturally occurring cellulosic materials. A quantity of the substance is taken which will give between 0·075 and 0·1 g. of furfural. The distillation is carried out as above. In the case of pine wood and the cellulose obtained from it, the distillation required no longer than 100 minutes (250 ml. of distillate), provided the wood was in the form of fine meal. To the distillate is added 2 ml. (or 3 ml. if the distillate reaches 350 ml.) of HCl of *d*, 1·19, and the liquid is then made up to the mark with 13·15 per cent. HCl.

From this volume 100 ml. are withdrawn for redistillation in the same apparatus. To the flask is added 19–20 g. of salt, and every 25 ml. which distils over is replaced by 25 ml. of fresh acid of 13·15 per cent. When 100 ml. have distilled all the furfural or methylfurfural will have come over.

The liquid is neutralised and titrated as before, care being taken to ensure that the bromate is in excess.

The calculation is carried out in the same way, with the addition that to the values for xylose, etc., 3·1 per cent. must be added to compensate for the furfural destroyed during distillation (p. 381). If rhamnosan is present the formula for pentosans in general is used, which gives the combined rhamnosan and pentosan.

C. Method for the Estimation of Pentosan in Pulps and Paper by Launer and Wilson.

The following solutions are required :—

(*a*) Hydrochloric acid 12 per cent. (*b*) Sodium thiosulphate solution 0·1 *N*. (*c*) Potassium iodide 10 per cent. (*c*) A 0·2 *N*-bromate-bromide solution containing 5·57 g. $KBrO_3$ and 50 g. KBr per litre.

One gram of the pulp is put into a 500 ml. distillation flask,

fitted with a tap funnel, containing 400 ml. of 12 per cent. HCl. Rubber bungs may be used. 100 ml. of the acid is run into the flask and the remainder added dropwise so as to maintain this volume throughout. A water-cooled condenser is used, fitted with an adapter which delivers into a 1 litre bottle. The time taken for distillation must be 100 minutes for 300 ml. of distillate. The importance of this rate, together with the necessity of avoiding loss of furfural in the early stages, is emphasised.

To the 300 ml. of distillate are added 50 ml. of water and about 250 g. of crushed ice. When the temperature has reached 0 to 2°, 20 ml. of bromate-bromide solution are added with the minimum of agitation, the bottle is stoppered and well shaken. Five minutes afterwards 10 ml. of 10 per cent. KI are added. After shaking well to permit absorption of the bromine vapour, the free iodine is titrated with 0·1 N-thiosulphate (say v_1 ml.).

A blank correction is obtained by diluting 270 ml. of the 12 per cent. acid to 350 ml., adding ice, bromate-bromide and KI, and titrating as before (say v_2 ml.). The pentosan content as

$$\text{Pentosan per cent.} = 1{\cdot}03[6{\cdot}60 \times N \times (v_2 - v_1)/\text{W}] - \text{C}.$$

Here C is volatile material arising from cellulose, etc. It has the value 0·9 per 300 ml. of distillate; N, the normality of the thiosulphate, and W the weight of sample taken after correcting for moisture, ash, resin and starch.

The factor 1·03 is the correction necessary for loss of furfural during distillation based on the authors' expertments. The factor 6·60 is the value of

$$100 \times 0{\cdot}048 \div 0{\cdot}727$$

where 0·048 is the weight of furfural ≡ 1 ml. of N-thiosulphate and 0·727 is the theoretical conversion factor for pentosan to furfural. This gives minimum values for pentosan, but the authors prefer this to using any arbitrary correction which is of doubtful accuracy. If, however, values comparable with those given by the Kröber tables are desired (where the conversion of pentosan to furfural is assumed to be 80 per cent, giving a conversion factor of 0·582), the following formula may be used, the furfural loss and cellulose correction being disregarded.

$$\text{Pentosan per cent.} = 8{\cdot}25 \times N \times (v_2 - v_1)/\text{W}.$$

D. Other Methods for the Estimation of Furfural

A number of other methods have been described, but they have not come into general use. The gravimetric method with barbituric

acid and the volumetric method with phenylhydrazine will be described, as they may be useful in special cases.

Volumetric Estimation by Means of Phenylhydrazine (Ling and Nanji).[1]—The formation of furfural phenylhydrazone was one of the first methods employed for the gravimetric estimation of furfural. The above authors have devised a convenient volumetric method in which the furfural is treated with excess of a standard solution of phenylhydrazine, the uncombined portion of which is estimated by means of iodine solution. It has been shown (v. Meyer, 1887) that in the presence of excess of iodine (at least 4 equivalents to 1 molecule of phenylhydrazine) the reaction proceeds as follows :—

$$Ph.NH.NH_2 + 2I_2 = PhI + 3HI + N_2.$$

Materials Required.—Standard aqueous solution of phenylhydrazine about 2 per cent. ; $N/10$ iodine solution ; $N/20$ thiosulphate solution ; approx. $3N$-sodium hydroxide.

The distillate is made up to 250 ml. Of this 25 ml. is neutralised with $3N$-NaOH to methyl orange, rise of temperature being avoided. Acetic acid is added, followed by 10 ml. of standard phenylhydrazine solution, and the liquid is heated to 50–55° for 20 minutes, when the precipitation of hydrazone is complete. After cooling the volume is adjusted to 100 ml., and the excess of phenylhydrazine is determined in an aliquot portion of the filtrate, thus : 10 ml. of $N/10$ iodine solution and 10 ml. of the filtrate are mixed and diluted to 100 ml. and the excess of iodine titrated with thiosulphate. The results obtained by the authors agreed closely with those given by the phloroglucin method.

Estimation with Barbituric Acid.[2]—This reagent does not precipitate hydroxymethylfurfural in dilute solution. It reacts with furfural, giving a yellow precipitate according to the equation :

$$C_4H_3O.CHO + H_2C.(CO.NH)_2.CO = H_2O + C_4H_3O.CH{:}C.(CO.NH)_2.CO.$$

The compound is soluble in 12 per cent. HCl to the extent of 1·22 mgm. per 100 ml., for which a correction must be applied. The following illustrates the working of the process : 0·2 g. of xylose gave 400 ml. of distillate and 0·2417 g. of condensation product. Weight remaining in solution, $4 \times 1{\cdot}22 = 4{\cdot}9$ mgm.

Wt. of product formed = 0·2417 + 0·0049 = 0·2466 g.

$$\text{Ratio wt. furfural/wt. product} = \frac{96{\cdot}03}{206{\cdot}13} = 0{\cdot}4659$$

$\therefore$ Wt. furfural $0{\cdot}2466 \times 0{\cdot}4659 = 0{\cdot}115$ g. or 57·5 per cent.

[1] A. R. Ling and D. R. Nanji, *Biochem. J.*, 1921, **15**, 466.
[2] R. Jäger and E. Ungar, *Ber.*, 1903, **36**, 1222.

E. Interpretation of the Results of Furfural Estimation

It has hitherto been the custom to estimate the proportion of furfural in cellulosic materials and to express the value as pentosan by using the figures of Kröber. The pentosan figure may have a value for comparative and statistical purposes, but it does not give a true indication of the origin of the furfural, for the following reasons :—

(i) It is increasingly apparent that the characteristic unit-sugar of the cell wall of lignified materials is xylose. The furfural found in such cases should be calculated to xylan.

(ii) It is now known that the uronic acids are widely distributed, and they give furfural and carbon dioxide on distillation with mineral acid. The proportion of furfural is much below the theoretical, but that of carbon dioxide is quantitative. The presence of uronic acid therefore makes the pentosan value of little account, since, for example, 20 parts of furfural could be produced from about 32 parts of xylan, from 100 of pectin, or from 61 parts of a hemicellulose from rye straw (p. 413). The use of the Kröber factor for pentosan would indicate 35 parts of pentosan in each case.

Norris *et al.*[1] have examined this question. Estimations of furfural were made by the standard process with mixtures containing hexosans, pentosans and uronic acids and the results submitted to mathematical analysis. The method of least squares was used to give a linear equation most satisfactorily showing the relation between substance and phloroglucide. The standard error was calculated and linear equations of the form

$$S = a + bP \pm e$$

were derived where S is weight of substance, P that of phloroglucide, and e the standard error.

The following equations apply to pure substances and the original Kröber process : here P is as above and C_{ga}, etc., is the weight of CO_2 obtained from the uronic acid named, giving ($\times$ 4) the weight of uronic acid anhydride.

Furfural (F)	$= 0{\cdot}5030\ P + 0{\cdot}0018$	$\pm 0{\cdot}0003$.
Anhydro-arabinose (A)	$= 0{\cdot}9253\ P + 0{\cdot}0050$	$\pm 0{\cdot}0007$.
Anhydro-xylose (X)	$= 0{\cdot}7673\ P + 0{\cdot}0069$	$\pm 0{\cdot}0009$.
Galacturonic acid (as CO_2)C_{ga}	$= 0{\cdot}5778\ P + 0{\cdot}0013$	$\pm 0{\cdot}0009$.
Pectolic acid (as CO_2)C_p	$= 0{\cdot}5744\ P + 0{\cdot}00076$	$\pm 0{\cdot}0008$.
Glucuronic acid (as CO_2)C_{gl}	$= 0{\cdot}6613\ P + 0{\cdot}0026$	$\pm 0{\cdot}0006$.

[1] S. Angell, F. W. Norris and C. E. Resch, *Biochem. J.*, 1936, **30**, 2146.

The values for xylan agree fairly well with those obtained from Kröber's table, but the values for araban are somewhat lower.

For mixtures of arabinose with galacturonic acid (as pectolic acid) the following equation gives the weight of arabinose:

$$A = 0{\cdot}9942\ P - 1{\cdot}9081\ C_p + 0{\cdot}01313 \pm 0{\cdot}00305.$$

Xylose in admixture with glucuronic acid (as euxanthic acid) is given by

$$X = 0{\cdot}7859\ P - 1{\cdot}146\ C_{gl} + 0{\cdot}006 \pm 0{\cdot}0006.$$

The presence of galactose does not affect the yield of furfural from arabinose or pectolic acid in a mixture of these substances unless the proportion of galactose exceeds one-half of the total content. In that case the arabinose is estimated by the above equation and the uronic acid by the CO_2 formed. The effect of glucose on the furfural yield from xylose is negligible, but in this case the phloroglucide must be washed with alcohol.

An example of an investigation in which an attempt has been made to assign the furfural produced to the units producing it will be found on p. 413.

Part II

Estimation of Uronic Acids

The method, due to Lefèvre, depends upon the decomposition of, for example, glucuronic acid by hydrochloric acid, according to the equation :—

$$C_6H_8O_6 = C_5H_4O_2 + 2H_2O + CO_2.$$

It has been shown that, while the yield of furfural is not quantitative, the yield of carbon dioxide accurately measures the amount of glucuronic acid. Four times the weight of carbon dioxide obtained gives the weight of acid lactone present. The method gives satisfactory results in the presence of pentoses and hexoses, and has been largely employed in the investigation of pectic substances and hemicelluloses. As other acids of a similar type may be present, it is usual to express the carbon dioxide obtained in terms of "uronic acid anhydride." The original method has been modified in minor detail by Nanji, Paton and Ling,[1] by Dore,[2] and by Dickson.[3]

Principle of the Method.—The substance to be examined is heated with HCl (*d*, 1·06), as in the estimation of furfural, except

[1] *J. Soc. Chem. Ind.*, 1925, **44**, 253T.
[2] W. H. Dore, *J. Amer. Chem. Soc.*, 1926, **48**, 232.
[3] A. D. Dickson *et al.*, *ibid.*, 1930, **52**, 775.

that a vertical condenser is employed to prevent the acid distilling over. A current of air, free from carbon dioxide, is passed through the apparatus which sweeps over the carbon dioxide produced. This is passed through various drying tubes and either absorbed and weighed in a potash bulb, or absorbed in excess of standard baryta solution.

Procedure.—The original method is described in the book of van der Haar (p. 407). The following slightly modified technique, by W. H. Dore, we have found satisfactory. A round-bottomed distillation flask, heated on a gauze or sand bath, is fitted with a cork carrying an inlet tube for the air stream and a vertical double-surface condenser. The tube of the condenser is connected to a U-tube containing aniline, to which a few drops of hydrochloric acid have been added. This will retain any furfural that may escape. It is connected to a vertical tube containing metallic zinc to absorb hydrochloric acid, followed by a calcium chloride drying tube. A potash bulb, with a calcium chloride guard tube, completes the train.

An absorption train including in succession 4 per cent. $NH_2OH.HCl$ (to remove furfural); dil. H_2SO_4 (to remove HCl), with $CuSO_4$, 72 per cent. H_2SO_4, and calcium chloride (to remove water) has been employed, the carbon dioxide being weighed in soda-lime tubes.[1]

The air must be purified by passing through a series of soda lime and potash tubes (2 parts potassium hydroxide to 3 parts of water). We prefer to drive the air through the apparatus from a gas-holder rather than to draw it through with a pump, as in the original method. A refinement consists in the use of a current of nitrogen purified by passage through a de-oxidant and through soda lime. The calcium chloride tube must be treated previously with carbon dioxide. The potash bulb is filled with potassium hydroxide solution of the strength above mentioned. All rubber joints should be made with thick-walled tubing.

Into the flask is poured 100 ml. of the hydrochloric acid, and a current of air is passed through the apparatus for some time. The substance is then introduced and the hydrolysis carried out as in the furfural estimation, beginning gently to avoid bumping and gradually increasing the heat as the distillation continues. The operation takes 3½ to 5 hours from the commencement of boiling. Hexoses, pentoses, and methylpentoses do not seriously interfere with the results (see notes below). In any special case a blank could be carried out with the equivalent weight of such sugars and a correction applied.

[1] O. Wurz *et al.*, *Papier-Fabrik.*, 1940, **38**, 299.

The apparatus used by Nanji, Paton and Ling (1925) consists of a 750 ml. flask fitted with air inlet and a vertical double-surface condenser. This flask contains 100 ml. of hydrochloric acid (*d*, 1·06) and enough substance to yield 0·2–0·5 g. of uronic acid. The upper end of the condenser is attached to two cylinders of 150 ml. capacity with ground-in stoppers each containing a known volume of standard baryta solution (100 ml. *N*/10). After heating for 3½ to 4 hours in the air current the barium carbonate is allowed to settle

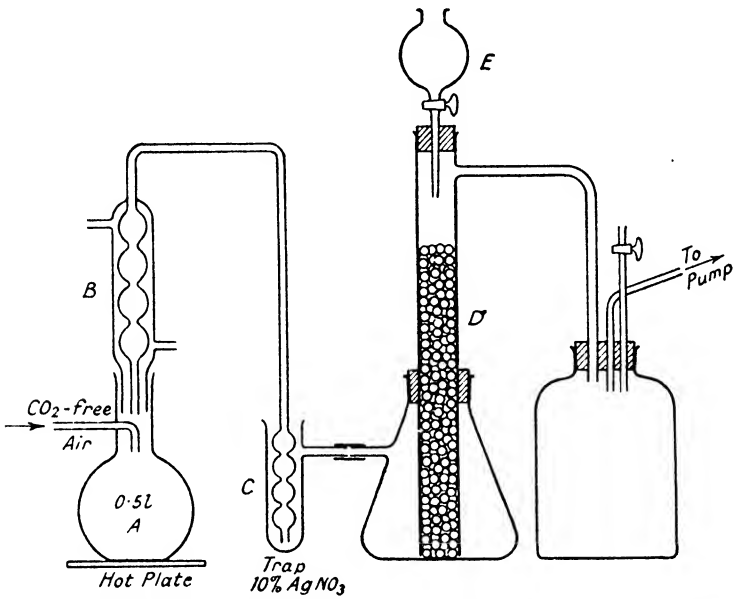


FIG. 73.—Apparatus for the estimation of uronic acids (Dickson *et al.*, *J. Amer. Chem. Soc.*, 1930, **52**, 775).

and 25 ml. portions of the supernatant liquid titrated, using methyl orange.

Per cent. CO_2 found $\times$ 4 = Uronic acid anhydride per cent.

Most recent workers prefer the apparatus of Dickson (*loc. cit.*) which is shown in Fig. 73. The half litre flask A is fitted with a side inlet attached to the air purifying train. B is a 25 cm. Allihin condenser connected with a trap C containing 10 per cent. silver nitrate solution. The absorption tower D is 2/3 filled with glass beads and fitted at the top with a tap-funnel E and soda-lime guard tube. The exit from D is attached to the water pump through a guard bottle.

Substance yielding 0·2 to 0·5 g. of uronic acid and 100 ml. of 12 per cent. hydrochloric acid are placed in A, and E is charged with

a known amount of $N/5$ barium hydroxide solution. A slow current of air is passed for 15 minutes. Heating is then begun, and as soon as the acid boils the baryta solution is allowed to enter slowly and is washed in with several quantities of CO_2-free water. The air current must be increased while this is done, but afterwards it is set at the rate of 2–3 bubbles per second through the tower. At the end of the reaction the tap-funnel is opened and the contents of the tower washed into the flask and titrated with $N/10$ HCl, using phenol- or thymol phthalein indicator.

Very sharp end-points are obtained by the use of achromatic indicators,[1] *e.g.* a mixture of methyl red-methylene blue-phenolphthalein (2 : 1 : 100) is very satisfactory in this titration.

Notes on the Uronic Acid Estimation.—(1) Little importance can be attached to small yields of carbon dioxide obtained from plant products since these may arise from sources other than uronic acid. Thus using Dickson's apparatus and working in a current of nitrogen it was found [2] that most common hexoses, pentoses and various starches gave 0·4 to 0·5 per cent. of carbon dioxide, *e.g.* glucose (0·4), galactose (0·46), xylose (0·4), arabinose (0·47), sucrose (0·52), rice starch (0·45). Values for fructose (0·55), inulin (0·6) and rhamnose (0·9) were higher: for cellulose (0·17) and 2 : 3 : 6-trimethyl glucose (0·2) lower than this, while mannitol, which cannot give rise to a reducing sugar, gave no yield at all.

A. G. Norman [3] finds that with substances in which uronic acid is a main constituent the rate of evolution of carbon dioxide reaches a maximum between 20 and 30 minutes after commencement of the boil (bath 140°) and some 50 per cent. of the total is evolved in the first hour. The only sugars giving such a maximum were sucrose and fructose, but with them only 15 per cent. of the total was produced in the first hour. His values for total carbon dioxide are lower than those given above, *e.g.* simple sugars, sucrose and starches (0·2), esparto cellulose (0·16), cellulose from spruce (0·4), from oak (0·5) and from jute (0·8) per cent.

(2) Factors have been given [4] for the relation between the weight of furfural phloroglucide produced by the standard method and the weight of uronic acid, pure or combined. Estimations of the pure acid as CO_2 gave a purity of 96 to 100 per cent. The following results were obtained, using Kröber's tables, the precipitate not washed with alcohol.

[1] E. Lester Smith, *Quart. J. Pharm.*, 1930, **3**, 499.
[2] W. G. Campbell *et al.*, *Nature*, 1938, **142**, 912.
[3] *Nature*, 1939, **143**, 284.
[4] F. W. Norris and C. E. Resch, *Biochem. J.*, 1935, **29**, 1590.

	Ratio of Uronic Anhydride to		Ratio of Uronic Acid to	
	Phloroglucide.	Furfural.	Phloroglucide.	Furfural.
Galacturonic acid . .	2·37	4·3	2·61	4·74
,, as Pectolic acid	2·33	4·2	2·56	4·63
Glucuronic acid (as Euxanthic acid)	2·61	4·7	2·88	5·14

(3) For a micro-method see H. W. Buston, *Analyst*, 1932, **57**, 220. In this 6–10 mg. of substance are distilled in a modified Pregl-Zeisel apparatus with 4 ml. of 13 per cent. HCl, 90 per cent. saturated with salt. Gases are scrubbed through a little silver sulphate solution below a pack of glass wool covered with a paste of silver sulphate. Time 60–70 minutes. The CO_2 is absorbed in $N/50$ barium hydroxide and titrated with $N/100$ oxalic acid.

Part III

Estimation of Methoxyl

The principle of the methods employed (which with some modification are also used for the estimation of ethoxyl) consists in the conversion of the methoxyl group into methyl iodide, which is estimated either gravimetrically or volumetrically.

The original Zeisel method has been simplified and some modifications will be briefly described. They are (1) the method of Hewitt and Moore [1]; (2) the method of W. H. Perkin [2]; (3) the method of Kirpal and Bühn [3]; (4) Micro-methods.

Methods (1) and (2) can be used in the case of compounds containing chlorine, bromine, or nitro-groups. When sulphur is present, as in the lignosulphonic acids, method (3) or the Vieböck process described under (4) must be employed. These methods are, however, suitable for all estimations and are recommended.

Reagents Required.—(*a*) *Hydriodic Acid* (*d*, 1·7) should have the constant b.p. 127° and contain 57 per cent. of hydrogen iodide. It should be prepared from iodine and red phosphorus, the fraction b.p. 125–127° being retained. For the method of Kirpal and Bühn

[1] J. T. Hewitt and T. Moore, *Chem. Soc. Trans.*, 1902, **81**, 319.
[2] W. H. Perkin, *ibid.*, 1903, **83**, 1369.
[3] A. Kirpal and T. Bühn, "Methoxyl-Bestimmung schwefelhaltigen Verbindungen," *Ber.*, 1914, **47**, 1084; J. T. Hewitt and W. J. Jones, *Chem. Soc. Trans.*, 1919, **115**, 193.

the acid may be obtained by saturating an aqueous suspension of iodine with hydrogen sulphide. The liquid is distilled, and the fraction boiling at 123–127° is retained.

(*b*) *Carbon Dioxide.*—Made from white marble and 15 per cent. hydrochloric acid. The gas is washed through dilute silver nitrate solution and dried through sulphuric acid.

(*c*) *Aqueous-alcoholic Silver Nitrate Solution.*—4 g. of fused silver nitrate dissolved in 10 ml. of water are mixed with 90 ml. of absolute alcohol. The solution is kept in the dark and, for use, is filtered through a dry paper and 1 drop of nitric acid added to it.

The Distillation Process.—(1) After Hewitt and Moore. A round-bottomed flask of 150–200 ml. is fitted with a vertical fractionating column of seven or eight bulbs and an inlet tube for CO_2 which reaches to within 1–2 cm. of the liquid. A thermometer with the bulb at the top of the fractionating column should read 20–25° during the operation. The gases are passed down a long glass tube and *bubble through* the silver nitrate solution contained in two small flasks. As a preliminary test these are disconnected and 16 ml. of the hydriodic acid are placed in the large flask, which is immersed in a glycerine bath and heated at about 130°, a slow current of CO_2 being passed. This removes impurities from the acid. After cooling, 0·2–0·3 g. of the methoxy-compound is weighed in a small tube or otherwise, and introduced into the flask, which is then connected to the absorption vessels. The acid is heated to 130° in a slow current of CO_2. The operation is usually complete in 45 minutes, but to make certain a check tube of silver nitrate solution can be used for a final 10 minutes.

This method is suitable for the analysis of cellulose ethers. For the estimation of *ethoxyl* the glycerine is maintained at 140° and the temperature at the top of the column at 27°. The current of CO_2 must be rapid at the end of the operation.

(2) After W. H. Perkin, senr. This apparatus is the simplest and most convenient for the distillation, and no column is required. It consists of a bulb of 100–150 ml. capacity with a long neck so that the exit tube is 8 in. from the top of the bulb, the neck projecting some 2 in. more. The cork through which the carbon dioxide tube enters is thus very little exposed to the acid vapours. The side tube slopes upwards and connects with the usual two small flasks, but in this method the inlet tube to the first flask does not enter the solution. The flasks are connected with a syphon tube, the end of which in the first flask comes down close to the silver solution, whilst in the second flask it passes into it. A small V-shaped tube is employed to determine the end of the reaction. A modified form

of this apparatus used for the estimation of methoxyl in wood is shown in the figure (W. H. Dore).

15 ml. of hydriodic acid is placed in the flask and the V tube, containing a little of the silver solution, is attached. The temperature of the bath is raised to 130°, and a slow stream of CO_2 is passed until no further turbidity is observed in the silver solution. The

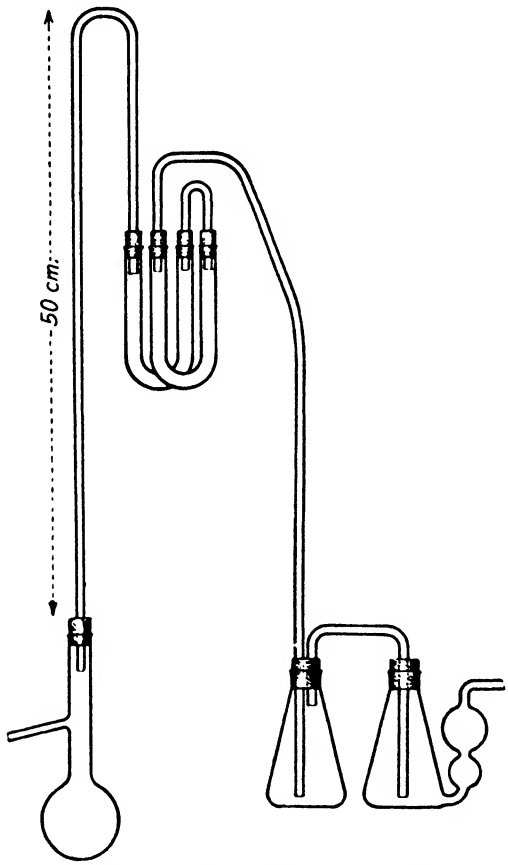


FIG. 74.—Apparatus for the estimation of methoxyl in wood.

apparatus is allowed to cool and the absorption flasks attached, the first containing 20 ml. and the second 15 ml. of the silver nitrate solution. The substance, 0·3 to 0·5 g., is weighed in a small tube and pushed down with the CO_2 tube. The inlet bath is heated at 130–140°, a stream of CO_2 being passed at the rate of about two bubbles per second. Towards the end the temperature of the bath may be raised until the acid just begins to boil. After 45 to 60 minutes the V-tube is substituted, and if no appreciable precipitate forms in 15 minutes the distillation is complete.

Some substances tend to resinify, causing difficulties in obtaining the true methoxyl content, even of some of the methylated sugars, the values found being too low. In such cases it is best to dilute the hydriodic acid with 6 to 8 per cent. of its volume of acetic anhydride, or, in extreme cases, hydriodic acid (*d*, 1·85) may be diluted with an equal volume of acetic anhydride and 20 ml. of the mixture used for the estimation.

The white precipitate which forms in the absorption flasks—a compound of silver nitrate and silver iodide—is decomposed on boiling with water. The contents of the absorption vessels are added gradually to 50 ml. of boiling water made acid with nitric acid. The boiling is continued until all the alcohol is driven off, any masses of precipitate being broken up with a glass rod. Water is added from time to time until the precipitate is converted into yellow silver iodide. It is then collected on a Gooch crucible in the usual manner.

Volumetric Methods of Estimation.—The excess of silver in the absorption flasks may be estimated volumetrically with thiocyanate in the usual way. The details are given under (i), but the modification due to Hewitt and Jones (ii), and the Vieböck process described on p. 399 are better volumetric methods.

(i) The reagents required are an *N*/10 aqueous alcoholic silver nitrate solution made by dissolving 17 g. of $AgNO_3$ in 50 ml. of water and diluting to 1 litre with absolute alcohol. *N*/10 KCNS solution is also required, with ferric alum solution as indicator.

A known volume of the silver solution is put into the absorption flasks, and when the reaction is at an end the contents are washed into a beaker and made up to 300 ml. The beaker is heated on the steam bath until the contents have evaporated to 50 ml. A little nitric acid is added and the silver iodide filtered off and washed with hot water containing nitric acid. The filtrate is then made up to 250 ml. and aliquot portions titrated with potassium thiocyanate.

1 ml. of 0·1*N*-$AgNO_3$ ≡ 0·0031 g. OCH_3.

(ii) **The Kirpal-Bühn Method applied to the Rapid Estimation of Methoxyl.**[1]—Distillation is carried out in a current of carbon dioxide in the usual manner, but the absorption apparatus is replaced by two test tubes in series, each containing 10 ml. of pyridine. About 20 ml. of hydriodic acid (*d*, 1·7), or a suitable quantity of acid (*d*, 1·9) diluted with acetic anhydride is placed in the flask. After heating for 1 hour the contents of the test tubes are washed out and made up to 100 ml. An aliquot

[1] J. T. Hewitt and W. J. Jones, *Chem. Soc. Trans.*, 1919, **115**, 193.

portion is put into a glass stoppered bottle of 250 ml. capacity, diluted with 70 ml. of water, and then in order, 25 ml. of aqueous $N/10$ silver nitrate solution and 30 ml. of approximately $10N$-nitric acid are added. The bottle is shaken by hand for 5 minutes and 5 ml. of ferric alum solution added. The liquid is titrated with $N/10$ thiocyanate until a permanent orange colour is produced.

The results tend to be up to 1 per cent. low.

The Estimation of Methoxyl Groups in Compounds containing Sulphur.—The Zeisel method, using silver nitrate solution as the absorbent, breaks down in the presence of sulphur. Many suitable modifications have been suggested. Of these the best are contained in (*a*) the method of Kirpal and Bühn, and (*b*) in that of Peniston and Hibbert described below, p. 401.

The modification of Kirpal and Bühn depends on the quantitative absorption of methyl iodide by pyridine and the titration of pyridine methiodide by silver nitrate.

The distillation is conducted in the usual manner. The absorption apparatus consists of two test tubes each containing 3–4 ml. of pyridine connected to a small flask to absorb the pyridine vapour. The contents of the tubes are evaporated to dryness on the water bath, the residue taken up with water and titrated with $N/10$ silver nitrate in the presence of sodium chromate until a red coloration is obtained.

4. Micro- and Semi-micro Methods.—The technique of Pregl ("Quantitative Organic Micro-Analysis," 1936) is frequently employed. The apparatus is similar to that shown in Fig. 75, and the estimation follows standard lines. The two modifications to be described embody the volumetric iodine method of Vieböck,[1] which can be recommended for general use. The estimation depends on the oxidation of methyl or ethyl iodide by bromine water as follows :—

$$CH_3I + Br_2 \rightarrow CH_3Br + IBr,$$
$$IBr + 2Br_2 + 3H_2O \rightarrow HIO_3 + 5HBr.$$

After removal of the excess of bromine by means of phenol, iodine is liberated by reaction of the iodate with potassium iodide and estimated in the usual way.

The process has many advantages in the estimation of methoxyl. It has a high titration factor ($CH_3I \rightarrow 31_2$) and is unaffected by the presence of phosphine, sulphur compounds, etc., so that ordinary hydriodic acid can be used. The same acid may be used for at least

[1] F. Vieböck *et al.*, *Ber.*, 1930, **63**, 3207.

three successive samples and substances containing sulphur give no trouble.

(i) **Micro-method for General Use.**[1]—The apparatus is shown in Fig. 75 where A is an ordinary Pregl micro-Zeisel flask. The leading tubes B are nearly of the same diameter as the two absorption vessels, C and D, so that the gas bubbles are flattened out as they rise, giving maximum absorption.

The *reagents* required are: (i) Hydriodic acid, *d*, 1·70; (ii) a suspension of purified red phosphorus; (iii) saturated bromine water; (iv) a phenol-water mixture, 10 per cent. phenol; (v)

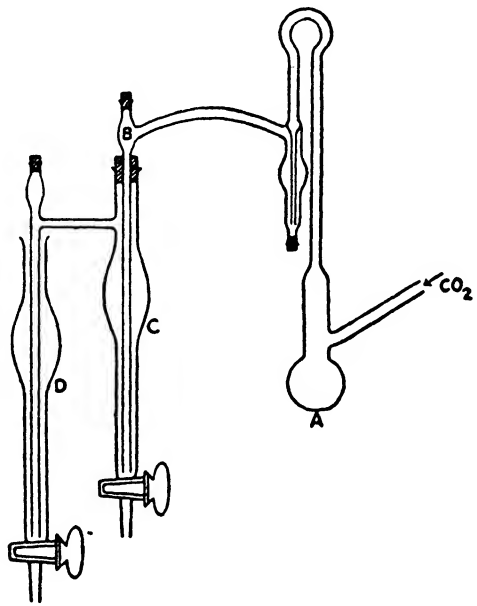


FIG. 75.—Apparatus for the micro-estimation of methoxyl.

freshly made potassium iodide solution, 20 per cent.; (vi) *N*-100 sodium thiosulphate solution.

Procedure.—A few crystals of phenol and 1·5 ml. of hydriodic acid are placed in bulb A and the washer charged with phosphorus suspension. The receivers contain, respectively, 4 ml. of bromine water (C) and 6 ml. (D). About 3 to 4 mg. of dried substance are weighed in a tin-foil cup. This is pushed into bulb A through the side tube, which is then connected with a source of CO_2 gas. The rate of flow must be two bubbles per second, carefully regulated, especially at the beginning. Gentle heat is applied till the tin-foil has dissolved. The acid is then heated briskly for a minute, then

[1] H. R. Nanji, *Analyst*, 1934, **59**, 96.

kept just warm for 5 minutes, then again raised just to boiling-point, kept warm for 5 minutes and the last two processes repeated. The reaction, with easily decomposable compounds such as pectin, is over in 15 minutes and there is no need to boil the acid for the whole period.

The liquid in the absorption tubes is run out into a flask and the tubes rinsed out with water. Ten ml. (and no more) of well-shaken phenol water are added all at once. After a few minutes 5 ml. of the potassium iodide solution are added and the iodine titrated with thiosulphate solution.

One ml. of *N*-100 thiosulphate solution is equivalent to 0·05171 mg. of CH_3O. The blank under the above conditions does not exceed 0·1 ml. of *N*-100 thiosulphate. Four estimations can be carried out in 2 hours.

(ii) **Semi-micro Method for Pulp and Plant Materials.**—The *TAPPI* standard methoxyl method T–209 M–34 follows the ordinary Zeisel process. The following [1] is recommended for convenience and accuracy. It can be used on pulp containing as little as 0·04 per cent. of methoxyl.

The apparatus, which can be modified if desired, is based on that of Clark,[2] which was designed for work with quantities of 20 mg. The essentials are given in Fig. 76. Water from a 2-litre Pyrex flask is circulated round the condenser B and the scrubber E, at a temperature of 45–55°. The current of dry CO_2 is supplied from a thermos flask filled with solid carbon dioxide and delivered through a pressure regulator.

Procedure.—Into the flask C are introduced phenol (7·5 g.) and hydriodic acid (15 ml.), together with one centimetre of nichrome wire to lessen bumping. The scrubber E is charged with a mixture of equal volumes of 5 per cent. cadmium sulphate and 5 per cent. sodium thiosulphate solutions—the gas inlet being covered to a depth of 4 mm.—requiring, say, 4 ml. The CO_2 current is adjusted to about 70 bubbles per minute and the apparatus " burnt out " by heating the oil bath D to 135° for up to 1 hour.

The absorption solution is made in a 10 ml. graduated cylinder by adding 7–8 drops of bromine to 10 ml. of 10 per cent. potassium acetate in glacial acetic acid solution. Of this 6 ml. are put into the first tube and the remainder into the other. The ground glass joint is sealed with a drop of water.

The sample (pulp, 0·1 to 0·5 g.; woodmeal, 0·1 to 0·2 g. of known moisture content) is put into the flask either as pills, or by

[1] Q. P. Peniston and H. Hibbert, *Paper Trade J.*, 1939, **109**, *TAPPI*, 230.
[2] E. P. Clark, *J. Amer. Chem. Soc.*, 1929, **51**, 1480.

pushing out of a glass tube with a glass rod, the whole being weighed before and after. The flask is sealed to the condenser tube with a drop of molten phenol at the ground glass joint.

The bath is again raised to 130–135° and distillation continued for about 1 hour.

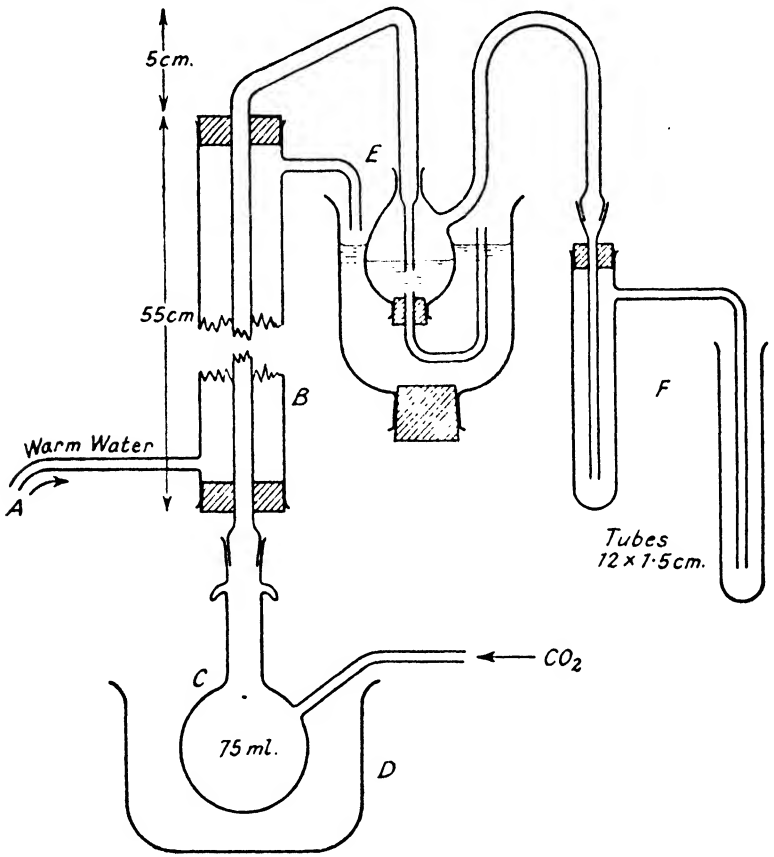


FIG. 76.

The contents of the absorption tubes are then transferred to a 250 ml.-flask containing 5 ml. of 25 per cent. sodium acetate, and made up to about 100 ml. Formic acid is added drop by drop till the yellow colour disappears (say 6 drops), after which 12 more drops are put in. After standing for 2 minutes 10 ml. of 10 per cent. sulphuric acid and 10 ml. of 10 per cent. potassium iodide are added and the titration carried out as usual.

$$\text{OMe per cent.} = \frac{\text{ml. thiosulphate} \times N \times 31{\cdot}02}{60 \times (\text{wt. of sample})}.$$

The " blank " will take about 0·1 to 0·2 ml. of 0·02*N*-thiosulphate.

N.B.—If any doubt exists as to the removal of all the bromine after reaction with formic acid, a drop of methyl red solution may be added. This is at once decolorised by bromine.

Determination of Methoxyl and Ethoxyl in Admixture.—This is sometimes required in the analysis of mixed cellulose ethers and in that of ethylated derivatives of lignin. A satisfactory method has been described [1] in which the alkyl iodides are absorbed in trimethylamine and the NMe_3EtI separated from the NMe_4I by extraction with a saturated solution of NMe_4I in alcohol.

Procedure.—(*a*) Total alkoxyl is determined, using the Vieböck oxidation method, and calculated as methoxyl.

(*b*) Methoxyl is estimated as follows: The sample (10–40 per cent. alkoxyl calc. as OMe) is weighed in tinfoil (10–20 mg.) and treated in the Zeisel apparatus with the standard mixture (HI, 5 ml., phenol 2·5 g.) as described above, except that three absorption tubes are used containing 6, 5 and 4 ml., respectively, of a 10 per cent. ethanol solution of trimethylamine.

After heating for 50 minutes the contents of the tubes are washed out with ethanol into a 50 ml. Erlenmeyer flask. The crystals of NMe_4I left in the first and second tubes are dissolved with 2 ml. portions of water followed by ethanol. The collected liquids are allowed to stand for 3 hours, after which they are evaporated nearly to dryness (steam bath) and the drying completed in a vacuum desiccator.

The NMe_3EtI is then extracted from the residue by adding 3 ml. of a saturated solution of NMe_4I in absolute ethanol with a drop pipette.* After shaking for a minute the flask is tilted to allow the crystals to settle and the liquid removed to a suction filter by means of a pipette. This process is twice repeated, and after the final decantation the pipette is dried in air and any traces of the tetramethyl compound removed by water. This water is added to a second flask which also contains the air-dry filter paper used. The contents of the first flask are freed from ethanol in a vacuum for 1–2 hours, after which the aqueous contents of the second flask are added and the aqueous solution of NMe_4I is ready for volumetric estimation.

For this it is treated with 10 ml. of a saturated solution of potassium acetate in glacial acetic acid containing 8–10 drops of bromine, for 2–3 minutes, followed by 5 ml. of 25 per cent. aqueous sodium

[1] L. M. Cooke and H. Hibbert, *Ind. Eng. Chem. Anal.*, 1943, **15**, 24.

* Ethanol alone may be used for the extraction of the NMe_3EtI in which case 0·2 ml. is added to the ml. of thiosulphate found for every 9 ml. of ethanol employed.

acetate. The bromine is removed by the addition of 10 drops of formic acid (80–90 per cent.) and the clear solution treated with 5 ml. of 10 per cent. KI + 5 ml. of 10 per cent. H_2SO_4. The liberated iodine is titrated with 0·05 *N*-thiosulphate solution. The results with pure compounds such as 3-ethoxy-4-methoxy-benzoic acid are very accurate.

$$\text{Per cent. OMe} = \frac{\text{ml. thiosulph.} \times N \times 31}{\text{wt. sample} \times 60}.$$

Per cent. OEt = (per cent. total alkoxyl as OMe − per cent. OMe) × 45/31.

CHAPTER XXII

THE HEMICELLULOSES.

THIS term was applied by Schulze (1891) to a group of constituents of the cell membrane which, unlike cellulose, were soluble in dilute alkalis and were readily hydrolysed to pentoses and hexoses. Their function would appear to be either that of reserve materials, as in kernels and seeds, in which case hexoses form the chief products of hydrolysis; or that of structural materials, as in seed and fruit husks, straws, woods, etc. The structural hemicelluloses, on hydrolysis, yield chiefly pentoses, of which xylose, and to a lesser extent arabinose, are most common. The pods of *Pisum sativum* and *Phaseolus vulgaris*, for example, were found to contain a hemicellulose which on hydrolysis gave galactose and arabinose, and the hemi-cellulose of the ivory nut was identified as lævulo-mannan.[1] The hemicellulose of American white oak, on the other hand, contained at least 70 per cent. of xylan and araban, coupled with smaller proportions of mannan and galactan.

Modern work on the hemicelluloses [2] has shown (i) that in most cases the crude product obtained by alkali extraction can be resolved into several fractions distinguished by their solubility and hydrolytic products; (ii) that many of these fractions contain uronic acids, and in some cases the uronic acid grouping, rather than the pentosan, constitutes the dominant factor. Such hemicelluloses it has been proposed to describe as polyuronides, leaving the older term hemicelluloses for those which yield no uronic acids on hydrolysis.

Hemicelluloses from a variety of plant materials have now been isolated and examined but few general conclusions can be drawn. The hemicellulose of woody tissue is almost always of a xylan-glucuronide type with a high ratio of xylose to uronic acid. The hemicellulose fractions from mesquite wood, for example, contain 6 to 12 xylose units to one of glucuronic acid.[3] The bark of trees, on the other hand, yields a hemicellulose of another type—a galactan-galacturonide: thus the bark of ash [4] (*Fraxinus excelsior*) gave 20 per cent. of hemicellulose, the hydrolysis products of which were

[1] J. L. Baker and T. H. Pope, *J. Chem. Soc.*, 1900, **77**, 703.

[2] See A. G. Norman, "The Biochemistry of Cellulose, Polyuronides," etc., Clarendon Press, Oxford, 1937; *Ann. Rev. Biochem.*, 1941, **10**, 79.

[3] L. Sands and W. Y. Gary, *J. Biol. Chem.*, 1933, **101**, 573; *ibid.*, 1935, **110**, 17.

[4] H. W. Buston and H. S. Hopf, *Biochem. J.*, 1938, **32**, 44.

mainly galactose (with a little mannose and arabinose) and galacturonic acid. In the hemicelluloses of leaves and pods also, galactose is the predominant carbohydrate, the "A" fraction of the leaves of bean and vine being almost pure galactan.[1]

Buston considers that the hemicelluloses derived from green non-lignified plant tissues are usually of the galacto-araban type, whereas those of older lignified tissue are of the gluco-xylan type. But there are exceptions to this, the predominant hemicellulose in cocksfoot grass,[2] for example, being xylan.

Hemicelluloses are usually isolated by extraction with cold 4 or 5 per cent. sodium hydroxide solution. The pre-treatment with boiling aqueous-alcoholic sodium hydroxide used, by some authors to remove lignin is not satisfactory in all cases. Polyuronide hemicelluloses show a loss of furfural which may indicate changes in their composition. The treatment should be used only if it is certain that it produces no substantial change in the hemicellulose. Lignin may be removed from isolated hemicellulose by brief chlorinations followed by washing with alcohol of about 70 per cent. strength or by suspension in alcohol and addition of sodium hypochlorite solution. Cold alcoholic sodium hydroxide used by some workers does not remove lignin to any extent, but minimises the amount of protein material subsequently extracted.

Chlorination enables more restrained methods of alkali extraction to be employed. An extensive removal of hemicellulose from wood, straws, etc., is achieved by chlorinating (15 mins.) the residue from the usual cold 4 per cent. alkali extraction (1 day), washing with a little cold water and treating again with alkali of the same strength (1 day). Extraction with 2 per cent. sodium carbonate at the boil for 30 minutes, followed by chlorination for 10 minutes and boiling for 30 minutes with 0·5 per cent. NaOH will also in many cases (*e.g.* straws) remove most of the hemicellulose.

Although isolated hemicelluloses are soluble in cuprammonium, they cannot be extracted from vegetable tissues by this reagent. A preliminary treatment of the material with hydrochloric acid, however, renders them completely soluble.[3] The action of very dilute boiling acid for 5 minutes, or cold 10 per cent. acid for 1 day, has been found effective for this purpose.

The general method of investigation of the hemicellulose obtained from any particular source is illustrated by the examples abstracted below, dealing with the hemicelluloses of wheat bran and maize cobs

[1] H. W. Buston, *Biochem. J.*, 1935, **29**, 196.
[2] *Ibid.*, 1934, **28**, 1028.
[3] E. Schulze, *Z. physiol. Chem.*, 1892, **16**, 410.

and with the composition of straws. Other examples will be found under Mannan and under Xylan (p. 424), where the nitric acid method of hydrolysis is described. Examination of the hemicelluloses of hard woods is illustrated by the work of O'Dwyer (p. 417), and an application of the methylation and acetylation methods developed by Irvine in the case of esparto cellulose (p. 421) illustrates a special method of treatment. The nature of the hemicellulose having been ascertained, reference may be made to the special sections on xylan, araban, mannan, etc.

The investigation of hemicellulose, it will be seen, involves (*a*) isolation of a crude product by extraction with alkali, with or without pre-treatment to remove lignin, pectin and other substances; (*b*) its purification, often by conversion to the copper compound (p. 425); (*c*) fractionation by various methods, the optinum *p*H for the precipitation being determined. Each fraction will require determination of (*d*) rotation in alkaline solution; (*e*) furfural yield and carbon dioxide yield and calculations of the distribution of the pentose and uronic acid constituents; also (*f*) estimation of methoxyl; and (*g*) hydrolysis, usually by sulphuric acid, but more conveniently by dilute nitric acid (p. 426) and the separation and identification of the individual sugars obtained.

If the product is sufficiently definite, as in the case of the mannans of yeast and ivory nut (p. 438), the araban of pectin (p. 523) and the ϵ-galactan of larch (p. 433), the methylation-hydrolysis treatment (*e.g.* p. 437) is applied and the structure of the complex deduced from the nature and proportion of the methylated carbohydrates obtained. In the case of a polyuronide hemicellulose the isolation of the acids formed on partial hydrolysis is attempted (see p. 416). The presence of uronic acids is best detected by the naphthoresorcinol test. A small portion is heated with an alcoholic solution of the reagent mixed with an equal volume of hydrochloric acid (*d*, 1·19). A clear violet-blue ring is formed.

The table on p. 408 gives some of the characteristics of the chief derived carbohydrates and uronic acids. For a summary of the reactions of the latter see Norman, " Biochemistry of Cellulose, Polyuronides, etc. ", and *Chem. Soc. Ann. Reports*, 1937, 396. For further details of identification of the sugars (*cf.* p. 418) the following may be consulted :—

A. W. van der Haar, " Anleitung zum Nachweis zur Trennung u. Bestimmung u.s.w. erhaltenen Monosaccharide und Aldehydsäuren " : Bornträger, Berlin, 1920.

Abderhalden, " Handbuch der biolog. Arbeitsmethoden," Abt. I, Pt. 5 (by G. Zemplén).

PROPERTIES OF SIMPLE SUGARS AND URONIC ACIDS DERIVED FROM ALKALI-SOLUBLE EXTRACTIVES OF VEGETABLE TISSUES

Name and form.		$[\alpha]_D^{20°}$ in Water.	Melting-point °C.	Osazone. Melting-point °C.
d-Xylose	α-	+ 18·10 (*c*, 0·87)	153	159–160
l-Arabinose	β-	+ 106·54 (*c*, 5·00)	158·5–159·5	166
d-Arabinose	β-	− 105·1 (*c*, 9·43)	158·5–159·5	
Fucose	α-	− 75·6 (*c*, 8·82)	145	178
l-Rhamnose	*α-	+ 9·43 (*c*, 5–45)	122–126	180
d-Glucose	α-	+ 52·76 (*c*, 4·5)	146–147	205
,,	β-		148–150	205
d-Mannose	α-	+ 14·25 (*c*, 2)	133	205
,,	β-	+	132	205
d-Galactose	α-	+ 80·72 (*c*, 5·60)	161–170	188
d-Fructose	β-	− 90·46 (*c*, 4·5)	95	205
d-Glucuronic acid	.	+ 11·7 → 36·3	156, 165	199, 215†
Quinine salt	.	−80	175–180	
Lactone	.	+ 18·5 − 20·7	180	144†
dl-Galacturonic acid	.	+ 51	157–159	150–151†
d-form ,, ,,	.	+ 98 → 50·9 (24 h.)	156–159	
l-form ,, ,,	.	+ 27 → 55·3 (24 h.)	160	
Cinchonine salt	.	+ 139	176–178	
d-Mannuronic acid	α-	+ 16 → − 6	120–130	
,, ,,	β-	− 47·9 → − 23·9	165–167	
Cinchonine salt	.	+ 113	152–154	
Lactone	.	+ 90, 93, 95	140–144	160†

* Anhydrous. † *p*-bromophenylhydrazone.

THE HEMICELLULOSES OF WHEAT BRAN AND MAIZE COBS.

These publications [1] represented a considerable advance in method in that they introduced (*a*) the use of alcoholic sodium hydroxide for the removal of lignin, and (*b*) the fractionation of the hemicellulose by precipitation with acetic acid followed by acetone, with the further purification of each fraction through the copper compounds.

The Hemicelluloses of Wheat Bran.—400 g. of the bran are treated with 2 l. of water for 1 hour and the mixture then poured into 2 l. of 1 per cent. ammonium oxalate previously heated to 90°. The whole is maintained at 90° for 2 to 3 hours, cooled, filtered through muslin, and the removal of pectin completed by another extraction with 0·5 per cent. oxalate. The mass is filtered and pressed.

To remove lignin the mass is (*a*) extracted twice with 3 l. of 50 per cent. alcohol containing NaOH 1 per cent., each extraction

[1] F. W. Norris and I. A. Preece, *Biochem. J.*, 1930, **24**, 60, 973; *ibid.*, 1931, **25**, 1304.

under reflux for 2 hours; (*b*) the residue is then treated under reflux with 3 l. of neutral 50 per cent. alcohol for 1 hour, and again filtered through muslin and pressed.

The hemicellulose is then extracted with 3 l. of 4 per cent. NaOH, the residue being further treated two or three times with the alkali. The combined extracts are filtered through glass wool.

To the filtrate is added glacial acetic acid in slight excess. The precipitate (hemicellulose A) is separated (centrifuge), repeatedly washed with water, the early washings being added to the main filtrate and dried by treatment with alcohol of gradually increasing strength and finally in a vacuum.

The filtrate is, if necessary, passed through paper pulp and half its volume of acetone added. After standing, hemicellulose B is removed, re-dissolved in 4 per cent. NaOH, the liquid neutralised with glacial acetic acid, and the hemicellulose thrown out by addition of half its volume of acetone. This is repeated several times before drying the product as above.

To the filtrate from B is added a volume of acetone equal to that previously added. This throws out hemicellulose C, which is purified by solution in water and precipitation by addition of an equal volume of acetone. This process is also carried out several times.

The yields of the dry products from 400 g. of bran were—A, 8·0 g.; B, 4·5 g.; C, 4·5 g.

Purification.—*Hemicellulose A.*—The product is dissolved in 1 litre of 4 per cent. NaOH and 250 ml. of Fehling's solution added. The copper compound is removed and decomposed by dilute HCl. The precipitation of the hemicellulose is aided by addition of acetone. The product is washed free from copper and acid by three or four changes of acetone. Drying is completed by alcohol. A trace of starch may still be left.

Hemicellulose B.—5 g. are dissolved in boiling water and the boiling continued for 5 minutes. The solution is filtered through glass wool, and after cooling NaOH is added to give a 4 per cent. solution. Fehling's solution (250 ml.) is then added with stirring and the precipitate (B1 copper complex) is removed through muslin. After further filtration through paper pulp the filtrate is diluted with half its volume of acetone and the second precipitate (B2) is filtered off. The precipitates B1 and B2 are decomposed separately with dilute HCl, acetone being added, and after washing with acetone are dried as above. The process may be repeated.

Hemicellulose C.—This is dissolved in 4 per cent. NaOH and Fehling's solution added. The liquid becomes viscous, but no

precipitate appears until acetone equal to half the volume is added. The precipitate (referred to as C2 in analogy with B2) is treated with HCl, etc., as with B2.

The hemicelluloses are white powders with ash content 0·3 to 2·0 per cent. A is slightly soluble in boiling water; B1, B2, and C2 are completely soluble. The solution of C2 is lævorotatory.

The following analyses were made by standard methods and calculated on 100 parts of dry ash-free material :—

Hemicellulose.	A.	B1.	B2.	C2.
Furfuraldehyde .	55·0	48·4	3·2	49·0
Carbon dioxide .	*Nil*	1·85	*Nil*	1·98
Uronic anhydride .	*Nil*	7·40	*Nil*	7·92
Chief products obtained on hydrolysis	Xylose Arabinose	Xylose Uronic acid	Glucose	Arabinose Uronic acid

The crude product B gave 31·1 per cent. of furfural. The fractions B1 and B2 are therefore present in the ratio 2 : 1. Product B2 is interesting as being apparently a pure hexosan.

From the hydrolysis of these fractions by 1 per cent. sulphuric acid, syrups were obtained which yielded the following results :—

Hemicellulose A.—Arabinose diphenylhydrazone, m.p. 202°, was isolated, as also the cadmium xylonobromide derivative of xylose. An osazone was prepared a small portion of which, insoluble in hot water, appeared to be glucosazone. The part soluble in hot water was seen microscopically to be a mixture of xylosazone and arabinosazone. Mannose hydrazone absent. The mucic acid test for galactose and the Pinoff-Selivanoff test for ketohexoses were negative.

Hemicellulose B1.—The syrup gave much cadmium xylonobromide, and another portion a little arabinosediphenylhydrazone. An osazone was prepared, and the portion insoluble in hot water gave needles from alcohol, quite different from the osazones of glucose and galactose; m.p. 158°. This may be derived from glucuronic acid. The osazone soluble in water m.p. 155°, was a pentosazone.

Hemicellulose B2.—As this only gave 3 per cent. of furfural and no CO_2 yield, pentosans and uronic acids were not present. An osazone was isolated which had a m.p. of 205° and was apparently glucosazone. Galactose and ketohexoses were absent.

Hemicellulose C2.—Arabinose diphenylhydrazone was obtained in quantity; m.p. 203°. An osazone was prepared of which the

part insoluble in water, m.p. 161–163°, resembled the supposed glucuronic acid derivative from B1.

The Hemicellulose of Maize Cobs.—Using similar methods, the hemicellulose of maize cobs was separated into four fractions.[1] One, A (8 per cent.), insoluble in water; B1 (6 per cent.), swelling in cold water, dissolved on boiling; C1 (1 per cent.), partially soluble in cold, quite soluble in hot water; C2 (0·5 per cent.), swells in cold water, quite soluble in hot. The furfuraldehyde phloroglucide obtained from B, C1 and C2 contained appreciable quantities of brown alcohol-soluble material derived from methyl pentosan. The following table shows the results obtained in per cent. on dry ash-free products:—

HEMICELLULOSE FRACTIONS FROM MAIZE COBS

Hemicellulose.	A.	B1.	C1.	C2.
Yield on cobs . . .	8·0	6·0	1·0	0·5
Methylpentosan . .	0·0	7·01	7·42	8·91
Furfuraldehyde . . .	61·49	57·31	54·57	43·90
Carbon dioxide . . .	0·94	1·30	1·85	1·39
Uronic anhydride . .	3·76	5·20	7·40	5·56
Rotation $[\alpha]_D^{20°}$ (in NaOH) .	−96°	−108°	−90°	—

Hydrolysis showed that A and B1 were almost entirely xylans, containing respectively 94·4 and 87·6 per cent. of xylan. C1 yielded some xylose, while C2 gave arabinose, but no xylose.

Using these results, and assuming that 100 g. of uronic anhydride yield 16·7,* 100 g. of xylan 64·5, and 100 g. of araban 53·5 g. of furfuraldehyde, the following table was calculated:—

Hemicellulose.	A.	B1.	C1.	C2.
Total furfural per cent. .	61·49	57·31	54·57	43·90
Furfural from uronic anhydride per cent.	0·63	0·87	1·23	0·93
Furfural from pentosan ,,	60·86	56·44	53·34	42·97
Xylan . . . ,,	94·36	87·50	82·70	—
Araban . . . ,, .	0	0	0	80·32
Methyl pentosan . ,, .	0	7·01	7·42	8·91
Uronic anhydride . ,, .	3·76	5·20	7·40	5·56
Total accounted for . ,, .	98·12	99·71	97·52	94·79

[1] I. A. Preece, *Biochem. J.*, 1930, **24**, 973.

* This gives a ratio anhydride to furfuraldehyde of 6 to 1. Norris and Resch (p. 395), find 4·3 to 1.

More recent examination [1] has shown that the fractions are seldom sharply defined, but tend to merge into one another. The A fraction is the most definite, and is often the only one investigated, but unless an optimum *p*H is found for the precipitation, a proportion of A will pass over into the B fraction. Thus practically the whole of the hemicellulose of maize-cobs was found in the A fraction when thrown down at the optimum *p*H of 4·0. It contained [1] xylan 94·8, uronic anhydride 5·1, and methoxyl 0·5 per cent., so that the B1 fraction of Preece above consisted chiefly of unprecipitated A fraction.

The B2 and C2 fractions also may contain material which should fall under B1 and C1 respectively, since the precipitation of hemicelluloses with Fehling's solution is seldom complete. The use of a mixture of copper sulphate and glycerol has been suggested as giving better results, the copper gel being decomposed by acetic acid instead of hydrochloric acid.

The use of alkali of 4 to 10 per cent. concentration employed in the initial extraction removes some cellulosan, *i.e.* the less resistant fraction of the cellulose. In the cases discussed this would be xylan with some glucosan, and as xylan is precipitated by Fehling's solution it will appear largely in fraction B1, a little remaining in fraction A. The hexosan is not precipitated as a copper compound and would therefore be found in fraction B2

Extraction of various materials with 1 *per cent. NaOH in* 50 *per cent. alcohol for* 1·5 *hours at boiling-point. Results given as per cent. of original material.*

	Residue.	Total Furfural.	Furfural from Polyuronide.	Lignin.
Oak	—	13·37	4·2	22·3
extracted	79·6	11·35	3·5	17·6
Jute	—	9·82	4·1	11·7
extracted	76·0	7·97	2·9	6·5
Bean Straw	—	10·92	5·1	12·7
extracted	70·1	8·56	3·7	10·1
Vetches (old)	—	11·52	7·5	14·3
extracted	53·8	7·54	3·8	7·6
Vetches (young)	—	5·71	3·8	11·2
extracted	33·6	3·53	1·7	3·4

[1] S. Angell and F. W. Norris, *Biochem J.*, 1936, **30**, 2155.

which is usually a small one. The B2 fraction of wheat bran (p. 410), for example, is a glucosan and this supports the view that it is derived from the cellulose and not the hemicellulose. Its quantity is small—since cold 4 per cent. NaOH does not remove very much of the hexosan—but if boiling alkali is used the amount may be much greater.

The pre-treatment with alcoholic sodium hydroxide, whilst removing soluble lignin, certainly affects the hemicellulose, as may be seen from the table given on p. 412.[1]

Preece, after further examination,[2] agrees that the use of alcoholic sodium hydroxide at the boiling-point is best omitted. It may be used cold or a simple extraction with alcohol may be given.

The Nature and Quantity of the Furfuraldehyde-Yielding Substances in Straws [3]

ANALYSIS OF THE SAMPLES OF STRAW EMPLOYED

	Oat Straw. Per cent.	Rye Straw. Per cent.
Ash	7·07	3·46
Total furfuraldehyde yield	16·08	17·05
Carbon dioxide yield	1·21	1·15
Calcium pectate yield	1·10	0·34
Cellulose (Cross and Bevan) *	53·14	55·27
Furfuraldehyde from cellulose	5·99	5·64
Lignin	18·54	19·5
Protein	1·8	1·9

* Extraction with 1 per cent. NaOH, followed by chlorinations of 12, 7 and 5 minutes.

Determination of Hemicellulose Content.—The total furfural obtained from oat straw may be derived from the pentose and uronic groups in the hemicelluloses, from the pectin, and from the rather obscure substances in the Cross and Bevan cellulose. It is possible from the data above to calculate the amount derived from hemicellulose, but many assumptions are made. Angell, Norris *et al.*,[4] for example, have shown that the yield of furfuraldehyde from pentose and uronic groupings together is not the sum of the yields given separately by each.

Let A represent total furfural yield; B furfural from cellulose

[1] A. G. Norman, " Biochemistry of Cellulose, etc. ", 1937.

[2] I. A. Preece, *Biochem. J.*, 1940, **34**, 251.

[3] A. G. Norman, *Biochem. J.*, 1929, **23**, 1353. Both oat straw and rye straw were examined. The details given relate to oat straw.

[4] *Biochem. J.*, 1936, **30**, 2146.

fraction; C that from pectin (19·5 per cent. on calcium pectate); D that from total uronic acid anhydride (16·66 per cent.); and E that from uronic acid anhydride in pectin (11·6 per cent. on calcium pectate).

From this (C—E) represents furfural from the arabinose group in pectin. The furfural arising from the pentose groups of the hemicelluloses present in 100 g. of straw is given by

$$[A - \{B + D + (C - E)\}]$$

which in the case of this straw is per cent.

$$[16{\cdot}08 - \{5{\cdot}99 + 0{\cdot}81 + (0{\cdot}21 - 0{\cdot}13)\}] = [16{\cdot}08 - 6{\cdot}88] = 9{\cdot}2$$

To interpret this in terms of hemicellulose the actual furfural yield of the hemicellulose was determined, since it is not possible to assume that only pentose groups are present. The method of extraction was the following: 100 g. of the straw were digested on a boiling-water bath with 1 l. of 0·5 per cent. ammonium oxalate twice for periods of 4 hours to remove pectic substances, and then washed with boiling water. Two treatments for 2 hours each with a litre of 55 per cent. alcohol containing 1 per cent. NaOH, to extract the more readily soluble lignin, followed, and after washing with 55 per cent. alcohol alone, the hemicelluloses were extracted by four treatments with 4 per cent. NaOH, the first for 4 hours, and the others for 2 hours each. The combined alkaline extracts were filtered and acidified with glacial acetic acid. A colloidal solution was obtained, from which the crude hemicellulose was precipaitted by alcohol. After purification the product, dried with alcohol and ether, gave the following figures on analysis :—

	Per cent.
Furfuraldehyde yield on ash-free basis	43·0
CO_2 yield on ash-free basis	3·9
Uronic acid anhydride	15·6
Furfuraldehyde due to uronic groups	2·6

By difference, the furfural due to pentose units of hemicellulose was 40·4 per cent. Since the amount of furfural arising from the pentose groups of the hemicelluloses present in 100 g. straw was 9·20, and the pentose units in the hemicelluloses themselves yield 40·4 per cent. furfural, an approximation for the actual hemicellulose content is given by the quotient—namely, 22·8 per cent.

The Nature of the Hemicelluloses Present.—The mixed product was separated into two portions, A and B, by the method of O'Dwyer (p. 419), the amount of A being three or four times that of B. Their properties are shown in the following table :—

Oat Straw Hemicellulose

	Hemicellulose A. Per cent.	Hemicellulose B. Per cent.
Furfuraldehyde yield on ash-free basis	42·9	43·3
CO_2 yield on ash-free basis	2·7	7·95
Uronic acid anhydride	10·8	31·80
Furfuraldehyde due to uronic groups	0·65	1·90
Furfuraldehyde due to pentose groups	42·25	41·5

Qualitative tests on the hydrolysis products from hemicellulose A showed that arabinose, xylose and galactose were present, while hemicellulose B showed arabinose alone.

It is probable, therefore, that hemicellulose A consists of about 11 per cent. of uronic acid anhydride, 79 per cent. of arabinose and xylose (as anhydroarabinose), and 10 per cent. of anhydrogalactose, while hemicellulose B, yielding about the same percentage of furfural, contains 32 per cent. uronic acid anhydride and 68 per cent. arabinose.

The Furfuraldehyde-yielding Substances in the Cross and Bevan Cellulose from Straw.—The small yield of CO_2 (0·2 per cent.) obtained from oat-straw cellulose shows that the xylan present is different from the free hemicelluloses isolated by alkali extraction.

The relationship of the xylan to the true cellulose is a matter of interest, since the xylan is so intimately associated that removal is a matter of considerable difficulty. To investigate this point, 100 g. straw were treated as before to remove pectin. This was followed by four treatments of an hour with 4 per cent. NaOH, and finally with water. For this residue the following analytical figures (second row) were obtained :—

	C. and B. Cellulose. Per cent.	Total Furfurald. Per cent.	Furfurald. on 100 g. C. and B. Cellulose. g.	Furfurald. on Cellulose in 100 g. Material. g.	Carbon Dioxide Yield. Per cent.	Uronic Acid. Per cent.
Oat straw	53·14	16·08	11·32	5·99	1·21	4·84
Residue	91·68	9·09	7·83	7·18	0·46	1·84
100 g. original straw	50·3	5·0	—	3·9	0·25	1·00

It was not possible to determine the actual loss during this treatment, but an approximate calculation was made, however, from the figures, assuming that there was no loss of true cellulose during extraction. The result obtained gave the loss as 45·2 per cent. From this the analytical figures of the residue calculated back on 100 g. of original straw were found. These are given in the third

horizontal row of the table above. While the furfuraldehyde yield from groups unassociated with the cellulose has decreased from 10·08 to 1·1 per cent., a loss of nearly 90 per cent., that from the xylan has fallen from 5·99 to 3·9 per cent., a loss of only 35 per cent.

The final interpretation of the analyses of these straws is given below.

COMPOSITION OF STRAWS

	Oat Straw. Per cent.	Rye Straw. Per cent.
Ash	7·07	3·46
Free hemicellulose	22·8	33·40
" Pure " cellulose	43·8	46·53
Xylan associated with cellulose	9·3	8·34
Pectin (calcium pectate yield)	1·1	0·34
Protein	1·8	1·9
Lignin (72 per cent. H_2SO_4)	18·5	19·50

The Hemicellulose of Oat Hulls.[1]—The composition of this product is of interest in that it is made up of 1 glucuronic acid unit to 2 galactose units and 20 to 65 pentose units. The pentoses are present in the proportion of 9 xylose : 1 arabinose units.

The crude hemicellulose was hydrolysed (4 per cent. H_2SO_4 for 15 hours) on the water bath. After removal of " body X " the liquid was neutralised with barium carbonate, filtered, taken to dryness and extracted with alcohol to remove sugars. The barium salt of the uronic acid dissolves in water and is reprecipitated by alcohol giving $[\alpha]_D^{20°} + 79·6°$; carbon dioxide 7·55 per cent. Barium uronate + 2 mols. of hexose requires 7·51 per cent. Heated in an autoclave at 120° with 4 per cent. sulphuric acid it gave crystalline *d*-galactose, $[\alpha]_D^{20°} + 78°$. Oxidised with bromine and hydrobromic acid, or with nitric acid, saccharic acid was obtained and isolated as acid potassium salt. This result confirms the presence of glucuronic acid in the original product.

The alcoholic solution containing the sugars gave much xylose and a little arabinose (10 per cent. of total).

HEMICELLULOSE OF WOODS

Pioneer investigations on oak wood abstracted below have been continued, the original fractions being further resolved. Attention has recently been given to the hemicelluloses obtained from different parts of the tree at various stages of growth. O'Dwyer has examined the changes observed in the transition from sapwood to heart-

[1] E. Anderson and P. W. Krznarich, *J. Biol. Chem.*, 1935, 111, 549.

wood and A. Allsopp and P. Misra [1] have studied the hemicellulose from ash, elm and Scotch pine, examining the mature sapwood, newly formed wood and the cambium.

Some woods, *e.g.* mesquite,[2] do not give up the whole of the hemicellulose on extraction with alkali. The remainder can be obtained by extraction with cold 10 per cent. sodium hydroxide after removing some of the lignin by chlorination treatments. E. Anderson *et al.*[3] have studied a number of hardwoods in this way and the results have led them to revive a suggestion originally made by O'Dwyer and by Campbell [4] that starch may be the precursor of hemicellulose in the life of the tree.

Nearly all the hemicelluloses from woods appear to be of the xylan-glucuronide type. Their molecular size has been measured by viscosity and osmotic pressure methods.[5] The galacto-araban from larch, the mannan from spruce and the xylan from beechwood all showed a degree of polymerisation varying within the limits of 150–220 units. This was unchanged after acetylation. In comparison the methods employed gave, with beechwood cellulose, a value of 1500 units.

The Hemicellulose of American White Oak.[6]—The hemicellulose obtained from this wood appears to be a mixture containing xylan + araban 70 per cent. and mannan + galactan 30 per cent. It yielded, roughly, 51·5 per cent. of xylose and 18·5 per cent. of arabinose on the weight of original wood. It was prepared as follows: 600 g. of sawdust, after extraction with hot water, were stirred for two days with 6 l. of 4 per cent. NaOH solution. The extract was acidified with acetic acid and the sticky precipitate removed. The filtrate on mixing with an equal volume of 95 per cent. alcohol gave a flocculent precipitate which was added to the other, and the total solid matter washed with 50 per cent. alcohol. The product was purified by solution in NaOH, filtering and reprecipitating with acetic acid and 95 per cent. alcohol. It was finally washed with alcohol and ether. Yield, about 10 per cent.

For further purification it was extracted with 2 per cent. NaOH on the water bath and fitered through glass wool. Fehling's solution was added in excess and the precipitate washed with very weak

[1] *Biochem. J.*, 1940, **34**, 1078.
[2] L. Sands and P. Nutter, *J. Biol. Chem.*, 1935, **110**, 17.
[3] *Ibid.*, 1940, **135**, 189.
[4] W. G. Campbell, *Biochem. J.*, 1935, **29**, 1068.
[5] E. Husemann, *Naturwiss.*, 1939, **27**, 595.
[6] M. H. O'Dyer, *Biochem. J.*, 1923, **17**, 502; 1934, **28**, 2116; 1937, **31**, 254; 1939, **33**, 713.

alcohol. The copper compound was decomposed with cold dilute acetic acid and the mixture washed, first with very weak acid and then with dilute alcohol. The precipitate was boiled out with absolute alcohol and washed with cold 95 per cent. alcohol to remove traces of acid.

Properties.—The product was greyish-white, free from nitrogen and ash, soluble in hot water, forming a gelatinous mass on cooling. It did not reduce Fehling's solution. Rotation $[\alpha]_D$ — 75° in 1 per cent. NaOH.

The Identification of Xylose, Arabinose, Mannose and Galactose as the Hydrolysis Products of the Hemicellulose of American White Oak.[1]—The hemicellulose was hydrolysed with ten times its weight of 1 per cent. sulphuric acid for 6 hours. The acid was precipitated and the filtrate mixed with a little alcohol to remove any further barium sulphate, and the filtrate concentrated and allowed to evaporate over sulphuric acid. A white mass was obtained which gave crystals A and mother liquor B. The solid A was treated, as usual, with phenylhydrazine and sodium acetate giving an osazone of m.p. 160°, which indicated either arabinose or xylose. A syrupy solution of the crystals was therefore treated with excess of diphenylhydrazine with sufficient alcohol to form a clear solution. On boiling for half an hour and cooling, crystals separated which, after recrystallisation, had m.p. 199°. This points to arabinose diphenyl-hydrazone, as it is difficult to obtain a melting-point for this substance higher than 200°.

The mother liquor B gave an osazone of m.p. 160°, identified as xylose osazone. The presence of xylose was confirmed as under.

(*a*) By Bertrand's reaction (see p. 427). The solution readily gave boat-shaped needles of the xylono-cadmium salt

$$(C_5H_9O_6)_2Cd + CdBr_2 + 2H_2O.$$

(*b*) A portion of the syrup was boiled with paraformaldehyde. After a time white crystals, m.p. 55°, separated : *d*-xylose diformal has m.p. 56°.

Another hydrolysis product was concentrated to a syrup, taken up with alcohol and evaporated three times. The syrup was dried over sulphuric acid, precipitated with hot absolute alcohol, and filtered immediately. As xylose is much more soluble in hot alcohol than the other three sugars, the filtrate contained xylose in a comparatively pure condition. The residue was dried and just sufficient water added to dissolve the crystals, and the solution was again left in a desiccator. The crystals that separated had m.p. 167°

[1] M. H. O'Dwyer, *Biochem. J.*, 1923, **16**, 503.

and $[\alpha]_D$ in 5 per cent. aqueous solution + 82°; phenylhydrazone, m.p. 156°. Galactose has m.p. 168° (rapid) and $[\alpha]_D$ + 80·3°.

The mother liquor was concentrated and treated several times with hot absolute alcohol. By this means mannose was removed, and the residue which remained after recrystallisation from absolute alcohol gave m.p. 160°, $[\alpha]_D$ in 10 per cent. aqueous solution + 103°, agreeing with the figures for *l*-arabinose.

Fractions A and B of the Hemicellulose from White Oak.—Fraction A was obtained by precipitation with acetic acid, and fraction B by subsequent addition of 2 volumes of alcohol. Both fractions from sapwood contain some 10 per cent. of anhydroglucose units, whilst those from heartwood contain less than 1 per cent., but on removal of the glucose by means of taka-diastase the fractions from both become chemically similar.

The following analytical figures per cent. were obtained before removal of glucosan. The figures for B under uronic anhydride are for monomethyluronic anhydride.

HEMICELLULOSE A

	$[\alpha]_D^{20°}$. (2 per cent. NaOH).	Ash.	Uronic Anhydride.	Xylan.	OMe.
Sapwood *	− 63	1·0	9·8	82·5	2·0
Heartwood *	− 83	0·8	10·7	85·0	2·2
HEMICELLULOSE B					
Sapwood †	− 63·6	3·9	13·9	52·2	1·95
Heartwood †	− 53·0 (water)	3·0	17·2	79·5	2·09

* Kiln dry, 41°. † Oven dry.

	Uronic Anhydride.	OMe.	Xylan.
Polysaccharide	17·9	3·1	81·75
Complex of 6 xylose + 1 methyl hexuronic acid requires	17·8	3·1	80·24

All fractions give two common products on hydrolysis, *viz.*, xylose and a water-soluble polysaccharide of $[\alpha]_D^{20°}$ − 51·2°, in the proportion of 2 : 3. The polysaccharide is a complex of one monomethyl hexuronic acid and six xylose residues.

Hydrolysis was achieved either by prolonged action of taka diastase (95–210 hours, 38°, *p*H 4·5) or by dilute mineral acids. The xylan was estimated as xylose by Lane and Eynon's method. The polysaccharide (from hemicellulose A), precipitated and purified by alcohol, gave the figures shown on p. 419, ash free, per cent.

Hydrolysis of the Polysaccharide.—A sample (4·66 g.) from fraction B was heated 3 hours at 100° with 1 per cent. sulphuric acid. After treatment with barium carbonate a barium salt 1·35 g., $[\alpha]_D^{20°}$ + 70° and xylose 2·23 g. were obtained. The barium salt gave Ba, 16·9; uronic anhydride, 42·9; OMe, 7·0; free aldehyde, 6·9 per cent.; furfural phloroglucide equivalent to 41 per cent. of xylose.

The Hemicellulose of Mesquite Wood.[1]—Extraction was made at ordinary temperature with 5 per cent. NaOH. Fractions A and C were obtained as under wheat bran (p. 408), fraction B being neglected. A and C were separated by solution in 2·5 per cent. NaOH and addition of alcohol to give 35 per cent. (for A1 and A2) and 55 per cent. (C1 and C2). The following results were obtained on analysis.

FREE HEMICELLULOSE FROM MESQUITE WOOD

	A1.	A2.	C1.	C2.
Uronic anhydride	10·2	17·5	18·0	17·8
Xylan	84·5	79·1	82·0	81·8
Methoxyl	1·96	—	3·05	—
"Body X"	6·6	5·2	0·5	0·3
Minimum molecular weight	1732	1009	976	993

It would appear that the last three fractions are identical. Hydrolysis of A1 and C1 with 1 per cent. H_2SO_4 was not complete but 2·5 per cent. acid proved satisfactory. The sugars were removed by crystallisation from alcoholic solution and the uronic acid precipitated as barium salt. It was found to be a complex of one molecule of uronic acid with two pentose groupings.

To examine the residual hemicellulose the wood, after extraction as above (5 per cent. NaOH), was chlorinated four times and extracted with alkali after each treatment. The fractions were obtained as before. The results show that the residual hemicellulose is very similar to the free hemicellulose. For example :—

[1] L. Sands and W. Y. Gary, *J. Biol. Chem.*, 1933, **101**, 573; L. Sands and P. Nutter, *ibid.*, 1935, **110**, 17.

RESIDUAL HEMICELLULOSE FROM MESQUITE WOOD

	After two chlorinations.				After four chlorinations.			
	A1.	A2.	C1.	C2.	A1.	A2.	C1.	C2.
Uronic anhydride . .	8·4	14·3	14·7	16·2	3·3	5·9	11·3	15·9
Xylan	77·1	76·7	80·1	81·2	32·1	65·3	78·0	79·0
Methoxyl groups per one uronic acid . . .	1·03	0·91	1·04	0·96	0·66	0·89	0·89	0·76
Xylan groups " ditto " .	12·3	7·2	7·3	6·7	13·1	14·9	9·3	6·7

The second A1 fraction contained 56 per cent. of the dark-coloured " body X " which is a common residuum from hydrolysis. It is probably a condensation product of lignin and furfural. In the case of hemicellulose from cottonseed hulls [1] it is found that by giving each fraction several chlorination or bromination treatments " X " is removed and white products result. The effect of chlorination with and without sulphite extraction has also been studied by Norman.[2]

ESPARTO CELLULOSE

The existence of more than one type of cellulose has been the subject of considerable discussion. It was thought that in addition to cotton cellulose, there might be other celluloses in which a proportion of the units are pentose groupings ; or they might be compounds of cellulose (of the hexose type) with hemicelluloses of the pentose type.

Irvine and Hirst [3] examined esparto cellulose with a view to investigating these problems. Esparto grass, digested with sodium hydroxide under pressure, gives about half its weight of " cellulose ", which in many ways functions as a homogeneous substance and is a valuable paper-making raw material. Esparto cellulose, however, contains " pentosan ", which can be eliminated only by repeated digestion with alkaline solutions. It yields about 80 per cent. of cellulose of the true hexose type.

Esparto cellulose might be, therefore, either a mixture of polysaccharides derived from hexose and pentose units, or a mixed polysaccharide in which the hexose and pentose units were condensed together.

The cellulose used (*loc. cit.*) gave 12 per cent. of furfural, corresponding to 18·5 per cent. of pentosan. This constituent was

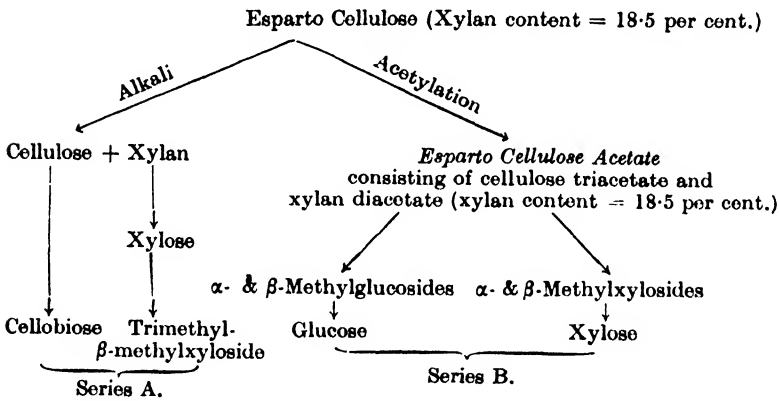
[1] E. Anderson *et al.*, *J. Biol. Chem.*, 1938, **126**, 175.
[2] A. G. Norman, *Biochem. J.*, 1935, **29**, 2259.
[3] J. C. Irvine and E. L. Hirst, *Chem. Soc. Trans.*, 1924, **125**, 15.

removed by extraction with boiling sodium hydroxide solution. Three products were therefore examined—(*a*) esparto cellulose purified from lignin, (*b*) the pentosan constituent extracted from it, and (*c*) the pentosan-free cellulose remaining. Product (*b*) proved to be a xylan, and product (*c*) was converted both into cellobiose and into 2 : 3 : 6-trimethyl glucose, and appeared to be chemically identical with cotton cellulose.

Product (*a*) was acetylated and gave, without loss of pentosan, a product containing hexosan triacetate and pentosan diacetate, the yield being almost quantitative. By the action of methyl alcoholic hydrochloric acid this was converted into a mixture of methylglucoside and methyl xyloside from which a mixture of glucose 84 per cent. and xylose 16 per cent., was obtained.

This ratio of 4 to 1, however, was variable, and the cellulose may contain any proportion of xylan from 20 per cent. downwards which seems to indicate that the cellulose is a mixture, or more probably a solid solution, of hexose and pentose units.

The experimental work is summarised in the scheme below.



The esparto cellulose acetate was soluble in chloroform and acetone, insoluble in alcohol; $[\alpha]_D$ (chloroform) about $-20°$. Found: C, 49·8; H, 5·46; $CH_3.CO$, 44·9; furfural, 6·9. Calculated for a mixture containing 18·5 per cent. of xylan before acetylation: C, 50·0; H, 5·55; $CH_3.CO$, 43·6; furfural, 6·8 per cent., showing that no loss of pentosan had occurred.

Conversion of Esparto Cellulose Acetate into Methylglucoside and Methylxyloside.—4 g. of the acetate were heated with 60 ml. of methyl alcohol containing 1·5 per cent. HCl at 130° for 120 hours. After treatment with animal charcoal 2·49 g. of syrup were obtained (about 92 per cent.), which crystallised, m.p. 105–150°; $[\alpha]_D + 90°$

(acid methyl alcohol). Recrystallisation (ethyl alcohol) gave pure α-methylglucoside (m.p. 164°). A polarimetric study of the original mixed product showed that it consisted of α- and β-methylglucosides and α- and β-methylxylosides ; thus 0·414 g. in 25 ml. of 3 per cent. aqueous HCl heated at 100° with a little charcoal gave the following figures (*c*, 1·656) :—

Time in minutes . .	0	45	90	240	
$[\alpha]_D$	+ 90°	59·1°	46·2°	45·6° *	(constant)

* Concentration calculated on weight of sugar formed during hydrolysis.

The equilibrium value for a mixture of glucose (84 per cent.) and xylose (16 per cent.) is + 46·6°.

The Xylan from Esparto Cellulose.—Haworth and Hirst have shown (*loc. cit.* p. 437) that in this xylan an arabinose residue forms the terminal group of a chain of 16–17 xylose residues. A portion of the arabinose can be removed by hydrolysis, leaving a fairly definite product described as xylan A. The chain-length of xylan A (from viscosity) is the same as that of the original xylan, but if the arabinose is completely removed by the action of oxalic acid (xylan B), it falls to one-half its value. The chain-length of all three types determined by end-group assay is, however, the same, *viz.* about 18 units.

The properties of these products are given below.

Methylated product.	Xylan.	Xylan A.	Xylan B.
M.P.	197°	202°	—
$[\alpha]_D$	− 98·3 †	—	− 91·2 †
	− 109·5 ‡	− 111 ‡	—
Apparent chain-length (units) by viscosity	92	88	44

† In chloroform. ‡ In 6 per cent. NaOH.

Preparation of Xylan.—Esparto half stuff (500 g.) was extracted at the boil for 12 hours with 5 l. of 12 per cent. NaOH solution. After cooling to 35° an equal volume of methylated spirit was added. The precipitate settled in 12 hours and after separation was triturated with a mixture of glacial acetic acid and alcohol (1 : 1), then with water, alcohol and ether in succession. Yield, 125 g.

Hydrolysis was effected by boiling 2·3 g. with 110 ml. of 3 per cent. nitric acid for 1 hour as described on p. 426. After separation of xylose the residual syrup, when treated with benzylphenyl hydrazine as p. 427 (*c*), gave the arabinose derivative, m.p. 171°.

Preparation of Xylan A.—Xylan (20 g.) was boiled for 1 hour with *N*/200-nitric acid (2 l.). The xylan A was separated by centrifuge and triturated with water, alcohol and ether. Yield, 17·5 g. The clear liquid contained arabinose detected as above.

Xylan A was methylated in the usual way giving finally a fraction with OMe content 38 per cent. On hydrolysis with methyl alcoholic HCl the following products were obtained: (*a*) 2 : 3-dimethyl methylxyloside (85–90 per cent.), (*b*) 2 : 3 : 5-trimethyl methyl arabinoside (2 per cent.), (*c*) 2 : 3 : 4-trimethyl methylxyloside (4 per cent.), (*d*) 2-monomethyl methylxyloside (6 per cent.).

Preparation of Arabinose-free Xylan.—Xylan (15 g.) made into a paste with water was diluted with water (1·6 l.) and the mixture heated at 100° for 2 hours. Oxalic acid (4·5 g.) was added and the heating continued for 5 hours more. At this point 8 per cent. of arabinose had been formed and the amount was not increased on further heating. Yield of product 86 per cent.

Xylan

Xylans are widely distributed, especially in lignified cells, and form a high proportion of the alkali-soluble extract known as " wood gum ". This substance, which is probably a cell wall constituent and not a gum in the usual sense, represents the caustic alkali extract of lignified tissues. Its proportion is considerable in the hard woods, particularly beech and birch, where it amounts to 20 to 26 per cent. of the total, but low in the conifers, usually 4 to 6 per cent., some species, *Abies firma* for example, giving as little as 1 per cent. Wood gum usually contains methoxyl 2 to 3 per cent., and in dilute NaOH solution is lævorotatory, the values recorded for $[\alpha]_D$ ranging around 92–96° for birch, 70–80° for beech, and 75° for white oak. The xylan content of the wood gum both from beech wood and from straw, is about 83–86 per cent. The wood gum from cherry wood also is rich in xylan,[1] but it may be noted that the true gum from the bark of the cherry tree gives arabinose on hydrolysis. Highly purified preparations of xylan [2] are white powders, which swell and form colloidal solutions in water, but are readily soluble in dilute alkali and sodium carbonate solutions. They are insoluble in alcohol and similar solvents, and give no blue colour with the zinc-chlor-iodide reagent; with the phloroglucinol reagent they are coloured only on warming, whereas lignin reacts in the cold. Xylan

[1] E. W. Allen and B. Tollens, *Ann.*, 1890, **260**, 296; E. Kröber and C. Rimbach, *Z. angew Chem.*, 1902, **15**, 508.

[2] H. I. Wheeler and B. Tollens, *Ann.*, 1889, **254**, 321.

and araban in alkaline solution are precipitated by Fehling's solution, giving difficultly soluble copper alkali compounds which, according to Heuser,[1] have the composition $2C_5H_8O_4$: Cu : 2Na.

I. **Preparation of Xylan.**—It is advisable in all cases to digest the raw material with a cold 2 per cent. ammonia solution for one or more periods, each of one day.

(*a*) *The Preparation of Xylan from Wood Gum* (Wheeler and Tollens).—Beech wood sawdust is exhaustively treated with 2 per cent. ammonia, washed with water and extracted with 5 per cent. NaOH for 48 hours at ordinary temperature with frequent shaking. The extract is filtered and an equal volume of 95 per cent. alcohol added. The precipitate is separated by decantation and collected on a filter cloth, in which it is squeezed by hand and washed with alcohol. As it retains alkali, it is suspended in alcohol and treated with hydrochloric acid until acid, then washed with alcohol and dried with ether.

(*b*) *Preparation of Xylan from Straw Cellulose* (Heuser [2]).—300 g. of bleached straw cellulose (about 100 g. of dry substance) are boiled for three-quarters of an hour with 150 g. NaOH in 2·3 l. of water. The liquid is filtered on a Buchner funnel without a paper, and to the filtrate 1 l. of Fehling's solution is added. The bulky precipitate is filtered through fine-wire gauze, pressed and kneaded twice with 300 ml. of 80 per cent. alcohol, and finally converted into a fairly fine suspension in 1 l. of 96 per cent. alcohol. Hydrochloric acid gas is passed in until the precipitate becomes white. The precipitate is then separated and washed many times by decantation with 30 per cent. alcohol and finally left 20 hours with ether. Yield, 22 g.; xylan content by furfural estimation, 96 per cent.

To avoid the lengthy copper precipitation the sodium hydroxide solution may be mixed with an equal volume of 95 per cent. alcohol and treated with HCl gas. The product in this case is less pure.

II. **The Hydrolysis of Xylan to Xylose.**—The wood gum is usually hydrolysed with dilute sulphuric acid. Dilute nitric acid gives very good yields (p. 426) and is recommended.

The apparent loss of pentose sugars during the hydrolysis of pentosans is considerably greater than the destruction of the pure sugar when heated with acid under comparable conditions. Xylose is more readily decomposed than arabinose. Tollens early (1892) found that when the pure sugars were heated with twenty-five times their weight of 10 per cent. sulphuric acid for 12 hours only 73·8

[1] E. Heuser, *Papier Fabrik.*, 1927, **25**, 239.
[2] E. Heuser, *J. Prakt. Chem.*, 1921, **103**, 88; *ibid.*, 1922, **104**, 261.
[3] E. Heuser and G. Jayme, *J. Prakt. Chem.*, 1923, **105**, 232.

per cent. of xylose and 84·5 per cent. of arabinose remained unaltered.

1. *Hydrolysis of Xylan with Sulphuric Acid.*—The following is a typical method of working [1]:—

50 g. of beech wood gum are heated on a boiling-water bath with 400 ml. of water and 20 g. of conc. sulphuric acid. After about 12 hours the liquid is filtered, neutralised with calcium carbonate, and the filtrate concentrated to a syrup. This contains unchanged gum and calcium sulphate, which are removed by taking up in warm alcohol, filtering and evaporating. These operations are repeated. When the gum is removed the liquid, on evaporating, crystallises after several days. Total yield, 26 per cent. of pure xylose.

2. *Hydrolysis of Xylan with Dilute Nitric Acid* (Heuser and Jayme [2]).—This process possesses a number of advantages. No furfural is formed and the yield is consequently higher. Thus from a sample of xylan a yield of 68 per cent. of xylose was obtained by the sulphuric acid method, whilst with nitric acid the yield was 85 per cent. Less barium carbonate is needed for neutralisation and a saving of time is effected since the treatment of a large precipitate of barium sulphate is avoided.

Experiment showed that the maximum of xylose was obtained with 3 per cent. nitric acid acting for 1 hour at 100°, and amounted to 97 per cent. of theoretical. On heating with forty-five times its weight of 3 per cent. nitric acid under these conditions the xylan dissolved in 1 to 2 minutes. An estimation by the Bertrand method [3] at this stage showed an apparent xylose content of nearly 60 per cent, of theory, although only a colloidal body, probably a xylodextrin, could be obtained.

Procedure.—10 g. of xylan are heated under a reflux, with 450 g. of 3 per cent. nitric acid and raised to the boiling-point. After an hour from this point the solution becomes clear. It is cooled and neutralised with barium carbonate, filtered and evaporated at 80–90°. Barium nitrate separates and is removed, the crystals being washed with a little cold water and the washings added to the filtrate. When the liquid is concentrated to some 50 ml. the removal of the crystals is discontinued, and when the liquid has become viscous it rapidly crystallises on working with a glass rod. The mass is finely powdered, ground with 100 ml. of alcohol, brought into a round flask with 300 ml. of additional alcohol

[1] H. I. Wheeler and B. Tollens, *Ann.*, 1889, **254**, 308; E. Salkowski, *Zeit. Physiol. Chem.*, 1901, **34**, 35, 240; E. Heuser *et al.*, *J. Prakt. Chem.*, 1922, **104**, 279.

[2] E. Heuser and G. Jayme, *J. Prakt. Chem.*, 1922, **105**, 232.

[3] G. Bertrand, *Bull. Soc. Chim.*, 1906, **35**, 1285.

and boiled for 3 hours under reflux with shaking. After filtering, the alcohol is distilled off, and at a volume of 50 ml. the liquid is poured off and the flask washed out with alcohol. On cooling crystallisation begins at once.

III. **The Identification of Xylose.**—The following reactions are useful :—

(*a*) *Preparation of the Osazone.*—1 g. is mixed with a solution of 2 g. phenylhydrazine hydrochloride and 3 g. sodium acetate in 20 ml. of water. If no precipitation takes place after half an hour, not more than a trace of mannose is present. The mixture is then heated on the water bath for 1½ hours. It should remain clear if glucose is absent. On cooling, xylose osazone comes out in yellow crystals, which are washed with water and crystallised from acetone. The mass should dissolve completely in sufficient cold acetone, any residue being probably glucosazone. A further crystallisation from hot water, and finally from acetone, gives a product m.p. 157°.

(*b*) *Preparation of Xylonic Acid-Cadmium Bromide Double Salt.*—1 g. of xylose in 20 ml. water is mixed with 2·5 g. of cadmium carbonate and gradually with cooling mixed with 2 g. of bromine. The mixture is allowed to stand for 20 hours, then brought to boiling-point, and concentrated to 7 ml. The liquid is filtered at the boiling-point and the residue washed with boiling water. The filtrate is mixed with alcohol, and the double salt comes out in the characteristic boat-shaped crystals, m.p. 163° (*cf.* p. 418).

(*c*) *Detection of small amounts of Arabinose in Xylose Preparations.*—After removing the bulk of the xylose by crystallisation the syrup (0·5 g.) in 75 per cent. alcohol (6 ml.) is treated with α-benzyl-phenylhydrazine (0·5 g.). After 12 hours arabinose benzyl-phenyl-hydrazone is precipitated and is crystallised from alcohol, m.p. 172°.

Araban

The presence in the cell wall of substances yielding arabinose alone, on hydrolysis, is by no means common. The wide distribution of pectin—of which an araban is a component—makes it probable that the arabinose occasionally obtained from hemicellulose preparations is derived from that source. The cell membranes of fruits and seeds (*e.g.* bran, p. 408, maize, p. 411, etc.) appear to contain araban, but arabinose units more often occur united with other sugars as in the xylo-araban of esparto cellulose (p. 423), and especially in galacto-arabans, which are of frequent occurrence. Galacto-arabans are found [1] in the bean leaf (12 per cent.), bean pod (30 per cent.), sweet pea (30 per cent.) and Iceland moss (10 per cent.). These

[1] H. W. Buston, *Biochem. J.*, 1935, **29**, 213; *ibid.*, 1934, **28**, 1028.

are non-lignified tissues. In fruits the amount ranges from 15 to 35 per cent. (figures include pectin). Grass (lignified) contains about 6 per cent. of galacto-araban with 20 per cent. of xylan.[1] The ε-galactan of larch is also a galacto-araban (p. 439).

Arabinose has been identified among the products of the hydrolysis of white spruce (*Picea canadensis*) and in the hemicellulose from beech and American white oak.[2] But the more usual sources of arabinose are from the vegetable gums. The hydrolysis of the gum and the isolation of the sugars follow on similar lines to those described under wood gum. General methods for the examination of an araban will be found under the araban of pectin (p. 523).

Mannan

Substances yielding mannose on hydrolysis are very widely distributed. They occur in woods, being characteristic of the gymnosperms. They have been detected in a whole series of American woods (*Pinus* species), white pine (*P. strobus*), pitch pine (*P. rigida*), and Japanese larch (*Laryx leptolepis*). It is probable that mannan occurs in all gymnosperms, and Bertrand[3] considered that in them mannan fills the place occupied by xylan in the hard woods. In spruce (*Picea excelsa*) it is found not only in the wood, but also in the needles and seeds.[4] Mannan has, however, been detected in small amount in some hard woods, *e.g.* in white oak (*Quercus pedunculata*), but Schorger and others[5] failed to obtain mannose by direct hydrolysis in a series of deciduous woods (*e.g.*, *Populus tremuloides*), and Dore reports its absence from live oak (*Quercus agrifolia*). The following table gives some idea of the distribution of mannan in the woods of forest trees :—

Mannan in Woods

Douglas fir (*Pseudotsuga taxifolia*)	6·65	*
Western larch (*Larix occidentalis*)	5·13	*
Arborvitæ (*Thuja occidentalis*)	1·44	*
White spruce (*Picea canadensis*)	7·12	*
California swamp pine (*Pinus muricata*)	3·07	*
Western white pine (*Pinus monticola*)	6·93	*
Redwood (*Sequoia sempervirens*)	3·21	†
Western yellow pine (*Pinus ponderosa*)	6·37	†

* A. W. Schorger, *Ind. Eng. Chem.*, 1917, 9, 748.
† W. H. Dore, *Ind. Eng. Chem.*, 1920, 12, 476.

[1] H. W. Buston, *Biochem. J.*, 1935, **29**, 213 ; *ibid.*, 1934, **28**, 1028.
[2] E. C. Sherrard and G. W. Blanco, *Ind. Eng. Chem.*, 1923, **15**, 611 ; C. A. Browne and B. Tollens, *Ber.*, 1902, **35**, 1466 ; M. H. O'Dwyer, *Biochem. J.*, 1923, **17**, 501.
[3] G. Bertrand, *C.R.*, 1899, **129**, 1025.
[4] J. B. Lindsey and B. Tollens, *Z. angew. Chem.*, 1892, **5**, 154.
[5] A. W. Schorger and D. F. Smith, *Ind. Eng. Chem.*, 1916, **8**, 494, and W. H. Dore, *ibid.*, 1920, **12**, 984.

The proportion of mannan in woods is thus usually 3 to 6 per cent. These values are probably low, although the use of an improved method of estimation [1] (p. 445) on the whole confirms them. The mannan is largely or wholly associated with cellulose as shown by the following results [1] :—

DISTRIBUTION OF MANNAN IN WOOD

	Per cent. on the Wood.			Per cent. on the Cellulose.	
	Mannan total.	Mannan not in Cellulose.	Cellulose.	Mannan in Cellulose.	Xylan in Cellulose.
Canadian spruce	5·75	2·6	63·72	4·92	9·19
Douglas fir .	7·06	0·2	57·46	10·14	5·54
Silver fir . .	5·96	2·3	52·90	7·01	7·34
Redwood . .	2·62	0·3	49·08	4·77	11·61

Wood pulps consequently contain mannans. Thus a sulphite pulp free from lignin had the following composition [2] : Cellulose, 87·0 ; mannan, 6·0 ; xylan, 4·5 ; and lævulan, 2·5 per cent.

Mannan occurs in much larger quantities in seeds and mucilages, notably in the ivory nut and in salep mucilage. It has also been obtained from yeast gum and from *Cetraria islandica*.

The association of mannan with polysaccharides based upon glucose is of interest. *Tubera Salep*, for example, contains mannan 30 ; hexose dextrins 13 ; and starch 30 per cent. Konjak mannan is said to be a molecular compound of glucose and mannose units. The mannans of ivory nut and salep are formed entirely of chains of mannopyranose units combined by β-1 : 4-glucosidic linkages.[3] The same structure is found in alginic acid,[4] which is built up of β-*d*-mannuronic acid residues linked through positions 1 and 4. Yeast mannan, on the other hand, has a structural unit consisting of mannopyranose residues arranged in a branched chain.[5]

Some of these are described below.

I. Isolation of Mannan, Mannan A and Mannan B from the Perisperm of Phytelephas Macrocarpa (Ivory Nut).—Early workers, *e.g.* Baker and Pope,[6] by extraction with cold alkali, obtained up to 70 per cent. of a carbohydrate ($[\alpha]_D$ −44·1) which

[1] A. Nowotnowna, *Biochem. J.*, 1936, **30**, 2177.
[2] E. Hägglund and F. W. Klingstedt, *Cellulosechem.*, 1924, **5**, 57.
[3] F. Klages, *Annalen*, 1934, **509**, 159 ; **512**, 185 ; 1936, **523**, 224.
[4] E. L. Hirst *et al.*, *J. Chem. Soc.*, 1939, 1880.
[5] W. N. Haworth *et al.*, *J. Chem. Soc.*, 1937, 784 ; 1941, 833.
[6] J. L. Baker and T. H. Pope, *Proc. Chem. Soc.*, 1900, **16**, 72.

gave only mannose on hydrolysis. The residue left after alkali extraction also gave mannose and as it responded to the zinc chloride-iodine test for cellulose it was described as a " manno-cellulose ". Lüdtke [1] obtained two forms of mannan (A and B) which differed in solubilities and he confirmed the presence of cellulose.

Lüdtke[1] found that the carbohydrates of the seeds are easily soluble in Schweizer's solution to which ammonium carbonate has been added. On addition of 2*N*-NaOH the mannans are precipitated, leaving cellulose (7·8 per cent.) in solution.

Mannan A was extracted from the precipitate by means of 5 per cent. NaOH, leaving a mannan B insoluble. Mannan A is identical with the product isolated by Baker and Pope. It is easily soluble in Schweizer's solution of a definite concentration, whilst B is insoluble. Mannan B, however, goes into solution on addition of ammonium carbonate. Mannan B gives mannose in almost quantitative yield, and has the interesting property of giving a blue colour with zinc chlor-iodide. Their properties are shown in the table :—

	Mannan A.	Mannan B.	Cellulose.
$[\alpha]_D^{20}$ in *N*-NaOH . . .	−44·94	insoluble	insoluble
$[\alpha]^{20}$ in Schweizer's solution .	+0·88	almost insoluble	−3·44
$[\alpha]^{18}$ ditto, after addition of $AmHCO_3$	+0·61	+0·52	−2·05
$[\alpha]_D^{20}$ of Acetate (in $CHCl_3$) .	−29·41	−25·2	−19·3
Zinc chlor-iodide . . .	−	+	+

By the aid of these reactions, followed under the microscope, some light has been thrown on the nature of the structures of the cell wall of the ivory nut. Treatment with chlorine dioxide removes the substance of the middle lamella, which is identified by some with pectin and amounts to one-third of the weight of the nut. The inner membrane, which is coloured with zinc chlor-iodide, is a cellulose membrane, and the middle lamella, which only colours feebly, is composed of a mixture of mannan A and mannan B.

Preparation of Mannan A.—Ivory nut chips are treated three successive times with chlorine dioxide and sodium sulphite solution by the procedure of Schmidt (p. 359). The residue is then treated with ten times its weight of 5 per cent. NaOH and left for 2 days at ordinary temperature. The liquid is made acid with acetic acid and the mannan washed with water and with alcohol and ether.

[1] M. Lüdtke, *Ann.*, 1927, **456**, 202.

Preparation of Mannan B.—The residue from the above, from which mannan A has already been extracted, is used. A further extraction with 10 per cent. NaOH is given, after which the residue is treated with 100 ml. of 25 per cent. ammonia solution to each gram of substance. Copper hydroxide is added little by little until each 4 mgm. equivalents of $C_6H_{10}O_5$ have received 7–10 mgm. equivalents. After shaking for 12 to 15 hours at ordinary temperature, CO_2 is passed into the solution. Excess should be avoided, otherwise a slimy precipitate forms. A small suspension is removed by the centrifuge and the solution is mixed, with shaking, with sufficient 2*N*-NaOH, added gradually until the liquid corresponds to 0·2*N*-NaOH. The precipitate is removed and washed in the centrifuge with a mixture of ammonia and sodium hydroxide. It is then dissolved in water, the solution acidified with 50 per cent. acetic acid, and the mannan separated by adding an equal volume of methyl alcohol, after which it is washed with 5 per cent. acetic acid and finally with methyl alcohol. The yield of dry mannan B is about 18 per cent. on the dry extracted ivory nut. A further 7 per cent. is left in the extract with 10 per cent. NaOH which may be recovered by acidification and solution of the dry precipitate in Schweizer's solution. After some hours mannan A dissolves, whilst mannan B for the most part remains.

The ivory nut therefore contains about 5 per cent. of cellulose, less than 66 per cent. of mannans A and B (in the ratio of 1 : 2), and about 33 per cent. of substances removable by chlorine dioxide.

Preparation and Methylation of Mannan A (Klages).—300 g. of ivory nut shavings were shaken 1 day with water and acetone, then treated for 5 days with chlorine dioxide, washed 1 day with water and dried. 50 g. portions were then treated for 3 days with 1 litre of 5 per cent. NaOH, the extract acidified with 70–80 ml. glacial acetic acid and an equal volume of methyl alcohol added. The precipitate was collected and digested overnight in 2 l. of methyl alcohol, and then again extracted for 1 day with methyl alcohol and ether. Yield 35–40 per cent.; $[\alpha]_D^{20}$ — 44·7°.

Methylation was difficult owing to resinification which was avoided by using benzene as a solvent. About 15 g., ground under NaOH, were suspended in 45 per cent. NaOH, washed into a flask (total volume about 500 ml.) and 100 ml. of dimethyl sulphate slowly added with stirring and cooling, followed by 50 ml. of benzene. On warming to 80° (reflux) reaction began and when completed 350 ml. of dimethyl sulphate were added over 2 hours. The mixture was heated for an hour at 100° mixed with 1 litre of water and the

methyl mannan separated by shaking out three times with chloroform at 45–50°. The product had QMe, 42–44 per cent. To complete the methylation it was dissolved in 50 ml. of benzene and 350 ml. of 45 per cent. NaOH added, followed by 300 ml. of dimethyl sulphate.

The methyl derivative was hydrolysed by dilute acid. It was dissolved in so much water that on addition of $N/10$-HCl a 1 per cent. solution was formed. After 16 hours hydrolysis was complete and the liquid was treated with barium carbonate as usual. Three extractions with chloroform in the cold removed 1·1 to 1·4 per cent. of tetramethyl mannose: The extracted liquid was evaporated to dryness and the residue, extracted many times with hot chloroform, gave crude 2 : 3 : 4-trimethylmannose (87 per cent.).

Hydrolysis for a shorter time with similar treatment gives oligosaccharides. They are methylated by Purdie's method and the simple methylated sugars isolated by high vacuum distillation.

II. **Hydrolysis of Mannans for the Maximum Yield of Mannose.**—According to Lüdtke,[1] the following procedure gives an optimum yield : Sulphuric acid 75 per cent. is allowed to act for 12 hours at 20°. The liquid is diluted with fifteen times the volume of water and heated on the water bath for 5 hours ; for example the mannan, 2·3 g., is treated with 16 ml. of 75 per cent. acid as above, 240 ml. of water are then added, and the solution heated for 5 hours on the water bath. The acid is removed by means of baryta, the precipitate washed with boiling water and the filtrate concentrated to 100 ml.

Mannose may be isolated and identified by precipitation with *p*-bromophenylhydrazine.

III. **Estimation of Mannose by Hypoiodite Solution** (Lüdtke)[2]—A solution containing 20–30 ml. of $N/10$ iodine, 20 ml. each of 0·2 molar sodium carbonate and bicarbonate, water to 200 ml. is prepared. 30–60 mgm. of mannose in solution are treated with the above quantity of reagent for 100–130 minutes in the dark. The solution is then acidified with 25 per cent. sulphuric acid and the excess of iodine titrated as usual.

ml. of $N/10$ iodine consumed $\times$ 9·005 = mannose in mgm.

NOTE.—For the estimation of mannan in wood, see p. 444.

GALACTAN

Among the hydrolysis products of wood a galactose-yielding carbohydrate was early observed, and the work of Schorger and

[1] M. Lüdtke, *Ann.*, 1927, **456**, 213, 216.
[2] *Ann.*, 1927, **456**, 220.

Smith [1] showed that galactans are characteristic of coniferous woods. Their presence in small amounts has been ascertained in other woods, such as those of *Populus tremula* and *Quercus agrifolia*.[2]

A water-soluble galactan is characteristic of larchwood. The so-called ϵ-galactan or galacto-araban of Western larch (see below) has been closely examined.[3] It is a white powder soluble in cold water to a mobile liquid and is not precipitated by lead acetate from this solution: $[\alpha]_D^{20°} + 12{\cdot}1°$. Yield of furfural, 6·2 per cent. The araban is largely removed by hydrolysis with 0·02 *N*-sulphuric acid at 100° though complete removal is not possible. The wood of European larch is said to yield a pure galacto-araban,[4] giving negative results for the presence of glucose, mannose, methoxyl and uronic acid. On hydrolysis it gives 12 per cent. of arabinose and 82 per cent. of galactose (p. 439).

A polygalactose has been shown to be the basis of agar.[5] The linear chain is composed of nine *d*-galactose residues joined by 1 : 3-glucosidic linkages. At the reducing end of the chain and joined to it at C4 is a residue of *l*-galactose which is itself esterified at C6 with sulphuric acid.

Preparation of the Water-soluble ϵ-Galactan from the Western Larch (*Larix occidentalis*).[6]—This wood contains 8 to 17 per cent. of galactan. 500 g. of the sawdust are boiled under reflux with 2·5 l. of water for 24 hours with frequent shaking. The extract is filtered through cheese cloth and the residue again heated for 24 hours with 1½ l. of water. A third extraction (6 hours) may be given. The total extract is concentrated to 2 l.

Hydrolysis to Galactose.—To the 2 l. of solution are added sufficient sulphuric acid to give 2·5 per cent. H_2SO_4 by weight. The liquid is boiled for exactly 10 hours under reflux and immediately neutralised by adding barium carbonate in slight excess. The mixture is shaken and heated until it gives a neutral reaction with Congo red paper. When neutral the precipitate is at once filtered and washed with hot water. Some barium always remains, and must be removed by adding sulphuric acid until no further precipitate appears. The liquid should still not change the colour of Congo red paper.

Basic lead acetate solution in excess is added, the precipitate

[1] A. W. Schorger and D. F. Smith, *Ind. Eng. Chem.*, 1916, **8**, 494.
[2] W. H. Dore, *J. Ind. Eng. Chem.*, 1920, **12**, 476.
[3] E. V. White, *J. Amer. Chem. Soc.*, 1941, **63**, 2871; 1942, **64**, 302, 1507; E. L. Hirst, J. K. Jones and W. G. Campbell, *Nature*, 1941, **147**, 25.
[4] F. C. Petersen *et al.*, *Cellulosechem.*, 1934, **15**, 109.
[5] W. G. Jones and S. Peat, *J. Chem. Soc.*, 1942, 225.
[6] A. W. Schorger and D. F. Smith, *Ind. Eng. Chem.*, 1916, **8**, 494; E. L. Hirst, J. K. Jones and W. G. Campbell, *Nature*, 1941, **147**, 25.

filtered off and the excess of lead in the filtrate removed with hydrogen sulphide. A pale straw-coloured filtrate results.

To obtain crystals of galactose this liquid is concentrated (low pressure) to about 76 per cent. total solids, which may be determined on the sugar scale of the Abbé refractometer. An equal volume of glacial acetic acid is added with shaking. Crystals should form at once, and after 2 or 3 days crystallisation is complete. After filtering as dry as possible, the mass is mixed with glacial acetic acid to a thick paste and filtered. This is repeated once with glacial acetic acid and several times with 95 per cent. alcohol until the filtrate shows no acid reaction. A final washing with absolute alcohol is given, and after leaving to dry, the crystals are dried in a vacuum desiccator, or in a vacuum oven at 70° for 3 hours. Yield of *d*-galactose 15 to 18 per cent. on the sawdust.

Preparation of Galactan from the Eastern Larch (*Larix decidua*).[1]—Alcoholic precipitation did not remove impurities from the aqueous extract so that the lead acetate-tannic acid process of Schorger and Smith [2] was used. A white powder (3 per cent. of the wood) was obtained which was purified by the electro-dialysis method of Holmes and Elder,[3] the ash being reduced from 1·5 to 0·1 per cent. The galactan had $[\alpha]_D$ + 12·2° and a molecular weight (by iodine value) 7,600 to 8,900.

Determination of Galactan.—This is based on the conversion of galactan into the difficultly soluble mucic acid. The oxidation, however, is not quantitative. With pure galactose and galacturonic acid reproducible results can be obtained, the yield of mucic acid being about 62 per cent. of the theoretical in each case.[4] This suggests a conversion factor for mucic acid to galactan of about 1·25 as compared with the 1·12 used in the method given below. There is little doubt that with difficultly hydrolysable polygalacturonides and galactans the yield of mucic acid is even lower. The usual method of working is to oxidise the substance directly with nitric acid. The mucic acid is extracted with ammonium carbonate, or alternatively, the filtered solution is concentrated to yield crystals of mucic acid. The presence of oxalic and other acids formed from lignin and hemicelluloses may, however, easily cause a small amount of mucic acid to escape unnoticed. A. W. Schorger [5] recommends the following method. The nitric acid used in the preliminary extraction is of such a strength that it acts chiefly as a hydrolytic agent.

[1] F. C. Petersen *et al.*, *Cellulosechem.*, 1934, **15**, 109.
[2] *Ind. Eng. Chem.*, 1916, **8**, 494. [3] *J. phys. Chem.*, 1931, **35**, 1351.
[4] E. L. Hirst and J. K. Jones, *J. Chem. Soc.*, 1938, 502.
[5] A. W. Schorger, "Chemistry of Cellulose and Wood," 1926, p. 538.

Procedure.—10 g. of wood powder are extracted with alcohol-benzene and treated with 150 ml. of 3 per cent. nitric acid in a flask fitted with reflux which is heated on a water bath for 2 hours. The contents are filtered and washed with 250 ml. of boiling water. The filtrate is concentrated to 100 ml., cooled and filtered. The filtrate from this is again concentrated to 10 ml. and transferred to a 100 ml. beaker with the aid of 50 ml. of 25 per cent. nitric acid (*d*, 1·15). The beaker is suspended in a bath kept at 85 to 87° and the liquid concentrated to 20 ml. If no mucic acid has separated after a day the liquid is further concentrated to 5 to 10 ml. at a very gentle heat and left for 2 or 3 days. Sufficient water is added to dissolve any oxalic acid, and after 2 or 3 days the residue is filtered on a Gooch crucible, dried and weighed. The mucic acid should be a white crystalline powder or crust: m.p. 212 to 215°.

$$\text{Wt. of mucic acid} \times 1{\cdot}12 = \text{galactan.}$$

As galactans in wood seem to be largely soluble in boiling water the presence of mucic acid should be confirmed by the oxidation of the water extract of the wood. 50 g. of wood powder are boiled with water for 2 hours and the filtrate concentrated to a syrup which is oxidised as above.

The proportion of oxalic and mucic acids in mixtures of the pure acids can be determined by regulated oxidation with potassium permanganate.[1]

Lichenin

This substance is believed by some authors to be a hemicellulose, since it is converted quantitatively to dextrose by the enzyme lichenase,* which is not able to resolve cellulose to any extent. It is a cell-wall component of Iceland moss (*Cetraria islandica*), from which it was first obtained by Berzelius in 1814. Whether it is a constant constituent of the lichens has not been definitely ascertained. P. Karrer and his co-workers have obtained it from *Evernia vulpina*, *Usnea barbata*, and *Parmelia furfuracea*, after a preliminary treatment to remove the lichen acids.

The properties of lichenin agree with those ascribed by Schulze to a hemicellulose. It is a white powder, soluble in dilute alkalis, and giving a clear colloidal solution with boiling water. It is easily hydrolysed to dextrose with dilute acids at ordinary pressure, giving 64·86 per cent. of this sugar. The general properties of lichenin resemble those of cellulose. It gives, after methylation and

[1] E. O. Whittier, *J. Amer. Chem. Soc.*, 1923, **45**, 1391.

* From the snail *Helix pomatia*; see P. Karrer, *Helv. Chim. Act.*, 1924, **7**, 144, 518.

hydrolysis, 2.3.6-trimethyl glucose and if heated in a vacuum forms lævoglucosan.[1]

Preparation of Lichenin.[2]—The procedure of Hess and Friese is as follows : 300 g. of *Cetraria islandica* are extracted three times with 6 l. of 2 per cent. KOH solution at the ordinary temperature to remove tannins. The washed product is covered with water and exposed for 4 hours to a fairly rapid stream of chlorine ; or a 2·5 per cent. solution of chlorine dioxide may be used. After washing and pressing it is covered with 2 per cent. sodium sulphite solution, allowed to stand 1 day, and washed with running water for many hours. The residue, after boiling for 6 hours with 4 l. of water, gives up most of the lichenin, but after filtration a second extraction with 4 l. for 3 hours is desirable.*

The mother liquors deposit a jelly which is best separated by freezing the whole mixture. After thawing, the lichenin deposits well and can be separated centrifugally. It is washed in the centrifuge with cold water till the water gives no colour with iodine. After treatment with alcohol and ether lichenin is left as a grey-brown powder. Yield between 18 and 25 per cent.

Purification of the Crude Lichenin.—This is best done by precipitation from *alkaline* solutions ; for example, the product is treated with seventy times its weight of cold water and NaOH solution added till solution takes place in the cold. The liquid is filtered and CO_2 gas passed until phenolphthalein indicator is decolorised, after which concentrated NaOH solution is added to restore the red colour. After freezing, the lichenin is white and filters easily. The treatment is repeated once or twice. The rotation in copper solution of such preparations, *viz.* $[\alpha]^{20}_{435\cdot8}$, is $-2\cdot25°$ not quite equal to the purest preparations ($-2\cdot33°$), but much purer than those obtained by the old methods using hot water as solvent.

Triacetyl Lichenin may be prepared by Barnett's method : 4 g. of dry lichenin with 25 ml. of glacial acetic acid are exposed for a quarter of a minute to a stream of dry chlorine, allowed to stand 30 minutes, and then, after addition of 30 ml. of acetic anhydride, treated for half a minute with dry SO_2 gas. The mass is kept for 12 hours at 65°, when most of the solid goes into solution. The liquid is poured into water and the acetate washed : Yield, quantitative. It is taken up in acetone and precipitated by ether.

[1] P. Karrer and K. Nishida, *Helv. Chim. Act.*, 1924, **7**, 363 ; *ibid.*, 129.

[2] M. Hönig and S. Schubert, *Monat.*, 1887, **8**, 453 ; A. Ulander and B. Tollens, *Ber.*, 1906, **39**, 402 ; K. Hess and H. Friese, *Ann.*, 1927, **455**, 190.

* The residue contains a hemicellulose remarkable in yielding *d*-glucose (89 per cent.), galactose (7·6 per cent.) and mannose (3 per cent.) with *d*-glucuronic acid (E. G. Percival, *J. Chem. Soc.*, 1943, 54).

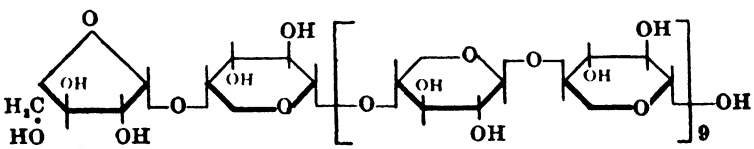
Final rotation, $[\alpha]_D^{22}$, $-35{\cdot}8°$ in chloroform; $-53{\cdot}7°$ in pyridine. Soluble with difficulty in methyl and ethyl alcohols, insoluble in ether and light petroleum.

NOTE.—The mucopolysaccharides, which include bacterial dextrans, levans and other mould polysaccharides, chitin, etc.. have recently been reviewed in *Chem. Soc. Ann. Reports*, 1936, and *Chemistry and Industry*, 1943, **62**, 110.

MOLECULAR STRUCTURE OF HEMICELLULOSES

The hemicellulose is purified, often by conversion to the acetate, and the product methylated. After hydrolysis the methyl-derivatives are separated by elaborate fractionation and their proportion estimated by means of refractive index and methoxyl values as in the cellulose " end-group " estimation.

Xylan from esparto (p. 423) has been found in this way to consist of chains of xylopyranose units linked 1 and 4, the glucosidic linkages being β- in type so that the structure resembles that of cellulose.[1] The terminal group, however,[2] proves to be an *l*-arabinose unit in the furanose form. The hydrolysis products of the methy-



Gives 2 : 3 : 5-trimethyl arabofuranose.

Gives 2 : 3-dimethyl xylose

(I) Xylan

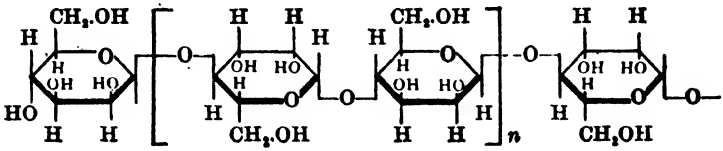
lated xylan consisted of 2 : 3-dimethyl xylose (*ca.* 90 per cent.), 2 : 3 : 5-trimethyl arabinose (*ca.* 6 per cent.) and about 5 per cent. of 2-monomethyl xylose the significance of which is obscure. The simplest structure for xylan based on these results would be that shown above (I), but an alternative and not unlikely one is a chain of xylopyranose units linked 1 and 4 with an arabofuranose unit attached as a side chain at intervals of 16 to 18 xylose units. Further work (*loc. cit.* 1940) tends to exclude this hypothesis and to confirm the view that the xylan is made up of primary chains of arabofuranose-(xylose)$_{16\text{-}17}$-xylose linked together by some type of union between the reducing group of the free xylose and a hydroxyl grouping of another chain. This latter grouping may be in the

[1] W. N. Haworth, E. L. Hirst *et al.*, *J. Chem. Soc.*, 1929, 1739; 1931, 2850.

[2] *Ibid.*, 1934, 1917; 1940, 1983.

3-position which would explain the production of equal weights of trimethyl arabinose and monomethyl xylose.

Mannans A and B from ivory nut (p. 429) have a similar constitution.[1] Mannan A gives 2 : 3 : 6-trimethyl mannose with 1 to 1·4 per cent. of 2 : 3 : 4 : 6-tetramethyl mannopyranose.



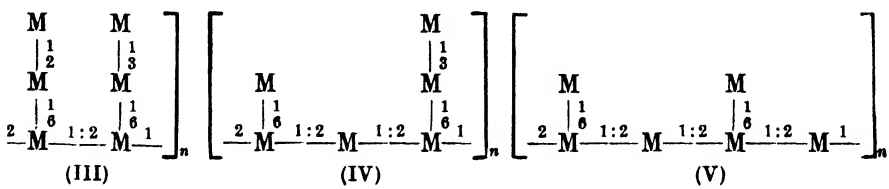
Gives 2 : 3 : 4 : 6-tetramethyl mannose

Gives 2 : 3 : 6-trimethyl mannose

(II) Mannan A

These scission products lead to the constitution shown in the formula (II) above, *viz.* a terminated chain of mannopyranose units linked through positions 1 and 4, in which some of the mannosidic linkages may be alpha. The chain-length of the methylated mannan is about 80 mannose units. The structure is confirmed by the isolation through the graded hydrolysis of methylated mannan of mannobiose and mannotriose derivatives which, after methylation and hydrolysis, give the same cleavage products as the original mannan. Mannan B behaves similarly.

The mannan of yeast gum has a different structure. It consists of a main chain of mannose units, glucosidically linked, with side chains branching from the central one. The side chains may consist of one mannose unit (V), or two units (III), or an equal number of side chains may contain one and two units respectively (IV) as in the formulæ below where M is a mannose unit and the numerals represent the carbon atoms of each unit involved in the glucosidic linkages. The value of n is 30 to 60.



(III) (IV) (V)

Methylated yeast mannan gave [2] on hydrolysis, etc., tetramethyl methylmannopyranoside ; 2 : 4 : 6- and 3 : 4 : 6-trimethyl mannose in equimolecular proportions with about 10 per cent. only of the 2 : 3 : 4-derivative ; and 3 : 4-dimethyl methylmannopyranoside. The

[1] F. Klages, *Annalen*, 1934, **509**, 159 ; **512**, 185 ; 1936, **523**, 224.
[2] W. N. Haworth *et al.*, *J. Chem. Soc.*, 1937, 784 ; 1941, 833.

fractions "tetra", "tri" and "di" were present in equimolecular proportions. On these results the mannan unit would appear to be made up of six mannose residues joined so that two can give tetramethyl mannose; two can give 3 : 4-dimethyl mannose; one, 3 : 4 : 6-trimethyl mannose and one 2 : 4 : 6-trimethyl mannose. These requirements are embodied in the typical formulæ (III), (IV), (V) above.

The **Galactan** of larchwood, the so-called ϵ-galactan (p. 433), is now considered to be a mixture of an araban and a galactan.[1] The latter gives rise to equimolecular proportions of 2 : 3 : 4 : 6-tetramethyl *d*-galactopyranose, 2 : 4-dimethyl *d*-galactopyranose and (probably) 2 : 3 : 4-trimethyl *d*-galactose. The galactan therefore may be of the branched chain type shown in the scheme below where G represents a galactopyranose residue.

$$\begin{array}{l} \ldots\ 6\,G\,1,\ 6\,G\,1,\ 6\,G\,1,\ 6\,G\,1\ \ldots \\ \qquad\quad \begin{matrix}3\\1\\G\end{matrix} \qquad\qquad \begin{matrix}3\\1\\G\end{matrix} \end{array}$$

E. V. White,[2] however, considers that the arabinose unit is combined with the galactan, being joined, at C1, to the C6 of a galactose unit which is linked also to two other galactose units.

The example given below illustrates the general method of dealing with these problems.

Constitution of Yeast Mannan.[3]—Yeast mannan was methylated by treating 20 g. in water (100 ml.) and NaOH, 30 per cent. solution (50 ml.), with methyl sulphate (250 ml.) and 30 per cent. NaOH solution (650 ml.). On raising the temperature to 100° the methylated product separated. This treatment was repeated eight times, acetone being used as an additional solvent. The product, in chloroform, was dried ($MgSO_4$), concentrated, and light petroleum added to turbidity. The small precipitate, which contained most of the ash, was removed (centrifuge) and the clear liquid run into a large volume of petroleum. The methylated mannan was dried (vacuum) at 60° and finally at 100°. Yield, 70 per cent.; $[\alpha]_D$ +88° in chloroform; OMe, 44·1 per cent.

It was purified by dissolving 108 g. in chloroform, concentrating and adding light petroleum till about 20 g. had separated (fraction A) This was continued to a final fraction F. Each fraction was then given a similar purification. Their properties are given in the following table.

[1] E. L. Hirst, *J. Chem. Soc.*, 1942, 73; *Nature*, 1941, **147**, 26.
[2] E. V. White, *J. Amer. Chem. Soc.*, 1941, **63**, 2871; 1942, **64**, 302, 1507.
[3] W. N. Haworth *et al.*, *J. Chem. Soc.*, 1937, 784; 1941, 833.

Fraction.	Wt. g.	OMe per cent.	$[\alpha]_D^{17°}$ in $CHCl_3$.	$\eta_{sp./c.}$ (c = g./100 ml.).	M from Os. Pr.	M (Hexose Units.)
A . .	23·5	43·5	+ 88·1°	0·212	76,000	380
B . .	20·5	44·1	+ 88·3	0·211	76,000	380
C . .	24·0	44·3	+ 89·1	0·195	72,000	360
D . .	23·0	44·3	+ 87·9	0·175	59,000	295
E . .	8·5	44·4	+ 88·7	0·121	35,000	175
F . .	0·5	41·8	+ 88·4	0·062	18,000	90

Hydrolysis of Methylated Mannan.—Instead of heating with methyl alcoholic HCl under pressure it was found better to use the following less severe method. Fraction A (21·3 g.) was dissolved in glacial acetic acid (213 ml.) and 5 per cent. HCl (213 ml.) added. The mixture was heated (water bath) till the $[\alpha]_D$ became constant (+2·04° to +0·4° in 12 hours). The HCl was neutralised with barium carbonate to Congo Red and the acetic acid solution taken to dryness at 50°. The residue was repeatedly extracted with boiling chloroform and the product converted to methyl glucosides by boiling with 2 per cent. methyl-alcoholic HCl until rotation became constant (12 hours). The liquid was neutralised with silver carbonate and the product isolated as usual.

Fractions B–E were combined and treated in the same way.

The mixed glucosides were fractionated in a high vacuum, any residue being hydrolysed again until 15 fractions were finally obtained.

On the basis of their methyl content and refractive index the proportions of (*a*) tetramethyl methylmannoside ($n_D^{20°}$, 1·4475; OMe, 62·0 per cent.), (*b*) trimethyl methylmannoside ($n_D^{20°}$, 1·4575; OMe, 52·6 per cent.), and (*c*) dimethyl methylmannoside ($n_D^{20°}$, 1,4705; OMe, 41·9 per cent.) were calculated. Fractions 2–4 (n_D, 1·4465/70; OMe, 58·9) consisted entirely of (*a*), fractions 6 to 8 (n_D, 1·4572, OMe, 51·5) of (*b*), and fractions 11–13 (n_D1·4708, OMe, 40) of (*c*).

The weight ratio found for tetra : tri : di was 34·4 : 33·3 : 27·6 which gives a molecular ratio of 1·00 : 1·02 : 0·90.

CHAPTER XXIII

THE ANALYSIS OF WOOD

THE methods which have been described for the estimation of the constituents of plant tissues have been co-ordinated by several workers to the proximate analysis of woods. Such analyses are of value for purposes of standardisation and for the study of the biological changes which accompany growth or decay. From them have been derived standard methods, such as those of *TAPPI*,[1] (p. 452) for the evaluation of pulping woods used in the manufacture of paper and rayon.

The more important schemes of analysis are those devised by König and Becker (1919), Schwalbe and Becker (1919), W. H. Dore (1920), and Schorger, Ritter, Fleck, and others, of the United States Forest Products Laboratory (1917–1922). That of König and Becker [2] differs most, and the results obtained by it are not readily comparable with any of the others. In the tables given below will be found references, and typical results obtained by the use of the other methods, from which it will be seen that there is a general resemblance between them.

The results obtained by the methods of Schwalbe and Becker agree very well with those of Ritter and Fleck. In each case the sum of the values for ash, fraction soluble in hot water, ether extract, acetic acid, pentosan, lignin and cellulose (free from pentosan) gives a figure approximating to 100.

The scheme of Dore represents an attempt to determine fractions of the wood substance so chosen that 100 per cent. of the material is accounted for. The method may be recommended, not only for the analysis of wood, but for other lignified plant tissues (see, for example, p. 350). As originally issued, it was open to the criticism that no information was available as to the total pentosan content of the wood, and a revised procedure is given below.

The general method of working in any of these processes can be inferred from the typical analyses on pp. 443 and 444. A few notes will be given on particular points of procedure in each case. Additional determinations which may be required include estimation of (i) nitrogen (protein) (p. 451), (ii) uronic acids (p. 391), and (iii) methoxyl (p. 395) and furfural (p. 375), in various fractions.

[1] Tentative *TAPPI* methods, "Sampling and Analysis of Wood", *Paper Trade J.*, 1942, **115**, *TAPPI*, 152.

[2] J. König and E. Becker, *Zeit. angew Chem.*, 1919, **32**, 155.

Analysis of Wood (W. H. Dore [1])

The table on p. 444 gives results from the work of W. H. Dore. It will be noted that the procedure for the coniferous woods differs from that recommended for the hard woods. The schemes have proved satisfactory and are still in use, with the exception that the method used for the determination of " soluble pentosans " under coniferous woods or " pentosans not otherwise accounted for " under hard woods not proving satisfactory, the author now prefers to obtain this value by subtracting the pentosan content of the cellulose from total pentosan.

A. **Procedure for Coniferous Woods.**—In the case of these woods it was found that preliminary extraction with water and alkali gave unsatisfactory (low) results for cellulose and lignin. The dry wood is therefore extracted with benzene and alcohol only, before making the cellulose determination. The sample is used in the form of sawdust which passes a sieve having fifty meshes to the linear inch. It may be pointed out that the rejection of the coarse particles prevents a true picture of the composition of the wood from being obtained.

1. *Benzene Extract.*—2 g.* dried at 100° are extracted with benzene for 6 hours. The extract is dried at 100° and weighed.

2. *Alcohol Extract.*—The residue is extracted for 6 hours with 95 per cent. alcohol, the extract dried and weighed as before.

3. Extraction with cold water, and 4. extraction with cold 5 per cent. NaOH are omitted with coniferous woods.

5. *Cellulose.*—2 g. of the material, extracted with alcohol and benzene, are transferred to a Gooch crucible containing a mercerised cloth filtering disc and washed with water. The cellulose is determined by the method of Sieber and Walter (p. 355). It is tested for lignin by digestion in 72 per cent. sulphuric acid, and if any quantity is present this is weighed and a correction applied.

6. *Lignin.*—2 g. of wood extracted with alcohol and benzene are air-dried at about 60° and placed in a 750 ml. flask. 20 ml. of 72 per cent. sulphuric acid are added and the mixture allowed to stand at room temperature for 3·5 hours. 50 ml. of cold water are added, then 500 ml. of hot water. The residue is filtered, washed with hot water, dried and weighed. The methods (p. 373) are now preferred.

7. *Soluble Pentosans.*—The furfural content of the cellulose (No. 5) is estimated and calculated to pentosan from 100 parts of

[1] *Ind. Eng. Chem.*, 1920, **12**, 476, 984.

* We prefer to use 4 to 5 grams.

Analyses of American Woods (Mean Values by the United States Forest Products Laboratory)

(Results as percentage of oven-dry (105°) samples)

	Ash.	Solubility in				Acetic Acid.	Meth-oxyl.	Pen-tosan.	Methyl Pen-tosan.	Cellu-lose.	Lignin.	In Cellulose.				
		Cold Water.	Hot Water.	Ether.	1 per cent. NaOH.							Pen-tosan.	Methyl Pen-tosan.	α	β	γ
Western yellow pine (*Pinus ponderosa*)	0·46	4·09	5·05	8·52	20·30	1·09	4·49	7·35	1·62	57·41	26·65	6·82	1·98	62·10	10·56	30·13
Redwood (*Sequoia sempervirens*)	0·21	7·36	9·86	1·07	20·00	1·08	5·21	7·80	2·75	48·45	34·21	7·40	2·09	78·81	2·95	18·24
Douglas fir (*Pseudotsuga taxifolia*)	0·38	3·54	6·50	1·02	16·11	1·04	4·95	6·02	4·41	61·47	—	5·34	1·20	—	—	—
White spruce (*Picea canadensis*)	0·31	1·12	2·14	1·36	11·57	1·59	5·30	10·39	3·55	61·85	—	9·63	0·72	—	—	—
Tan bark oak (*Quercus densiflora*)	0·83	4·10	5·60	0·80	23·96	5·23	5·74	19·59	—	58·03	24·85	22·82	—	56·77	19·92	23·03
Hickory (shellbark) (*Hicoria ovata*)	0·69	4·78	5·57	0·63	19·04	2·51	5·63	18·82	0·80	56·22	23·44	21·89	1·41	76·32	2·82	20·35
Basswood (*Tilia Americana*)	0·86	2·12	4·07	1·96	23·76	5·79	6·00	19·93	3·73	61·24	—	24·28	1·54	—	—	—
Yellow birch (*Betula lutea*)	0·52	2·67	3·97	0·60	19·85	4·30	6·07	24·63	2·69	61·31	—	28·30	1·16	—	—	—
White pine *:																
(*a*) Sapwood	0·23	3·55	5·15	5·46	17·16	1·68	4·16	9·31	2·14	54·25	26·51	6·81	2·09	54·56	17·47	27·97
(*b*) Heartwood	0·42	5·97	7·68	3·62	19·15	1·43	4·60	8·56	1·00	50·23	26·14	7·12	2·02	57·29	22·42	19·29
White ash:																
(*a*) Sapwood	0·61	5·81	6·41	1·17	21·77	3·23	4·70	19·85	2·40	50·38	26·95	18·83	1·60	74·67	13·67	11·66
(*b*) Heartwood	0·30	2·24	3·40	0·43	19·59	2·31	5·36	19·90	2·25	53·56	27·39	16·75	1·34	64·68	24·58	10·84
White oak:																
(*a*) Sapwood	0·57	2·55	4·11	0·46	21·11	3·44	5·95	23·25	0·90	49·53	32·34	24·74	0·88	68·07	15·27	16·66
(*b*) Heartwood	0·43	7·33	10·15	0·71	25·81	2·59	6·18	21·82	1·57	48·68	32·74	24·22	0·58	67·33	11·84	20·83

* G. J. Ritter and L. C. Fleck, *Ind. Eng. Chem.*, 1923, **15**, 1056.

COMPOSITION OF VARIOUS WOODS (Method of W. H. Dore)
(Per cent. on dry weight)

	Redwood.	Western Yellow Pine.	Sugar Pine.	Live Oak.
(1) Benzene extract	0·34	2·22	2·84	0·52
(2) Alcohol extract	4·39	1·49	1·90	4·52
(3) Soluble in cold 5 per cent. NaOH	—	—	—	19·53
(4) Soluble in cold water	—	—	—	3·82
(5) Cellulose	54·89	57·72	59·18	47·47
(6) Lignin	34·50	29·47	29·50	21·14
(7) Pentosans not otherwise accounted for	3·67	3·49	1·86	1·97
(8) Mannan	3·21	6·37	6·63	0·00
(9) Galactan	0·50	0·78	0·50	1·56
Total	101·50	101·54	102·41	100·53

ANALYSES OF EUROPEAN WOODS (by Schwalbe and Becker)[1]
(Per cent. on dry weight)

	Spruce (*Picea excelsa*).	Pine (*Pinus silvestris*).	Beech (*Fagus sylvatica*).	Birch (*Betula verrucosa*).	Poplar (*Populus tremula*).
Ash	0·77	0·39	1·17	0·39	0·32
Fat [ether extract]	0·78	1·92	0·31	0·71	1·08
Wax [alcohol extract]	1·52	1·53	1·47	1·09	2·08
Fat and Wax	2·30	3·45	1·78	1·80	3·16
Resin [by alcohol-benzene]	2·34	3·32	1·20	1·68	2·87
Methyl	2·36	2·20	2·96	2·77	2·57
Pectin (*v.* Fellenberg)	1·22	1·11	1·75	1·61	1·82
Acetic acid (Schorger)	1·44	1·40	2·34	4·65	4·17
Protein ($N \times 6{\cdot}25$)	0·69	0·80	1·05	0·74	0·63
Furfural	7·49	7·04	14·90	16·08	12·64
Pentosan	11·30	11·02	24·86	27·07	23·75
Methyl pentosan	3·00	2·23	1·02	0·84	0·72
Cellulose (Cross and Bevan)	63·95	60·54	67·09	64·16	62·89
Pentosan in cellulose	9·55	11·27	20·35	29·40	24·94
Cellulose (pentosan-free)	57·84	54·25	53·46	45·30	47·11
Lignin (Willstätter)	28·29	26·35	22·46	19·56	18·24

wood. The difference between this value and that of the total pentosan of the extracted wood gives soluble pentosans.

8. *Mannan.*—The method[2] originally used is first described, but the modification given below is preferable. 10 g. of the extracted wood (1 and 2) are boiled for 3·5 hours with 150 ml. of hydrochloric

[1] C. G. Schwalbe and E. Becker, *Z. angew. Chem.*, 1920, **33**, 14.
[2] A. W. Schorger, *Ind. Eng. Chem.*, 1917, **9**, 748.

acid (*d*, 1·025) under reflux. The mixture is filtered, and the residue digested with 100 ml. of water for a few minutes on a hot plate. The solution is poured through the filter and the residue treated as before, until about 500 ml. of filtrate are obtained. This is neutralised with sodium hydroxide, slightly acidified with acetic acid and evaporated to 150 ml. It is then filtered into a glass-stoppered Erlenmeyer flask, and 10 ml. of phenylhydrazine in 20 ml. of water, acidified with acetic acid, are added. Mannose hydrazone is precipitated. After standing for 2 hours with shaking the hydrazone is filtered on a Gooch crucible fitted with a disc of mercerised cotton, washed several times with cold water and then with acetone, dried at 100° and weighed. The weight × 0·6 = mannan.

The amount of mannose present is frequently small, and it has been shown that its complete precipitation in Schorger's method depends upon its concentration in the solution,[1] and is only approximately quantitative (90–95 per cent.) when the concentration exceeds 1 per cent. If salt is present, however, a recovery of 90 per cent. can be obtained in a concentration of 0·5 to 0·6 per cent. Below this no precipitation occurs, so that small quantities of mannose are not detected. The salt is provided by the neutralisation of the acid used for hydrolysis. A reaction time of 6 hours is necessary.

Modified Procedure.[1]—10 to 15 g. of wood, finely ground, or 35 to 40 g. of wet wood-cellulose are boiled under reflux for 3½ hours with 100 to 150 ml. of 5 per cent. HCl. The residue is separated and washed well with about 300 ml. of hot water. The total filtrate is neutralised with NaOH, made faintly acid with acetic acid and evaporated to a volume of 25 to 30 ml. The concentrated solution is filtered into a small marked flask and the paper washed till the volume is 50 ml. (or in some cases 75 ml.). After cooling 2·5 to 4 ml. of phenylhydrazine and up to 5 ml. of 50 per cent. acetic acid are added. The flask is closed and kept for 6 hours at ordinary temperature with shaking. The final volume is noted, the precipitate filtered on a Gooch crucible, washed with about 50 ml. cold water, then with acetone, dried and weighed.

If the final concentration in the solution from which the hydrazone is precipitated is less than 0·5 per cent. another estimation employing larger quantities of the wood should be made.

9. *Galactan.*—Generally, only small quantities of galactan are present, and may originate in a pectic substance. The method (p. 434) may be employed.

[1] A. Nowotnowna, *Biochem. J.*, 1936, **30**, 2177.

B. **Procedure for Hard Woods.**[1]—Several modifications had to be made to adapt the scheme to the analysis of hard woods. It was found that with hard woods extraction with benzene and alcohol, did not remove adventitious substances, so that, following extraction with benzene, and with alcohol, successive digestions in cold water and cold dilute sodium hydroxide solutions are given.

The wood of *Quercus agrifolia* was prepared by sifting the sawdust through a sieve having fifty meshes to the linear inch and grinding the over-size particles again until they also passed the sieve.

The procedure with regard to drying and (1) *benzene extraction* and (2) *alcohol extraction* is the same as for coniferous woods.

3. *Soluble in Cold Water.*—The residue from the alcohol extraction (2) is dried and digested for 1 day with 200 ml. of cold water. It is then filtered through a Gooch crucible fitted with a disc of mercerised cotton cloth, washed, dried for 16 hours * at 100° and weighed. The amount soluble in cold water is calculated by adding together the percentage figures for the loss on drying, benzene and alcohol extract and residue after water extraction, and subtracting this sum from 100 per cent.

4. *Soluble in cold 5 per cent. Sodium Hydroxide Solution.*—The residue from the above is treated with 100 ml. of 5 per cent. NaOH solution for 24 hours and the solution filtered through the same crucible as before. The residue is washed with water, dilute acetic acid, and with water. After drying as before, it is again weighed, the loss in weight on the previous weighing representing material soluble in cold 5 per cent. NaOH solution.

5. *Cellulose.*—This is determined on the residue from the above treatment.

6. *Lignin.*—Four samples are run at the same time. Amounts of 1 g. each extracted under Nos. 1 to 4 inclusive, are placed in 10 × 1 in. test tubes and treated with 10 ml. of concentrated hydrochloric acid. Each tube is closed with a rubber stopper, carrying an inlet tube leading almost to the bottom, and an outlet tube. Hydrochloric acid gas is passed through for 2 hours. The tubes are left closed for 24 hours, the contents mixed with water and filtered off, the residues of lignin washed thoroughly, dried at 100° and weighed.

7. *Pentosans not otherwise accounted for.*—If this value is required, estimations of furfural are necessary (*a*) in the benzene-alcohol extracted wood, (*b*) in the cellulose, the value being calculated to 100 of original wood, (*c*) in the liquors from the extraction with 5 per cent. NaOH solution. These may be neutralised with HCl,

[1] W. H. Dore, *Biochem. J.*, 1920, **12**, 984.

* We prefer to dry for a shorter time than this.

evaporated to dryness, and distilled preferably as in Kullgren's process, p. 385. The result is again calculated to 100 parts of wood.

8. and 9. Mannan and Galactan, as before.

Interpretation of the Results.—In the case of *Quercus agrifolia*, figures for which are given in the table (p. 444), the benzene extract, probably oil-wax-resin, is very small, as would be expected. The alcohol extract, a red-brown material, is high, and probably consists of tannin and colouring matter. The cold-water soluble contains colouring substances not soluble in alcohol. The fraction removed by 5 per cent. NaOH solution contains a considerable amount of pentosan of the wood, *e.g.* 11·2 per cent. of pentosan was found in the alkali extract shown in the table.

The extract also contains acetic acid, for whilst the original wood gave on hydrolysis 4·7 per cent. of acetic acid (after correction for formic acid),[1] only traces of volatile acid could be obtained similarly from the alkali-extracted wood. It may be noted that after extraction by reagents 1 to 4 the wood contained only a few tenths of a per cent. of nitrogen and a similarly small quantity of ash.

A study of the distribution of the furfural-yielding groups makes it probable that they consist of three kinds. Those removed by 5 per cent. alkali are of the nature of wood gum; those in the cellulose are closely associated hemicelluloses, while the third portion may be of a polyuronide type.* The general distribution of pentosan in *Quercus agrifolia* is shown in the following table :—

DISTRIBUTION OF FURFURAL-YIELDING GROUPS IN OAK
(As percentage of air-dry wood—moisture 4·2 per cent.)

In the	Furfural.	Pentosan.
1. Untreated wood	12·90	22·01
2. Extracted wood : (1)–(4)	6·83	11·69
3. Extract by 5 per cent. NaOH	6·60	11·29
4. Extract by cold water	—	—
Total compare with (1)	13·43	22·98
5. Cellulose	6·11	10·68
6. Chlorination liquors	1·10	1·89
7. Lignin	—	—
Total compare with (2)	7·21	12·57

[1] W. H. Dore, *Ind. Eng. Chem.*, 1920, **12**, 474.

* Compare the study of the furfuraldehyde-yielding components of straw, on p. 413.

Comparing the value (1) with the sum of (2), (3), and (4), and again comparing (2) with that of (5), (6), and (7), it will be seen that more furfural is obtained from the fractions than is directly separated from the wood, or the cellulose, respectively.

Examination of the distribution of methoxy groups in oak shows that these are largely associated with lignin. A small portion, 0·8 per cent., is apparently lost during the hydrochloric acid treatment, probably from an ester methoxyl present in lignin.

DISTRIBUTION OF METHOXY GROUPS IN OAK

(As percentage of air-dry wood—moisture 4·2 per cent.)

	OMe per cent.
1. Untreated wood	5·56
2. Wood after benzene-alcohol (1), (2)	5·56
3. Wood after complete extraction : (1)–(4)	4·33
4. Lignin from wood extracted by benzene-alcohol	3·56
5. Lignin from wood completely extracted	3·53

For the additional estimations needed to complete the statistical examination referred to above, see furfural (p. 375), methoxyl (p. 395), acetic acid (p. 449), uronic acid (p. 391).

C. **Notes on the Methods employed by Schwalbe and Becker in the Analyses of Woods given in the Table.**—The wood was taken from 60- to 80-year-old branches and reduced to powder. The moisture was determined at 105°, the sample being then ashed. The extraction with ether and alcohol was carried out as usual.

For the residual fat-wax (resin in the table) the material was dried at 50 to 60° and extracted with equal parts of benzene and alcohol.

The lignin was determined in three ways which showed general agreement—(*a*) with sulphuric acid (König and Becker), (*b*) concentrated hydrochloric acid (Willstätter), and (*c*) gaseous hydrochloric acid (Krull).

For (*c*) 1 g. of wood was moistened with 6 ml. of concentrated hydrochloric acid and HCl gas passed, with ice cooling, the mass being allowed to stand 24 hours.

The pectin was obtained from the formula, MeOH × 10 = pectin.

The acetyl value was determined by Schorger's method (p. 449); the cellulose by Cross and Bevan or Sieber and Walter (p. 355).

Notes on the Methods of A. W. Schorger, S. A. Mahood and D. E. Cable, G. J. Ritter and L. C. Fleck.[1]—These methods are not summative and are designed to give information as to the

[1] A. W. Schorger, *Ind. Eng. Chem.*, 1917, **9**, 556; S. A. Mahood and D. E. Cable, *ibid.*, 1922, **14**, 933; G. J. Ritter and L. C. Fleck, *ibid.*, 1923, **15**, 1056, 1264; 1924, **16**, 47, 947. See table, p. 443.

quantitative action of reagents on the wood. The sample is made to pass an 80-mesh, but retained by a 100-mesh sieve. The coarse material is reground and the 80–100 fraction mixed with the rest of the sample. The powder is preserved air-dry in a sealed bottle. The moisture content being once determined, all measurements are made on the air-dry material, correction being made for the known moisture content.

For loss on drying 3 to 4 g. are dried at 105° to constant weight. This usually requires 4 to 6 hours. The following measurements are made each on a sample of the original wood.

1. *Soluble in cold Water.*—2 g. are digested with 300 ml. of water at room temperature with frequent stirring during 4 hours.

2. *Soluble in hot Water*, and 3. *Soluble in Alkali.*—These are carried out as p. 452 or as under pulp, p. 475.

4. *Ether and Alcohol Extracts.*—3 to 4 g. of dry wood powder is extracted with ether in a Soxhlet apparatus for 6 hours. The residue is dried and weighed. The wood is then extracted with alcohol for 8 hours.

5. *The Ash.*—3 to 5 g. in a platinum dish are incinerated in an electric muffle furnace at a dull red heat.

6. *Acetyl Groups as Acetic Acid.*[1]—The wood is hydrolysed with dilute sulphuric acid, and the acetic acid distilled over.

2 g. of wood are boiled for 3 hours under reflux with 100 ml. of 2·5 per cent. sulphuric acid. After cooling the condenser is rinsed and the contents of the flask washed into a 250 ml. graduated flask, which is filled to the mark with CO_2-free water. After standing several hours with shaking the liquid is filtered. For hard woods 100 ml. of the filtrate will be required, for soft woods, 200 ml. For the distillation a 750 ml. round-bottomed flask is fitted with a rubber stopper carrying (i) a dropping funnel, (ii) a glass tube drawn to a capillary which reaches to the bottom of the flask, closed at the top with a rubber tube and pinch clip, and (iii) a bulb trap joined to a condenser. A 500 ml. distillation flask is used as receiver connected with suction pump and manometer.

The appropriate quantity of the filtrate, with a few pieces of pumice, is placed in the flask, which is heated in a bath kept at 85°. The pressure is regulated to 40 or 50 mm. When only some 20 ml. are left in the flask, distilled water free from CO_2 is run in at the same rate that distillation is taking place.* When 100 ml. have

[1] A. W. Schorger, *Ind. Eng. Chem.*, 1917, **9**, 559; see also W. H. Dore, *ibid.*, 1920, **12**, 472.

* An alternative method recommended is to add at this point 100 ml. of distilled water and to distil 100 ml. over, then to add another 100 ml. of water and again distil 100 ml., after which the reaction is complete.

distilled over, the distillate is titrated with $N/20$ NaOH solution to phenolphthalein. If 200 ml. were taken for distillation, then the total ml. of alkali used will be obtained by multiplying the titration value by 5/4, etc. 1 ml. of $N/20$ alkali ≡ 0·0030 g. acetic acid.

Formic acid, which is frequently present, is estimated by concentrating the neutralised distillate obtained and adding excess of a saturated solution of mercuric chloride. The liquid is heated for 2 hours on the water bath, and the mercurous chloride formed by reduction is filtered through a Gooch crucible, and dried at 100°.

The weight of precipitate × 0·0975 = weight of formic acid. This value may be calculated to acetic acid and a correction applied to the acetic acid estimation.

An alternative method for the estimation of formic acid is to add to the neutralised distillate a few ml. of $N/10$ silver nitrate solution. After warming on the water bath for several hours the silver reduced is filtered off, dissolved in nitric acid, and estimated as silver chloride. The weight of precipitate × 0·40 gives the weight of acetic acid equivalent to the formic acid present.

A useful volumetric method for the estimation of formic acid in the presence of acetic acid is that of Fouchet,[1] which requires the following solutions: potassium permanganate 5 g. per l.; sodium carbonate 50 g. per l.; ferrous ammonium sulphate 20 g., sulphuric acid 30 g. in 1 litre; sulphuric acid 500 ml. in 1 litre.

40 ml. of the sodium carbonate and 20 ml. of the permanganate are placed in each of two flasks, and to one of these the solution equivalent of 0·05 g. of the material to be examined is added, the same volume of water being added to the other. The flasks are warmed on the water bath for 3 minutes, cooled, and 50 ml. of the ferrous ammonium sulphate added to each, the excess being estimated by the permanganate. The difference represents the formic acid present, each ml. of permanganate solution being equivalent to 0·00351 g. of formic acid.

7. *The lignin* is determined as follows: 2 g. of wood are extracted for 4 hours with a mixture of benzene-alcohol (2 : 1 by volume). The solvent is removed and the sample treated with ten times its weight of 72 per cent. sulphuric acid. After 16 hours the acid is diluted to a concentration of 3 per cent., and the solution boiled under reflux for 2 hours. Compare recent criticism, p. 370.

Estimation of Methyl Alcohol and Pectin.—The method of v. Fellenberg[2] has been employed for the estimation of pectin in woods. The methyl alcohol yielded on hydrolysis is converted to

[1] A. Fouchet, *Chem. Soc. Abstr.*, 1912, ii., 499.
[2] T. von Fellenberg, *Biochem. Z.*, 1918, **85**, 68.

pectin, assuming the relation MeOH × 10 = pectin. In view of the small amount of pectin, if any, present in woods and the uncertainty of the above relation, it is perhaps better to examine the carbon dioxide yield. A description of von Fellenberg's technique is given by A. W. Schorger, " Chemistry of Cellulose and Wood ", 1926.

Determination of Nitrogen in Wood.[1]—3·5 g. are placed in a 550 ml. Kjeldahl flask with 10 g. of sodium sulphate anhydrous, 0·3 g. of copper sulphate crystals, and 25 g. of concentrated sulphuric acid. The flask is heated below the boiling-point of the acid until frothing is over, after which the acid is boiled briskly until oxidation is complete.

After cooling, 200 ml. of water are added with a few pieces of pumice stone. About 60 ml. of saturated NaOH solution are then poured down the side of the flask, so that the alkali does not mix at once with the acid. The liquid must be strongly alkaline. The flask is at once connected with a bulb attached to a condenser. An adapter leads to the bottom of a vessel containing 50 ml. of *N*-HCl and 0·5 ml. of methyl red indicator. The flask is shaken and 150 ml. distilled over, the distillate being titrated with 0·1 *N*-alkali. A blank experiment, using 3·5 g. of cane sugar, may be run.

The nitrogen found × 6·25 gives the protein.

ASH CONTENT OF WOOD AND OTHER PLANT MATERIALS

Name of Material.	Per cent. Ash.	Name of Material.	Per cent. Ash.
Conifers	0·22–0·33	Esparto	3·6
Deciduous trees	0·37–0·57	Bamboo	1·6–2·0
Bark of fir	5·8	Cotton, American	0·1–1·8
„ „ beech	8·8	„ Egyptian	0·25
Cork	4·1	Flax	1·0
Bran from barley	4·4	Hemp	0·6–0·8
„ „ rye	5·3	Jute	0·7
„ „ wheat	5·8	Ramie	0·25
Straw of barley	5·5	China grass	2·9
„ „ rye	3·2	Apple peel	2·7
„ „ wheat	5·8	Potato peel	9·0
„ „ maize	4·0	Hay	7·5–8·0

The chemical composition of the ash naturally varies considerably. The ash of the wood of forest trees may contain per cent.; CaO, 20–45; MgO, 2–8; Fe_2O_3, 1–5; Mn_3O_4, 0·1–22, or even 40; Na_2O, 1–10; K_2O, 10–40; SiO_2, 1–10; P_2O_5, 1–10.

[1] " Methods of Analysis ", A.O.A.C., 1919, p. 6.

Evaluation of Pulping Woods.—The *TAPPI* standards (T 1, m, 1934) recommend the distillation method for the estimation of moisture (p. 14). For *solubility in cold water* 2 g. of sawdust are digested with 300 ml. of water for 48 hours at ordinary temperature, washed with water and dried at 105°. *Solubility in hot water* is similar, except that 100 ml. of water is used, heated on a boiling water bath for 3 hours. *Solubility in alkali* is determined on wood screened to pass a 60-mesh sieve, of which 2 g. (oven dry) are digested for 1 hour on a boiling water bath with 100 ml. of a solution containing 1 g. NaOH. The mixture is stirred 10, 15 and 25 minutes after the start. Residue washed with hot water, acetic acid and water.

CHAPTER XXIV

THE INVESTIGATION OF PULP AND PULP PROCESSES

PART I

The Preparation of Cellulose (Pulp) from Wood and other Lignified Materials

THE cellulose prepared on the technical scale from wood and other lignified materials is not a normal cellulose, as it may contain hemicellulose, pentosans, and other constituents of the original wood. The term " pulp " is therefore appropriately used to describe such products. The resolution of wood on the large and small scale may be effected (i) by the action of caustic soda—the soda process ; (ii) by the action of sulphurous acid, alone or in the presence of soluble bisulphites—the sulphite process ; (iii) by the sulphate process, in which a mixture of sodium hydroxide and sodium sulphide is employed ; (iv) by the chlorination process.

The sulphite and sulphate processes are now of major importance in pulp production. The sulphate process is so called on account of the addition of sodium sulphate to the waste liquors, which are concentrated and incinerated for the recovery of alkali. The sulphate becomes reduced to sulphide, and in this way the loss of alkali during the cook is made good. The soda process is employed to a limited extent in America for the processing of hard woods to give a pulp of good bulking quality. It is employed entirely for the resolution of esparto and other lignified fibres, and is useful in the laboratory for isolating cellulose from natural products. The chlorination process has been worked on a limited scale for the production of pulp from cereal straws for local consumption, in Italy, South America and South Africa.[1]

The sulphite process owed its former predominance to the ease with which light coloured, easy-bleaching pulp could then be obtained. This was not possible with the alkaline cooking processes. With modern bleaching methods, however, white pulps can readily be produced from alkali-cooked products and as this opens up a wider range of raw materials, including the use of resinous and hard woods, the alkaline (Kraft) processes have made relatively large

[1] See " Cellulose by Chlorination ", Pomilio, *Ind. Eng. Chem.*, 1939, **31**, 657; " Recent Progress in the Manufacture of Pulp ", Hägglund, *Z. angew. Chem.*, 1939, **52**, 325.

advances in recent years. In addition the normal use of sulphate pulps for the manufacture of wrapping and packaging materials has very greatly increased so that the present world production capacity of sulphate pulp has reached some 7 million tons, compared with 10 million for sulphite and 9 million for mechanical wood.

A study of these processes involves a definition of the conditions of working and a progressive estimation of the pulp yield, the rate of the removal of lignin, etc. Such experimental work is illustrated in the curves shown in Figs. 77 to 80. The analytical values which may require to be determined in a sample of pulp [1] are given in Part II, p. 462.

Production of Pulp by the Action of Sulphurous Acid and Bisulphites.—The general physical action of these reagents is to render soluble the middle lamella (lignin and hemicellulose) and leave the cellulose fibres in loose bundles. The chemical action is less clear, but the sulphurous acid appears to act in two main directions—those of hydrolysis and of sulphonation. Sulphonation, by the addition of sulphurous acid ions at unsaturated groupings in the lignin and by reaction with aldehydic groupings, plays an important part. The fact that acid hydrolysis can also take place is held to be equally important. It has been shown that the proportion of free sulphurous acid exerts a dominating influence on the yield and character of the pulp produced, and that the curves showing the rate of production of sugar during the sulphite cooking of wood are almost parallel with those similarly obtained by the action of other mineral acids. The relative incidence of these reactions is difficult to gauge, but it has been found that at 110° the acid ion penetrates the wood faster than the sulphonic ion, so that irregular action will take place unless sufficient time for complete penetration is given.

The rate at which the action takes place is largely a function of the temperature of working; the acid concentration and the pressure being restricted in technical practice. The lower the temperature which can be employed to effect the removal of the non-cellulose constituents, the greater the strength of the pulp obtained for a given lignin content or bleachability.

The rate of reaction on the large scale is comparatively slow owing to the time taken for the liquor to penetrate the wood chips. Under experimental conditions the rate of change can be greatly increased. Miller and Swanson,[2] for example, working with powdered wood in a small apparatus, with efficient stirring, found that the time required for the reaction was reduced by about one-half

[1] For examples see S. D. Wells, *Ind. Eng. Chem.*, 1921, **13**, 936.
[2] *Ind. Eng. Chem.*, 1925, **17**, 843.

for every 10° increase in temperature between 120° and 150° and that by increasing the concentration of sulphurous acid from 1 to 3 per cent. the time required was again reduced by one-half. In one test they were able to remove 90 per cent. of the lignin in 80 minutes, using a liquor containing 4 per cent. free SO_2 at 150°. A typical laboratory experiment is given in the table, p. 456. Solutions of calcium or magnesium bisulphites were employed to which the necessary amount of free SO_2 had been added.

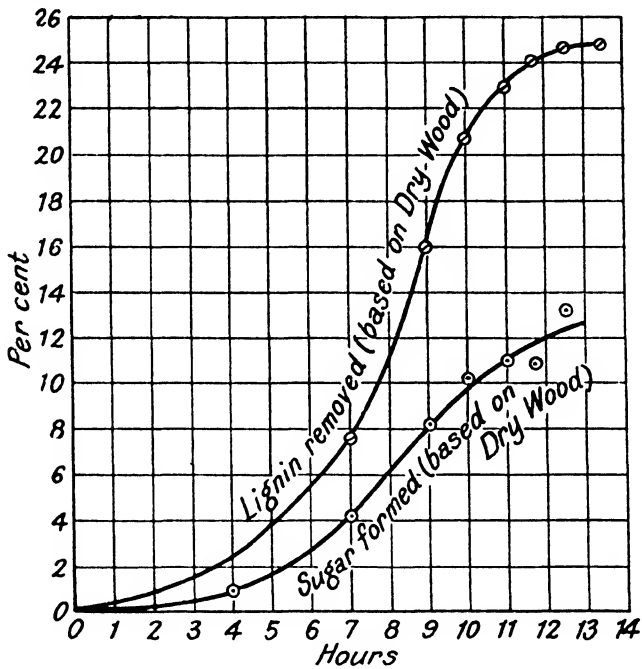


FIG. 77.—Showing the rate of formation of sugar compared with rate of removal of lignin in a sulphite cook, 2·4 per cent. free, and 1·4 per cent. combined, SO_2. (*After Sherrard and Suhm.*)

There were formerly three modifications of the sulphite process —the Mitscherlich, in which indirect heating was used over a long period; the Ritter-Kellner, in which direct heating at a higher temperature for a shorter time was used, and the "quick cook" process. Pulps were classified under these names, which still occur in commercial descriptions. Indirect heating by piping in the digester, however, is no longer used. The adoption of forced circulation in digesters by externally pumping the cooking liquor has made possible the heating of the liquor in a tube system outside the digester. In sulphite pulping direct steam may be introduced at one stage to increase the speed at which the maximum temperature is reached.

In the older methods the total SO_2 varied from 2 to 5 per cent. The modern tendency is towards stronger acids and higher pressures, so that a total SO_2 of 7 to 10 per cent. on the liquor is commonly used. The combined SO_2 should not be less than 1 per cent. generally in the form of calcium or magnesium bisulphite.

As a result of the positive forced circulation of the liquor and improved control of the process, pulps can now be made to close specifications for degree of cooking, bleachability and physical characteristics.

The following table illustrates the laboratory investigation of the sulphite process by Miller and Swanson. The particular series given deals with the variation in the time of the cook :—

ACTION OF SULPHITE LIQUOR AT 120° FOR VARYING TIMES

White spruce, 40–60 mesh—benzene-alcohol extracted—containing cellulose 58·88, lignin 28·55 per cent. Total SO_2, 3·0 ; free SO_2, 2·0 ; combined SO_2, 1·0 and excess SO_2 1·0 per cent. About 15 g. oven-dry wood in each case, 250 ml. of liquor.* Results all oven dry.

Time in hours.	Yield of Oven-dry Pulp on Oven-dry Wood.	Lignin in the Pulp on Basis of the Wood.	Lignin removed on the Original Lignin.	Cellulose in Pulp calc. on the Wood.	Cellulose removed on Original Cellulose.	Residue not accounted for as Lignin or Cellulose on the Wood.
1	92·85	25·42	10·96	54·58	7·32	12·85
3	80·35	21·78	23·71	50·35	14·48	8·22
6	69·93	16·54	42·06	49·04	16·71	4·35
9	62·66	10·95	61·64	48·66	17·37	3·05
12	56·03	5·67	80·14	48·15	18·22	2·21
15	53·19	3·66	87·18	47·16	19·90	2·37
18	51·80	2·66	90·68	47·29	19·68	1·85
21	50·94	2·02	92·92	46·70	20·68	2·22

The results of further laboratory trials in which other factors are determined will be found summarised in Figs. 78, 79, 80.

In addition to these processes sulphurous acid alone at a concentration of 7 per cent. SO_2 and a temperature of 100–115° for 15 to 48 hours resolves the wood substance, but a better bleaching pulp is obtained by the addition of 0·1 to 0·5 per cent. of ammonia (NH_3) on the weight of the liquor used, the temperature being 95–110°.

This was demonstrated by experiments in which the action of

* Compared with commercial cooks the total SO_2 is low and the proportion of liquor to wood very high.

ammonia was compared with that of equivalent quantities of lime or soda.[1] The digester employed consisted of an 8 in. drawn steel tube 50 cm. high flanged at both ends. The tube and flanges were

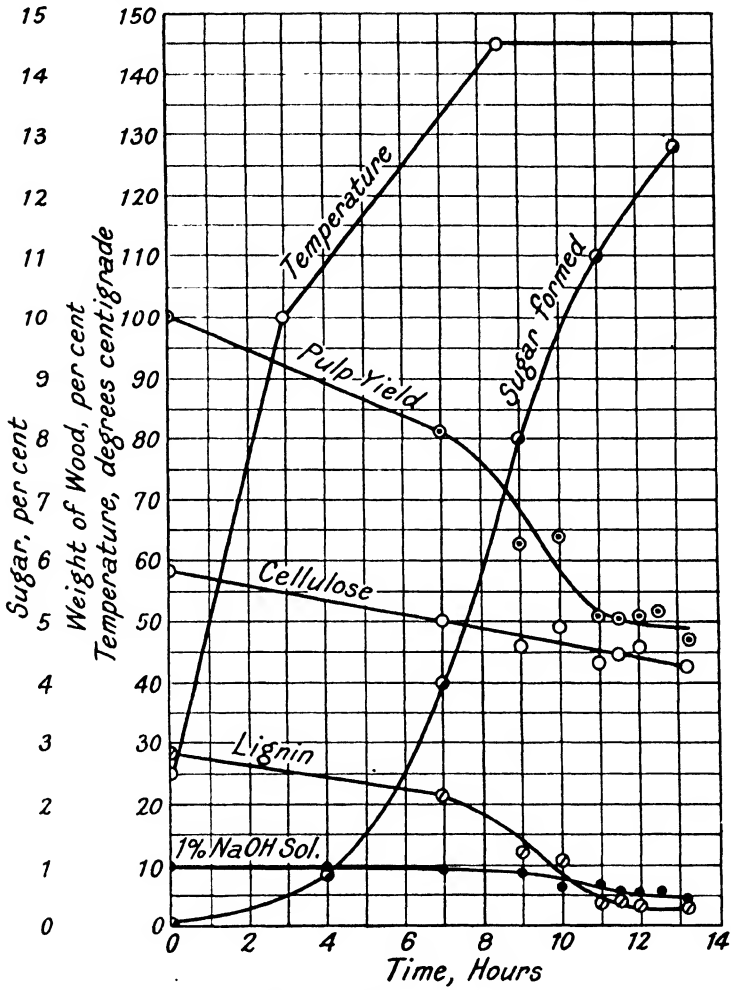


FIG. 78.—The action of sulphite liquor (2·4 per cent. free SO_2) on spruce wood. (Miller and Swanson, *Paper Trade J.*, 1922, **74**, 295; Bray and Andrews, *ibid.*, 1923, **76**, 49; Sherrard and Suhm, *Ind. Eng. Chem.*, 1922, **14**, 931.).*

lined with lead. Volume 14 litres. The cover contained holes for thermometer, gauge, and relief valve for SO_2. Around the cylinder

* The curves shown in Figs. 77, 78, 79 are taken from Hawley and Wise, "The Chemistry of Wood", Chemical Catalog. Co. Inc., 1926, by courtesy of authors and publisher.

[1] C. F. Cross and A. Engelstad, *J. Soc. Chem. Ind.*, 1924, **43**, 253 T; 1925, **44**, 267 T.

was wound a spiral of nichrome wire for electrical heating. At the conclusion of the operation the SO_2 was blown off through cooled water.

In each case 1·8 kg. of air-dry chips was heated with 10 l. of liquor (8·53 g. SO_2 per 100 ml.) and kept at 100° for 24 hours (pressure 6·9 kg./cm.^{2}).

Experimental Methods for the Investigation of the Sulphite Process.—The majority of the following methods are those used in the United States Forest Products Laboratory, described in "The Chemistry of the Sulphite Process", by Miller, Swanson and others.[1]

The experimental autoclave was an ordinary upright digester In addition to the connections for direct steam heating a lead coil was installed in the lower half of the digester for indirect heating. A small lead pipe cooler was attached to the sample plug to enable cold samples to be drawn.

The digester was filled full of bone-dry wood chips (100 lb.) and these were steamed for half an hour, whereby they acquired regularly 22 per cent. of moisture. The blow-off valve was closed and the acid run in until the digester was completely filled. It was then allowed to stand overnight. Heating was by indirect steam in the coil. Temperature reached 100° in 3 hours, 145° in 8·5 hours, at which it was maintained. The other conditions were: Gallons of cooking liquor, 61–65; SO_2 per cent. total, 3·80—free, 2·40; combined, 1·40. Yield of screened pulp 80 to 48. For further details see Kress, Wells and Edwards, "The Equipment and Operation of an Experimental Pulp and Paper Laboratory", *Paper*, June, 1920.

D. E. Cable has described a laboratory digester equipment. A small lead-lined bronze autoclave was employed which was heated in a large electric oven. The outlet pipe from the digester carrying the gauge and needle valve was led outside the oven, opening of the oven being avoided. An oil seal was used to protect the gauge and valve from the sulphur dioxide.

The digester carried three 12 oz. wide-mouth bottles and each produced about 30 grams of pulp. They rested on a porcelain desiccator disc. 65 grams of chips were placed in each and covered with a thin pad of cheese cloth weighted with glass rods to prevent floating when the liquor (a 6 per cent. solution of SO_2) was added.

Analytical Control.—The iodine method of Winkler, generally employed for the estimation of the total SO_2, has been found unsuitable for samples taken during the progress of the cook, errors being caused by the organic products present. The following procedure is recommended by Miller and Swanson (*loc. cit.*):—

[1] The Lockwood Trade Journal Co., 10 East 39th Street, New York.

(*a*) The liquor is titrated with alkali till neutral to phenolphthalein, allowed to stand half an hour, and then titrated with *N*/16 iodine solution with starch indicator. The figure gives the total sulphur dioxide.

(*b*) The combined SO_2 is measured by an adaptation of the Sander Method.[1] This ostensibly gives both total and combined SO_2, but it would appear that loose or reversible SO_2 is partly brought into reckoning during the necessary titration,[2] so that only the combined SO_2, which depends upon the difference of two titrations, is considered reliable.

A 2 ml. sample of liquor is diluted with water to about 100 ml. and titrated with *N*/8 NaOH, using methyl orange, or bromophenol blue, as indicator. When neutral an excess of a saturated solution of mercuric chloride is added, upon which the mixture becomes acid again. Titration is continued till the contents are again neutral to the indicator. 0·4 times the second titration gives the percentage of total SO_2. 0·2 times the difference between the second and first gives the percentage of combined SO_2.

The first neutral point is reached when all the excess SO_2 is present as bisulphite. Mercuric chloride reacts with this, forming, according to Sander, a complex of the formula $Ca(HgCl.SO_3)_2$, liberating 1 molecule of HCl per HSO_3 ion ; thus :

(1) $H_2SO_3 + Ca(HSO_3)_2 + NaOH \rightarrow NaHSO_3 + Ca(HSO_3)_2 + H_2O$

(2) $NaHSO_3 + Ca(HSO_3)_2 + 3HgCl_2 \rightarrow NaHgCl.SO_3 + HCl + Ca(HgCl.SO_3)_2 + 2HCl.$

The loosely combined SO_2 which is split off by alkali, may also be estimated by the method given by *TAPPI* (Analysis of Sulphite Waste Liquor, O 403, sm–40, corrected 1940). For this 5 ml. of the liquor is shaken with 5 ml. NaOH (10 per cent.) to set free the loosely combined SO_2. After 1 hour, 60 g. of ice are added and the liquid neutralised with dil. H_2SO_4 and titrated with 0·1 *N*-iodine using starch. The SO_2 found includes the free SO_2 which is estimated as follows and subtracted : 5 ml. of liquor are run on to 50 g. of ice in 25 ml. of water and the liquid titrated with iodine as before.. A full investigation of the problems involved has been given by E. Oman.[3]

The total calcium is determined by heating the liquor with

[1] A. Sander, *Paper Trade J.*, 1920, **81**, No. 10.

[2] P. Klason, " Beitrage zur Kenntnis der Chem. Zusammensetzung der Fichtenholz ". He notes that one molecule of SO_2 is so loosely bound that it may be partially titrated by iodine.

[3] E. Oman, *Cellulosechem.*, 1927, **8**, 117 ; also M. Hönig and W. Fuchs, *Ber.*, 1927, **60**, 782.

nitric and sulphuric acids until a pale yellow solution is obtained. After dilution the calcium is precipitated as oxalate and the oxalic acid estimated as usual.

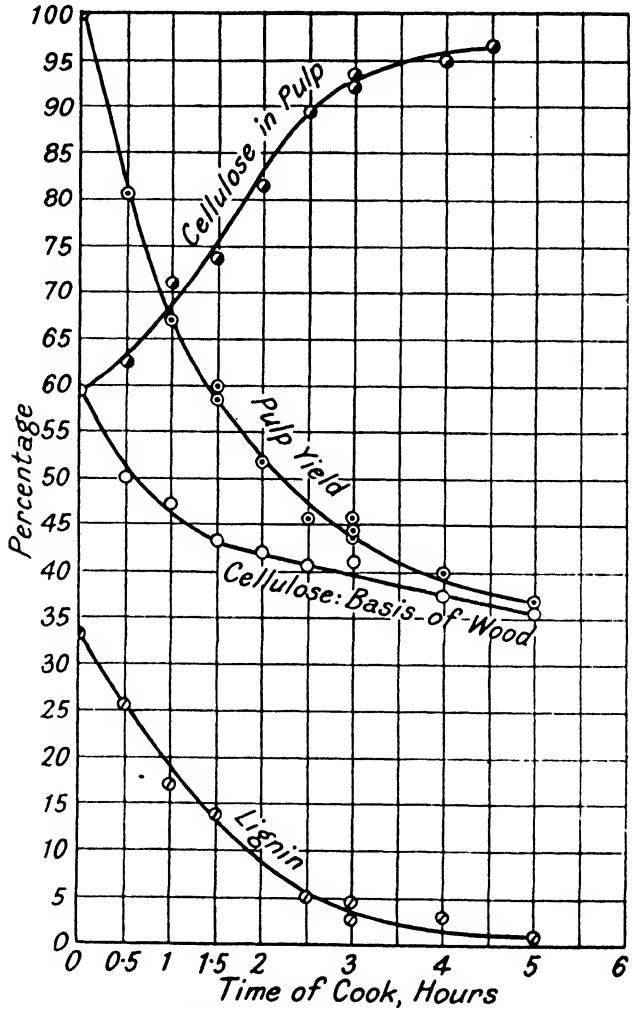


FIG. 79.—The action of soda liquor on jack pine wood.

Production of Pulp by the Action of Caustic Soda Solution.—The lignin in this process is removed as a soluble sodium compound. Experience has shown that it requires more than 20 per cent. of NaOH (on the dry wood) to produce a satisfactory pulp, so that in practice the amount used is from 25–35 per cent. About 900 gallons of solution containing 6–10 per cent. of NaOH are used per cord of wood chips. The process is relatively short, as a high

temperature is employed such as 170–180°, which is reached in 1 to 2 hours. The temperature is then maintained for 2 to 8 hours more. The cooking time depends on whether it is desired to make strong, or easy bleaching pulp. To obtain movement in the digester the pressure is released from time to time. The pulp yield is about 40

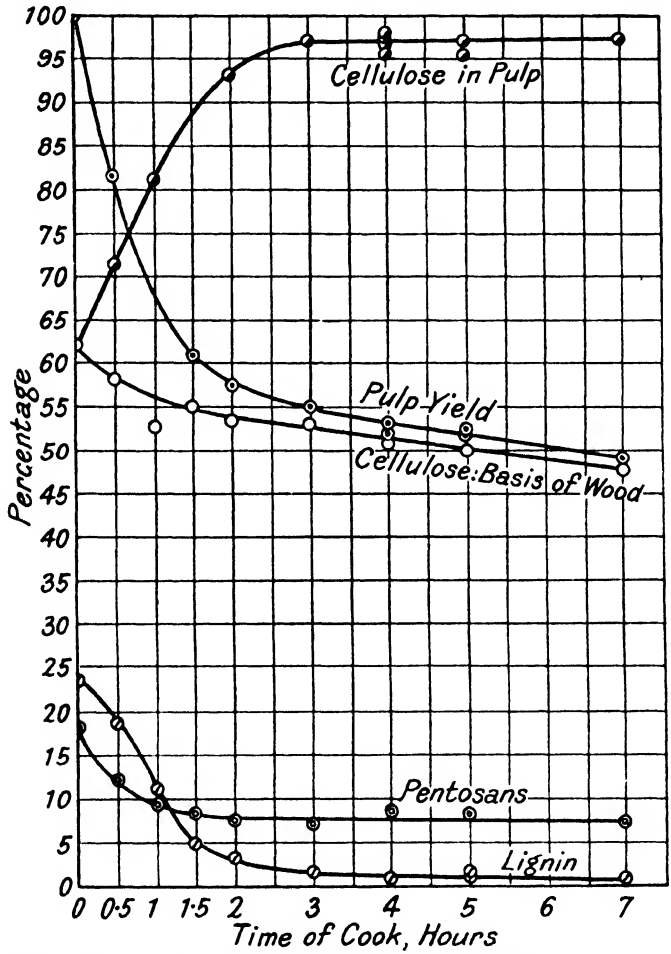


FIG. 80.—The action of soda liquor on aspen wood. (Bray and Andrews, *Paper Trade J.*, 1926, **76**, 49; S. S. Aiyar, *Ind. Eng. Chem.*, 1923, **15**, 714.)

per cent., but lower yields, of course, are obtained with the longer cooks. Hard woods require less time (about 4 hours), and less alkali than coniferous woods, such as spruce, which require 6 to 7 hours.

A series of experimental cooks on aspen (hardwood) and pine species was carried out by Bray and Andrews [1] under the following

[1] M. W. Bray and T. M. Andrews, *Paper Trade J.*, 1923, **76**, 19, 49; *cf. ibid.*, *TAPPI*, 1936, 48.

conditions: 100 lb. of dry chips; 20 lb. NaOH; initial volume of cooking liquor, 25 gals. Liquor raised to the maximum of 170° in 1 hour. Some of the results are shown in Figs. 79 and 80. It will be seen that the lignin is dissolved very rapidly from the beginning and is completely removed in 3 to 4 hours. The volatile acid reaches a maximum in 1·5 hours. The methoxyl content of the pulp from pine wood decreased rapidly in the first 2 hours and reached a constant value after the third hour.

The Sulphate Process.—Saw-mill waste or a mixture of waste and round wood is generally used in this process. The older type of digester rotated, but external circulation of the liquor by pumping is now more usual. External heating also has largely replaced direct steaming, with the advantage of maintaining reagent concentration.

The cooking liquor is made from a mixture of black liquor from earlier cooks and re-causticised liquor from the recovery plant. The sodium sulphate added during the recovery cycle is reduced to sulphide during the burning and smelting, which is controlled to 25 to 33 per cent. of the total alkalinity.

A typical industrial charge would be: chips (22–25 per cent. moisture), 37 cubic metres; white liquor (3·2 per cent., Na_2S; 9·2 per cent. NaOH), 7 cubic metres; black liquor, 3·8 cubic metres. Owing to more rapid penetration of the chips the cooks are much shorter than in the sulphite process. Temperatures up to 180°; normal time 5–6 hours, reduced to 3 in some mills.

Sulphate pulp can now be produced to close specification, both in regard to bleachability and any particular physical characteristic, such as burst or tear quality.

Part II

The Examination of Pulps

The general information required in handling a sample of pulp is similar for all types, but special points arise as between pulps intended for paper making and those intended for the manufacture of rayon. These will be considered separately.

The determination of physical characteristics (strength, colour, etc.) is of importance in paper making, and the necessary standard physical tests will be found in the "Second Report of the Pulp, Evaluation Committee", Paper Makers' Association, London, 1936, and J. Grant, "Wood Pulp", London, 1938.

The chemical tests to be considered below include references to the standard methods of the Technical Association of the Pulp and

Paper Industry of America (*TAPPI*). Some or all of the following factors are usually determined :—

(1) Identification of the fibres present in the sample, its fibre composition and process of manufacture. (2) The cellulose content and/or the α-, β- and γ-fractions. (3) Bleachability. (4) Resin. (5) Solubility in alkali and in water. (6) Lignin. (7) Copper number. (8) Acidity. (9) Methoxyl. (10) Ash. (11) Viscosity.

The moisture content is determined by drying in a boiling water oven, or at 105° in the electric oven. About 5 hours is sufficient to reach constant weight. The distillation method is also used.

1. **Identification of the Nature and Method of Preparation of a Pulp.**—Various staining reagents are used in conjunction with the microscope to identify the fibre material employed and, in the case of a mixture, by counting the fibres specifically stained, it is possible to estimate the proportion of each fibre present.

Some of the reagents may be applied directly to the pulp, and the effect examined with a hand lens. For the microscope test a minute bundle of fibres is pulled from the moist pulp, and added to a drop of water placed on a glass slide. The bundle is then teased out into separate fibres and slides are prepared so that about 10 fibres are present in each circular field of the microscope. The slide is warmed until the fibres just dry out, when they will adhere closely to the glass.

A drop of the stain is then placed on the cover glass, which is inverted and placed over the dried pulp, care being taken to exclude air-bubbles. Staining requires about 1 minute. For qualitative reactions see under the separate stains (p. 347), of which Herzberg's is the most useful for general purposes. For quantitative estimation the number of fibres stained with each colour is counted together with the total number in the field. At least ten fields should be counted and the results averaged.

Recent investigation shows that the results obtained by microscopic estimation are far less accurate than previously supposed. A conservative report on a fibre furnish would give a range of 5 per cent., *e.g.* mechanical wood, 45–50 per cent., with a probable error of ± 5 per cent., giving an overall range of 15 per cent. For identification other characters such as resin and pentosan content, strength, etc., give more reliable information.

The following tests are used to determine the method of preparation of a sample of pulp :—

(*a*) *Distinction between Sulphite and Soda Pulps* may be effected by the use of Alexander's stain.[1] The following solutions are required :—

[1] E. P. Cameron, *Paper*, 1924, **33**, 26, 138.

A. 0·2 g. of Congo Red in 300 ml. of water ; B. 100 g. of calcium nitrate in 50 ml. of water ; and C. Herzberg's iodine stain, made by mixing solutions of (1) 20 g. zinc chloride in 10 ml. of water with (2) 2·1 g. of KI and 0·1 g. of iodine in 5 ml. of water.

The sample is stained by treating with 2 drops of A for 1 minute. The excess is removed with blotting paper and the sample allowed to dry. It is then placed on a microscope slide and covered with 3 drops of B for 1 minute, after which 1 drop of C is added and the liquids quickly mixed. The cover glass is put on, and after 3 or 4 minutes the sulphite is uniformly stained pink and the soda blue.

A difference is also found in that the chloroform extract from sulphite pulps gives the reactions of cholesterol, whilst that from soda pulp does not. Abietic acid gives the cholesterol tests, and the difference is probably due to the fact that the soda cook removes resin more completely than the sulphite cook.

About 0·5 g. of pulp is boiled with a little chloroform and the extract filtered. To the cold filtrate 0·5 ml. of acetic anhydride is added and then about 1 ml. of concentrated sulphuric acid is poured down so that the liquids do not mix. A rose colour, becoming green on adding excess of acid, indicates sulphite pulp, whilst soda pulp gives only a yellowish colour.

(*b*) *Distinction between Unbleached Sulphite and Sulphate Pulp by the Lofton-Merritt Stain.*[1]—The solutions required are :—

A. 2·0 g. of malachite green in 100 ml. of water ; B. 1 g. of basic fuchsine crystals in 100 ml. of water ; C. 1 ml. concentrated hydrochloric acid in 1 litre of water.

One volume of A is mixed with two volumes of B immediately before use. The pulp is treated with 2 drops of the mixture for 2 minutes and rinsed with 4 drops of the acid C, soaking for 10 seconds, after which the acid is absorbed with blotting paper, the pulp treated with a few drops of water, and again dried with blotting paper. Unbleached coniferous sulphite pulp shows violet or lavender and unbleached coniferous sulphate pulp appears green. It is advisable to make comparison tests with samples of known origin.

(*c*) *Distinction between Bleached and Unbleached Sulphite Pulp.*[2] —The lignin residue in the unbleached pulp will reduce the ferric ferricyanide reagent, giving a green or blue colour, which is thrown into contrast by the use of a red dye. The following solutions are required :—

A. 2·7 g. of ferric chloride ($FeCl_3.6H_2O$) in 100 ml. of water ; B. 3·29 g. of potassium ferricyanide in 100 ml. of water ; C. 0·4 g.

[1] R. E. Lofton and M. F. Merritt, *Bur. Standards, Tech. Paper*, 189, 1921.
[2] C. G. Bright, *Ind. Eng. Chem.*, 1917, **9**, 1044.

Benzopurpurin 4B extra and 0·1 g. Oxamine Brilliant Red BX in 100 ml. of hot water.

A mixture of equal volumes of A and B is brought to 35°, the pulp immersed in it, and the liquid kept at 35° for 15 minutes. The material is washed six times in water and warmed in water. The pulp is then stained in solution C at 45° for 5 minutes. On rinsing the bleached fibres will be dyed red and the unbleached blue.

2. **Estimation of the Total Cellulose and the α-, β- and γ-fractions.**—The chlorination method is always employed and is given on p. 355. For the *TAPPI* modification, see p. 356.

The determination of α-cellulose is given fully on p. 363. The corrected official *TAPPI* method (T 203, m-44, 1944) given below, is similar in detail, but differs essentially in that the dilution period is omitted. The pulp to alkali ratio is also different.

Procedure.—Three grams of shredded pulp are broken up under 35 ml. of 17·5 per cent. (wt./wt.) solution of pure NaOH (*d*, 1·197, 15°), and after 5 minutes 40 ml. more are added gradually in 10 ml. portions during 10 minutes. The whole is kept at 20° for 30 minutes, mixed well with 75 ml. of water at 20° and filtered *at once* by suction, the cellulose forming its own mat. The filtrate is passed through several times till clear. Washing with 750 ml. of water is followed by soaking in 40 ml. of 10 per cent. acetic acid at 20° for 5 minutes, applying suction, and washing till neutral. The α-cellulose is dried at 105°, weighings being made every hour after the first 6 hours. This period may be shortened by the use of alcohol and ether.

If desired, especially with unbleached pulps, a correction can be made for lignin present in the α-cellulose. The α-cellulose is soaked in 5 ml. of water for a day, then treated with 45 ml. of sulphuric acid (76·76 per cent. by weight, H_2SO_4) at 25° for 16 hours, after which 1·57 l. of water is added and the mixture boiled 2 hours under reflux. The lignin left is separated, washed and dried.

The question of a dilution stage in the α-cellulose estimation is of some importance. It has been urged that as industrial mercerisation in the viscose process is not followed by dilution the α-cellulose content of pulps intended for viscose manufacture should be determined without a dilution period as in the above and other methods. For the estimation of β- and γ-cellulose see p. 364.

3. **Estimation of the Bleach Requirement, or Bleachability, and the Degree of Cooking of Pulps.**—The more completely the lignin, resin and other extractives are removed during the cooking and washing processes the less bleach will be required for a good colour and, in this way, an indication of the extent to which cooking

has proceeded can be obtained. Control methods are based either on the amount of chlorine absorbed by the pulp or on the amount of an oxidising agent, such as hypochlorite, permanganate or bromate, which reacts with the pulp under specified conditions.

The absorption of chlorine, either gaseous or in solution, gives a direct measure of lignin content and degree of cooking. The value can be determined quickly, but rather elaborate apparatus is required for the gaseous absorption (Roe value). The bromate (Tingle) method is essentially a laboratory process, but the determinations of the so-called Sieber number, in which the pulp is allowed to react with bleaching powder solution, and in particular that of the Oestrand number—the amount of permanganate required for oxidation under standard conditions—are quick and accurate, and need no special apparatus. There are a number of modifications of each of these methods in use.

Curves and tables have been published with the object of interpreting one value in terms of another, the Roe value being generally taken as the standard. Thus D. Johansson [1] has shown that the relationship between chlorine number and permanganate number can be represented by a straight line, and Bergman [2] has correlated the chlorine number with bleachability. A critical examination of the relationships between all the more important methods in technical use, carried out by the leading Scandinavian laboratories, was brought before the Pulp Purification Committee of the Technical Association of the Pulp and Paper Industry of the United States at the autumn meeting of 1941.

From general experience it may be said that curves connecting the various methods can be constructed, but no absolute relationship exists. A curve from which, for example, the Oestrand number can be read from the Roe number is valid for one mill and one process only and as such has a definite utility. But a curve made for sulphite pulp is not valid for sulphate, and variations in processing change the relationship. If the Roe values are plotted as abscissæ the ordinates of the lines representing the various permanganate numbers are higher for sulphate than for sulphite pulp. Thus a Roe number of 5 may give a permanganate number of 20 for sulphite and 25 for sulphate pulp. Again, for sulphite pulp the Sieber chlorine number and one-tenth of the Oestrand number are almost identical in terms of Roe number, but for sulphate pulp they are quite different.

[1] *Paper Trade J.*, 1935, **101**, *TAPPI*, Sect., 197. See also p. 474.
[2] *Papier Fabrik.*, 1926, **24**, 744.

(*a*) *The Bromate Method of A. Tingle.*[1]—The following reagents are required :—

(*a*) Sodium bromate solution.—8 g. of bromine are shaken with 100 ml. of *N*-sodium hydroxide until dissolved ; the liquid is boiled for some time and diluted to 1 litre. The reagent is standardised by adding potassium iodide, acidifying with hydrochloric acid, and titrating with 0·1 *N*-sodium thiosulphate solution.

(*b*) The acid solvent.—50 ml. of sulphuric acid (*d*, 1·84) are poured slowly into 450 ml. of hydrochloric acid (*d*, 1·19) ; the mixture is shaken, cooled and kept in a cool place.

Procedure.—0·5 to 0·75 g. of the dried pulp in a glass stoppered bottle is treated with 30 ml. of the acid solvent, and shaken to dissolve the pulp, which may take half an hour. Meanwhile 300 ml. of water are adjusted to 23–28°, and when ready the bottle and its contents are brought to the same temperature, the water poured in, and the whole thoroughly shaken. 10 ml. of the bromate solution are allowed to trickle slowly down the side of the bottle, which is then closed and the contents shaken. After standing for 20 minutes with occasional gentle shaking 2 g. of KI in 25 ml. of water are added and the liberated iodine titrated at once. The reaction is slow at the finish as iodine is adsorbed by the cellulose. The end-point is known by the mass becoming white or cream-coloured. If A is the weight of chlorine in 1 ml. of 0·1 *N*-solution, *i.e.* 0·00355 g., B, the number of millilitres of 0·1 *N*-bromate solution consumed, and X the weight of pulp taken, then the

$$\text{Chlorine number} = 100 \times A \times B/X,$$

the chlorine number being the weight of chlorine reacting with 100 parts of dried pulp.

In practice the weight of chlorine required is considerably more than this, and is found by multiplying the chlorine number by an empirical factor K. The value of K is about 3 for sulphite pulp and from 3·6 to 4·9 for soda pulps.

(*b*) *Estimation of the Chlorine absorbed by Lignified Products.*—The method described by R. B. Roe [2] for estimating the chlorine absorption of pulp is now generally adopted. It is described below, and the *TAPPI* standard modification of it on p. 356. A somewhat different apparatus was used by H. W. Strong.[3] A simple method in which chlorine water is used is given on p. 469.

[1] A. Tingle, *Ind. Eng. Chem.*, 1922, **14**, 40 ; T. M. Andrews and M. W. Bray, *ibid.*, 1923, **15**, 934.

[2] R. B. Roe, *Ind. Eng. Chem.*, 1924, **16**, 808.

[3] H. W. Strong, *J. Soc. Chem. Ind.*, 1928, **47**, 88T.

Determination of the Chlorine Number or Roe Number.—The apparatus is shown in Fig. 81. A levelling bottle L, joined to cock K and another bottle J, joined to clamp I, are omitted. The burette A is calibrated into 100 ml. × 0·2. It carries a three-way cock C (fitted with a side capillary) and is surrounded by an air jacket. The capillary at the top of the burette carries a rubber stopper with a small one just above, as shown. The former carries a water jacket D and the latter a reaction bulb E. The burette H is an inverted Mohr burette. The bottle L contains a filtered solution of calcium chloride of *d*, 1·285. The bottle J and burette H are filled with water. The top of the bottle L is connected by rubber tubing with a draught cupboard.

Procedure.—The apparatus is first disconnected above C. Burette A is filled with liquid from L and the side capillary of C is connected with the chlorine cylinder. On opening the cock chlorine displaces the liquid in A and is allowed to bubble slowly through the liquid in L for about a minute. The gas is then expelled into the air by raising L and the process repeated. At the third time the chlorine is shut off when the level stands between 90 and 100 ml. in burette A. The chlorine is expelled from the upper capillary of cock C by means of a piece of finely drawn out glass tubing. The level in A is then approximately adjusted to give atmospheric pressure.

2 g. of oven-dry pulp in thin sheet are weighed, immersed in water, squeezed between blotters, and replaced on the balance, water being added if necessary to make the weight 4·5 g. It is then placed in bulb E and with a bent wire brought down, leaving the upper one-third of the bulb empty. D and E are then fitted and D filled with water at 25°. The water in burette H is brought to some definite point in the capillary bridge G, clamp F being shut, C is then opened so as to connect the burette and reaction bulb, and the levels adjusted and the volume noted. The bottle L is now raised so as to put the gas under a slight positive pressure and clamp I is opened. At an observed minute F is opened slowly and the water level in H allowed to fall till about 10 ml. of air have passed into H. Clamp F is then shut and the level of the water in H is adjusted to that of the bottle J, after which clamp I is closed. The absorption of chlorine is very rapid during the first 5 minutes and the level in A is frequently adjusted to that in L, cock K being closed between each adjustment.

Exactly 14 minutes from the time clamp I is opened the water in H is forced up by opening clamp I, cock K, and clamp F in order. When the water has reached the original mark on the capillary

bridge, clamps F and I are shut and the volume at once read at atmospheric pressure.

The number of grams of chlorine absorbed by 100 g. of oven-dry pulp less a " blank " correction of 0·4 per cent. is called the " chlorine number ".

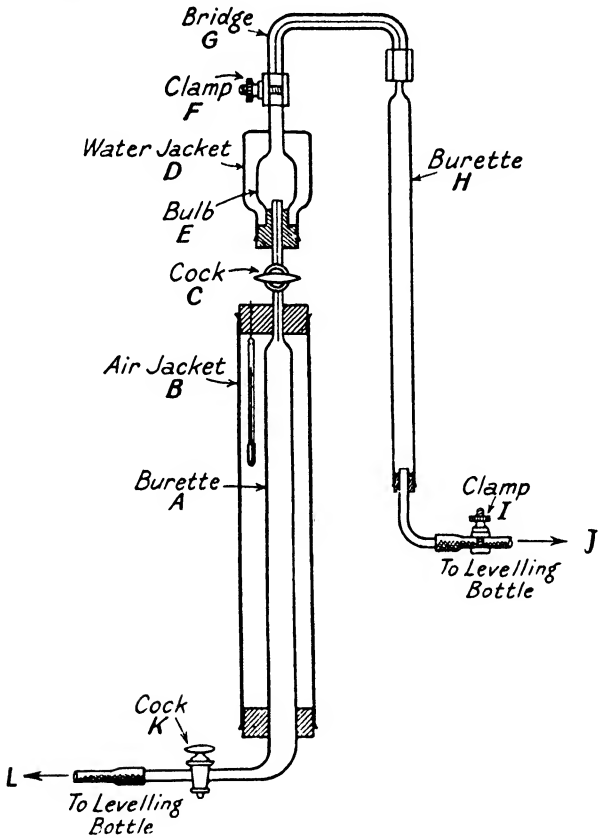


FIG. 81.—Apparatus for the determination of the chlorine number. (*After R. B. Roe.*) Levelling bottles L, on the left, and J, on the right, are omitted. (From *Ind. Eng. Chem. loc. cit.*)

Each determination takes about 20 minutes, and the average error is 0·8 per cent.

Weight of 1 litre of chlorine at 25° :—

Pressure in mm. .	735	740	745	750	755	760
Weight in grams .	2·807	2·826	2·845	2·864	2·883	2·912

Chlorine Absorption using Chlorine Water.—The chlorine number can readily be determined as follows : [1] Air-dry pulp

[1] A. Kung, *Papier Fabrik.*, 1935, **33**, 60 ; L. R. Benjamin and J. L. Somerville, *Bull. Council Sci. Ind. Res.* (Australia), 1928, **37**, 26.

equivalent to 1·5 g. bone dry, are weighed into a filter flask and steamed until there is an increase of 5 g. in weight. The flask is closed with a rubber bung carrying a glass tube drawn to a jet. The side-arm is connected with a 3-bulb absorption bubbler containing 10 ml. of 30 per cent. KI solution. The apparatus and all solutions used are now adjusted to 20° and 100 ml. of fresh chlorine water (about 0·6 per cent.) are run in through the glass tube (which is first filled with chlorine water) from a constant feed burette. The jet is closed with a clip on the rubber tube connector and the flask shaken gently for 15 minutes. The KI solution is run into the flask from the bubbler followed by an additional 10 ml. of iodide solution. The iodine liberated is titrated with 0·5 *N*-thiosulphate solution and the blank of the chlorine water estimated at the same time.

(c) *Permanganate Methods (Oestrand Number).*—(i) The original Oestrand process [1] is as follows: Air-dry pulp, well disintegrated, corresponding to 1 g. of oven-dry pulp is weighed into a 600 ml. tall type beaker and 180 ml. of distilled water and 20 ml. of sulphuric acid (1 vol. acid *d*, 1·84, with 9 vols. of water), all at 20°, are added. The mixture is stirred with a glass stirrer, at first slowly and then at 500 (or better 350) r.p.m. The temperature is maintained at 20° and 50 ml. of 0·1 *N*-permanganate (at 20°) added from a beaker. The stirring is continued for exactly 5 minutes, immediately after which 50 ml. of 0·1 *N*-ferrous ammonium sulphate containing 100 ml. conc. sulphuric acid per litre are added. When the liquid has become colourless it is back titrated with the 0·1 *N*-permanganate until the first pink colour appears, stirring being continued throughout. Alternatively one-half (150 ml.) of the liquid may be removed and titrated.

The permanganate (Oestrand) number is now expressed as the number of millilitres of 0·1 *N*-potassium permanganate consumed by 1 g. of oven-dry pulp (although the original number was calculated on 2 g. of pulp).

(ii) The following variation,[2] based on the Swedish standard Committee's report, is also recommended.

Solutions (A) of permanganate (3·161 g. $KMnO_4$ per litre) and (B) of ferrous ammonium sulphate (40 g. per litre) are required. The equivalent of 2 g. of dry pulp are disintegrated in water with high speed stirring, made up to 200 ml. with water and the temperature brought to 20°. The whole is then stirred at 700–800 r.p.m. with a propeller-shaped glass rod, and when well mixed 100 ml. of sulphuric acid (1 to 4 by vol.) are added and then, rapidly, 50 ml.

[1] D. Johanssen, *Paper Trade J.*, 1935, **101**, *TAPPI*, 197.
[2] *Svensk Papperstid.*, 1930, 930.

of solution A. After exactly 5 minutes 40 ml. of B are added and the excess titrated with the 0·1 *N*-permanganate to faint pink, the stirrer being kept running. If the excess of permanganate falls below 10 ml. the test is repeated, using 100 ml. of A.

The blank experiment is made, omitting the pulp, and the permanganate number calculated on 2 g. of pulp.

Comparisons of this process with the Sieber number show that for Sieber numbers 1, 1·5, 2 and 3 the permanganate numbers were, for sulphite pulps 16, 28, 40 and 68, and for sulphate pulps 15, 20, 26 and 42 respectively (Cross and Bevan).

(iii) The Soederquist modification of the Oestrand process gives a reaction time of 3 minutes with a temperature of 25°.

(iv) The *TAPPI* Tentative Standard, T 214, m-37, 1937, defines the test as the number of ml. of 0·1 *N*-permanganate solution absorbed by 1 g. of dry pulp. The necessity for varying the amount of permanganate with the bleachability of the sample is recognised, but in every case the liquid is diluted to give *N*/300 $KMnO_4$ and 0·133 *N*-H_2SO_4. The excess of permanganate is estimated by means of potassium iodide and sodium thiosulphate.

Solutions required: 0·1 *N*-$KMnO_4$; 0·1 *N*-$Na_2S_2O_3$; *N*-KI; H_2SO_4 about 4*N*-, made by adding 106 ml. H_2SO_4 to 0·5 l. of water and making to 1 litre.

The equivalent of 1 g. oven-dry pulp is broken up in a known volume of water. The reagent is prepared by mixing equal volumes of acid and of permanganate with water to give, when added to the wetted pulp, a total volume which will make the permanganate *N*/300. For pulps of average bleachability 25 ml. each of acid and permanganate with water to a total of 750 ml. is used; pulps of higher bleachability 40 ml. of each solution with water to 1,200 ml. With exceptional pulps these quantities may be modified, the relative proportions being kept the same.

The calculated quantity of water is mixed with the measured volume of acid, temperature of this and all solutions is adjusted to 24–26°, and the acid is poured on to the pulp contained in a beaker. The mixture is stirred at 500 r.p.m., the volume of permanganate quickly added and stirring continued for 5 minutes. The reaction is then stopped by adding 5 ml. of the KI solution and the iodine titrated in the usual way in the beaker without filtration. The $KMnO_4$ consumed is the difference between the volume added and the titration number.

Factors are given for the conversion of permanganate number to chlorine number.

(v) Permanganate numbers obtained by the Soederquest modifi-

cation are usually 1 to 1·5 units lower than those found under the Oestrand conditions both for sulphite and sulphate pulps.

More rapid methods of using permanganate have been suggested and are frequently employed. The Björkman number, for example, is the number of millilitres of 0·02 *N*-permanganate solution consumed by 2 g. of the pulp in 30 seconds. The Roschier number, on the other hand, is the time in seconds which 2 g. of air-dry pulp require to decolorise 80 millilitres of 0·01 *N*-permanganate.

A critical examination of all the variables in the Oestrand process (i) has been made in connection with the cooking of Eucalypt Sulphate pulps.[1] The rate of stirring can be varied from 180 to 500 r.p.m. without affecting the result. A rate of 350 r.p.m. is recommended. No difference was observed when the rate of back titration was varied between 4·5 and 35 ml. per minute. An examination of the influence of temperature showed that there was a straight line relationship between permanganate number and temperature over the range 20–30°, the increase in the number being 0·13 unit per degree of rise in temperature.

A study of the time factor showed that the major part of the oxidation was complete within 2 minutes, but that it still proceeded slowly even after 5 minutes. Well cooked pulps, for example, gave an average increase in permanganate number of 3 units per minute during the first 15 minutes, and an increase of 0·4 only during a further 5-minutes. These values indicate that for practical purposes the reaction is complete in the standard time of 5 minutes.

This is not the case with under-cooked pulps which react with the greater part of the permanganate present, and an investigation into the influence of the weight ratio of pulp to permanganate showed that if more than 25 ml. of the solution were consumed the mass effect of the permanganate is so reduced that the numbers obtained are too low. It was found, however, that, provided there is a sufficient excess of permanganate, a maximum value is reached which corresponds to the normal figure obtained by the Oestrand method when the absorption of permanganate is less than 25 ml.

This maximum value, which the authors (*loc. cit.*) refer to as the "true" permanganate number, requires that the ratio of permanganate added to that consumed is not less than 50 : 25. To give a safe margin they recommend that the ratio 50 : 20 should be employed. Working with 1 g. of pulp, therefore, in the standard process, if the absorption amounts to more than 20 ml., check values are carried out in which additional solution is added to give the

[1] P. B. Edwards and A. W. Mackney, *Jour. of Council for Scientific and Industrial Research* (Melbourne), 1938, **11**, 185.

ratio 50 : 20 recommended. At the same time acid and water must be added so that the ratio permanganate : sulphuric acid : water remains as in the Oestrand method at 5 : 2 : 18.

The effect of this modification on the larger permanganate numbers is given in a curve which shows that pulps with Oestrand values of 28, 35 and 40 give " true " values of 30, 40 and 50 respectively, values 10 and 20 being the same in each case.

(*d*) *The Sieber Number.*—This determination utilises the direct action of bleaching powder solution on the pulp. The solution is standardised as to active chlorine and alkalinity. It contains 6 g. of active chlorine per litre with alkalinity equivalent to 200 ml. of 0·1 *N*-alkali per litre. It may be made up by mixing a strong and a weak solution of bleaching powder until these values are obtained or better by grinding 200 g. of bleaching powder with 600 ml. of water and diluting to 2 l. with the addition of the necessary quantity of saturated lime water. The active chlorine is estimated with 0·1 *N*-sodium arsenite solution and the alkalinity with 0·1 *N*-HCl after addition of sufficient hydrogen peroxide of known alkalinity.

Five grams of air-dry pulp are disintegrated and shaken with 200 ml. of water at 20°. Fifty millilitres of the standard chlorine solution are run in with shaking, and the whole kept at 20° for 1 hour in a dark place, again shaken and screened or filtered clear. Fifty millilitres of the filtrate are titrated with arsenite solution and the " Sieber Number " calculated as the weight of chlorine consumed by 100 g. of pulp under the above conditions.

The process as described above employs 6 per cent. of available chlorine on the pulp taken and is generally used for sulphite pulps. For sulphate pulps, however, many laboratories increase the amount of chlorine to 9 per cent.

Variations of the Sieber method are also used in Scandinavian countries. The Bergman number, for example, measures the amount of active chlorine in the form of a calcium hypochlorite solution of definite alkalinity which is consumed in 5 hours at 10° by a 3·33 per cent. suspension of the pulp. The Enso number is determined similarity ; time, 1 hour, temperature 40° and 8·86 per cent. of active chlorine on the weight of pulp used.

(*e*) *Comparison Method for Estimating the Bleach Requirement of a sample Pulp.*—A simple method, of which there are several variations,[1] is to add the bleaching agent to the pulp (10 per cent. consistency in water) until, when the reagent is completely exhausted (iodide-starch test with hypochlorite bleaches), the colour matches that of a standard bleached pulp. The comparison is made

[1] " The Testing of Wood Pulp," Sindall and Bacon, 1912, p. 101.

with standard powders, colorimeters or other methods. About 80 per cent. of the bleach is added first and then small additions are made until the requisite shade of colour is obtained. This makes the process rather slow, but the consumption of bleach liquor under these conditions is very close to that required on the works scale.

Relationship between the Permanganate Number and the Chlorine Number, Lignin Content and Solubility in Sodium Hydroxide.—To determine to what extent these values agree in giving a measure of the degree of cooking of a pulp, 55 pulps prepared from *Eucalyptus* species by the sulphate process were examined.[1] The total alkali varied from 15 to 27 per cent. The permanganate number (P) was the "true" value (p. 472), the chlorine number (C) was measured as on p. 469, and the lignin determination carried out by the U.S. Forest Products (1932) method (p. 373). Solubility (S) was estimated as the loss per cent. after boiling for 1 hour in 0·5 per cent. NaOH. The table gives a few of the values obtained with *E. Sieberiana*.

PULPS FROM *E. Sieberiana*

Pulp.	True $KMnO_4$ Number. P.	Solubility 0·5% NaOH. S.	Lignin per cent. L.	Sum of Lignin and Alkali Soluble. L + S.	Chlorine Number. C.
J. 3 . .	49·8	4·2	4·1	8·3	9·4
J. 8 . .	27·4	3·5	2·2	5·7	6·7
J. 9 . .	16·0	2·7	1·5	4·2	4·4
J. 10 .	12·3	3·2	1·0	4·2	3·3
J. 16 .	34·9	3·3	2·8	6·1	8·1

The results were treated statistically, and the following relationships deduced from the curves drawn :—

$$L = (0{\cdot}086 \times P - 0{\cdot}55) = (0{\cdot}47 \times C - 0{\cdot}88).$$
$$L + S = (0{\cdot}17 \times P + 0{\cdot}51) = (0{\cdot}95 \times C - 0{\cdot}17).$$
$$C = 0{\cdot}16 \times P + 1{\cdot}44.$$

The statistical analysis showed that the permanganate number gives a more accurate measure, both of lignin and lignin and alkali soluble (*i.e.* total non-carbohydrate), than the chlorine number. The permanganate number, however, gives a more accurate measure of total non-carbohydrate (L + S) than it does of lignin alone.

4. **The Resin content** is determined by extraction with ether for 3 hours and then with alcohol, or with alcohol-benzene mixture, for

[1] P. B. Edwards and A. W. Mackney, *loc. cit.*

3 or 4 hours. The total is returned as resin. The ether extract may vary from 0·1 to 0·7 and the alcohol extract from 0·2 to 0·5 per cent.

The official *TAPPI* method (T 204, m, 1935) requires a much longer extraction period. The pulp is soaked in water and split into sheets which are dried and cut into pieces of 2 × 4 inches. These are folded by creasing first one side and then the other in the manner of a folded filter paper, and in this form 5 g. are extracted with ether in a Soxhlet apparatus for 16 hours at least. The extract is filtered and evaporated, the residue dried at 105°.

The pulp is then extracted with alcohol for 16 hours and the weight of alcoholic extract obtained. The resin is returned as total extract on 100 g. of dry pulp.

Acetone is often used as a single solvent for resin estimation.

5. **Solubility in Alkali and in Water.**—The extent to which a pulp dissolves in dilute alkali gives a measure of the degradation of the cellulose due to processing. The official *TAPPI* method (*TAPPI*, T 212, m-44, 1944) is as follows: The equivalent of 2 g. of oven-dry pulp is broken up in 100 ml. of NaOH (1 per cent.), the vessel is covered and heated on a boiling water-bath for 1 hour with initial stirring, which is repeated after intervals of 10, 15 and 25 minutes. The residue is filtered by suction through a tared crucible, washed with hot water, with 50 ml. 10 per cent. acetic acid and with water and dried at 105°. The percentage soluble (dry on dry) is corrected for the solubility of the pulp in hot water.

For this (*TAPPI*, T 207, m, 1934) 2 g. of air-dry pulp are digested with 100 ml. of water on a boiling water bath for 3 hours under reflux, washed and dried as before.

6. **Determination of the Lignin Content of Pulps.**—The following rapid method for estimating the lignin content of pulp can be used for examination of samples taken during the digestion process.[1]

Sulphuric acid made by mixing 4 parts of concentrated acid with 1 of water is required. A sample of pulp weighing 0·022 g. (0·020 g. dry) is placed in a 50 ml. stoppered tube, 20 ml. of the acid poured on, and the mixture shaken until the pulp is dissolved. The colour is compared with that of a similar solution made from a pulp of known lignin content (*cf.* p. 374).

The method originally standardised for wood by the Forest Products Laboratory of the United States[2] is also employed to

[1] P. Klason, *Papier Fabrik.*, 1910, **8**, 1285; G. Von Zweigbergk, *Papier-Ztg.*, 1912, **37**, 2506.

[2] G. J. Ritter, R. Seborg and R. L. Mitchell, *Ind. Eng. Chem., Anal.*, 1932, **4**, 202.

estimate lignin in pulp. The air-dry sample is extracted 4 hours with a mixture of alcohol-benzene (1 : 2 by vol.). After drying the residue is digested with cold 72 per cent. H_2SO_4 in a flask fitted with a reflux condenser for 16 hours. The acid is then diluted to a concentration of 3 per cent. H_2SO_4 and raised to boiling for 2 hours. The residue is washed with hot water till neutral, and dried at 105°.

Since it has been shown that in some cases as much as 30 per cent. of this residue is non-lignin many workers [1] nowadays give the wood or pulp a preliminary extraction with 0·125*N*- (or even 0·5*N*-) NaOH solution on the water bath for 80 minutes—afterwards treating the residue with dilute acetic acid, etc., before carrying out the standard process.

The Phloroglucinol Absorption Value of Lignified Substances.—The coloured substance produced by the action of phloroglucinol on lignified tissue involves only a small part of the phloroglucinol absorbed.[2] The main reaction appears to be with the aldehydic groupings in lignin, and experiment showed that the total amount of phenol combining with the lignified product was constant and furnished a measure of the amount of lignin present. By utilising the interaction of phloroglucinol with formaldehyde or furfural a method was devised for determining volumetrically the amount of phloroglucinol absorbed. It has proved useful in indicating the proportion of mechanical wood present in paper and in research.[3]

Solutions Required.—(1) Hydrochloric acid (*d*, 1·06), Solution A. (2) A solution of 0·5 g. of crystalline phloroglucinol per 100 ml. of this acid, Solution B. (3) A standard aldehyde solution containing either 0·4 g. of furfural or 0·2 g. of 40 per cent. formaldehyde dissolved in 100 ml. of the same acid, Solution C.

Procedure.—10 ml. of solution B are diluted with 20 ml. of solution A and the liquid heated to 70°. The standard solution C is added from a burette 1 ml. at the time with an interval of 2 minutes between each addition. At 70° the reaction is complete in this time. Towards the end of the titration smaller quantities are added, but with the same intervals between each addition. As indicator a piece of ordinary newspaper is employed. A spot of the liquid placed on this will give a red stain so long as phloroglucinol is present. As the end-point approaches it is necessary to put a

[1] P. B. Edwards and A. W. Mackney, *J. Council Sci. and Ind. Research* (Melbourne), 1938, **11**, 186.

[2] C. F. Cross, E. J. Bevan and J. Briggs, *Ber.*, 1907, **40**, 3119.

[3] C. F. Cross and C. Dorée, "Researches on Cellulose", IV.: Longmans, Green & Co., 1922, pp. 159, 168.

drop three times on the same spot and to dry the spot of liquid each time, in order to detect the red colour. In this way the aldehyde solution is standardised against crystalline phloroglucinol.

For the estimation of the phloroglucinol absorption 2 g. of the wood, fibre or paper, either dry or of known moisture content, are placed in a small flask, and treated with 40 ml. of solution B. After standing for 16 hours the liquid is strained through glass or cotton wool and quantities of 10 ml. taken for titration. The difference between the titrations gives the quantity of phloroglucinol reacting with the lignocellulose. This is expressed as a percentage on the fibre substance. In the case of papers the fibre substance is estimated approximately by deducting the weight of the ash and 1·5 per cent. for sizing constituents on the dry weight of the paper. The following are examples of the values found for raw materials :—

	Phloroglucinol absorbed, per cent.
Wood flour	7·50
Mechanical wood pulp	6·71
Jute (best white)	3·98
Jute (ordinary)	4·23
Sulphite wood pulp	0·75
Esparto cellulose	0·50
Cotton	0·20

The percentage, H, of mechanical wood pulp in a sample is given by the equation :—

$$H = 100(x - y)/(z - y),$$

where y, z and x are the weights of crystalline phloroglucinol reacting with 100 g. of chemical pulp, mechanical wood pulp and the sample under examination, respectively.

Cross and Bevan gave $y = 1$ and $z = 8$ as average values.

A further examination of the method [1] suggests a temperature of 35° for the absorption reaction and gives a revised formula.

7. **Copper Number.**—The Schwalbe-Braidy method (p. 31) is usually employed. The *TAPPI* modification (T 215, m-38, 1938) requires in addition to the solutions A and B (p. 32), another solution C. This is made by adding 100 g. of sodium molybdate ($Na_2MoO_4.H_2O$) and 75 ml. phosphoric acid (83 per cent.) to a mixture of 275 ml. conc. sulphuric acid and 1·75 l. of water. A solution D of sodium carbonate (about 5 per cent.) is also required.

The test is suitable for pulps free from groundwood or other

[1] H. B. Dunnicliff, *Analyst*, 1932, **57**, 354.

highly lignified fibres. The sample may be disintegrated in a grinder which must not cause heating.

1·5 g. of the sample (duplicates for moisture, ash, etc.) is weighed into an Erlenmeyer flask. Solutions A (5 ml.) and B (95 ml.) are mixed, raised to boiling in 2 minutes, and poured over the sample, which is kneaded with a glass rod. The flask is submerged in a bath at 100° for 3 hours with occasional shaking. The pulp is filtered with suction, flooded with 100 ml. of D at about 20° and then with 250 ml. of hot water. The fibres and filter paper are then treated with 25 ml. of solution C and well worked with a glass rod, transferred to the filter funnel, and washed with cold water till the blue colour is removed. The filtrate is diluted to 700 ml. and titrated with 0·05 N-$KMnO_4$.

$$\text{The Copper Number} = 6{\cdot}36 \times \text{ml. } KMnO_4 \times N/W.$$

The weight W of the sample is the weight corrected for moisture, ash, etc.

8. **Acidity of Pulp.**—10 g. of air-dry pulp are shaken for half an hour with 200 ml. of water at 20°. The suspension is filtered by suction and the pulp washed until the wash-water is neutral to litmus paper. Filtrate and washings are titrated with 0·1 N-alkali (or acid) using methyl orange.[1]

9. **Methoxyl Content.**—This may be determined by any of the methods given on pp. 395 *seq.*

10. **Ash Content.**—The determination of this quantity and especially the presence in it of metals with catalytic activity has become of increasing importance, especially in the case of viscose pulps (see p. 482). Most laboratories have adopted a definite procedure, ashing either at about 450° or at 850–1000°, and in some cases sulphating the ash. The *TAPPI* method (T 211, m-44, 1944) uses 5 g. of well-sampled air-dry pulp, which is dried to constant weight. The crucible and pulp are then ignited in an electric muffle or other furnace at a low red heat to constant weight. The time allowed for cooling in the desiccator before weighing should be the same after each ignition including the preliminary ignition of the crucible.

11. **Viscosity.**—This is sometimes determined for paper pulps but is essential for rayon pulps (p. 481). For methods see pp. 52–59, where the *TAPPI* modification is also given.

The following analyses (from the Cross and Bevan laboratories) illustrate values for some of the factors in the case of paper pulps.

[1] *Cf. Paper Trade J.*, 1939, **108**; *TAPPI*, 41.

ANALYSES OF PULPS FOR PAPER MAKING

	American Bleached Sulphite.		Swedish E.B. Sulphites.		Swedish E.B. Sulphates.		Canada Sulphate.	Bleached "Soda" Pulps.	
Cellulose									
α- .	88·9	90·2	87·3	87·4	86·2	89·0	90·3	63·3	76·6
β- .	0·9	1·5	0·7	0·5	4·0	1·0	0·02	27·8	15·7
γ- .	10·2	8·5	12·0	12·1	9·8	10·0	9·7	8·9	7·7
Ash, p.c. .	0·13	0·10	—	—	0·72	0·58	0·56	—	—
Resin, p.c. .	0·34	0·32	1·0	0·87	0·02	0·05	0·19	0·38	0·44
Pentosan, p.c.	3·3	3·4	5·9	5·1	8·4	8·2	8·9	—	—
Viscosity(Cp.)	42	44	88	70	12	20	52	7·4	9·0

EXAMINATION OF PULPS FOR VISCOSE MANUFACTURE

The following comments and analyses are from the practice of the Cross and Bevan laboratories.[1] The pulp sample should not be prepared for chemical examination by dry grinding in the laboratory mills which are frequently recommended for sub-division. This procedure may seriously affect results, *e.g.*, a fall of 5 per cent. in α-value was observed after grinding a rag stock in such a mill, and if heating takes place the copper number also will be increased. The best method is to bring the pulp to a standard open, fluffy condition by teasing out on a rotating device covered with a " file card ".

The influence of the state of division on copper number is very marked. A pulp prepared in the standard open condition gave a copper number of 2·0. The same sample used in the form of squares of 2, 5 and 10 mm. side, respectively, gave values of 2·5, 3·0 and 3·2 respectively. This variation is worthy of note, since it might have been expected that the value would decrease as the state of division became less fine.

Routine determinations on pulps required for viscose manufacture include :—

(1) Moisture content.

(2) The α-, β- and γ-cellulose.

(3) Ash content at high and low temperature and after sulphating : estimation of calcium, iron, manganese, etc., in the ash.

(4) The copper number or the alkali-solubility.

(5) Cuprammonium viscosity.

(6) Viscose viscosity, including estimation of insoluble material or filtration characteristics of the viscose.

[1] *Cf.* " Wood Pulp for the Rayon Industries ", L. Hebbs (Cross and Bevan), *J. Text. Inst.*, 1936, **27**, 169P.

(7) Resin, usually by extraction with acetone.

(8) Physical characters of the sheet as received, and after swelling in mercerising soda (swelling factor).

(9) Colour as received and after alkali treatment.

Moisture is determined at 105°, about 5 hours being required for constant weight. The following table gives typical values obtained for viscose pulps (1940) of normal and low viscosity. Calculated dry on dry pulp.

TYPICAL VALUES FOR VISCOSE PULPS.

	Normal Viscosity.*	Low Viscosity.
Cuprammonium viscosity (Cp.)	24·8	11·4
Viscose viscosity (relative)	1·44	1·07
Viscosity ratio C.V. to V.V.	17·3	10·7
Copper number	1·74	1·77
Alpha cellulose, p.c.	91·4	89·3
Beta cellulose, p.c.	3·4	6·0
Gamma cellulose, p.c.	5·2	4·7
Resin (acetone), p.c.	0·17	0·32
Insoluble matter in viscose, p.c.	0·07	0·10
Ash (1000°), p.c.	0·07	0·09
Iron, p.p. million pulp	7	11
Calcium (CaO), p.c.	0·034	0·047
Sheet weight, g., p. sq. metre	590	552
Sheet thickness, mm.	0·91	0·79
Apparent sp. g.	0·65	0·70
Swelling factor	5·2	5·0
Capillary rise, time	730	2000

* Values typical of alkali-refined pulp.

The α-cellulose is determined by the methods on pp. 363, 364. The need for standardising the conditions of the dilution stage must be emphasised. With the *TAPPI* method in which the pulp is filtered immediately after dilution, it is more difficult to obtain reproducible results than with the Cross and Bevan method. The results, also, are somewhat higher as shown by the following comparisons made on three different bleached sulphite pulps. Sample I gave 89·9 (Cross and Bevan method), 90·8 (*TAPPI*); II gave 89·4 and 90·7; and III gave 91·3 and 92·3 respectively.

The cuprammonium viscosity is determined by the methods of Clibbens (pp. 52–59). It is absolutely essential to keep the nitrous acid content of the solvent below 0·5 per cent., especially when dealing with low viscosity pulps. As only 0·2 g. of pulp is used it is difficult to make this representative of a large consignment, but

a series of measurements made on the samples drawn for moisture estimation give both an average and the range of variation, which should not exceed ± 7 per cent. in a single consignment.

Viscose Viscosity.—The "quick" viscose viscosity methods generally in use are based on lower cellulose concentrations than those employed industrially and use relatively high proportions of caustic soda. These methods give straight line relationships with cuprammonium viscosity at 1 per cent. cellulose and the cuprammonium value can preferentially be employed.

It is, however, possible to prepare viscose in the laboratory to industrial concentrations and from the experimental trial useful information can be obtained. Experience shows that small quantities, say 10 to 20 g. of pulp, can be processed with greater accuracy than the 10 to 20 kg. used in "semi-commercial" viscose plants, where difficulties of mechanical control may introduce larger variations than those due to the pulps under test.

The process should be carried out as far as possible in a thermostat, using times and temperatures approximating to industrial conditions. After steeping in mercerising alkali the pressing down to a ratio of 1 part of pulp to 3–4 of liquor requires close control. A small grinding mill is needed to reduce the pressed soda cellulose to the crumb condition. During the period necessary for the alkali-cellulose to mature—which may be up to 72 hours according to temperature—the vessel containing the crumbs should be totally immersed in the water of the thermostat and rotated to obtain even temperature conditions throughout the mass.

At the xanthating stage when adding carbon disulphide the container should be connected to a manometer and the pressure conditions controlled. The xanthated cellulose is dispersed in water or sodium hydroxide solution, according to the ratio of mercerising liquor left in the pulp after pressing. A ratio of NaOH to cellulose of 1 : 1 in the final viscose is suitable because it approaches the point of maximum viscose stability, although on the large scale the proportion of caustic soda will be lower. The industrial ratio may be matched, if desired, but then the speed of ripening and the rate of change in viscosity will be very much greater.

The ripening process is followed by measurement of the salt point (p. 268) or combined sulphur (p. 264) at different periods. The viscosity of the product is measured either by the falling sphere or by the Ostwald viscometer, such as the B.S.I. 2D. 50 (p. 65). Viscosities determined in viscose dispersions, however, if converted directly into absolute units, cannot be compared with results obtained by another method (*cf.* p. 58).

It is, however, not always possible to obtain reproducible results in the above process, and a standard pulp should be kept and processed in duplicate in each series of tests and used as an internal standard of comparison.

The filtration characteristics of the viscose prepared may be examined by filtering the diluted solution and weighing the undispersed material separated. Alternatively, the viscose is forced through small filters comparable with industrial practice and the necessary pressures recorded, or again, the quantity flowing in a given time under fixed pressure may be measured.

Physical Characters.—The thickness of the sheet and the apparent specific gravity are determined as they have some bearing on steeping conditions.

The swelling factor can be determined in two ways. The gravimetric result is usually reported as the final weight of the pulp swollen in mercerising soda, less the weight of the pulp, compared with the original oven-dry weight. It may also be given as the increase in the height of a stack of sheets or discs of pulp, when immersed in the alkaline solution.

Capillary tests are made to measure either the rate of climb of mercerising soda solution up a strip of pulp or, alternatively, the rate at which the sheet can be immersed in water or mercerising soda. These factors have a bearing on the rate of admission of liquor in the press.

Ash Content and Analysis.—The conditions used in ashing should be fixed. Ashing may be carried out by burning slowly and heating to a low temperature, say 450°, or to a high temperature such as 850–1000°. The sulphated ash, obtained by moistening the pulp with sulphuric acid and burning slowly at a low temperature, is reported for comparison to indicate the volatile sodium salts present.

A bleached pulp gave an ash content of 0·11 per cent. at 1000° and 0·17 per cent. when burnt slowly and finished at 450°. The ash in the second case showed on analysis (per cent. on dry pulp):

CaO	0·0418	Fe_2O_3	0·0019	Cl	0·0055
Na_2O	0·0400	Mn_3O_4	0·0022	SO_4	0·0071
MgO	0·0325	CO_2	0·0272	——	——
Al_2O_3	0·0049	SiO_2	0·0090		0·1721

For the analysis the following methods may be used, 20 g. of pulp, ashed in a platinum vessel, being taken for each estimation.

Calcium.—The ash is fused with fusion mixture (3 g.), the melt treated with boiling water (20 ml.), HCl added in small quantities to slight excess and CO_2 boiled off. About 1 g. of AmCl and excess of ammonia are added, the filtrate boiled, about 0·5 g. ammonium

oxalate added and the liquid kept at 70–80° for 1 hour. The precipitate is separated and washed till the washings give no reaction with barium chloride. It is then extracted with boiling $2N$- H_2SO_4 in portions up to a total of 70–80 ml. and finally washed with cold water. The solution obtained is titrated at 70° with $N/25$ permanganate.

Manganese.—The ash is fused with 3 g. of potassium bisulphate, the melt dissolved in $2N$-H_2SO_4 (10 ml.) and diluted to 25 ml. The solution is then heated with an excess (say 0·3 g.) of potassium periodate for some 15 minutes. The colour could be compared directly with permanganate solutions by the Nessler test, but it is better to reduce the known permanganate solution with SO_2 and to treat it as above before making the comparison.

Copper and Iron.—After fusion with bisulphate (3 g.) the melt is dissolved in 20 ml. of $2N$-H_2SO_4, heated to boiling, ammonia added in excess, and after further boiling a precipitate (A) and a filtrate and washings (B) are obtained.

A. This contains the iron. It is dissolved in hot $2N$-HNO_3, filtered, and filtrate and washings diluted to 100 ml. when cold. Of this solution 25 ml. in 50 ml. Nessler tubes are treated with 0·2 ml. of thioglycollic acid and 5 ml. conc. ammonia solution and made up to 50 ml.

The colour is matched against that obtained with known quantities of iron. The standard iron solution is made by dissolving 7 g. ferrous ammonium sulphate in 50 ml. N-H_2SO_4 and diluting to 100 ml. One mil. of this with 50 ml. of N-H_2SO_4 is treated with permanganate till faintly pink and then diluted to 100 ml., so that 1 ml. contains 0·0001 g. iron.

B. This filtrate is concentrated to 30 ml. and treated with 1 ml. of strong ammonia and 10 ml. of sodium diethyl dithiocarbamate (0·1 per cent.). The solution is extracted with chloroform until no further colour is removed and the extracts matched in Nessler tubes against standards prepared in the same way. As the copper complex seems more easily removed if mineral salts are present, it is best to add 2–3 g. of potassium sulphate before the chloroform extraction.

The standard copper solution (1 ml., 0·0001 g. Cu) is made by dissolving 0·393 g. $CuSO_4.5H_2O$ in 1 litre.

CHAPTER XXV

THE CHEMISTRY OF ISOLATED LIGNIN.

THE nature of lignin and its relationship to cellulose and other constituents of lignified tissue, is still not fully explained despite the progress made in recent years.* During the early stages of research on lignin (1897–1926) methods of isolation more or less severe, were employed. The products obtained, although differing in detail, showed a general similarity which pointed to a common origin in a basic lignin-substance existing in the plant. The reaction capacity of lignin lies in the possession of hydroxyl groups, more or less methylated, in the possession of potential reducing groups and possibly in a measure of unsaturation. The changes in these

THE COMPOSITION OF TYPICAL LIGNINS

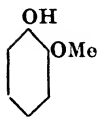
No.	Nature.	Author.	Formula.	Groups indicated.
1.	Alkali lignin from straw	E. Beckmann, O. Liesche and F. Lehmann.	$C_{40}H_{44}O_{15}$	$C_{36}H_{28}O_7$ $\{(OCH_3)_4$ $(OH)_4$
2.	Alkali lignin from flax	J. Powell and H. Whittaker.	$C_{45}H_{48}O_{18}$	$C_{40}H_{30}O_6$ $\{(OCH_3)_4$ $(OH)_5$ CHO
3.	Alkali lignin A from wood	H. Hibbert and F. Brauns	$C_{67}H_{71}O_{22}$	$C_{21}H_{46}O_{10}$ $\{(OCH_3)_6$ $(OH)_7$
4.	Alkali lignin B from wood		$C_{102}H_{107}O_{27}$	$C_{33}H_{39}O_{17}$ $\{(OCH_3)_9$ $(OH)_{11}$
5.	" Primary " liguin	A. Friedrich and J. Diwald	$C_{29}H_{48}O_{14}$	$C_{23}H_{20}O_5$ $\{(OCH_3)_5$ OH $(OH)_2$ CO
6.	Lignosulphonic acid (spruce)	C. Dorée and E. Barton-Wright	$C_{40}H_{48}O_{15}S_2$	$C_{20}H_{24}O_2$ $\{(OH)_2$ $(OMe)_2$ CO $(SO_3H)_2$
7.	Lignosulphonic acid	P. Klason	$C_{40}H_{44}O_{17}S_2Ba$	$C_{20}H_{22}O_7$ $\{(SO_3)_2$ Ba $(OCH_3)_4$
8.	Lignosulphonic acid (spruce)	E. King and H. Hibbert	$C_{47}H_{54}O_{19}S$	$C_{42}H_{32}O_6$ $\{(OCH_3)_5$ $(OH)_5$ SO_3H_2
9.	Methanol lignin	F. Brauns and H. Hibbert	$C_{46}H_{54}O_{16}$	$C_{42}H_{32}O_8$ $\{(OCH_3)_6$ $(OH)_4$
10.	Glycol lignin	K. R. Gray F. Brauns H. Hibbert	$C_{49}H_{58}O_{17}$	$C_{42}H_{32}O_8$ $\{(OCH_3)_5$ $(OH)_4$ $O.C_2H_5O$
11.	Basic (native) liguin	H. Hibbert	$C_{47}H_{52}O_{16}$	$C_{42}H_{42}O_6$ $\{(OCH_3)_6$ $(OH)_5$

* Excellent reviews by the leading workers in the field are available. See W. Fuchs, " Die Chemie des Lignins ", J. Springer, Berlin, 1926—a valuable monograph ; A. G. Norman, " Biochemistry of Cellulose, Lignin, etc.", Clarendon Press, Oxford, 1937 ; K. Freudenberg, *Ann. Rev. Biochem.*, 1939, **8**, 88 ; *Chem. Soc. Ann. Reports*, 1939, 382 ; *ibid.*, 1942, 142 ; H. Hibbert, *Ann. Rev. Biochem.*, 1942, **11**, 183.

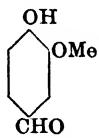
reactive groupings, together with processes of condensation and polymerisation, account for the differences observed between individual isolated lignins. The table on p. 484 contains data of some of the types which have been described. The general similarity is apparent, although no exact agreement can be found even when the results are calculated to the primary " lignol," *i.e.* to a completely demethylated, deacetylated and desulphonated product.

The fact that solutions of lignin are colloidal and show a great capacity for dispersing insoluble substances such as barium sulphate, also accounts for variations. It is now recognised that lignin solutions may contain insoluble lignin, hemicellulose, or even cellulose in colloidal suspension.

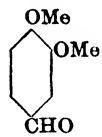
The early period was marked by a singular failure to achieve any constitutional results by the use of oxidation methods. Under the action of standard oxidising processes lignin either breaks down completely to oxalic and carbonic acids, or gives polymerised products. The occurrence among the oxidation products of 1 : 2, and 1 : 2 : 4-phenols such as catechol, guiacol (I) and vanillin (II) in minute amount, and in larger yield as the result of potash fusion led, however, to the assumption of an aromatic basis for the lignin complex. Klason [1] (1920) suggested a constitution on the theory



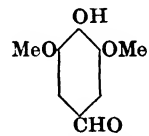
(I) Guiacol.



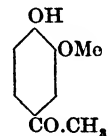
(II) Vanillin.



(III) Veratric Aldehyde.

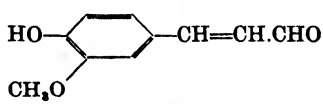


(IV) Syringyl Aldehyde.

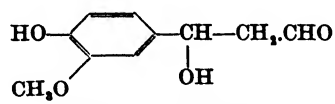


(V) Aceto-vanillone.

that lignin is built up of units of coniferyl aldehyde, or of α-hydroxy-coniferyl aldehyde, condensed into straight chains of a semi-acetal type, the chains being subsequently polymerised to larger aggregates. This theory is quite in keeping with more recent observations.



Coniferyl aldehyde.



α-hydroxy coniferyl aldehyde.

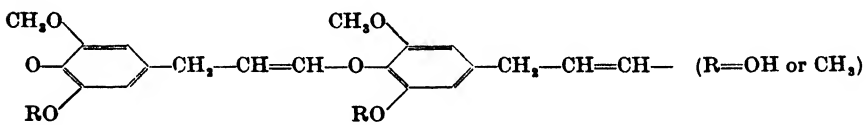
The " protolignin " of the plant is no doubt a polymerised form of some unit structure, but not necessarily a very highly polymerised one. The molecular weight of isolated lignin shows a minimum value of 800 to 1,000, corresponding to a C_{40} to C_{45} formulation, and it has been shown that relatively simple units can be polymerised and depolymerised and that colloidal properties develop with a

[1] P. Klason, *Ber.*, 1920, **53**, B, 1864 ; *ibid.*, 1922, **55**, B, 448.

comparatively limited degree of polymerisation.[1] Determinations of the molecular weight of lignins isolated by acid and alkali methods, and of methanol lignin from maple and spruce,[2] have been made. Osmotic pressure and boiling-point methods give values of the order of 3,900 ± 300, while diffusion methods give about 10,000. Viscosity measurements indicated that lignin dispersions approach monodispersion, so that the true molecular weight of isolated lignin is considered to be about 3,900.

During the period 1926–1933 new methods were devised with the object of obtaining lignin with the minimum of change. These included the use of weaker acids, *e.g.* formic acid ; alcoholysis—the action of methyl and ethyl alcohols, glycol, etc., in the presence of hydrogen chloride—and the use of cuprammonium.

The hydroxyl and other groups were characterised by extensive use of methylation methods, the Grignard reagent, etc. The action of sodium ethoxide at 150° led to a product from which on oxidation 3 : 5-dimethoxy-benzoic acid and vanillic acid were obtained.[3] From this result von Wacek deduced a straight chain structure for lignin such as



and similar views were advanced by Freudenberg (1931).

The period from 1934 onward has been marked by great progress in the isolation of phenolic compounds in sufficient quantity to enable more precise formulation, based on a propylphenol unit, to be suggested. The development of method has included extensions of the alcoholysis technique, the pressure hydrogenation of wood and lignin (Hibbert), the use of a " cuproxam " lignin isolated with the minimum of change, together with a new alkali nitrobenzene oxidation technique introduced by Freudenberg. The last method has proved of great value. It was known, for example,[4] that whereas vanillin only can be obtained from soft woods, hard woods gave vanillin (II) and syringyl aldehyde (IV) in about equal proportions. The yields obtained, *e.g.* by the action of 9 per cent. NaOH on the sulphonic acids, were small, but by oxidation with nitro-benzene Freudenberg has shown that from soft woods a maximum of 20 to 25 per cent. of vanillin can be obtained. From

[1] H. Staudinger *et al.*, *Ber.*, 1936, **69**, B, 1729.
[2] D. L. Loughborough, *J. phys. Chem.*, 1936, **40**, 113.
[3] A. von Wacek, *Ber.*, 1930, 63 [B], 282.
[4] W. L. Hawkins, H. Hibbert *et al.*, *J. Amer. Chem. Soc.*, 1937, **59**, 2447.

the hard woods maple and aspen, however, a mixture of vanillin and syringyl aldehyde amounting to 46 to 48 per cent. is produced,[1] indicating that in these angiosperms 58 to 62 per cent. of the protolignin is aromatic. Nitro-benzene oxidation has in fact furnished a definite chemical differentiation between the angiosperms and the gymnosperms. All recognised gymnosperms (pine species, etc.) give vanillin only, whereas angiosperms (monocotyledons such as rye, corn, bamboo, and dicotyledons such as maple, aspen and jute) give both vanillin and syringyl aldehyde.[2]

Further evidence has been derived from pressure hydrogenation of woods such as spruce and maple,[3] whereby the protolignin is converted in part into (*a*) 4-*n*-propylcyclohexanol, and (*b*) 3-(4′-hydroxycyclohexyl) propanol-1 in yields of 19·5 and 5·8 per cent., respectively, on the lignin content of the wood. The total yield of propylcyclohexanol derivatives represented a recovery of some 36 per cent., based on the methoxyl-free lignin in the wood.

Alcoholysis studies have also contributed. Maple wood after ethanolysis with 2 per cent. ethyl alcoholic HCl gives 35 per cent. (on the lignin) of aromatic compounds. These include vanillin and syringyl aldehyde, together with α′-ethoxy α-hydroxypropiovanillone — $R.CO.CHOEt.CH_3$; vanilloyl methyl ketone — $R.CO.CO.CH_3$, and the corresponding syringyl derivatives (R, a vanillin, or a syringyl residue).

The "cuproxam" lignin[4] is claimed to be less complex than acid-isolated lignins, and is recommended for exact work on structure. Ordinary lignins on methylation show an increase in OMe content from about 15 to 29 per cent., while cuproxam lignins increase no more than 2 per cent. Their composition is given as follows:

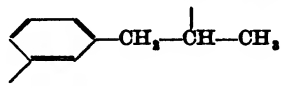
(*a*) Spruce cuproxam lignin C, 65–66; H, 6·1; OMe, 15–16; O_2CH_2, 4; OH, 10; ·O·, 9; C–CH_3, 2·7 per cent.

(*b*) Beech cuproxam lignin C, 60·5; H, 5·8; OMe, 21·5; O_2CH_2, 2; C—CH_3, 7 per cent.

The hydroxyl groupings are largely secondary and can be characterised by reaction with methylating and tosylating agents, but a small proportion are tertiary, and can be acetylated only. The C—CH_3 grouping is the source of the acetic acid (*ca.* 6 per cent.) obtained by oxidation with chromic acid. The production of formaldehyde by heating with mineral acid is held to originate in the methylene-dioxy-grouping.[5]

[1] H. Hibbert, *J. Amer. Chem. Soc.*, 1941, **63**, 312.
[2] H. Hibbert *et al.*, *ibid.*, 1939, **61**, 2556; 1940, **62**, 2803, 3049.
[3] H. Hibbert, *J. Amer. Chem. Soc.*, 1941, **63**, 3061.
[4] K. Freudenberg, *Ber.*, 1936, **69**, 1415; *ibid.*, 1938, **71**, 1810.
[5] K. Freudenberg *et al.*, *Annalen*, 1935, **518**, 62. See also M. J. Hunter and H. Hibbert, *Ber.*, 1938, **71**, 734.

Based on these results, Freudenberg considers that the lignin chain can be explained as a phenylpropane chain member

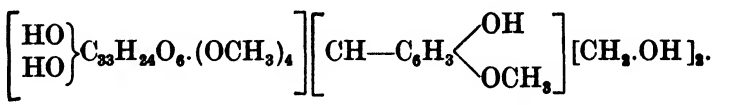


capable of condensation to complex molecules.

General Methods of Investigation

The usual methods of isolating lignin are (*a*) by the action of hydrochloric acid under various conditions (Willstatter lignin, Primary lignin, etc.), and of formic acid; (*b*) by the action of sulphurous acid and bisulphites (lignin sulphonic acids); (*c*) by the action of sodium hydroxide solutions (alkali lignin); (*d*) by alcoholysis, *i.e.* the action of various alcohols in the presence of hydrogen chloride (methanol lignin, glycol lignin, etc.) One of the hydroxyl hydrogens is replaced by the alcohol radicle in this process; (*e*) as a condensed product by reaction with phenol (phenol lignin).

The most restrained conditions employed have probably been those of Beckmann,[1] who used 2 per cent. NaOH in dilute alcoholic solution in the cold for 2 days. The molecular weight of the lignin obtained was about 800 and its composition $C_{40}H_{44}O_{15}$. Isolated lignin is a brown or yellow powder with a limited range of solubility. It contains methoxyl groups—the content of which is its most definite quantitative property (p. 367)—and hydroxyl groups, some of which may be formed during the isolation process. The hydroxyl groups are secondary, tertiary, and phenolic in character, and they accordingly vary in their reactivity. An investigation in which the aliphatic hydroxyl groups are removed by hydriodic acid, which leaves the aromatic and carboxylic groups unchanged, is described on p. 502. For beech lignin Freudenberg found a ratio of aliphatic to aromatic hydroxyl of 4·6 : 1.[2] Tomlinson and Hibbert[3] state that of the five hydroxyl groupings present in "native" lignin one is characterised by exceptional reactivity. Of the others three are aliphatic and one phenolic. They represent these differences in the schematic formula



[1] E. Beckmann *et al.*, *Z. angew. Chem.*, 1921, **34**, 285; *Biochem. Z.*, 1923, **139**, 491. Also M. Phillips and M. J. Goss, *J. Biol. Chem.*, 1936, **114**, 557.

[2] K. Freudenberg and K. Hess, *Annalen*, 1926, 448, 121.

[3] *J. Amer. Chem. Soc.*, 1936, **58**, 340, 345, 348.

The presence of hydroxyl groups is more definitely revealed by methylation. Most lignins reach a maximum content of about 25 per cent. OMe when methylated 5 or 6 times with dimethyl sulphate. Harris *et al.*,[1] by the progressive methylation of Klason lignin (72 per cent. sulphuric acid method), found the high maximum of 32 per cent., which was also reached with methanol lignin.[2] The alkali used, however, produces changes in the lignin with the development of new hydroxyl groups. This is especially marked when a large excess of alkali is used at higher temperatures such as 60°. The best conditions, if change is to be avoided during the alkali-dimethyl sulphate treatment, are given as [3] (*a*) use of acetone as solvent, (*b*) a slight excess (5 to 10 per cent.) only of alkali, and (*c*) a temperature of 20°.

Diazomethane,* whilst reacting with great ease, does not always give maximum methylation. This is achieved by following the action of diazomethane with repeated treatments with dimethyl sulphate. In other cases (*a*) the substance is fully acetylated and treated with dimethyl sulphate and alkali; or (*b*) the substance, methylated with diazomethane, is acetylated and then treated with dimethyl sulphate. In each case the action of the alkali unmasks the acetylated hydroxyl groups in a reactive condition. As an example a phenol lignin (OMe, 9 per cent.), methylated with diazomethane, gave OMe, 21·5 per cent. The product when acetylated contained OMe, 19 per cent.; $COCH_3$ 11 per cent. A single treatment with dimethyl sulphate gave a product (OMe, 24·3 per cent.), and after three more treatments the methoxyl became constant at 27·5 per cent. The same value was reached by complete acetylation of the phenol lignin (pyridine, acetic anhydride) and methylation with dimethyl sulphate and alkali in slight excess.

Lignin reacts with phenylhydrazine and hydroxylamine, but the products obtained are not very definite, though they are generally taken to indicate the presence of carbonyl groupings. The observation [4] that formic acid lignin adds a small, but consistent, amount of Grignard reagent is held to confirm this view and since the "carbonyl value," measured in this way, does not change during various reactions, enolisation apparently does not take place. Conversion of a CO into a CHOH grouping may explain the increase in

[1] E. E. Harris *et al.*, *J. Amer. Chem. Soc.*, 1934, **56**, 889.
[2] F. Brauns and H. Hibbert, *Can. J. Research*, 1935, B, **13**, 28.
[3] J. Compton and H. Hibbert, *ibid.*, 1937, B, **15**, 39.
[4] G. F. Wright and H. Hibbert, *J. Amer. Chem. Soc.*, 1937, **59**, 125.

* For the preparation and use of diazomethane see Gattermann, "Practical Organic Chemistry", London, 1937, p. 271, or Fieser, "Experiments in Organic Chemistry", New York, 1941.

hydroxyl content observed [1] after treatment of lignin with reducing agents.

The action of sulphurous acid and bisulphites is usually explained as an addition at some unsaturated centre with the formation of sulphonic acids or their salts.[2] The presence of such a centre has been assumed in several formulations to explain polymerisation, etc., but the alternative hypothesis that sulphurous acid brings about direct sulphonation of an aromatic nucleus is also quite possible.[3]

A characteristic reaction of lignosulphonic acids is that with β-naphthylamine hydrochloride. This reagent gives a precipitate with sodium or calcium lignosulphonates, the formation of which was considered by Klason [4] as due to reaction between the amine and the aldehydic and sulphonic groupings, a ring compound being formed. The precipitate, which is given only by the so-called α-lignin sulphonic acid, was stated to have the composition

$$(3C_{10}H_{10}O_3 + 2H_2O) + H_2SO_3 + C_{10}H_9N—H_2O.$$

The β-lignin sulphonic acid can be precipitated in the filtrate by means of basic lead acetate.

Other aromatic amines, *e.g.* quinoline (used as 5 per cent. hydrochloride solution), produce similar precipitates though the amount of α-form removed is not the same in each case.[5]

The action of the ordinary oxidation processes yields only small quantities of aromatic substances and in general bring about a complete breakdown of the complex. Oxalic acid is generally one of the end products. Dilute nitric acid, besides giving a considerable amount of oxalic acid, forms red nitro-compounds which can be reduced with zinc or magnesium in acid solution to nitrogen-free substances, possibly ketones.[6]

Practical Methods of Preparation and Examination

The methods used in the investigation of lignin are illustrated by the abstracts which follow of typical experimental work in this field. They include the following examples :—

A. Metalignin (alkali lignin).
B. " Primary " Lignin.
C. Willstätter Lignin.
D. Formic Acid Lignin.
E. Methanol Lignin.
F. Glycol Lignin.
G. Phenol Lignin.
H. " Cuproxam " Lignin.
J, K. Lignosulphonic Acids.
L. The Hydroxyl Groups in Spruce Lignin.

[1] R. G. Moore and H. Hibbert, *Can. J. Research*, 1937, **15**, B, 533.
[2] *Cf.* I. Kolker and A. Lapworth, *J. Chem. Soc.*, 1925, **127**, 307.
[3] E. G. King, F. Brauns and H. Hibbert, *Can. Jour. Research*, 1935, B, **13**, 88.
[4] P. Klason, *Ber.*, 1920, **53**, 706.
[5] G. H. Tomlinson and H. Hibbert, *J. Amer. Chem. Soc.*, 1936, **58**, 340.
[6] C. Dorée and L. Hall, *J. Soc. Chem. Ind.*, 1924, **43**, 257T.

General working methods common to all are :—

1. Purification of the Wood or Other Material.—The removal of resin is especially important, as this cannot easily be separated from lignin. The wood, etc., is powdered (65–100 mesh) and extracted for 12–24 hours successively with benzene, alcohol and sometimes water, or a mixture of benzene and alcohol is used. Hemicelluloses are removed by digestion 4 or 5 times with cold 5 per cent. NaOH solution. The product is dried under reduced pressure at moderate temperature, if possible in an inert atmosphere.

2. Examination of the Hydroxyl Groupings.—These are usually characterised by the preparation of (*a*) acetyl-, (*b*) benzoyl- and (*c*) tosyl-derivatives, and their number is determined by estimation of active hydrogen, (*d*) by the Grignard machine [1] or similar technique, and (*e*) by Zerervitinoff's [2] method.

(*a*) *Acetylation.*—Methods vary with the solubility of the lignin employed. Acetyl chloride, catalysed by a drop of sulphuric acid, gives rapid reaction (Example A). A reliable method is the use of acetic anhydride in pyridine solution,[3] *e.g.* 2 g. of lignin in 10 ml. dry pyridine mixed with 5 ml. acetic anhydride and left for 1 day. The mixture is poured into ice-water and the solid washed and purified by fractionation from solvents (Example E).

(*b*) *Benzoylation.*—If the lignin is soluble in alkali the Schotten-Baumann method is used (Examples A and B). Treatment in pyridine or quinoline solution with benzoyl chloride is also effective, *e.g.* 2 g. in 15 ml. of dry quinoline with 6 ml. of benzoyl chloride Substituted benzoyl derivatives are employed similarly, and are useful in determining the size of the lignin complex combined, for example, with one atom of bromine as bromo-benzoyl compound.

(*c*) *Tosylation.*—The reaction with *p*-toluene sulphonyl chloride is usually taken as giving a measure of the hydroxyl groups present. 3 g. of lignin and 5 g. *p*-toluene sulphonyl chloride (tosyl) in 50 ml. of dry pyridine are left at ordinary temperature up to 3 days and then poured in a fine stream into a litre of 2·5 per cent. potassium bicarbonate solution. The mixture is well stirred and the precipitate fractionated, *e.g.* from chloroform by ether.

(*d*) *Methylation.*—Methods are discussed on p. 489.

A. **Metalignin,**[4] $C_{20}H_{20}O_6$.—*Preparation of Metalignin.*—Spruce wood (fine sawdust) was extracted with benzene, alcohol and

[1] E. P. Kohler *et al.*, *J. Amer. Chem. Soc.*, 1930, **52**, 3736.
[2] See Gattermann, " Practical Organic Chemistry ", 1937, p. 84.
[3] E. Heuser and W. Ackermann, *Cellulosechem.*, 1924, **5**, 13.
[4] C. Dorée and E. Barton-Wright, *Biochem. J.*, 1927, **21**, 290; E. B. Colegrave, *Thesis*, London University, 1940.

water, and then digested with four changes of 5 per cent. NaOH for 36 hours to remove hemicelluloses. The wood was heated with a 4 per cent. NaOH solution at 8 at. pressure (or with 10 per cent. NaOH at 4 at.) for 1 hour. The solution was poured off and the metalignin precipitated by the addition of HCl, washed by decantation, dissolved in 95 per cent. alcohol, and the solution evaporated to dryness. A lustrous black solid was obtained.

It was purified by solution in glacial acetic acid and addition of water. It appeared to melt at 180°, raised finally to 185°, but this is only a sintering-point due to traces of solvent. After drying in a vacuum the sintering-point became 245°.

The metalignin gave C, 67; H, 5·6; OMe, 17·4 per cent. $C_{20}H_{20}O_6$ requires C, 67·3; H, 5·6; OMe, 17·4 per cent. with two methoxyl groupings.

Treatment with 95 per cent. alcohol separates it roughly into a soluble fraction A, with the above sintering-point, and a less soluble fraction B, without melting-point. On analysis fraction A gave C, 66·5; H, 5·5; OMe, 15·5 per cent. $C_{22}H_{22}O_7$ requires C, 66·3; H, 5·5; OMe, 15·5 per cent., and fraction B gave C, 67; H, 5·5; OMe, 17 per cent. corresponding with the C_{20} formula given above.

M.wt. by freezing-point in acetic acid and in naphthalene was 342.

Monobenzoyl-metalignin is a pale yellow solid, m.p. 184°; very soluble only in pyridine, from which it was precipitated with alcohol.

Found: C, 70·1; H, 5·1; OMe, 13·8 per cent. $C_{27}H_{24}O_7$ requires C, 70·4; H, 5·2; OMe, 13·4 per cent.

Monoacetyl-metalignin. 5 g. metalignin and 20 g. acetyl chloride were mixed and a few drops of concentrated sulphuric acid added.[1] The metalignin rapidly went into solution, which was then heated for 1 hour at 80°. The derivative is very soluble in pyridine, alcohol and acetone, insoluble in other solvents.

Found: C, 66·0; H, 5·5 per cent. $C_{22}H_{22}O_7$ requires C, 66·3; H, 5·5 per cent.

Methyl-metalignin. 5 g. were dissolved in 12 ml. of 10 per cent. NaOH and dimethyl sulphate added with shaking. The product slowly precipitated. Purification was effected by solution in pyridine and addition of dilute alcohol. The derivative is yellow, soluble in pyridine, acetone and alcohol.

Found: OMe, 25·4 per cent. $C_{18}H_{13}O_3(OCH_3)_3$ requires OMe, 25·1 per cent.

Metalignin dioxime. The presence of carbonyl groupings was shown by the reduction of Fehling's and ammoniacal silver solutions and by the formation of a dioxime. 3 g. metalignin were mixed

[1] *Chem. Soc. Trans.*, 1924, **125**, 357.

with 3 g. hydroxylamine hydrochloride and an 8 per cent. NaOH added gradually. The oxime was precipitated by the addition of ammonium chloride.[1]

Found : N, 6·9 per cent. $C_{20}H_{22}O_6N_2$ requires N, 7·2 per cent.

From these results the formula $C_{16}H_{12}O(OCH_3)_2OH.CO.CHO$ was assigned to metalignin.

An alkali lignin prepared by a similar method [2] was separated by dioxan-ether fractionation into alkali lignins A and B. Fraction A had the composition $C_{61}H_{46}O_{10}(OMe)_6(OH)_7$, confirmed by acetylation and complete methylation. Fraction B, soluble in ether-dioxan, with the composition $C_{99}H_{69}O_{17}(OMe)_9(OH)_{11}$ was also capable of complete methylation to $C_{99}H_{69}O_{17}(OMe)_{20}$.

B. **Primary Lignin,**[3] $C_{34}H_{33}O_9(OMe)_5$.—The lignin is isolated by hydrolysis with 17 per cent. HCl. The purification of the wood is similar to that under example A. When dry it is at once ground up with its own weight of HCl (one vol. HCl, *d*, 1·17 ; one vol. of water) and allowed to stand for 2 days. The mass is then boiled with ten times its weight of 96 per cent. alcohol for 8 to 10 hours. These details are important, as, if the acid is removed before treatment with alcohol, no lignin passes into solution.

The solution is filtered, concentrated to a third of its volume, and mixed with ten times the volume of water, a little acid being added to cause the lignin to clot. Primary lignin is thrown down as a light brown, amorphous precipitate. Solution and precipitation are repeated several times.

The yield is 8 to 10 per cent. on the wood, the product, which is very hygroscopic, containing 8 per cent. of water.

The reactions of primary lignin were originally explained on the assumption of the presence of three methoxyl, three hydroxyl, and two methyl ester groupings. The two ester methoxyls were said to be removed by gentle heating with alkali. King and Hibbert,[4] however, find that this is not the case. The methoxyl content of about 19 per cent. remained unchanged after heating at 50° for 2 hours with 2*N*-NaOH solution. They conclude that carboxyl groupings are not present in primary lignin. Methanol lignin (p. 495) also contains none.

(*a*) *Primary lignin* is easily soluble in alkali and most solvents except ether and benzene. Analysis gave : C, 63·34 ; H, 6·41 ;

[1] O. L. Brady and F. Dunn, *Chem. Soc. Trans.*, 1913, **103**, 1613.

[2] H. B. Marshall, F. Brauns and H. Hibbert, *Can. J. Research*, 1935, B, **13**, 109.

[3] A. Friedrich and J. Diwald, *Monatsheft.*, 1926, **46**, 33, 597 ; *Z. physiol. Chem.*, 1928, **176**, 127.

[4] *Can. J. Research*, 1936, B, **14**, 12.

OMe, 20·90. $C_{34}H_{33}O_9(OMe)_5$ requires C, 63·22; H, 6·53; OMe, 20·95. It reduces Fehling's solution and reacts with phenylhydrazine and sodium bisulphite. On methylation it gives a product $C_{34}H_{32}O_8(OMe)_6$, as a powder, decomposing at 110°. Benzoylated by Schotten-Baumann, it gives a derivative, $C_{34}H_{30}O_6(OMe)_5(OBz)_3$, less soluble than the original lignin.

C. **Willstätter Lignin.**—The following modification [1] of the Willstatter procedure is recommended as giving lignin comparatively unchanged and free from cellulose: Pine shavings, previously freed from resins and fats by extraction with a mixture of alcohol-benzene (1 : 1), are shaken for 15 minutes with ten times their weight of fuming hydrochloric acid (*d*, 1·22), then poured into excess of hot water, thoroughly stirred, and at once diluted with a large excess of cold tap water. The lignin settles first, and the lighter cellulose precipitate is separated from it by decantation followed by filtration through muslin. The residue is extracted twice with the fuming acid (10 minutes' shaking each time with five, and then with two and a half times its weight of acid), and finally washed with water and dried. The lignin thus prepared has the composition C, 58·8; H, 6·8–7·0; CH_3, 5·5 per cent. It is only slightly soluble in boiling phenol, and in general is resistant to the action of solvents. It dissolves at once, however, in trichlor-acetic acid, giving a violet-brown solution, from which it is reprecipitated by water in a form soluble in alkalis, acetone, etc. It dissolves with difficulty in hot sulphite solutions, but addition of cellulose facilitates solution. It acts on a photographic plate in the dark more strongly than lignin prepared by other methods. The product still contains pentosans (about 8 per cent.).

Lignin prepared by this method reduces ferric chloride and colours Schiff's reagent, but does not reduce Fehling's solution. Heated at 200°, pine lignin, prepared in this way, gave about 60 per cent. of its weight as a sublimate of vanillic acid with some vanillin (Kürschner, p. 505).

D. **Formic Acid Lignin.**[2]—Formic acid removes about 17 per cent. of lignin from spruce wood. Partial demethylation takes place so that the methoxyl content is low (12–14 per cent.), but extraction is easy and rapid and the products, obtained by fractionation, are readily soluble in a range of solvents. The more soluble fractions have higher hydroxyl and lower methoxyl values than the more insoluble ones. The crude lignin, by active hydrogen measurement

[1] K. Kürschner, *Brennstoff-Chem.*, 1925, **6**, 117, 158, 177, 188, 208, 304.

[2] K. Freudenberg *et al.*, *Ber.*, 1936, **69**, 1415; H. Staudinger and E. Dreher, *ibid.*, 1936, **69**, 1729; G. F. Wright and H. Hibbert, *J. Amer. Chem. Soc.*, 1937, **59**, 125.

and by tosylation, is shown to contain four hydroxyl groups per kilogram, of which two are phenolic.

Purified spruce wood (75 mesh) is refluxed with 300 ml. of formic acid (80–95 per cent.) for 6–12 hours. The meal is filtered and washed with 100 ml. of formic acid (95 per cent.) cold. The solution is taken nearly to dryness (25 mm.) and the residue washed with water to remove soluble carbohydrates. An acetone-water mixture (17 : 3) dissolves out the lignin which can, if required, be separated into chloroform-soluble and insoluble, portions and these further separated by acetone extraction. Methoxyl, about 13·5 per cent.; active hydrogen, 4 per kg.; RMgX added per kg. 0·6. The details following are by Wright and Hibbert (*loc. cit.*).

Methylation with Diazomethane.—1 g. in 15 ml. of dry dioxan was treated at 25° with 4 ml. of an ether solution of the reagent prepared from 0·5 g. of nitrosomethyl-urethane. After 5 hours gas evolution ceased (total 48 ml.) and after 12 hours the solution was taken to dryness (30 mm.) and the product dissolved in benzene or acetone and the liquid centrifuged to remove diazomethane polymer. Precipitation into a tenfold volume of ether gave about 1 g. of product; OMe, 18·5 per cent.

Methylation with Dimethyl Sulphate.—1 g. in a mixture of acetone 40 ml., water 10 ml. was stirred, preferably under nitrogen, while 3·8 ml. (0·09 mole) of dimethyl sulphate and 0·05 mole of alkali (*e.g.* 7·5*N*-NaOH) added over 90 minutes, alkali being kept in slight excess. After stirring for 30 minutes more the liquid was diluted with water to 200 ml. and made just acid with acetic acid. The precipitate was removed by chloroform and the concentrated extract precipitated by pouring into a volume of ether or light petroleum. OMe, 28 per cent.

The presence of carbonyl was inferred from the addition of about 0·6 of phenyl magnesium bromide per kg. from an etherial solution of the reagent.

E. **Methanol Lignin,**[1] $C_{42}H_{32}O_6(OMe)_6(OH)_4$.—Spruce wood meal (375 g.), dried (low pressure) at 50°, was placed in an autoclave lined with glass-enamel and treated with 3 l. of a 2 per cent. solution of anhydrous HCl in methanol for 3 days at 90–100° at 55–60 lb. pressure. The mixture was filtered and the residue washed with methyl alcohol (weight, air dry 333 g.). During concentration of the filtrate (40°, low pr.) to about 200 ml. crystals of α-methyl-*d*-mannoside, m.p. 191°, were separated. The clear filtrate was run into water, with stirring, and the lignin removed and washed with

[1] F. Brauns and H. Hibbert, *Can. J. Research*, 1935, B, **13**, 28; *ibid.*, 1936, B, **14**, 12, 55, 115; J. Compton and H. Hibbert, *ibid.*, 1937, B, **15**, 38.

water. Yield 26·4 g. or 25 per cent. of theoretical. OMe, 22·5 per cent.

Fractionation from dioxan solution with ether resolved the crude lignin into two products: (*a*) an ether dioxan-soluble product identical with the methanol lignin originally obtained (*loc. cit.*, 1935) of the above formula (OMe, 21·5), and (*b*) a second ether-dioxan soluble form (OMe, 23·6). The ratio of the two is of the order 4 : 1, but higher temperature in methanolysis increases the proportion of the second derivative. They were separated by the methods given below.

Fractionation of Crude Methanol Lignin.—(*a*) The crude product (26 g.) in 260 ml. of dioxan was added in a stream, with stirring, to ten times the volume of dry ether. After a repetition, the weight of precipitate was 13 g.; OMe, 22 per cent. Of this 8 g. in 80 ml. of dioxan were added dropwise to 800 ml. of dry benzene. The precipitate, washed with benzene and light petroleum, weighed 7 g.; OMe, 21·8, which, after two repetitions, became 21·0 per cent. The formula given above requires 21·5 per cent.

The ether-dioxan filtrates were concentrated to 100 ml. and added to light petroleum. Wt. of precipitate 13·3 g.; OMe, 22·9 per cent. Of this 8 g. in a mixture of 70 ml. of benzene and 10 ml. of dioxan were dropped into 800 ml. of light petroleum. The precipitate was redissolved in benzene-dioxan, 9 : 1 (vol.) and after repetitions gave OMe, 23·9 per cent.

(*b*) Long continued ether extraction of the crude methanol lignin removed the fraction of OMe, *ca.* 24 per cent., showing that this is a true ether-soluble material.

(*c*) Methanol lignin dissolved in fifty times its weight of warm 5 per cent. NaOH was filtered after 2 hours (sintered glass funnel) and the insoluble part washed with acetic acid and water, dried and precipitated by ether from dioxan. Yield 14 per cent.; OMe, 23·2 per cent. The filtrate was added dropwise to 1 per cent. HCl. The precipitate was purified by solution in dioxan and addition of ether. Yield 86 per cent.; OMe, 21·5 per cent.

Acetylation of Methanol Lignan.—1 g. (OMe, 21·6 per cent.) with dry pyridine (5 ml.) and acetic anhydride (3 ml.) was allowed to stand for 48 hours. The solid obtained by pouring on to ice was dried, dissolved in dioxan and precipitated by anhydrous ether. Further purification was effected by solution in benzene and running into light petroleum. Yield 1·2 g.; OMe found, 17·6 per cent. $C_{42}H_{32}O_6(OMe)_6(OAc)_4$, [1054·5], requires OMe, 17·8 per cent. The derivative is soluble except in ether and light petroleum.

Methylation with Diazomethane.—2 g. of methanol lignin in 20 ml. of dioxan were treated with the diazomethane prepared

from 10 ml. of nitrosomethyl urethane, at 5°. After 18 hours the liquid was heated to 50° for 15 minutes. A slimy precipitate forms which, after centrifuging, floats to the surface and can be filtered off. The clear filtrate was run into dry ether. The pale brown precipitate was dissolved in dioxan and thrown out by addition of ether. Found: OMe, 24·8. $C_{42}H_{32}O_6(OMe)_7(OH)_3$ requires 24·1 per cent. The derivative is insoluble in dilute alkali, but otherwise resembles the original lignin.

Fully Methylated Methanol Lignin.- The above product (OMe, 24·8) was acetylated in the same way as the original lignin, giving $C_{42}H_{32}O_6(OMe)_7(OAc)_3$. The acetyl derivative (from 2·6 g. of lignin) in 30 ml. of acetone was treated at 40° with 30 ml. of dimethyl sulphate and 65 ml. of NaOH (30 per cent. solution) over 2½ hours, the mixture being kept slightly alkaline. The acetone was distilled off and the mass ground with water, dried and methylated again in acetone solution. The product in dioxan was precipitated into dry ether. Found: OMe, 32·3. $C_{42}H_{32}O_6(OMe)_{10}$ requires OMe, 32·9 per cent.; insoluble in ether and light petroleum.

Further treatment with methylating and acetylating agents gave no increase. It was later found [1] that, by methylation with excess alkali, hydroxyl groups are developed, since a product with a methoxyl content of 37 per cent. was obtained.

F. **Glycol Lignin.**[2]—This substance, like methanol lignin, is probably an ether derivative of lignin. It is obtained (Hibbert *et al.*) by treatment of the wood with ethylene glycol containing 0·2, or sometimes 0·5 per cent., of hydrogen chloride. Although some 80 per cent. of the total lignin is obtained in four extractions with the weaker acid, only 40 per cent. was recovered after purification, owing to the presence of a soluble product which was lost on pouring into water.

Glycol lignin has an OMe content of 16·9 per cent. The presence of glycol in combination was demonstrated by using glycol monomethyl ether for extraction, when the OMe content rose to 20·5, *i.e.* one additional methoxyl on a M.wt. of about 900. As glycol yields methoxyl in the standard estimation the necessary correction was determined. This amounts to 0·97 per cent. (on a M.wt. of 916) on account of the glycol present.

Glycol lignin can be separated into chloroform-soluble and chloroform-insoluble fractions. Both have the same composition: C, 62·6–63·0; H, 6·2–6·4; OMe, 16·9 per cent. After diazomethane, OMe, 21 per cent.; after complete methylation, OMe, 32 per cent.

[1] J. Compton and H. Hibbert, *Can. Jour. of Research*, 1937, B, **13**, 39.

[2] B. Rassow and H. Gabriel, *Cellulosechem.*, 1931, **12**, 290, 318; H. Hibbert *et al.*, *Can. J. Research*, 1935, **13**, 35, 48.

Reaction with trityl chloride shows the presence of four hydroxyl groups, one being the free hydroxyl in the glycol residue and another phenolic. The latter is methylated with diazomethane, since, after treatment with this reagent, only three hydroxyl groupings are shown by the action of trityl chloride.

Preparation of Glycol Lignin.—Spruce wood meal (500 g.) is heated for 8 hours at 107–109° with 5 l. of anhydrous ethylene glycol containing 0·2 per cent. HCl, with stirring. A current of dry nitrogen is passed through the apparatus. The meal is separated, washed with hot glycol and filtrate and washings poured, in a fine stream, into four times the volume of water warmed to 50°. The light brown product is washed four times by decantation and dried (desiccator). The bulk of the lignin is removed after two extractions with glycol.

For purification 20 g. is dissolved in warm dioxan (100 ml.), clarified, the solution brought to about 10 per cent. lignin and then added dropwise to 1·2 l. of ether with agitation. The ppte. is washed several times with ether and light petroleum. Yield 55 g.

Glycol lignin is insoluble in ether, light petroleum and benzene, partly soluble in chloroform and absolute acetone and readily soluble in other solvents, including aqueous acetone and dilute alkaline solutions.

Analyses agree with the formulation

$$C_{42}H_{32}O_6(OCH_3)_5(OCH_2.CH_2OH)(OH)_4[916{\cdot}5].$$

The esters are all prepared in pyridine solution, *e.g. acetyl glycol lignin* : 2 g. glycol lignin in 10 ml. dry pyridine and 5 ml. acetic anhydride ; *p-nitrobenzoyl glycol-lignin* : 2 g. in 12 ml. pyridine mixed with 5 g. nitrobenzoyl chloride in 5 ml. dry chloroform ; *trityl derivative* : 2·5 g. in 15 ml. pyridine and 2·5 g. trityl chloride. Mixture heated to 70° for 15 minutes then left 2 days.

Methylation of Glycol Lignin.—2 g. of glycol lignin in 15 ml. of dioxan are treated with diazomethane (from 10 ml. of nitrosomethyl urethane) in 10 ml. of dioxan. Next day the same amount of diazomethane is added and after 1 day a slimy substance is coagulated by heating to 50° for 15 minutes. The clear filtrate concentrated (low pr.) is poured into dry ether giving 2·1 g. Found : OMe, 21, corrected to 20 per cent., the content required by the formula $C_{42}H_{32}O_6(OCH_3)_6(OCH_2.CH_2OH)(OH)_3$. On acetylation all the hydroxyl groups are esterified. For complete methylation 7 g. of the acetylated product in 100 ml. of acetone are treated three times with dimethyl sulphate as usual. Maximum OMe found, 31·4 per cent., which is that required for the fully methylated formula.

Acetylated glycol lignin methylated twice by the above process also gives this product.

G. **Phenol Lignin.**[1]—This condensation product is obtained from native or isolated lignin by reaction in the presence of a trace of catalyst. From spruce wood two different products are obtained, an ether-insoluble (A) and an ether dioxan-soluble (B) in the ratio of 3 : 1. The former appears to contain three new phenolic hydroxyl groups and also one which has formed an ether linkage with a hydroxyl of the lignin. In the latter a large number of phenolic groups, perhaps 15–21, have combined with the lignin unit. Phenol lignins prepared from Willstätter and other isolated lignins cannot be resolved into two fractions.

Preparation of Phenol Lignin.—Brauns and Hibbert use the following method (*loc. cit.*). Spruce wood was extracted with alcohol-benzene and with water and dried (60° low pr.). Pure phenol (2 kg.) was melted (80°) in a 3 l., 3-necked flask, fitted with stirrer and dropping funnel, and 180 g. of wood, also heated to 80°, added. With good stirring 200 ml. of dry ether containing 12 g. of HCl was added over 10 minutes from the funnel, the end of which was below the surface of the phenol. The stirring was continued and the temperature kept at 80–90° for half an hour, after which the phenol was distilled off in an atmosphere of nitrogen under reduced pressure (bath temperature below 80°).

The tarry product was dissolved in methyl alcohol (300 ml.) and the liquid, after centrifuging, added to about 4 l. of water. Phenol lignin is precipitated and the amount is increased by again extracting the residual " cellulose " with methyl alcohol. Yield 121 g. (67 per cent. on the wood) ; OMe, 6·4 per cent.

30 g. of crude substance in 300 ml. of dioxan were allowed to drop into seven or eight times the volume of ether. After four or five such treatments Phenol Lignin A was obtained : C, 69 ; H, 6 ; OMe 10·4 per cent.

To obtain Phenol Lignin B the residues from the above were evaporated (low pr.) to remove dioxan, then taken up in dioxan to give a 10 per cent. solution and added to ether to remove any A fraction present. This was separated, and the residue after removal of the ether added to dry benzene—a fine, light powder being obtained. It is often, however, very difficult to prepare a solid product. After purification analysis showed : C, 72·7 ; H, 6·0 ; OMe, 5·3 per cent.

It is soluble in most solvents except chloroform, pure benzene and dry ether. It dissolves readily in ether containing dioxan.

[1] A. Hillmer, *Cellulosechem.*, 1925, **6**, 169 ; F. Brauns and H. Hibbert, *Can. J. Research*, 1935, B, **13**, 61.

H. **Cuproxam Lignin.**[1]—Purified wood (200 g.) is ground with 1·2 l. of cold saturated (80 per cent.) calcium thiocyanate solution in a porcelain mill. The wood swells and is washed by decantation free from thiocyanate and then treated on the suction filter with 25 per cent. ammonia. The mash (from 400 g. of wood) is treated in an 8 l. flask with 5–6 l. of Schweizer's solution, the air above being replaced by propane. After standing on ice with occasional shaking for 1 day, the meal is separated (centrifuge) and the residue from two such flasks placed in a 4 to 5 l. flask which is completely filled up with Schweizer's solution. After 12 hours in the ice chest the solid is again separated and twice more treated in the same way, after which it is washed on the centrifuge, once with Schweizer's solution, four times with strong ammonia, and twice with water.

The mass is suspended in water and slightly acidified (H_2SO_4), washed and squeezed on the suction filter. It is brought, while moist, into 6 l. of 1 per cent. H_2SO_4. By introducing steam and outside heating the liquid is raised to the boil and after 1½ hours is poured into cold water and left for 2 hours. The light brown mass obtained by filtration is put into two flasks and the whole treatment with Schweizer's solution, etc., down to the acid boil repeated four more times.

From 400 g. of spruce wood (7 per cent. water) 102 g. of lignin (4 per cent. water) were obtained or 26 per cent. of the dry wood. The cuproxam lignin contains 1–2 per cent. of nitrogen and gives 3 per cent. of formalin on acid hydrolysis. Boiled repeatedly with bisulphite solutions, it dissolves as sulphonate. Its composition is given on p. 487.

J. **Lignosulphonic Acids.**—The following are laboratory methods of preparation. The treatment of commercial sulphite liquor is illustrated under example K.

(*a*) Spruce meal (1·4 kg.), air dry, is heated with 11·4 l. of sodium bisulphite liquor containing 1·2 per cent. free and 4·7 per cent. of combined SO_2. Temperature raised slowly over 2 hours to 110° then maintained 8 hours at 125°.

(*b*) Spruce meal, 200 g., similarly with 1·8 l. of calcium bisulphite liquor (6 per cent. total and 1·2 per cent. combined SO_2). Heating as under (*a*).

(*c*) Yellow birch chips, 13·5 kg., heated with 60 l. sodium bisulphite liquor (6 per cent. total, 1·1 per cent. combined SO_2) at maximum of 125° for 8 hours.

K. The Lignosulphonic Acid, $C_{40}H_{44}O_9.2H_2SO_3$, obtained from Spruce Wood by the Action of Sulphurous Acid in the

[1] K. Freudenberg, *Ber.*, 1928, **61**, 1760; *ibid.*, 1938, **71**, 1810.

Presence of Ammonia.[1]—Cross and Engelstad showed that a solution containing 7 per cent. SO_2 resolves wood at 110°, especially if about 0·1 to 0·5 per cent. of NH_3 on the total liquor is present.[2] An examination of the lignosulphonic acid from this process is described.

Purification of the Crude Liquor.—This was dialysed for 7 days in parchment paper bags. The solution was evaporated to dryness at 40° as higher temperatures resulted in the product becoming insoluble in water. It formed a brown, non-deliquescent solid, soluble in water and in alcohol-water mixtures, and slightly soluble in pyridine. It was purified by precipitating with ether from aqueous alcoholic solution.

The product contained nitrogen, which was removed by alkali, but was not affected by the addition of HCl and dialysis. Typical analyses were :—

Fraction	I. .	NH_3 1·5 per cent.,	S 7·3 per cent.,	S/N = 2·5/1.
,,	II. .	NH_3 1·8 ,,	S 7·36 ,,	S/N = 2·1/1.

The sulphur content indicates an acid $C_{40}H_{40}O_{12}$, $2H_2SO_3$, the nitrogen figures agreeing approximateiy with a monoammonlum salt ot the dibasic acid.

Preparation of the Free Acid, $C_{40}H_{44}O_9$, $2H_2SO_3$, *from the Ammonia Compound.*—Sodium hydroxide removed the nitrogen as ammonia with equivalent substitution of sodium, but the addition of HCl and dialysis did not remove the sodium and release the free acid. The sodium salt, therefore, was precipitated with β-naphthylamine, and the β-naphthylamine compound (1 mol. acid, 1 mol. amine) warmed for 2 hours with pyridine. On pouring into alcohol the free acid was precipitated. This was separated and washed with alcohol. It was soluble in water and free from nitrogen and sodium.

The acid, after fractionation, gave on analysis : C, 57·7 ; H, 5·9 ; S, 7·5 ; OMe, 10·8 per cent. $C_{37}H_{35}O_6(OMe)_3$, $2H_2SO_3$ requires C, 57·6 ; H, 5·7 ; S, 7·4 ; OMe, 11·17 per cent. The sodium salt gave C, 55·8 ; H, 5·3 ; S, 7·36 per cent. $C_{40}H_{44}O_9$, $NaHSO_3$, H_2SO_3 requires C, 56·2 ; H, 5·2 ; S, 7·5 per cent. The sodium salt corresponds with the ammonium salt for which calculated values would be N, 1·65 ; S, 7·54 per cent. Found : N, 1·30 ; S, 7·36 per cent.

The benzoyl derivative (Schotten-Baumann) contained three benzoyl groupings per C_{40}. A *phenyl hydrazine derivative* (sodium acetate method) also contained one N_2HPh grouping per C_{40} formula.

The Action of Nitric Acid.—One part of the acid was heated gently for 4 hours with 20 parts of nitric acid (5 per cent.), followed

[1] C. Dorée and E. C. Barton-Wright, *J. Soc. Chem. Ind.*, 1929, **48**, 9T.
[2] *Ibid.*, 1925, **44**, 267T.

by dialysis for 1 day. A red powder was obtained insoluble except in water and pyridine. It gave a red solution with alkalis evolving NH_3 on warming. Gelatin, heavy metals and alkaloids removed it from solution.

The nitro-compound in aqueous solution reacted vigorously with magnesium, and after addition of HCl and NaCl a product free from nitrogen was obtained which showed ketonic reactions.

L. **The Hydroxyl Groups in Spruce Lignin.**[1]—A fully methylated spruce lignin (OMe, 32·4 per cent.) was demethylated with hydriodic acid—a reagent which destroys the aliphatic hydroxyl groups, but leaves aromatic or carboxylic hydroxyl groups unchanged. The product was soluble in alkali and contained 8·3 active H_2 units per kg. (Zerewitinoff analysis in quinoline). After treatment with zinc and acetic acid to remove iodine the substance was free from halogen and methoxyl, and the active hydrogen content was unchanged.

The Zerewitinoff values were confirmed by methylation (Me_2SO_4) under such *p*H conditions that carbomethoxyl linkages were not hydrolysed. Found : OMe, 23 per cent., which accounts for all of the 8·3 active hydrogen units. Methylation with diazomethane (OMe, 21 per cent.) accounts only for 7·5 units. The balance 0·8 unit is probably the aliphatic OH group formed by reduction of the carbonyl group (0·8 group/kg.) present in spruce lignin (p. 495).

Tosylation should replace both aliphatic and aromatic hydroxyl, but only 7·7 groups per kg. were tosylated. The balance (8·3—7·7) or 0·6 group, corresponds to the residual active hydrogen (0·8 unit) found by Zerewitinoff analysis, so that 0·5 to 0·8 OH group is present, which is neither aliphatic nor aromatic. Saponification of the diazomethane methylated product (OMe, 21 per cent.) showed that this balance was carboxylic, since the methoxyl was reduced to 19·2 per cent., corresponding to about 0·6 hydroxyl group per kg.

The balance of 6·9 groups per kg. (7·5–0·6) must be aromatic, since any aliphatic enolic OH would not survive reduction with hydriodic acid.

Demethylation with Hydriodic Acid.—A solution of lignin (OMe, 32·4 per cent.) in glacial acetic acid (10 g. in 800 ml.) with 100 ml. hydriodic acid (*d*, 1·7) was boiled for 2 hours in a current of carbon dioxide.

Fractionation.—The liquid, concentrated to 200 ml., was poured into dilute sodium bisulphite (3 l.). After centrifuging, it was concentrated (20 mm.) and extracted with ether to remove tar.

[1] R. G. Moore, G. F. Wright and H. Hibbert, *Can. J. Research*, 1937, B, **15**, 532.

The lignin-like precipitate dissolved in dioxan and was precipitated by pouring into ether (ten times volume). Yield 0·9 g. The liquors were concentrated and poured into petroleum ether (ten times volume), giving 4·2 g.

De-iodination.—The crude product from HI reduction (1 part) was heated for 1 hour with 150 parts of glacial acetic acid and 5 parts of zinc dust. The solution concentrated (low pr.) was poured into 10 volumes of water and the product fractionated as above. Dioxan-ether soluble (15 per cent., fraction A) and dioxan-petroleum ether insoluble (80 per cent., fraction B) separated. B contained C, 60; H, 7 per cent.; active H_2, 8·3 per kg.

Modified Methylation with Dimethyl Sulphate.—A sample of B after methylation with gaseous diazomethane (0·3 g.) was acetylated (3 days) in pyridine (5 ml.), acetic anhydride (2 ml.) and the derivative in acetone solution at once treated with dimethyl sulphate (6 ml., 0·06 mole) and 30 per cent. NaOH (7 ml., 0·05 mole). The treatment was once repeated and, after solution in dioxan and precipitation with light petroleum gave OMe, 23 per cent.

Tosylation.—The aliphatic hydroxyl group which could not be methylated with diazomethane reacts with tosyl chloride. Thus 1·5 g. of product B was treated twice with 6 g. in 55 ml. of pyridine. The derivative contained S, 11·3 per cent.; active H_2, 0·8 per kg. Calculated for 7·7 tosyl groups per kg.: S, 11·3 per cent.

Isolation and Estimation of the Aromatic Aldehydes from Lignin

Alkaline treatment of lignosulphonic acid from spruce wood gives about 6 per cent. of vanillin with a little acetovanillone,[1] while products from hard woods give vanillin and syringyl aldehyde (total 6 per cent.) in about equal amounts with acetosyringone (about 1 per cent.), calculated on the lignin present.

Method for Maximum Yield.—The use of alkali in the presence of nitrobenzene or sodium *m*-nitrobenzene sulphonate,[2] gives maximum yields of aldehydes. The method and its application to the estimation of vanillin and syringyl aldehyde are illustrated by the following example.[3]

[1] H. Hibbert *et al.*, *J. Amer. Chem. Soc.*, 1936, **58**, 345; *ibid.*, 1937, **59**, 597; *Can. J. Research*, 1938, B, **16**, 54.

[2] K. Freudenberg and W. Lautsch, *Ber.*, 1940, **73**, 167; W. Lautsch and F. Klink, *Z. angew. Chem.*, 1940, **53**, 450; K. Freudenberg and E. Plankenhorn, *Ber.*, 1942, **75**, 866.

[3] R. H. Creighton, J. L. McCarthy and H. Hibbert, *J. Amer. Chem. Soc.*, 1941, **63**, 3049.

Oxidative Alkaline Cleavage.—20 g. of wood with 12 ml. of pure nitrobenzene and 400 ml. of 8 per cent. aqueous NaOH solution are heated for 8 hours at 160°, with violent agitation, in a stainless steel bomb of about 500 ml. capacity. Precautions must be taken against explosion due to sudden heat development. After cooling the nitrobenzene is removed in steam, the liquid filtered, the residue washed with alkali and water and the total filtrate and washings extracted continuously with benzene for 48 hours.

The benzene is extracted successively with solutions of (*a*) sodium bisulphite, 20 per cent., (*b*) sodium bicarbonate (8 per cent.), and (*c*) with sodium hydroxide (5 per cent.).

The bisulphite fraction is acidified and the SO_2 removed (low pr.) without heating. After filtration, the liquid is made up to 500 ml. and the total vanillin and syringyl aldehyde estimated in 50 ml. as *m*-nitrobenzoyl hydrazone after buffering with sodium acetate.

The rest of the solution is extracted with benzene to obtain the mixed aldehydes, and after removal of the solvent the aldehydes are separated by sublimation (the most satisfactory method). About 0·4 g. of the oil is heated in a small subliming tube ($5\frac{1}{2} \times \frac{3}{4}$ in.) fitted with a cold finger, for 8–10 hours at 61° (1·5 mm.).

The sublimate of vanillin is taken up in ether, the solvent removed (low pr.), leaving about 0·08 g. of vanillin, m.p. 65–75°. The cold finger is replaced and the bath temperature raised to 100° for 15–20 minutes, whereby about 0·02 g. of a mixture of aldehydes sublimes, and is washed off with ether. The sublimation is then continued (100°, 1·5 mm.) for 12 to 18 hours as before. About 0·25 g. of syringyl aldehyde is usually obtained, m.p. 105–110°, which when crystallised from water (loss 3 per cent.) gives m.p. 110–112°.

The crude vanillin sublimate is dissolved in 10 ml. of hot water, made just acid with acetic acid and mixed at 60° with a hot aqueous solution of *m*-nitrobenzoyl hydrazine (0·15 g. in 10 ml.). After 30 minutes at 60° and overnight the precipitate is separated, dried and weighed. M.p. 202–205°; OMe, 9·85 per cent.

N.B.—Pure vanillin has m.p. 80–81°; OMe, 20·4 per cent.; *m*-nitrobenzoyl hydrazone, m.p. 212°. Pure syringyl aldehyde has m.p. 110–112°.

Formation of Vanillin and Acetovanillone from Spruce Wood and Acetosyringone from Hard Woods.—Lignosulphonic acids, when heated with sodium hydroxide solutions, give vanillin (or the mixture of aldehydes) which are isolated by extraction with benzene and bisulphite as above.[1] Acetovanillone (V) or acetosyringone (*cf.* IV, p. 485), is left.

[1] G. H. Tomlinson and H. Hibbert, *J. Amer. Chem. Soc.*, 1936, **58**, 345; W. L. Hawkins and H. Hibbert, *ibid.*, 1937, **59**, 2447.

The sulphite liquor is either heated for 20 hours under reflux with sufficient NaOH to make a 24 per cent. solution, or heated (4 hours) under pressure (6 at.) with NaOH to a 9 per cent. solution. The amount of lignin in the liquor can be estimated from the methoxyl content of the solid residue, assuming that lignin contains 15 per cent. of methoxyl.

Acetovanillone.—The liquor (*e.g.* 3 l. from spruce wood containing 111 g. of lignin),[1] after heating with NaOH, is extracted with benzene and the extract shaken twice with 20 per cent. sodium bisulphite solution to remove vanillin (7·16 g). After evaporation of the benzene a viscous oil (1 g.) is left which is treated by the sublimation process given above. At bath temperatures, 55–100° (8 mm.), oily drops collect on the cold finger which is changed. No further sublimate forms till 136°, and after 200° nothing more collects. The sublimate, which is crystalline, is twice resublimed and crystallised from benzene and light petroleum, giving 300 mg. (0·2 per cent. on the lignin) of acetovanillone, m.p. 114°; OMe, 18·7 per cent.; semicarbazone, m.p. 166°.

As acetovanillone gives no precipitate with *m*-nitrobenzoyl hydrazine it does not affect the estimation of vanillin (p. 504).

Acetosyringone.—When the sulphite liquor from birch wood (3 l., 59 g. of lignin) was similarly treated the benzene solution, after bisulphite extraction, gave 1·5 g. of viscous oil. This, under sublimation (7 mm.), gave 100 mg. of oil from 50–100° and 500 mg. of crystalline sublimate between 100–200° (bath temp.).

The crystalline product, twice resublimed, crystallised from benzene-light petroleum and then from water, gives acetosyringone, m.p. 121–122°; OMe, 31·6; *p*-nitrophenylhydrazone, m.p. 195°.

α-Ethoxy-hydroxy-propiovanillone was obtained by ethanolysis of spruce wood, and the corresponding propiosyringone derivative from maple wood.[2]

Autoxidation Methods.—Kurschner [3] showed that when lignin is heated at about 200° in thin layers just below a cold surface, a sublimate of vanillic acid is formed, but that if air was entirely excluded no change took place. The material is heated in a dish, resting in a hole in a sheet of asbestos placed on the top of an air-bath. The condenser is a small Petri dish cooled with water.

The application of this method to metalignin [4] (p. 491) showed

[1] F. Leger and H. Hibbert, *J. Amer. Chem. Soc.*, 1938, **60**, 565; *Can. J. Research*, 1938, B, **16**, 54.

[2] H. Hibbert *et al.*, *J. Amer. Chem. Soc.*, 1939, **61**, 509, 576.

[3] "Zur Chemie der Ligninkorper", Stuggart, 1925.

[4] E. B. Colegrave, "The Aromatic Structure of the Lignin Complex", *Thesis*, London University, 1940.

that when heated as above for 12 hours at 200° vanillin itself was obtained and not vanillic acid. In a good vacuum, or an inert atmosphere, no change took place. To determine whether the para-hydroxyl group of vanillin resulted from a free phenolic group in metalignin, or whether it was derived from the rupture of an ether linkage, an experiment was made on fully methylated metalignin.

From this derivative an aromatic oil was obtained which was crystallised from the minimum of ethyl alcohol by cooling the solution in solid carbon dioxide. The odour, m.p. 40°, and comparison with an authentic sample showed that the product was veratric aldehyde (m.p. 41°), indicating that the nucleus in metalignin which gives rise to vanillin, contains a free phenolic group.

Autoxidation of Benzoyl Metalignin.—When 0·029 g. of benzoyl metalignin was heated (200°, 20 hours) as before, the sublimate weighed 0·016 g., or 55 per cent., so that each $C_{20}H_{20}O_6$ unit yields one mol. of vanillin on autoxidation. The sublimate was identified as benzoyl vanillin giving a 2 : 4-dinitrophenylhydrazone, m.p. 208°, and the result indicates that the vanillin residue is joined to the remainder of the lignin molecule by the carbon atom attached to the nucleus.

Nitrometalignin under autoxidation gave 5-nitrovanillin, m.p. 172°.

CHAPTER XXVI

THE PECTIC SUBSTANCES

THE extensive research which has been carried out in connection with the pectic substances and the related plant gums and mucilages has been well summarised, so that a brief introduction only is necessary. The following monographs may be consulted for further information:—

(i) " A Critical and Historical Study of the Pectic Substances of Plants ", by M. H. Branfoot (M. H. Carré)—Department of Scientific and Industrial Research, Special Report No. 33 : H.M. Stationery Office, London, 1929.

(ii) " Pektin ", Handbuch der biol. Arbeitsmethoden (Abderhalden, Berlin, 1936, **1**, (11), 1503, by F. Ehrlich.

(iii) " Recent Progress in the Chemistry of the Pectic Materials and Plant Gums ", by E. L. Hirst, *J. Chem. Soc.*, 1942, 70.

(iv) Chemical Society Annual Reports, 1937, **34**, 296-302 ; 1941, **38**, 150-167.

The following also, have historical and practical interest :—

Ehrlich, *Biochem. Z.*, 1926, **168**, 263 ; **169**, 13 ; 1933 ; **259**, 100.

Nanji, Paton and Ling, *J. Soc. Chem. Ind.*, 1925, **44**, 253 T.

G. G. Schneider *et al.*, *Ber.*, 1937, **70**, 132, 1617.

P. A. Levene *et al.*, *J. Biol. Chem.*, 1937, **120**, 591.

The varying nomenclature used in the past to describe the pectic substances has led to some confusion. A review of the evidence available up to 1929 led Branfoot (*loc. cit.*, p. 27) to state that the following points, relating to the names and nature of the pectic substances, might be considered as fairly well established. They are generally accepted to-day.

1. An insoluble compound occurs in unripe fruits and other plant tissues which is generally described as *protopectin* or *pectose*. It was formerly regarded as a pectin-cellulose complex with a constitution analogous to that of the glucosides.

2. *Pectin* is a neutral fully methylated methyl ester of pectic acid yielding 11·76 per cent. of methyl alcohol. Between pectin and pectic acid come the *pectinic* acids which are more or less demethylated and exhibit increasing acidic properties as their methyl content diminishes.

3. *Pectic Acid*, which constitutes the basal molecule of pectin, is a complex galacturonic acid associated with arabinose and galactose, and possibly with methyl pentose.

4. Pectin can be converted quantitatively into calcium pectate, the methyl groups being removed by hydrolysis and replaced by calcium. Calcium pectate is a definite compound containing 7·62 per cent. of calcium.

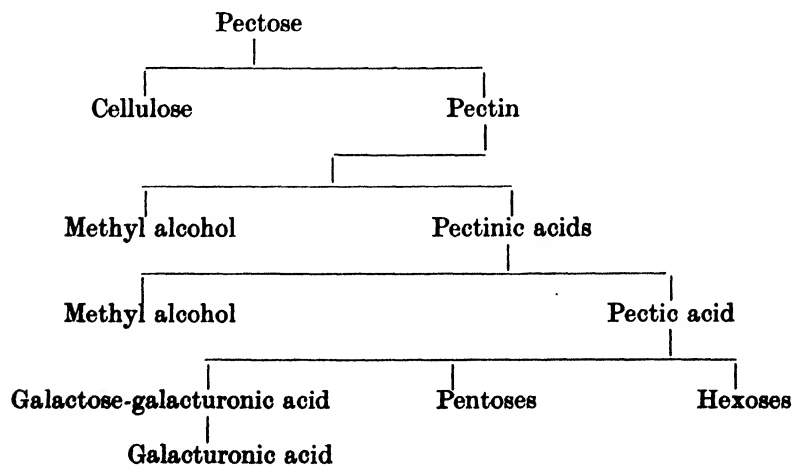
5. The formula $C_{39}H_{58}O_{33}$ or $C_{35}H_{46}O_{29}(OCH_3)_4$ might provisionally be assigned to pectin. Pectic acid would then be $C_{35}H_{50}O_{33}$, and calcium pectate derived from it as above would contain calcium 7·66 per cent.

These results were based upon the work of Ehrlich (*loc. cit.*), who, from beet residues, obtained a crude pectin from which an impurity—a lævorotatory araban—was easily removed. The purified product "pectinogen" (*i.e.* pectin) was found to be a calcium magnesium salt of esterified pectic acid. Treatment with acid and precipitation by alcohol gave pectic acid, $[\alpha]_D + 220°$; methoxyl, 9 per cent. Pectic acid hydrolysed by 1 per cent. oxalic acid gave galactose-galacturonic acid. More severe hydrolysis using oxalic acid under 2 to 3 atmospheres pressure gave galactose and galacturonic acid.

On treating pectic acid with cold sodium hydroxide a white solid was obtained, $[\alpha]_D + 270°$, which was found to be tetragalacturonic acid, giving galacturonic acid on hydrolysis. The araban was isolated as a strongly lævorotatory substance with $[\alpha]_D$ varying from $-25°$ to a maximum of $-173°$.

A microchemical study of the metabolic changes taking place in fruits during ripening and senescence [1] in the light of these results, made it possible to represent the transformation of the pectic substances of the life of the fruit as follows :—

Diagram representing the Pectic Changes in Apples



[1] M. H. Carré and A. S. Horne, *Ann. Bot.*, 1927, **41**, 1.

The relationship of these compounds in terms of the most probable formulæ were given as follows :—

Pectin

$$C_5H_8O_4—C_6H_{10}O_5—(C_5H_7O_4.COOMe)_4 \quad (C_{39}H_{58}O_{33}).$$

Pectic Acid

$$C_5H_8O_4—C_6H_{10}O_5—C_5H_7O_4(COOH)—C_5H_7O_4(COOH)—C_5H_7O_4(COOH)—C_5H_7O_4(COOH) \quad (C_{35}H_{50}O_{33}).$$

Arabinose Galactose Galacturonic acid.

Nanji, Paton and Ling (1925) proposed a six-ring formula for the basal molecule of pectin, consisting of four galacturonic acid residues united to anhydroarabinose and anhydrogalactose, with four free carboxyl groups. This molecule should give a calcium salt (Ca, 7·36 per cent.) and contain 69·7 per cent. galacturonic anhydride, 14·25 anhydroarabinose, and 16·55 per cent. anhydrogalactose. It should yield 20·85 per cent. of furfural, and 17·64 per cent. of carbon dioxide.

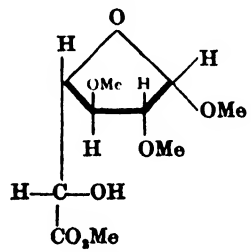
A large number of determinations with isolated pectin show an average yield of furfural of 20·5 per cent. and carbon dioxide 18 per cent.

The results of subsequent investigation show that pectin is essentially a *mixture* of pectic acid (a polygalacturonic acid) with a polyarabinose (araban) and frequently with a polygalactose (galactan or galactogen). These three components are present in most, if not all pectins, although their respective proportions vary. Further, the araban and galactan are not, as formerly supposed, combined with pectin, nor do they exist as a galacto-araban complex in the mixture.[1]

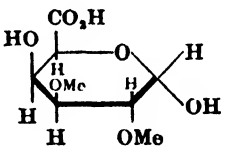
Pectin itself is a complex made up of a number of *d*-galacturonic acid residues more or less esterified. On hydrolysis it yields pectic acid which may still contain as many as 10 to 15 galacturonic acid residues.[2] The type of union between the uronic acid groupings was early assumed to be 1 : 4-glucosidic as this type seemed to be characteristic of the polysaccharides occurring in plant (and animal) tissues although, more recently, 1 : 2-, 1 : 3-, 1 : 5- and 1 : 6-linkages have been discovered. The correctness of the existence of the 1 : 4-linkage in pectic acid was shown by application of the methylation-hydrolysis method to pectic acid derived from strawberry

[1] E. L. Hirst and J. K. Jones, *J. Chem. Soc.*, 1938, 496 ; 1939, 452.
[2] *Chem. Soc. Ann. Reports*, 1937, **34**, 300.

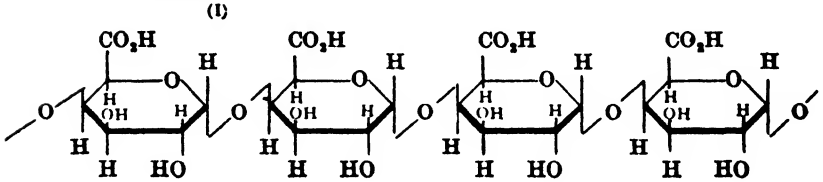
pectin [1] and citrus pectin,[2] and later from pectins obtained from white lupin seeds, apple, peanut and hawthorn. The sole product isolated in each case was the methyl ester of 2 : 3-dimethyl methyl *d*-galacturonoside (I). This shows that pectic acid is made up of galacturonic acid residues connected either by 1 : 4 or 1 : 5-glucosidic linkages. If the linking is 1 : 5 the galacturonic residues would be furanose, and although the 2 : 3-dimethyl derivative is isolated in that form (I) there is much evidence in favour of the view that they exist in pectic acid in the pyranose form (II), reverting under the conditions of methylation and hydrolysis. In that case the linking is 1 : 4-glucosidic, and taking into consideration the high positive rotation of pectic acid (above 200°) and its resistance to acid hydrolysis, the formulation (III) for pectic acid made up of 1 : 4-α-glucosidic linkages seems most probable. Levene *et al.*, however, still favour the 1 : 5-linkage on results obtained for the rate of hydrolysis of a methylated pectic acid.[2]



(I)



(II)



(III)

The similarity in structure between pectic acid and cellulose is apparent. Each is composed of chains of simple hexose residues linked in the 1 : 4-position, cellulose being based on β-glucose and pectic acid on α-galacturonic acid (*cf.* II). Stereochemical models show that the chain in each case is zig-zag, but that pectic acid with α-orientation at the 1-carbon position [3] has a flatter zig-zag and longer pyranose ring unit than cellulose.

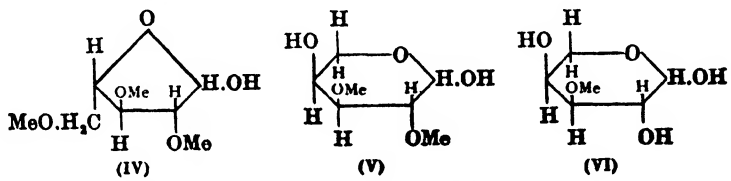
The open-chain structure of cellulose is shown by the production of a methylated "end group" fraction after methylation and

[1] S. Luckett and F. Smith, *J. Chem. Soc.*, 1940, 1106, 1506.
[2] P. A. Levene, G. M. Meyer and K. Kuna, *Science*, 1939, **89**, 370.
[3] G. V. Caesar and M. L. Cushing, *J. phys. Chem.*, 1941, **45**, 776.

hydrolysis (p. 178). If pectic acid also has an open-chain structure an end fraction—the methyl ester of trimethyl methylgalacturonoside —should be formed. It has not, however, been detected among the products of methylation and hydrolysis and this negative observation, if confirmed, would support the opinion that in pectic acid the chain is joined in a closed ring or loop.

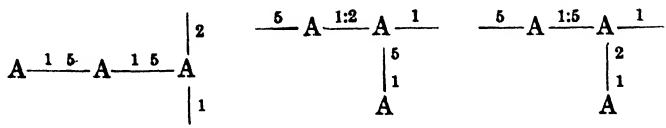
The polyglucuronic acid prepared by boiling pectin with dilute acid for a long time still contains 10 to 15 galacturonic acid residues. Pectin, when nitrated, shows a certain physical resemblance to cellulose nitrate and determinations [1] of its viscosity and use of the same K_m constant as for nitrocellulose have given figures for molecular weight between 50,000 (beetroot pectin) and 150,000–200,000 (apple and citrus pectins).

An araban seems invariably to be associated with the pectic acid in pectin. The arabans isolated from peanut (the best source), apple and citrus pectins are all similar and give after methylation-hydrolysis, equimolecular proportions of three sugars : (*a*) 2 : 3 : 5-trimethyl *l*-arabinose (IV), (*b*) 2 : 3-dimethyl *l*-arabinose (V) and (*c*) 3-methyl *l*-arabinose (VI).



Although sugars (V) and (VI) are isolated in the pyranose form they are present originally in the furanose form (IV). The absence of a methyl group at position 5 in their case permits isomerism to take place during hydrolysis.[2] This view is based upon the high negative rotation of the araban (which also indicates α-glucosidic linking) and the ease with which it undergoes hydrolysis.

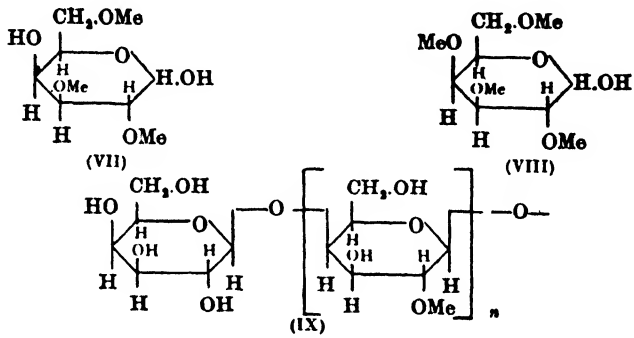
The following branched chain formulæ for the repeating unit of this araban would agree with the production of sugars (*a*), (*b*) and (*c*) above. A represents an α-arabofuranose residue, and the numbers indicate the carbon atoms at which linkage takes place.



[1] G. G. Schneider and H. Bock, *Ber.*, 1936, **69**, 321.

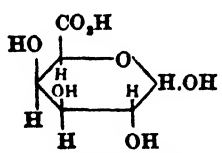
[2] E. L. Hirst and J. K. Jones, *J. Chem. Soc.*, 1938, 496 ; 1939, 452, 454 ; G. H. Beaven, E. L. Hirst and J. K. Jones, *ibid.*, 1939, 1865.

The galactan associated with pectin is difficult to isolate in a pure form. The seeds of *lupinus albus*, however, are rich in galactan, while the araban is present in small proportion. The latter is hydrolysed with 0·01 *N*-acid and the pectic acid removed as calcium pectate. The residual galactan has a low positive rotation, and on hydrolysis gives *d*-galactose at a rate which points to a pyranose structure. It forms a trimethyl-derivative which is hydrolysed to 2 : 3 : 6-trimethyl *d*-galactose (VII) with a small proportion of 2 : 3 : 4 : 6-tetramethyl *d*-galactose (VIII), results which indicate

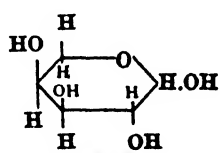


that the galactan is built up of chains of β-*d*-galactose units linked in the 1 and 4-positions (IX).

With regard to the mutual relationship and origin of the three chief components of pectin, it has long been a favourite hypothesis that the *d*-galacturonic acid is formed by direct oxidation, at C_6, of a galactan initially present, and that the araban is derived by simple decarboxylation of the pectic acid. The results outlined above, however, lead to the interesting conclusion that the natural processes are more complicated and must involve the breakdown of one of the complexes into a hexose, from which a uronic acid or a pentose is formed, followed by the building up of these simple units into new complexes. The galactan (IX), for example, which



d-galacturonic acid.
(X)



l-arabinose.
(XI)

is made up of a chain of β-*d*-galactose residues of the pyranose type linked 1- and 4-, could not produce the araban, which has a furanose ring structure (*cf.* IV), unless the galactan were first hydrolysed to

d-galactose and the araban synthesised from this through *l*-arabinose [1] (XI). The same mechanism would be required to produce the galacturonic acid residues present in pectic acid, from the galactan (IX).

That the direct decarboxylation of hexuronic acids may take place in plant metabolism is shown by the constant association of *d*-glucose with *d*-xylose and *d*-galactose with *l*-arabinose. A glance at the formulæ shows that *d*-glucuronic acid gives rise directly to *d*-xylose and *d*-galacturonic acid (X) to *l*-arabinose (XI).

Commercial Pectin and its Analysis

The Preparation of Pectin.—The usual sources on a large scale are apple pomace, the refuse from cider and vinegar manufacture, citrus peels and refuse, beet pulp and beet residues, and carrots. The proportion of " pectin " in these materials is given as follows (Wilson) :—

	Pectin in Fresh Material, per cent.	Pectin on a Water-free Basis, per cent.
Apple pomace	1·5–2·5	15–18
Lemon pulp	2·5–4·0	30–35
Orange pulp	3·5–5·5	30–40
Beet pulp	1·0	25–30
Carrots	0·6	7

(Pectin here means alcohol-precipitate less ash. Extract made by an arbitrary method consisting of ten successive extractions each of 1 hour with 0·5 per cent. sulphurous acid on the water bath.)

The principle of all the methods of isolation is the same—*viz.* the hydrolysis of the pectose of the tissue to pectin. The material is finely minced and treated either with superheated steam, with water under pressure, with boiling water containing copper sulphate (said to give a snow-white product), or with very dilute acids.

Pectin is usually " extracted " by acid solutions, of which citric, tartaric and lactic have been used among the organic acids, and hydrochloric, phosphoric and sulphurous among the inorganic. A commercial product sold as " citrus pectic acid " is prepared from citrus fruits by the action of citric acid. It corresponds closely to Ehrlich's pectolic acid, and being practically a pure polygalacturonide, is a useful starting material.

The following method suggested for the commercial preparation of a clear concentrated and tasteless extract of pectin appears satisfactory [2] :—

[1] E. L. Hirst, J. K. Jones *et al.*, *J. Chem. Soc.*, 1942, 71.
[2] H. D. Poore, *U.S. Dept. Agric. Bull.*, 1925, No. 1323.

1. The aqueous extract is concentrated and clarified through kieselguhr.

2. The pectin is precipitated with 95 per cent. alcohol.

3. The precipitate is treated with sufficient alcohol to make a thick paste. The mass is kneaded and the alcohol removed by pressing, the process being repeated several times and a temperature of 68° maintained throughout to ensure sterility.

4. The pectin is redissolved and concentrated as required.

For the preparation of small quantities of pectin in a powder form from these extracts the solution is dialysed against running water, or better by electro-dialysis, concentrated in a vacuum, not above 40°, and precipitated by alcohol. Greyish-yellow scales are obtained soluble in water.

The method described by Wilson [1] for the large-scale production of pectin from lemon refuse obtained in citric acid manufacture has been followed by a number of workers requiring material for laboratory investigation and is quite satisfactory.

Manufacture of Pectin (C. P. Wilson).—The lemon refuse is cut up or ground and heated to 95–98° for 10 minutes to destroy pectinase, which would convert pectin to pectic acid and cause cloudiness.

Extraction.—The ground peel, 500 to 1,000 kg., is run into wooden tanks with false bottoms covered with filter cloth. Sufficient of 1 per cent. sulphurous acid solution is added to suspend the pulp and the whole raised rapidly to 90°, at which it is kept 2 hours. The liquid is drawn off through the false bottom, the pulp forming its own mat. Two more similar extractions are then made. The extracts are filtered, if necessary, through paper pulp, and the solution, containing about 0·5 per cent. of pectin, is quickly cooled and stirred, or baffled, to remove sulphur dioxide.

Precipitation of the Pectin.—This is done by means of aluminium hydroxide, a positive colloid which neutralises the negative charge carried by pectin. It is produced by adding aluminium sulphate (25 per cent. solution) to ammonia in the bath.

A sample is tested and the quantities of reagents required for precipitation are determined and weighed out for the bulk quantity.

The pectin is violently agitated and the ammonia is introduced all at once, immediately followed by the aluminium sulphate solution. The best results are obtained when the mixture finally obtained has a minimum viscosity and a *p*H of 4·0–4·2 (to bromophenol blue).

Separation of the Precipitated Pectin.—The tank is fitted with a wooden agitator and side baffles so that it is possible to whip air into the mixture, bringing the precipitate to the top as a thick sponge.

[1] C. P. Wilson, *Ind. Eng. Chem.*, 1925, 10, 1066.

The mother liquor is withdrawn through a screen and the excess of aluminium sulphate washed out of the precipitate by a short agitation in cold water. The pectin is finally centrifuged and dried in hot air at 65°. The quicker the drying, the better the quality of the product.

The pectin contains at least 6 and probably 10 to 12 per cent. of ash, mostly alumina. The dry pectin may be suspended in 85 per cent. alcohol containing more than enough hydrochloric acid to neutralise the ash. The aluminium chloride is thus removed and the residue washed with alcohol and dried, giving a greyish powder.

Quantitative Estimation of Pectic Compounds.—The older method of precipitation by alcohol, frequently employed for the approximate estimation of pectin in fruit juices, is not reliable as a quantitative method. The procedure was to concentrate the pectin solution and add twice the volume of 96·5 per cent. ethyl alcohol. The coagulum, after standing, was filtered through a stretched linen surface, washed with alcohol and with ether.

The estimation of the methyl alcohol produced on hydrolysis also does not give accurate results, as the methyl content of any particular sample varies with the method of preparation.

The following methods are recommended :—

Estimation of Pectin as Calcium Pectate.[1]—This method depends upon the facts (*a*) that the various pectic substances present in any extract are all converted by treatment with sodium hydroxide into pectic acid ; (*b*) that calcium pectate is exceedingly insoluble and has a definite calcium content of between 7·5 and 7·8 per cent.

A quantity of pectin is taken which will yield 0·02 to 0·03 g. of calcium pectate ; this is neutralised and diluted such that after all reagents have been added the total volume measures about 500 ml. 100 ml. of $N/10$ NaOH are then added and the mixture allowed to stand at least 1 hour, or better overnight. 50 ml. of $N/1$ acetic acid are added, and after 5 minutes 50 ml. of $M/1$ calcium chloride.

The mixture stands 1 hour and is then boiled for a few minutes and filtered through a large fluted filter paper. If the precipitation has been properly done, filtration is rapid and washing easy. The washing is done with boiling water until chloride cannot be detected, after which the precipitate is put back into the beaker, boiled and filtered again. The washings are tested for chloride and the processes repeated until the filtrate gives no reaction with silver solution. It is then filtered into a small fluted filter, transferred to a dish, and finally to a Gooch crucible previously dried at 100°. The precipitate is dried at 100° to constant weight (about 12 hours).

[1] M. H. Carré *et al.*, *Biochem. J.*, 1922, **16**, 60, 704 ; *ibid.*, 1925, **19**, 257.

For larger quantities of pectin the amounts of sodium hydroxide and calcium chloride can be increased. The use of less acid and more calcium chloride than those given above has been found to facilitate washing. Thus, for 50 ml. of pectin solution containing the equivalent of 0·0235 g. calcium pectate, 50 ml. of $N/10$ NaOH, 100 ml. of $N/10$ acetic acid, and 100 ml. of $M/1$ calcium chloride were employed.

The precipitate is so insoluble that estimations can be carried out with very dilute solutions, whereas no precipitate is given by alcohol below a concentration of pectin of 0·06 per cent.

The presence of acids in the extracts which are able to give insoluble calcium salts, would obviously impair the results obtained. Of these, however, only calcium oxalate and calcium racemate are insoluble in the dilute acetic acid employed. In their presence, however, the following modification of the method can be employed.

Estimation by Precipitation of the Pectic Substances with Acid Alcohol and subsequent use of the Calcium Pectate Method.—It has been found [1] that acidified alcohol will precipitate pectin completely at practically all dilutions. In the presence of oxalic acid, therefore, the following procedure is adopted :—

The solution is treated with four times its volume of alcohol, which contains sufficient HCl to make the whole mixture of decinormal strength. After standing overnight the precipitate is filtered, washed once with acidified alcohol, and dissolved off the filter paper with hot water. It is then hydrolysed, and estimated as calcium pectate as above.

Estimation of the Calcium Pectate Number and the Distribution of Pectic Substances in Plant Tissues (Nanji and Norman [2]).—These authors have estimated the yield of calcium pectate from 100 g. of various plant materials (the calcium pectate number). They alter slightly the method given above, working as follows :—

The dried and powdered plant tissue is extracted with 200 ml. of 0·5 per cent. oxalic acid or ammonium oxalate for 24 hours at 85°. The liquid is filtered, the residue washed with more solvent, and the whole made to 250 ml. 100 ml. of this are gently concentrated to 25 ml. (If oxalic acid has been used it should be neutralised before concentration.) After cooling, 3½ volumes of 95 per cent. alcohol, acidified with 5 or 6 drops of concentrated HCl, are added. The final concentration of alcohol should be 70 per cent. After several hours the precipitate is filtered on a fluted paper and washed with acid alcohol till free from oxalate. The paper and precipitate

[1] A. M. Emmett and M. H. Carré, *Biochem. J.*, 1926, **20**, 6.
[2] D. R. Nanji and A. G. Norman, *Biochem. J.*, 1928, **22**, 599.

are placed in a beaker and the solid dissolved by boiling with about 50 ml. of water, or in the case of ammonium oxalate extracts, with very dilute ammonia (to dissolve any free pectic acid). The solution is filtered and the paper again boiled with dilute ammonia in the case of aqueous or oxalic acid extracts, and with water in the case of ammonium oxalate extracts. Finally, further water is added to the paper, which is triturated with a glass rod, got on to a filter, and washed with hot water and hot dilute ammonia. The total liquid, usually over 100 ml., is treated (cool) with 100 ml. of 0·4 per cent. NaOH and allowed to stand 12 hours. 50 ml. of $N/1$ acetic acid are added, together with 50 ml. of 11·1 per cent. calcium chloride solution, and the mixture boiled for 5 minutes. The calcium pectate is filtered off as hot as possible and the gel washed with boiling water till free from chloride. Sometimes 400 ml. of water will be needed. The precipitate is dried at 100° and weighed.

The authors differentiate the pectic substances according to their solubilities thus :—

A, water—removes free pectin ; B, 0·5 per cent. oxalic acid—removes free pectin, plus pectin combined with metallic ions ; C, 0·5 per cent. ammonium oxalate—removes free pectin, pectin combined with metallic ions and pectic acid, free and combined.

Therefore A = free pectin ; B — A = pectin combined with metallic ions ; C — B = pectic acid, free and combined.

Some of their experimental results follow :—

Distribution of Pectic Substances in Plant Tissues

	Calcium Pectate Number.						Moisture, per cent.
	A.	B.	C.	A.	B.–A.	C.–B.	
Leaves :							
Sycamore .	3·87	5·24	7·90	3·87	1·37	2·66	64·2
Laurel . .	2·87	4·52	4·95	2·87	1·65	0·43	77·9
Cereal Grains :							
Wheat . .	*Nil*	0·40	0·60	*Nil*	0·40	0·20	11·6
Fruits :							
Apples—							
Peel . .	9·15	11·89	17·44	9·15	2·74	5·55	80·3
Pulp . .	8·92	11·94	17·63	8·92	3·02	5·69	88·0
Oranges—							
Yellow rind	7·54	11·09	15·92	7·54	3·55	4·83	73·2
White peel .	18·53	20·59	38·75	18·53	2·06	18·16	76·3
Pulp . .	10·45	12·06	12·40	10·45	1·61	0·34	89·1

(All values expressed as per cent. of the dry powder.)

Nanji, Paton and Ling (1925) state that the percentage of carbon dioxide yielded by a preparation of pectin when distilled with hydrochloric acid × 5·66, gives the percentage of pectinogen (pectose) and pectic acid present. Gummy material should first be removed by extraction with cold water.

The determination of the methyl alcohol yield has been of service in the investigation of the chemistry of the pectic substances, although not reliable as a means of estimation. The micro-method given below can be recommended. Reference to that of von Fellenberg will be found on p. 450.

Micro-Method for the Estimation of Methyl Alcohol obtained in the De-esterification of Pectin.[1]—Most of the colorimetric methods proposed for the determination of methyl alcohol depend upon its oxidation to formaldehyde and determination by means of roseaniline bisulphite. The method now proposed is claimed to be free from many of the objections that can be urged against the older ones, and is much more expeditious. The authors proved by experiment that quantities of the order of 5 mgm. of methyl alcohol could be distilled out quantitatively from solutions likely to be used and that such quantities could be estimated in 7 minutes with a sensitiveness of the order of 0·05 mgm.

Procedure.—1. The distillation: The pectic solution, containing not more than 0·05 g. of the substance, is treated with 100 ml. of $N/10$ NaOH in a closed flask and kept overnight. The liquid is neutralised with sulphuric acid to a pH of about 4·5, transferred to a 200 ml. distillation flask and distilled until about nine-tenths have come over. The methyl alcohol is estimated in the whole distillate. Corks, previously repeatedly boiled out with water, should be used in fitting up the apparatus.

2. The estimation of methyl alcohol: The following solutions are required:—(*a*) Potassium permanganate (9·75 g./litre), (*b*) potassium permanganate $N/20$ (1·58 g./litre), (*c*) sodium hydroxide (150 g./litre), (*d*) oxalic acid (20 g./litre), (*e*) sulphuric acid (2 vols. concentrated acid with 5 vols. of water).

100 ml. of the permanganate solution (*a*) and 40 ml. of sodium hydroxide (*c*) are placed in a 500 ml. Erlenmeyer flask. The dilute methyl alcohol solution, containing not more than 10 mgm., is added and the mixture boiled under reflux for 3 minutes exactly after coming to the boiling-point. Without cooling 100 ml. of oxalic acid (*d*), followed by 40 ml. of sulphuric acid are added. The whole is shaken and the excess of oxalic acid titrated with $N/20$

[1] D. R. Nanji and A. G. Norman, *J. Soc. Chem. Ind.*, 1926, **45**, 337T.

permanganate. A control experiment *must* be carried out without the addition of methyl alcohol.

All flasks, pipettes, etc., used should be cleaned with alkaline permanganate. The pipettes should be double marked and very accurately calibrated. The strength of the dilute permanganate need not be exact, as the solutions must be standardised against methyl alcohol solutions of known concentration. The following results illustrate the accuracy of the method :—

Volume of $N/20$ $KMnO_4$ (1 ml. = 0·269 mgm.) equivalent to		Methyl alcohol.	
Blank * + MeOH taken, ml.	MeOH taken, ml.	Found, mgm.	Taken, mgm.
23·7	18·7	5·08	5·0
19·8	14·8	3·98	4·0
15·9	10·9	2·93	3·0
12·3	7·3	1·96	2·0
8·7	3·7	0·99	1·0

* The blank in each case was 5·0 ml.

Enzymic Degradation of Pectin.—Certain enzymes convert pectin into *d*-galacturonic acid, and by their action a better yield is obtained than by ordinary hydrolysis. These enzymes are contained in various commercial preparations (such as " Pectinol M " and " Pectinol 100D ") which are made from moulds and used for the clarification of fruit juices.

The specific enzymes functioning in the case of pectin are not yet clearly defined.[1] An esterase (pectin demethoxylase) presumably converts pectin into pectic acid, for it has been shown [2] that esterases from pancreas and castor oil seeds will form gels from pectin solutions at *p*H 5 to 8 in the presence of calcium. A polygalacturonase continues the hydrolysis to galacturonic acid. Whether this acid is also attacked by enzymes is uncertain.

The Scientific Examination of the Pectic Substances

Methods have been devised for the separation of the pectic acid, araban and galactan components so that fairly homogeneous products can be obtained. This is achieved partly by choosing the most suitable type of pectin, *e.g.* that from the seeds of *Lupinus albus*, to isolate galactan, and that from the peanut, *Arachis hypogœa*,

[1] See D. H. Clayson, *Chem. and Ind.*, 1942, **61**, 517.
[2] Z. I. Kertesz, *J. Amer. Chem. Soc.*, 1933, **55**, 2605.

which is low in galactan, as a source of araban. Separation of araban is also helped by the ease with which it undergoes hydrolysis. Methylation followed by separation of the methylated derivatives is an important aid. The methyl sulphate method cannot always be used, owing to the physical nature of the pectic products and seldom gives complete methylation. Considerable success has been attained in this direction by the use of thallium hydroxide [1] (Menzies), followed, if necessary, by the silver oxide-methyl iodide treatment of Purdie. Thallium hydroxide forms a compound with pectic acid which when ground to powder is very reactive. Great care must be taken in working owing to the poisonous character of the reagent.

The examples given relate chiefly to apple and citrus pectins. Pectin from turnip was used by Norris and Schryver,[2] and products from orange peel, orange juice, strawberry and currant have been examined.[3] Considerable attention also has been given to the pectic constituent of flax,[4] which may be extracted with water or dilute ammonium oxalate and purified as the copper compound. All these products are similar, with a uronic acid anhydride value of 70–80 per cent. and furfural yield 20 per cent.

The characteristic property of " pectin " of forming jellies in the presence of sugar has formed the subject of a number of technical investigations.[5]

General Methods for the Preparation of Pectin.—Orange peel, or the flesh of apples, is minced and percolated for 1 day with 95 per cent. alcohol. This is repeated till the liquid is colourless. The mass is dried, extracted with water and dried. Beet shavings are dried without treatment.

(*a*) *Extraction of Pectin with Water under Pressure.*—The material with ten times its weight of water is heated in an autoclave to 110° for 1 hour. The liquid is squeezed out and the residue extracted as before. The total extract is poured into so much 84 per cent. alcohol (containing 5 ml. of concentrated HCl per litre) that the alcohol content is not less than 70 per cent. The precipitated pectin is purified by solution in water and repetition of the alcohol treatment. After the third precipitation the pectin is filtered through kieselguhr set between layers of filter-paper pulp.

[1] C. M. Fear and R. C. Menzies, *J. Chem. Soc.*, 1926, 937; C. B. Purves and C. S. Hudson, *J. Amer. Chem. Soc.*, 1937, **59**, 49, 1170.

[2] *Biochem. J.*, 1925, **19**, 676.

[3] For composition see A. G. Norman, " Biochemistry of Cellulose, etc.", Clarendon Press, 1937, p. 80.

[4] F. W. Norris, *Biochem. J.*, 1929, **23**, 195.

[5] Thus Myers and Baker, *Delaware Agr. Exp. Sta. Bull.*, 1929, 160.

(*b*) *Extraction with Ammonium Oxalate Solution.*—Four successive extractions are made with this reagent at 80–85°, each for 1 hour. The bulky extracts are concentrated under diminished pressure to about 3 litres, and the pectin thrown out with acid-alcohol as above. It is redissolved in the minimum of water containing a little chloroform and the solution dialysed for 2 weeks, after which the pectin is purified twice by alcohol precipitation.

(*c*) *Extraction with Hot Water* (Ehrlich, 1932).—Beet shavings, or kilned hops (0·5 kilo.) are heated in an enamelled vessel with 10 l. of water for 1 hour at 50–55°. The residue is pressed in a muslin bag and the treatment continued until the liquid no longer gives a positive α-naphthol reaction. Extraction is continued with water at 75° and finally the material is boiled for 1 hour with three successive quantities of water and the united liquids filtered. The filtrate is either concentrated at low pressure to about 3 l. and the pectin precipitated by alcohol, or it is taken to dryness and the residue heated with successive amounts of 75 per cent. alcohol until the extract no longer gives the orcinol reaction. The insoluble portion is taken up in 1 litre of water, filtered (kieselguhr), and the pectin precipitated by pouring into 2 l. of 95 per cent. alcohol (containing 50 ml. concentrated HCl).

The Pectin of Apples and its Araban Component.—The composition of the pectins obtained by the different methods of extraction and purification varies somewhat. The following constants, for example, are given for apple pectin used by two sets of workers [1] :—

	OMe per cent.	Uronic Anhydride per cent.	Anhydro-araban per cent.
Apple pectin (Hirst and Jones) .	9·5	49·2	18
Apple pectin (Norris and Resch)	10·0	76·2	10·4

Hirst and Jones obtained pectin A (table below) in such a way that the pectic acid component remained as methyl ester freely soluble in water. Treatment with hot 70 per cent. alcohol left the pectic acid (C below) undissolved, araban and galactan (D below) going into solution. These were separated by methylation, a methylated araban being isolated. The araban is readily hydrolysed by *N*/20 mineral acid, leaving the galactan mixed with some methyl pectate (B). Pectic acid is obtained from this by conversion

[1] E. L. Hirst and J. K. Jones, *J. Chem. Soc.*, 1939, 454 ; F. W. Norris and C. E. Resch, *Biochem. J.*, 1937, **31**, 1950.

to the sodium salt and precipitation of the acid. The figures (C) show that this acid approaches very closely to a pure polygalacturonic acid anhydride of equivalent weight 176, and the uronic anhydride figure accounts for all but 3 or 4 per cent. Whether the impurity is galactan or very closely bound water is uncertain. The following are the results found on analysis of these products :—

	Apple pectin. (A)	Methyl pectate-galactan complex. (B)	Pectic Acid. (C)	Araban-galactose Mixture. (D)
Equivalent Weight . .	364	250	185	Not acid
$[\alpha]_D$ in water . . .	+178°	+230°	+276°	−30°
OMe per cent. . . .	9·5	10·2	*Nil*	*Nil*
Furfural per cent. . .	19·9	16·4	—	28
Uronic anhydride per cent. .	49·2	73	96·7	*Nil*
Pentosan per cent. (calc. as araban) . . .	20	*Nil*	*Nil*	54
Galactan per cent. (by difference)	25	21	<4	46

Some practical details follow.

Preparation of Apple Pectin.—Cider apple pomace was used. It was stirred for 5 hours with boiling water, cooled, pressed in a bag and the liquid poured into three times its volume of methylated spirit containing HCl 1 per cent. After drying in a vacuum at 40°, the residue, in water solution, was filtered through kieselguhr, precipitated with alcohol, and the pectin (A) obtained as a nearly white water-soluble powder. The figures for furfural and uronic anhydride indicate about 20 per cent. of pentosan, which was removed by treatment with $N/20$-H_2SO_4 at 90° for 4 hours. The liquid was filtered and poured into alcohol when the complex (B) was thrown out. The methoxyl figure shows that the methyl ester group of (B) had not hydrolysed. The equivalent weight 250 agrees with the amount of uronic anhydride (73 per cent.) and the furfural (16·4) is equivalent to uronic anhydride 74 per cent. Some 44 per cent. of mucic acid was obtained on oxidation.

Separation of Pectic Acid.—Complex (B) (3·6 g.) was dissolved in N-NaOH, diluted to 600 ml. and precipitated with dilute HCl. The product was dissolved in the calculated quantity of NaOH and precipitated, this being repeated three times more, after which the sodium salt was dissolved in water (600 ml.). Calcium chloride gave the insoluble calcium salt which was washed and triturated with alcoholic HCl. The acid obtained was converted to sodium salt and again precipitated, giving product (C).

The Araban-Galactan Complex (D).—Six extractions of 90 g. of pectin (A) with 800 ml. portions of hot 70 per cent. alcohol removed much araban with some galactan. These were thrown down on addition of acetone, giving mixture (D). This heated (90°) with $N/20$-H_2SO_4 was hydrolysed, the initial $[\alpha]_D^{18°}$ of − 30° becoming + 8 (1 hr.) and constant at + 94° (6 hrs.). Estimation of reducing sugar (in the methyl alcohol extract) showed that 62 per cent. of the polysaccharide had been hydrolysed. Alcohol insoluble portion mainly galactan.

Apple pectin (A) after repeated methylation, first with alkali and methyl sulphate, which largely destroys the pectic acid, then, as thallium salt, with methyl iodide, and finally with Purdie's reagents gave a methylated araban as an almost colourless powder, $[\alpha]_D^{20°}$ − 86° (methyl alcohol, *c.* 1·7), giving correct analytical figures and OMe content (38·8 per cent.) for $C_7H_{12}O_4$. On hydrolysis it gave the mono-, di- and trimethyl methylarabofuranosides in equimolecular proportions.

The araban is more easily obtained, however, from citrus pectin,[1] as given below.

The Araban Component.—The commercial citrus pectin used showed uronic anhydride 74·9; pentosan 6·9; galactan, 15·4 per cent.; $[\alpha]_D$ + 183°; equiv., 268. It contained a small amount of hesperidin. 1 kg. was stirred with hot 70 per cent. alcohol (2 l.) for 10 hours and the extract concentrated to small volume. Hesperidin was separated and addition of acetone (10 vols.) gave crude araban. Three such extractions gave 10 g. of hesperidin, m.p. 250°, acetyl derivative, m.p. 143°, and 26 g. of araban, $[\alpha]_D^{20°}$ − 34° in water.

The araban in water (clear by centrifuge) was thrown down by a large volume of acetone. The precipitate was treated in water with barium hydroxide till no further barium sulphate appeared. Alcohol (1 vol.) was added in the centrifuge, and a small precipitate removed. Addition of a large amount of alcohol gave crude araban (18 g.) as a brown solid, $[\alpha]_D^{20°}$ − 118°.

It was purified by acetylation, *e.g.* 8 g. in pyridine (80 ml.) and acetic anhydride (40 ml.) for 10 hours gave diacetyl araban (4·2 g.): $[\alpha]_D^{20°}$ − 94° (acetone); $CH_3.CO$, 40·5; furfural 29·2. $C_9H_{12}O_6$ requires 39·9 and 32 per cent. respectively.

The preparation of methylated araban (below) affords an example of the application of Menzies' method.

Methylation of Araban.—10 g. of the crude araban, $[\alpha]_D$ − 80° (water), was dissolved in water (100 ml.) and thallium hydroxide

[1] G. H. Beaven, E. L. Hirst and J. K. Jones, *J. Chem. Soc.*, 1939, 1865.

(2·5 equivs.) added. On taking to dryness under reduced pressure at 50° (CO_2 excluded) the grey-green residue was powdered (120 mesh) and treated with anhydrous MeI free from acid. After initial reaction the mixture was kept at 45° for 32 hours (light and moisture excluded). The excess of MeI was distilled off and the residue repeatedly extracted with methyl alcohol. The extract gave a brown solid (11·2 g.) of which 6·5 g., in benzene, were treated with thallous ethoxide (2·5 equivs.) and taken to dryness. The product (120 mesh) was boiled with methyl iodide as before. The methylated araban was then given two methylations by Purdie's method and one with thallous ethoxide, leaving 5·9 g. of crude product (OMe 36·5 per cent.).

Traces of thallous iodide were removed by solution in ether and the centrifuge. Additions of light petroleum gave (*a*) dimethyl araban as a pale brown solid (3·9 g.), $[\alpha]_D^{20°}$ — 128° (methyl alcohol); OMe, 38·8: a dimethyl pentosan requires OMe, 38·8 per cent.; (*b*) a syrup which was rejected.

The methylated araban was boiled with 2 per cent. methyl alcoholic HCl for 22 hours. After treatment with silver carbonate and fractionation under 0·001 mm. pressure four fractions were obtained, of which the n_D, OMe and $[\alpha]_D$ values showed that mono-, di- and trimethyl methylarabinosides were present in equimolecular proportion.

Araban from the Seeds of Arachis Hypogæa.—The "peanut" contains very little galactan, and after removal of oil and protein the alkaline extract (0·2 per cent. KOH) precipitated by alcohol gives an araban-pectic acid complex.[1] Its sodium salt had $[\alpha]_D$ + 120° (*c.* 1·5, water); equiv. 388. A pure araban was isolated from this,[2] through the acetyl derivative, as a hygroscopic powder, easily soluble in water, but insoluble in other solvents: $[\alpha]_D^{21°}$ — 160° (water, *c.* 1·44).

On hydrolysis it gave 97 per cent. of pure *l*-arabinose.

The Galactan Component.—The seeds of *Lupinus albus* are rich in galactan, and up to the present this is the only source from which a pure galactan has been isolated.[3] The small content of araban is removed by hydrolysis with 0·01*N*-acid and the pectic acid precipitated as calcium pectate, leaving the galactan. Hydrolysis gives *d*-galactose, the velocity indicating a pyranose structure. On methylation a trimethyl galactan is formed which, after hydrolysis, yields 2 : 3 : 6-trimethyl *d*-galactose with a small amount of the 2 : 3 : 4 : 6-derivative.

[1] E. L. Hirst and J. K. Jones, *J. Chem. Soc.*, 1938, 500.
[2] *Ibid.*, 1939, 453.
[3] E. L. Hirst, *J. Chem. Soc.*, 1942, 71.

Preparation and Properties of Pectic Acid.—Pectic acid has been isolated in a nearly pure state from apple, citrus, peanut and hawthorn pectins and from the seeds of white lupin by precipitation as the calcium and copper salts and subsequent purification.[1] Purity was indicated by the absence of any other hydrolytic product than *d*-galacturonic acid, together with high positive rotation, $[\alpha_D]$ + 170 to + 230° and equivalent weight approaching 176.

It is very conveniently prepared [2] from citrus pectin—a commercial product—by warming with 5 per cent. hydrochloric acid for 1¾ hours at 75–80°. In a particular case [3] the precipitate was separated by the centrifuge and washed in turn with water, alcohol (70 per cent.), alcohol (absolute) and ether. The white podwer (" tetragalacturonic acid "), insoluble in organic solvents, dissolved in boiling water, giving an acid solution, $[\alpha]_D^{19°}$ + 250° (*c.* 1·0). Suspended in water, it dissolved when one equivalent of NaOH was added (equiv. found, 203) and the solution (*c.* 0·4) had $[\alpha]_D^{19°}$ + 262°. If further 5*N*-NaOH is added a yellow sodium salt is thrown down. A 1 per cent. solution in water on boiling, slowly hydrolyses to galacturonic acid, the $[\alpha]_D$, for example, falling from + 235° to + 35° in 70 hours. On evaporation and extraction of the solid with alcohol a yellow glass was obtained. A solution of 1·9 g. of this dissolved in 2·8 per cent. methyl alcoholic HCl (100 ml.) and kept at room temperature showed the following values: $[\alpha_D]$ + 34 (initial), + 5·5° (6 hours), + 12° (22 hours) + 34° (63 hours), + 51° (136 hours). After 3 days more the solution was non-reducing (Fehling's solution). It was neutralised with silver carbonate, filtered and freed from solvent. The residue in the minimum of methyl alcohol was treated with Purdie's reagents and then three times with silver oxide and methyl iodide alone. Extracted with acetone a liquid (1·1 g.) b.p. (bath temp.) 130–140°/0·04 mm., $n_D^{21°}$ 1·4650; $[\alpha]_D^{21°}$ + 35° (*c.* 0·8) was obtained which gave crystals of 2 : 3 : 4-trimethyl methylgalacturonoside, m.p. 70°.

Methylation of Pectic Acid.—The precipitate from the hydrolysis of pectin (above) was washed in the centrifuge only to remove impurities and 50 g., still moist, treated for 3 hours with methyl sulphate (250 ml.) and sodium hydroxide, 30 per cent. with stirring. Undue excess of the alkali throws out the sodium salt and was avoided. After 9 hours the whole was acidified and the sodium sulphate dialysed out. The residue was made just alkaline and evaporated under reduced pressure. After 3 methylations in this way, followed by two more at 35–40°, the crude yellow sodium

[1] E. L. Hirst, *J. Chem. Soc.*, 1942, 72.
[2] F. Ehrlich and R. Guttman, *Biochem. Z.*, 1933, **259**, 100.
[3] S. Luckett and F. Smith, *J. Chem. Soc.*, 1940, 1109.

salt was dialysed 4 days, fresh sulphuric acid being added for the first 2 days to ensure conversion to the free acid. Evaporation gave a glassy yellow solid which had $[\alpha]_D^{16°} + 252°$ (water *c.* 1·0); OMe, 22·5 per cent.; equiv., 208. Dimethyl polygalacturonic acid $(C_8H_{12}O_6)_n$ requires OMe, 27·4 per cent.; equiv., 204.

This acid was esterified by neutralising an aqueous solution with silver oxide. The silver salt was boiled with MeI containing dry methyl alcohol. When esterified further additions of silver oxide and MeI were made. The product isolated with methyl alcohol, after remethylation (Purdie), gave a glassy solid, purified by solution in acetone and pouring into light petroleum, giving the methyl ester of methylated pectic acid—white powder $[\alpha]_D^{18°} + 201°$ (water, *c.* 0·3); OMe, 39·0 per cent. The methyl ester of methylated polygalacturonic acid $(C_8H_{14}O_6)_n$ requires OMe, 42·6 per cent.

The substance (8·4 g.) in acetone (50 ml.) was separated into four fractions by additions of ether. Fraction I contained inorganic impurities, II, III and IV each showed OMe about 41 per cent. Fraction V (OMe, 43·3 per cent.) was obtained by pouring the residue into light petroleum.

Fraction IV gave $[\alpha]_D^{20°} + 223·5°$ in water and in chloroform (*c.* 0·6); equiv. (heating with *N*/50-NaOH), 252; *M* (Rast), *c.* 800; $\eta_{sp.}^{20°}$ 0·096 (*m*-cresol, *c.* 0·836) giving (*K*, 10^{-3}), a value of *M*, 2,500; *M* (by osmotic pr.) 2,900.

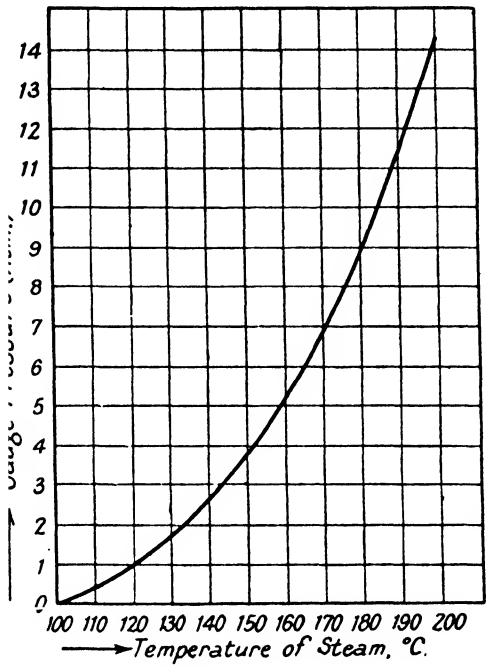
The fractions II and IV and III and V (5 g.) were hydrolysed with 5 per cent. methyl alcoholic HCl (150 ml.) for 18 hours, and after silver oxide treatment the products, being only partially ether-soluble, showing imperfect hydrolysis, were heated in sealed tubes with the same reagent (1 per cent. HCl) for 18 hours at 115°. Fractional distillation of the hydrolytic product gave the methyl ester of 2 : 3-*dimethyl methyl galacturonoside*, b.p. (bath temp.) 125–130°/0·01 mm.; $[n]_D^{18°}$ 1·4540; equiv. 250.

Use of a *degraded pectic acid ester* has to some extent overcome the difficulty of methylating pectic acid. By boiling pectic acid with methyl alcoholic HCl, ash and adsorbed galactan and araban are removed, the acid is partially hydrolysed and the carboxyl group esterified. Samples of pectic acid from all the common sources give in this way products with equivalent weight ± 200; specific rotation 200° or over, OMe 14 to 18 per cent., and Ba, in the barium salt, about 26 per cent. A methyl polygalacturonide methyl ester of eight units would require Ba, 27·7 per cent.

On methylation (Menzies) trimethyl derivatives are formed which require heating in a sealed tube with methyl alcoholic HCl to a high temperature, before they can be hydrolysed to give 2 : 3-dimethyl methyl-*d*-galacturonoside.

APPENDIX

Autoclave Pressures and Temperatures



Graph showing the relation between autoclave pressure and temperature of the steam.

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Table I

Comparison of Hydrometer Scales

Baumé (Rational), Twaddell and Specific Gravity

Sp. gr.	Tw.	Bé.	Sp. gr.	Tw.	Bé.	Sp. gr.	Tw.	Bé.	Sp. gr.	Tw.	Bé.
1·000	0	0	1·220	44	26·0	1·440	88	44·1	1·660	132	57·4
1·005	1	0·7	1·225	45	26·4	1·445	89	44·4	1·665	133	57·7
1·010	2	1·4	1·230	46	26·9	1·450	90	44·8	1·670	134	57·9
1·015	3	2·1	1·235	47	27·4	1·455	91	45·1	1·675	135	58·2
1·020	4	2·7	1·240	48	27·9	1·460	92	45·4	1·680	136	58·4
1·025	5	3·4	1·245	49	28·4	1·465	93	45·8	1·685	137	58·7
1·030	6	4·1	1·250	50	28·8	1·470	94	46·1	1·690	138	58·9
1·035	7	4·7	1·255	51	29·3	1·475	95	46·4	1·695	139	59·2
1·040	8	5·4	1·260	52	29·7	1·480	96	46·8	1·700	140	59·5
1·045	9	6·0	1·265	53	30·2	1·485	97	47·1	1·705	141	59·7
1·050	10	6·7	1·270	54	30·6	1·490	98	47·4	1·710	142	60·0
1·055	11	7·4	1·275	55	31·1	1·495	99	47·8	1·715	143	60·2
1·060	12	8·0	1·280	56	31·5	1·500	100	48·1	1·720	144	60·4
1·065	13	8·7	1·285	57	32·0	1·505	101	48·4	1·725	145	60·6
1·070	14	9·4	1·290	58	32·4	1·510	102	48·7	1·730	146	60·9
1·075	15	10·0	1·295	59	32·8	1·515	103	49·0	1·735	147	61·1
1·080	16	10·6	1·300	60	33·3	1·520	104	49·4	1·740	148	61·4
1·085	17	11·2	1·305	61	33·7	1·525	105	49·7	1·745	149	61·6
1·090	18	11·9	1·310	62	34·2	1·530	106	50·0	1·750	150	61·8
1·095	19	12·4	1·315	63	34·6	1·535	107	50·3	1·755	151	62·1
1·100	20	13·0	1·320	64	35·0	1·540	108	50·6	1·760	152	62·3
1·105	21	13·6	1·325	65	35·4	1·545	109	50·9	1·765	153	62·5
1·110	22	14·2	1·330	66	35·8	1·550	110	51·2	1·770	154	62·8
1·115	23	14·9	1·335	67	36·2	1·555	111	51·5	1·775	155	63·0
1·120	24	15·4	1·340	68	36·6	1·560	112	51·8	1·780	156	63·2
1·125	25	16·0	1·345	69	37·0	1·565	113	52·1	1·785	157	63·5
1·130	26	16·5	1·350	70	37·4	1·570	114	52·4	1·790	158	63·7
1·135	27	17·1	1·355	71	37·8	1·575	115	52·7	1·795	159	64·0
1·140	28	17·7	1·360	72	38·2	1·580	116	53·0	1·800	160	64·2
1·145	29	18·3	1·365	73	38·6	1·585	117	53·3	1·805	161	64·4
1·150	30	18·8	1·370	74	39·0	1·590	118	53·6	1·810	162	64·6
1·155	31	19·3	1·375	75	39·4	1·595	119	53·9	1·815	163	64·8
1·160	32	19·8	1·380	76	39·8	1·600	120	54·1	1·820	164	65·0
1·165	33	20·3	1·385	77	40·1	1·605	121	54·4	1·825	165	65·2
1·170	34	20·9	1·390	78	40·5	1·610	122	54·7	1·830	166	65·5
1·175	35	21·4	1·395	79	40·8	1·615	123	55·0	1·835	167	65·7
1·180	36	22·0	1·400	80	41·2	1·620	124	55·2	1·840	168	65·9
1·185	37	22·5	1·405	81	41·6	1·625	125	55·5	1·845	169	66·1
1·190	38	23·0	1·410	82	42·0	1·630	126	55·8	1·850	170	66·3
1·195	39	23·5	1·415	83	42·3	1·635	127	56·0	1·855	171	66·5
1·200	40	24·0	1·420	84	42·7	1·640	128	56·3	1·860	172	66·7
1·205	41	24·5	1·425	85	43·1	1·645	129	56·6	1·865	173	67·0
1·210	42	25·0	1·430	86	43·4	1·650	130	56·9			
1·215	43	25·5	1·435	87	43·8	1·655	131	57·1			

Table II

Specific Gravity 15°/4° and Strengths of Hydrochloric Acid Solutions

Parts by weight of HCl *in* 100 *parts by weight of solution*

Sp. gr.	HCl.	Sp. gr.	HCl.	Sp. gr.	HCl.	Sp. gr.	HCl.
1·000	0·16	1·055	11·18	1·105	20·97	1·155	30·55
1·005	1·15	1·060	12·19	1·110	21·92	1·160	31·52
1·010	2·14	1·065	13·19	1·115	22·86	1·165	32·49
1·015	3·12	1·070	14·17	1·120	23·82	1·170	33·46
1·020	4·13	1·075	15·16	1·125	24·78	1·175	34·42
1·025	5·15	1·080	16·15	1·130	25·75	1·180	35·59
1·030	6·15	1·085	17·13	1·135	26·70	1·185	36·31
1·035	7·15	1·090	18·11	1·140	27·66	1·190	37·23
1·040	8·16	1·095	19·06	1·145	28·61	1·195	38·16
1·045	9·16	1·100	20·01	1·150	29·57	1·200	39·11
1·050	10·17						

Table III

Specific Gravity 15°/4° and Strengths of Nitric Acid Solutions

Parts by weight of HNO_3 *in* 100 *parts by weight of solution*

Sp. gr.	HNO_3.	Sp. gr.	HNO_3.	Sp. gr.	HNO_3.	Sp. gr.	HNO_3.
1·000	0·10	1·135	22·54	1·265	42·10	1·395	64·25
1·005	0·20	1·140	23·31	1·270	42·87	1·400	65·30
1·010	1·90	1·145	24·08	1·275	43·64	1·405	66·40
1·015	2·80	1·150	24·84	1·280	44·41	1·410	67·50
1·020	3·70	1·155	25·60	1·285	45·18	1·415	68·63
1·025	4·60	1·160	26·36	1·290	45·95	1·420	69·80
1·030	5·50	1·165	27·12	1·295	46·72	1·425	70·98
1·035	6·38	1·170	27·88	1·300	47·49	1·430	72·17
1·040	7·26	1·175	28·63	1·305	48·26	1·435	73·39
1·045	8·13	1·180	29·38	1·310	49·07	1·440	74·68
1·050	8·99	1·185	30·13	1·315	49·89	1·445	75·98
1·055	9·84	1·190	30·88	1·320	50·71	1·450	77·28
1·060	10·68	1·195	31·62	1·325	51·53	1·455	78·60
1·065	11·51	1·200	32·36	1·330	52·37	1·460	79·98
1·070	12·33	1·205	33·09	1·335	53·22	1·465	81·42
1·075	13·15	1·210	33·82	1·340	54·07	1·470	82·90
1·080	13·95	1·215	34·55	1·345	54·93	1·475	84·45
1·085	14·74	1·220	35·28	1·350	55·79	1·480	86·05
1·090	15·53	1·225	36·03	1·355	56·66	1·485	87·70
1·095	16·32	1·230	36·78	1·360	57·57	1·490	89·60
1·100	17·11	1·235	37·53	1·365	58·48	1·495	91·60
1·105	17·89	1·240	38·29	1·370	59·39	1·500	94·09
1·110	18·67	1·245	39·05	1·375	60·30	1·505	96·39
1·115	19·45	1·250	39·82	1·380	61·27	1·510	98·10
1·120	20·33	1·255	40·58	1·385	62·24	1·515	99·07
1·125	21·00	1·260	41·34	1·390	63·23	1·520	99·67
1·130	21·77						

Table IV

Specific Gravity 15°/4° and Strengths of Sulphuric Acid Solutions (Lunge)

Parts by weight of H_2SO_4 *in* 100 *parts by weight of solution*

Sp. gr.	H_2SO_4.	Sp. gr.	H_2SO_4.	Sp. gr.	H_2SO_4.	Sp. gr.	H_2SO_4.
1·00	0·09	1·26	34·57	1·52	61·59	1·78	84·50
1·01	1·57	1·27	35·71	1·53	62·53	1·79	85·70
1·02	3·03	1·28	36·87	1·54	63·43	1·80	86·90
1·03	4·49	1·29	38·03	1·55	64·26	1·81	88·30
1·04	5·96	1·30	39·19	1·56	65·08	1·82	90·05
1·05	7·37	1·31	40·35	1·57	65·90	1·83	92·10
1·06	8·77	1·32	41·50	1·58	66·71	1·831	92·30
1·07	10·19	1·33	42·66	1·59	67·59	1·832	92·52
1·08	11·60	1·34	43·74	1·60	68·51	1·833	92·75
1·09	12·99	1·35	44·82	1·61	69·43	1·834	93·05
1·10	14·35	1·36	45·88	1·62	70·32	1·835	93·43
1·11	15·71	1·37	46·94	1·63	71·16	1·836	93·80
1·12	17·01	1·38	48·00	1·64	71·99	1·837	94·20
1·13	18·31	1·39	49·06	1·65	72·82	1·838	94·60
1·14	19·61	1·40	50·11	1·66	73·64	1·839	95·00
1·15	20·91	1·41	51·15	1·67	74·51	1·840	95·60
1·16	22·19	1·42	52·15	1·68	75·42	1·8405	95·95
1·17	23·47	1·43	53·11	1·69	76·30	1·8410	97·00
1·18	24·76	1·44	54·07	1·70	77·17	1·8415	97·70
1·19	26·04	1·45	55·03	1·71	78·04	1·8410	98·20
1·20	27·32	1·46	55·97	1·72	78·92	1·8405	98·70
1·21	28·58	1·47	56·90	1·73	79·80	1·8400	99·20
1·22	29·84	1·48	57·83	1·74	80·68	1·8395	99·45
1·23	31·11	1·49	58·74	1·75	81·56	1·8390	99·70
1·24	32·28	1·50	59·70	1·76	82·44	1·8385	99·95
1·25	33·43	1·51	60·65	1·77	83·32		

TABLE V

SPECIFIC GRAVITY 15°/4° AND STRENGTHS OF SODIUM HYDROXIDE SOLUTIONS

Parts by weight of NaOH *in* 100 *parts by weight of solution*

Sp. gr.	NaOH.	Sp. gr.	NaOH.	Sp. gr.	NaOH.	Sp. gr.	NaOH.
1·012	1	1·192	17	1·351	32	1·508	47
1·023	2	1·202	18	1·363	33	1·519	48
1·035	3	1·213	19	1·374	34	1·529	49
1·046	4	1·225	20	1·384	35	1·540	50
1·059	5	1·236	21	1·395	36	1·550	51
1·070	6	1·247	22	1·405	37	1·560	52
1·081	7	1·258	23	1·415	38	1·570	53
1·092	8	1·269	24	1·426	39	1·580	54
1·103	9	1·279	25	1·437	40	1·591	55
1·115	10	1·290	26	1·447	41	1·601	56
1·126	11	1·300	27	1·456	42	1·611	57
1·137	12	1·310	28	1·468	43	1·622	58
1·148	13	1·321	29	1·478	44	1·633	59
1·159	14	1·332	30	1·488	45	1·643	60
1·170	15	1·343	31	1·499	46	1·748	70
1·181	16						

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