

SOME ASPECTS OF VISCOSE RAYON SPINNING

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by

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Academic Record

The author received his B.Sc. (1st Class Honours) degree in June, 1965 at the Victoria University of Manchester, Faculty of Science and Technology. He then carried on for post-graduate studies in the Department of Polymer and Fibre Science, and has been engaged in this work since October, 1965.

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Abstract

This thesis reviews the literature relating to the formation of viscose rayons that contain a high proportion of skin-type structure. The experimental work reported is in two main sections, the first dealing with the influence of viscose salts on skin formation, and the second is an investigation into the possibilities of creating skin-type structure by spinning viscoses made from partially methylated cellulose. The physical properties of the resulting rayons have also been determined.

Summary

Two distinct investigations related to the fine structure of viscose rayons are reported. The first is concerned with the relation between the proportion of viscose salts in viscose and the proportion of skin-type structure in the corresponding rayon. In the second investigation an attempt has been made to influence the nucleation and crystallisation behaviour of cellulose during coagulation and regeneration from viscose by partially methylating the cellulose prior to its conversion to viscose.

It has been briefly reported in the literature that the production of skin-type structure is dependent on the presence of viscose salts and that no skin structure is obtained in their absence, even if modifiers are present. In the present investigation commercial tyre-cord viscose was freed from salts by an ion-exchange resin, mixed in varying proportions with untreated viscose, and the different viscoses spun by a two-bath process. The rayons were examined for gel-swelling value, proportion of skin and core structure, limiting-degree of polymerisation following acid hydrolysis, and for crystalline content. The data obtained are shown to be in complete agreement with the published claims.

The partially methylated celluloses used in the second investigation were produced by swelling a hydrocellulose derived from cotton linters to different extents with alkali solution and reacting the alkali cellulose with dimethyl sulphate. The preparation of the required products necessitated an investigation of methylation conditions, weight losses, and

changes in degree of polymerisation. Constant degree of polymerisation was obtained by ageing the alkali celluloses to different extents prior to methylation. A limited amount of work was done to characterise the hydrocellulose and the methylated derivatives.

The hydrocellulose and the methylated derivatives (meo contents 2.78, 5.77 and 7.87 per cent) were converted to viscose in the usual manner and their viscosities and ripening behaviour determined. The viscoses were spun by a one-bath process into baths containing 9, 12 and 15 per cent acid; viscoses with and without 3 per cent cyclohexylamine present were spun into 12 per cent acid. The resulting rayons exhibited a wide variation in structure from skin and core to all skin or all core depending on the acid concentration, the methoxyl content, and the absence or presence of modifier. The tensile properties of the rayons deteriorated with increasing methoxyl content owing to a corresponding decrease in crystalline content, an effect which made impossible any correlation between structure and tensile properties.

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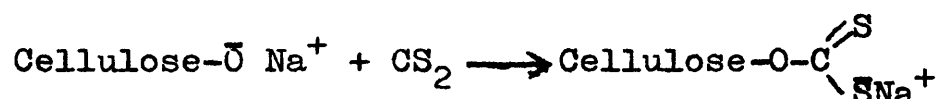
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SECTION 1.

GENERAL INTRODUCTION

1.1. Developments in Viscose Rayon Spinning.

In 1892 Cross, Bevan and Beadle (1) showed that carbon disulphide would react with alkali (or soda) cellulose to form a compound soluble in dilute caustic soda from which cellulose was precipitated by acids. The reaction product was the cellulose ester of dithiocarbonic acid, generally known as sodium cellulose xanthate; its formation is usually simplified to



A solution of this ester in dilute caustic soda is known as "viscose", a name which implies the viscous character of the solution.

The preparation of viscose as we know it today requires the following steps:

- (1) the conversion of cellulose into soda cellulose by steeping purified wood pulp in caustic soda solution of mercerising strength, and the removal of excess solution,
- (2) the shredding of the soda cellulose into crumbs,
- (3) subjecting the crumbs to controlled atmospheric oxidation to degrade the cellulose to a desired degree of polymerisation,
- (4) xanthation of these degraded soda cellulose crumbs with carbon disulphide to the required degree of substitution and removal of excess CS_2 , and
- (5) the dissolution of the xanthate in dilute caustic soda

solution to give concentrations of about 5-10 per cent cellulose and 5-10 per cent caustic soda.

To make this solution, or viscose, suitable for spinning into fibres it must undergo the additional processes of filtration, deaeration, and ripening. The last mentioned process is conducted at a controlled temperature; during this process the xanthate groups redistribute both intra- and intermolecularly among the cellulose molecules to give a more or less randomly substituted and therefore more homogeneous product. There is also a slow reduction in the degree of substitution by xanthate groups and spinning is begun when a level is reached that is appropriate to the composition of the coagulating and regenerating bath in use.

The process of fibre formation consists of forcing the viscose through an array of fine orifices, called a spinneret, into a spin bath containing a coagulating and regenerating medium of water, sulphuric acid, sodium sulphate, zinc sulphate, and relatively small amounts of surfactants and "modifiers".

Quite naturally the viscose spinning process has developed over a considerable number of years, the highlights in the developments (2) (3) being:

- (i) the introduction of stretch spinning by Thiele in 1903,
- (ii) the introduction by Müller in 1907 of spin baths containing sulphuric acid and metal sulphates,
- (iii) the improvements obtained by Napper in 1911 by adding small amounts (ca. 1 per cent) of

zinc sulphate to such a spin bath,

- (iv) the use of larger amounts of zinc sulphate (up to 4 per cent) reported by Bergen and Dreaper in 1924,
- (v) the discovery of modifiers by Cox (4) in 1946,
- (vi) the use of a two-bath process introduced by Courtaulds Limited (5).

The improvements in the properties of the rayon yarns resulting from the continuous development of the process are aptly illustrated by the data in Table 1, which show a continuous rise in filament strength over the years: (6).

TABLE I
Development of the Strength of Tyre Yarns

Yarn	Year	Conditioned tenacity g/den.	Wet tenacity g/den.	Cord-breaking load, lbs. (1650-den. yarn)
Textile	1907	1.1	0.4	
"	1913	1.4	0.5	
"	1917	1.7	0.8	
"	1939	2.1	1.1	
Tenasco	1937	3.4	2.2	23
Low acid process	1950	4.0	2.8	28.5
Super 1	1953	4.3	3.1	32.5
Super 2	1957	5.0	3.8	35
Super 3	1962	5.5	4.4	38
Super 4 (in devel- opment)	1965	6.0	5.0	42

An increase of tenacity can readily be achieved by increasing orientation, imposed by stretching during spinning, but the increase in ultimate strength so obtained is usually at the expense of breaking elongation (7). See Figure 1.1.

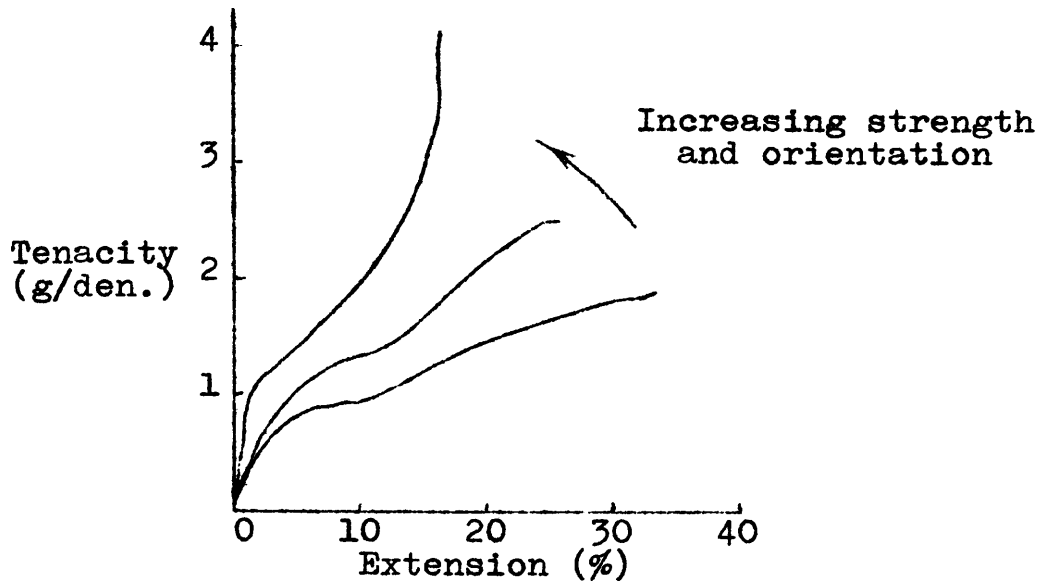


Figure 1.1. The effect of spinning stretch on the air-dry load-elongation properties of Tenasco-type rayons

Too low a breaking elongation is not desirable either for general textile purposes or for tyre cord rayons. It is to the credit of the rayon manufacturers that significant increases in strength have been achieved while ultimate elongation has been maintained or even increased.

Figure 1.2. illustrates this achievement (8):

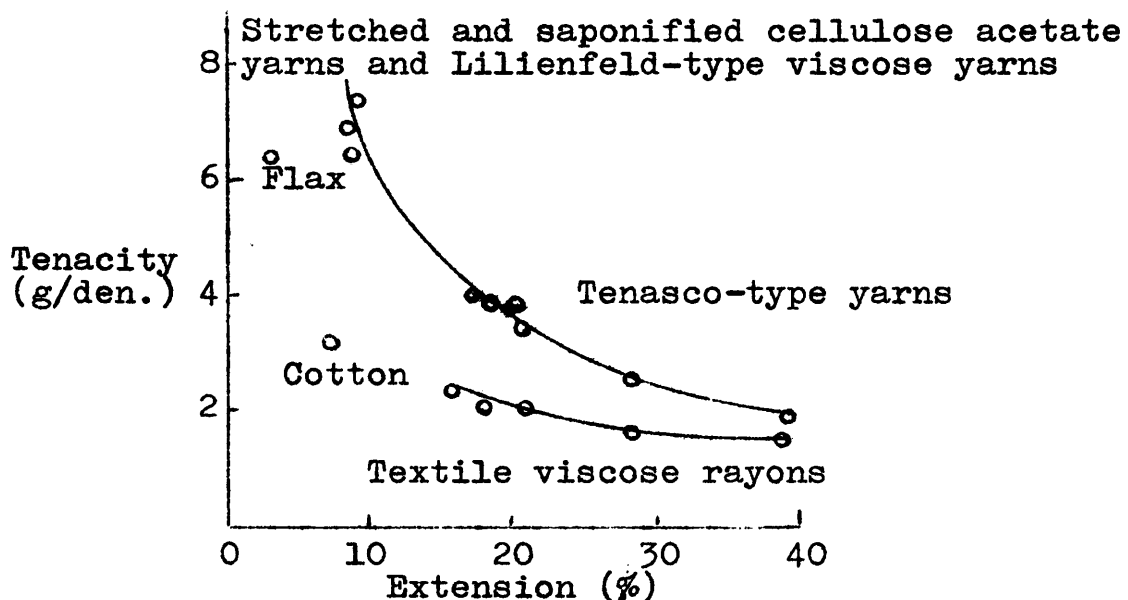


Figure 1.2. Load-elongation properties of air-dry regenerated cellulose fibres

The improvements that have been obtained in the mechanical properties of filaments are paralleled by significant changes in the shape of the filament cross-section and in the microscopic structural details within the cross-section. Three different types of structures may be discerned from microscopical examination of stained and unstained sections of filament, namely cuticle, skin and core (9) (see Figure 1.3.) though all three features are not necessarily present in any one filament.

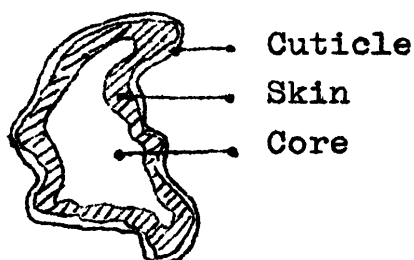


Figure 1.3. Cross-section of a viscose rayon fibre

Insofar as the shapes of the cross-sections are concerned it may be said that highly serrated sections go hand-in-hand with a relatively low content of skin structure and relatively low filament strength. Less serrated and nearly circular cross-sections have a higher, and sometimes an entirety of skin structure content, with corresponding superior physical properties.

The developments in the viscose spinning process previously enumerated are by no means the whole story, but simply the principal events. To these must be added the use of purer grades of cellulose, attention to the average molecular weight (MW) and MW distribution of the cellulose, and better filtration and deaeration to remove

sources of weak places in filaments. Attention to these factors has further upgraded the properties of viscose rayons. Still further improvements have been achieved by the realisation that in the early stages of existence an incompletely coagulated and regenerated filament is in a very fragile condition and susceptible to damage by the viscous drag exerted by the spin bath and by turbulence set up by the continuous replacement of the bath, a situation that worsens with increase of filament velocity. In this connection it has been observed that an advantage is gained, within limits, by spinning a yarn containing a high number of filaments, see Table II (10).

TABLE II
Effect of Number of Filaments

Denier	Number of filaments	Tenacity (g/den.) Conditioned	Elongation (%) Conditioned
<u>Textile "Cordura"</u>			
50	20	2.05	20.7
150	60	2.40	20.5
300	120	2.87	17.3
450	180	2.91	15.6
600	240	2.96	15.8
1100	720	5.05	11.5
<u>Industrial "Cordura"</u>			
650	1100	5.20	11.0
2200	1650	5.05	12.0
3300	2200	5.03	13.4

It would appear that neighbouring filaments support each other probably by inducing a well-defined flow of bath liquid in the filament direction. With increasing number of filaments the advantage is eventually lost possibly because the innermost filaments are starved of coagulation and regeneration chemicals. The same advantage may, however, be gained by passing the filaments, immediately they leave the spinneret, into a tube submerged in the spin bath.

For the sake of clarity two other developments in the history of viscose rayons have been omitted from the above more or less chronological account until now, namely the Lilienfeld process and the process(es) for producing rayons with a high wet modulus; the latter are sometimes classified as "Polynosics."

In 1925 Lilienfeld (11) produced very strong fibres by spinning viscose into a bath containing at least 50 per cent sulphuric acid and subsequently stretching the filaments about 200 per cent. The concentrated sulphuric acid produced a highly plastic xantho-sulphuric acid cellulose ester from which cellulose was regenerated by passage through cold water. Lilienfeld rayons had, owing to their relatively high degree of orientation, the highest tenacity for many years, but filaments exhibited a correspondingly high brittleness and low extensibility and consequently never became important for general textile purposes. Rose (12) produced some later variations on this theme but again without any great commercial success.

The high wet modulus rayons have sprung from an attempt to produce man-made fibres with the advantages of cotton, that is, to produce fibres which have better dimensional stability both in the dry and wet conditions, lower swelling in water, the ability to withstand mercerising, and a crisper and loftier handle. The modifications to the viscose spinning process referred to earlier have partly remedied these defects; the tenacity of viscose rayon has been increased, and the ratio of wet/dry strength has been greatly increased. Dimensional stability has been achieved by resin finishes. Even so the viscose rayon on its own is not the equal of cotton.

The origin of high wet modulus viscose rayon can be traced back to the fibre Lanusa manufactured by B.A.S.F. (13) from about 1933-55 through to the so-called Toramomen (or Tufcel) process of S. Tachikawa in Japan (14), and finally to Vincel and SM27 produced by Courtaulds and Courtaulds (Alabama) respectively. Spinning-process details of the last two mentioned processes are not disclosed but it is believed that they are similar in some ways to the Toramomen process. As far as one can ascertain the production of the high wet modulus rayons differ from the usual process in that:

- (i) Ageing is omitted to produce a fibre with a higher average degree of polymerisation.
- (ii) A higher degree of xanthation is achieved.
- (iii) The sodium cellulose xanthate is dissolved in water instead of dilute caustic soda.
- (iv) Ripening is omitted.

(v) Coagulation and regeneration are achieved in a spin bath containing only about 1 per cent sulphuric acid; in other words coagulation and regeneration are controlled to proceed more slowly.

(vi) Stretching is done in steps to the extent of 300 per cent.

It should be noted that little or no neutral salts are employed in the spin bath. It seems likely that the later variations on the process utilise neutral salts, including zinc sulphate, and modifiers to achieve the necessary slow coagulation and regeneration.

The fibres are characterised by an almost circular cross-section and a fibrillar micro-structure, the latter feature distinguishing them from other types of viscose rayon.

This thesis is principally concerned with factors that influence the skin/core structure of viscose rayons, consequently no further reference to the Lilienfeld and polynosic fibres will be made. Two separate aspects have been investigated, firstly the claim that the buffering action of "viscose salts" plays a significant part in the formation of the skin structure (15), and secondly an attempt has been made to influence the mode of crystallisation of the cellulose, following regeneration, by preparing viscoses from partially and heterogeneously methylated cotton. Before describing this work it is desirable to review the existing theories of skin/core formation and to indicate the relevance of the present work.

The opportunity will also be taken to introduce various terms and concepts used in the study of viscose spinning and in the characterisation of the fibres.

From the foregoing it should be clear that the viscose process is very versatile and that fibres of very different properties may be prepared by varying the composition of the viscose, even more so the composition of the spin bath, and the conditions of applied stretch. Table III (2) indicates the range of these variables.

TABLE III
The Variables of Spinning

Some variables of the spinning process	Technologically used range
The cellulose concentration of viscose	4-10%
The alkali " " "	3-8%
The amount of CS ₂ used in xanthation	30-60%
The degree of substitution of xanthate groups per 100 glucose units (=γ-number)	25-80
The H ₂ SO ₄ concentration in the spin-bath	3-15%
The Na ₂ SO ₄ " " " "	5-20%
The ZnSO ₄ " " " "	0-10%
The temperature of spin bath	20-100°C
The amount of stretch applied	0-150%

It is difficult in such a complex multi-variant system to produce a simplified view of the influence of the inter-related variables. Some success, however, has been achieved in terms of a quantity referred to as, "Ultimate Swelling Value", and denoted by (SV)_{lim}. Vroom (2) has

defined this quantity as the swelling value in water of an unstretched filament produced by passing the filament after the first wheels back to the spinning bath, keeping it there for some time, in practice about 10 minutes, and washing it until free from acid. The swelling value is then taken as the difference in weights of the centrifuged swollen samples and of the dried samples expressed as a percentage of the latter. If one varies only the acid strength in the spinning bath it is possible to produce a simple and useful correlation between $(SV)_{lim.}$, acid concentration and filament structure. See Figure 1.4.

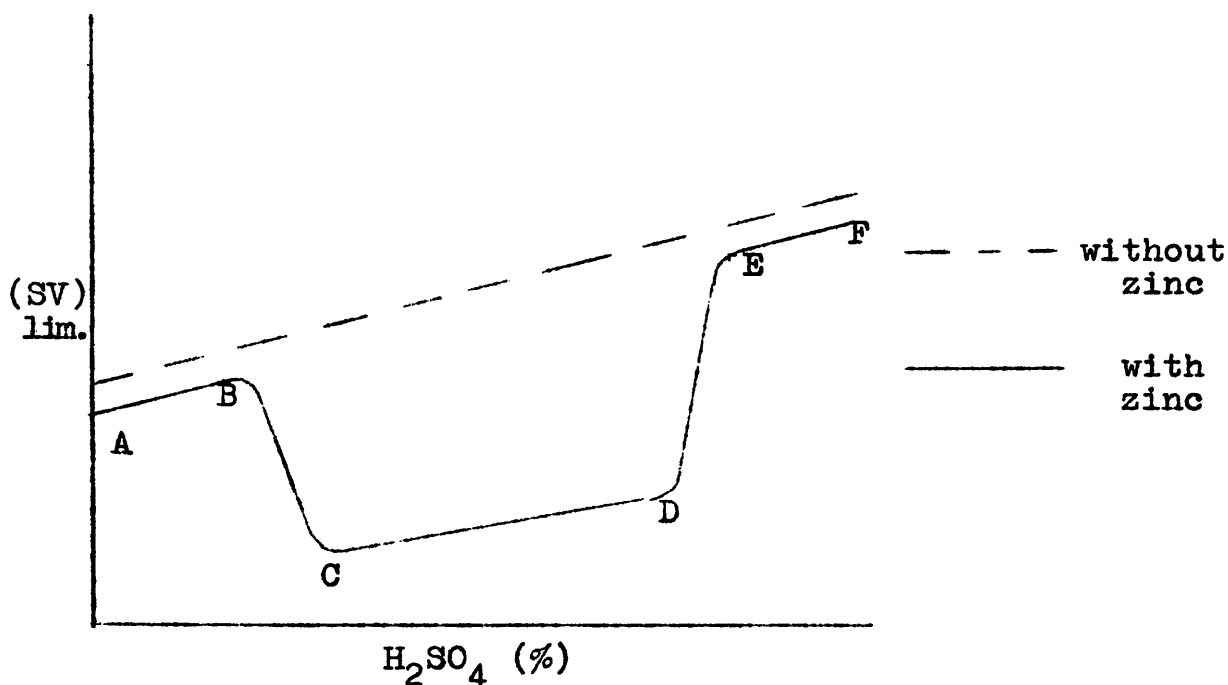


Figure 1.4. The relationship between ultimate swelling value and acid concentration

In the acid concentration region of AB high modulus filaments with all-core structure can be obtained. The spinning of a viscose, with a rather low cellulose content, high degree of polymerisation and high γ -number, into a cold sulphuric acid bath containing little or no

salt results in the formation of filaments of high modulus, low swelling and all-core structure. This is known as the Toramomen Process. The filaments so-produced resemble cotton in their mechanical properties. The cross-section of these filaments is circular and smooth!

In the BC region filaments with thin skin structure can be produced. These filaments have serrated cross-sections.

In the CD region filaments with thick skin structure can be produced. These filaments are suited for tyre reinforcement because of their high tenacity. The swelling value of these fibres is rather low. Tenasco type of filaments are spun in this region. It is in this region that the so-called modifiers or dopes (such substances as cyclohexylamine and polyethyleneoxide) in conjunction with a high degree of stretch are found to be particularly effective in the production of rayons with an all-skin structure. Super Tenascos are spun in this way.

In the DE region the filaments have serrated cross-sections with a thin skin surrounding the core. These filaments are suitable as ordinary textile rayons. The swelling values of these fibres are higher. The skin structure around the core is quite uniform in contrast to the skin surrounding the core structure of filaments produced in the region BC.

Finally, in the EF region the filaments have no skin structure. The cross-sections of these filaments are smooth and round. In this region viscose is cast into sheets and generally no zinc sulphate is used. Spinning of viscose

into a bath of at least 50% sulphuric acid results in the formation of Lilienfeld rayons.

The usefulness of the ultimate gel swelling value is that it is a measure or indication of the degree of swelling or alternatively of the cellulose concentration at the time of regeneration. Conditions at this time in the life of a filament determine the mode of crystallisation of the cellulose and hence its final physical properties.

1.2. Theories of Skin-Core Formation.

1.2.1. The Differential Orientation Theory.

The skin-core structure of viscose rayon filaments was first observed by Preston (16) in 1931, who postulated that skin formation was due to the orientation of the molecules on the outer layer of the extruded filaments in contrast to the unoriented cellulose chains in the centre of filaments. Preston believed that surface orientation resulted from friction between the filament surface and spin bath liquid. Schrameck and Zehmish (17) also accepted this theory that the skin-core structures resulted from a differential orientation of skin and core but considered that the cause was skin stretching and preferential orientation while the core was still liquid.

1.2.2. The Differential Crystallisation Theory.

A more convincing picture of skin-core formation was given later by Morehead and Sisson (18) who postulated that skin-core structures were due to a differential crystallisation of the outer layer in comparison to the centre of the filaments. They postulated that this differentiation was one of size and number or frequency of crystallites; a large number of small crystallites being in the skin structure and a relatively small number of large crystallites being in the core structure.

Some di-valent and tri-valent ions such as Al^{+++} , Fe^{++} , Ni^{++} and Zn^{++} were found to influence the skin formation; Zn^{++} ions being the most effective. These ions were believed to form an insoluble metal-cellulose-xanthate complex, and to crosslink the chains while they were in a more or less random conformation. These crosslinks then acted as nuclei for crystal growth during the regeneration of the primary gel, hence numerous small crystallites would ensue in the external regions penetrated by zinc ions.

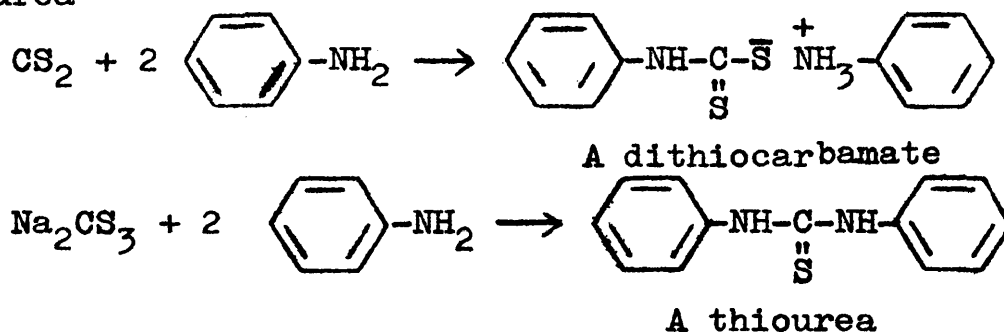
To explain how the zinc ions could penetrate a finite distance into the viscose and form a transient crosslinked structure when it was known that the larger zinc ions would diffuse more slowly than the smaller hydrogen ions, Morehead and Sisson argued that the metal ions formed a zinc-cellulose-xanthate membrane at the periphery, which allowed alkali to diffuse outwards more rapidly than acid could diffuse inwards. In this way suitable pH conditions were maintained for the existence of the short-lived crosslinked structure. Ultimately, of course, the faster diffusing hydrogen ions would overtake the slower diffusing zinc ions and the core of the filament would be regenerated without the intermediate formation of a crosslinked structure. Consequently, the number of nuclei in the core would be relatively low and a relatively small number of large crystallites would form.


Moore (19) agreed with Morehead and Sisson that the skin formation was due to the zinc ions present in the bath forming zinc-cellulose-xanthate gel, but considered that the function of the crosslinked structure was to increase the rate of dehydration and to decrease the rate of regeneration.

The advantage of rapid dehydration and slow regeneration is in getting a high polymer concentration, from which may result a greater number of nuclei during regeneration and hence smaller crystallites.

After the discovery of modifiers by Cox (4), Levine and Burroughs (20) studied gel swelling and rate of neutralisation of filaments spun from viscoses containing an amine-type modifier into baths containing zinc sulphate, sodium sulphate and dilute sulphuric acid. From their experimental work they concluded that zinc ions, modifier, and sulphur by-products, generally known as viscose salts or impurities which are sodium sulphide and sodium salts of perthiocarbonic and tri-thiocarbonic, as well as carbonic acids, had to be present in the system in order that skin structure could form. It was claimed that in the absence of free CS_2 and viscose salts the zinc-cellulose-xanthate formed quantitatively, i.e., one zinc ion combined with two xanthate units at pH values of 5-6 but when they are present in the system they also react with the zinc ions. The authors claimed that the modifiers formed a semipermeable membrane and that regeneration was delayed by the intermediate formation of xanthic acid from the zinc-cellulose-xanthate.

The reaction of CS_2 and viscose salts with the amine additive was considered to produce a dithiocarbamate or a thiourea



where -NH₂ represents an amine type of modifier. These compounds then formed zinc dithiocarbamate and zinc thiourea, which reacted with cellulose chains to result in semipermeable membrane formation.

Witkamp and Saxton (21) studied the effect of varying the amount of Na₂CS₃ in the viscose. They found that, with a spin bath free from zinc ions, the gel swelling value and the rate of regeneration were not affected by increasing the amount of Na₂CS₃ present in viscose. However, when zinc ions were present, an excess of Na₂CS₃ increased gel swelling initially and decreased the rate of regeneration. In contrast to the action of modifiers, which decrease the rate of regeneration in the early stages of spinning, the retarding action of Na₂CS₃ was found to occur in the later stages of spinning.

Cumberbirch, Gee and Ford (22) found that an increase in the zinc sulphate and a decrease in the acid concentrations in the spin bath increased the proportion of skin structure. The effect of the zinc sulphate became less marked as its concentration increased. They also found that an increase in the sodium sulphate concentration also favoured the formation of skin structure, provided that the cation concentration remained constant (assuming $\text{Zn}^{++} \equiv 2\text{Na}^{+}$). They differed with Morehead and Sisson (18) on finding that an increased proportion of skin structure was obtained by raising the temperature of the spin bath.

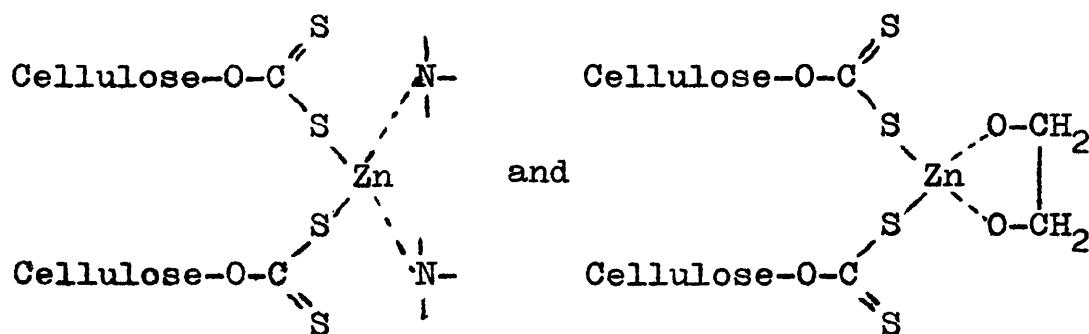
These authors favoured the view that the skin structure was formed from a region of freshly coagulated filament which was subjected to rapid de-swelling before regeneration

was complete, claiming that the skin region was not necessarily the region of penetration by zinc ions during coagulation and regeneration, but the region of higher deswelling. The cuticle was considered to be identical with the region of penetration of the zinc ions into the structure.

In a later paper Witkamp and Saxton (23) confirmed the conclusions they reached earlier (21) but went further and studied the effect of modifiers. The modifiers they used were polyethylene oxide (Carbowax 1500) and cyclohexylamine. They confirmed the formation of zinc-cellulose-xanthate as being the first step in skin structure formation. The modifiers were found to :

- (1) retard the rate of neutralisation, which was measured in terms of D-values. D-values are defined as the distances, in centimetres, from the spinneret to the point at which the filaments become neutral,
- (2) retard the decomposition of cellulose-xanthate initially but accelerate at later stages of the spinning,
- (3) lower the gel swelling. The filaments were more dehydrated even at the same level of regeneration in the presence of modifier,
- (4) require zinc sulphate in the bath to obtain skin formation,
- (5) give filaments of smooth, circular cross sections.

Witkamp and Saxton considered that the modifiers functioned by forming a semipermeable membrane on the outer surface of the filaments, thus separating the regeneration bath from the cellulose-xanthate gel. The suggested structures of the membranes are:



In this way the zinc-cellulose-xanthate was stabilised, and acted as a semipermeable membrane which retarded the diffusion of the spin bath ions into the gel structure. Regeneration of the primary gel was delayed, dehydration of the filament promoted, and regeneration occurred at a lower degree of gel swelling. Under these circumstances nucleation was facilitated and the growth of the large crystals prevented.

. According to A.M. Van de Ven (24) the formation of skin structure is a direct result of zinc-cellulose-xanthate formation and the thickness of skin structure depends on the depth of the penetration of zinc ions into the filament. In a modified viscose filament, if the zinc ions penetrate throughout the entire cross-section and form zinc-cellulose-xanthate intermediate, an all-skin structure thus forms.

. Klare and Gröbe (25) opposed the idea of zinc ions being present throughout the entire cross-section of the tyre cord filaments, and agreed with Cumberbirch (22) that they were present only in the cuticle.

. Klare and Gröbe (26) later confirmed their findings by spinning tyre cord filaments of 1000 mμ diameter from

a low acid bath, using a modifier, and concluded that zinc ions only penetrate the cuticle region of the filaments, regardless of whether modifiers are present, by using an autoradiographic technique with ^{69}Zn isotope.

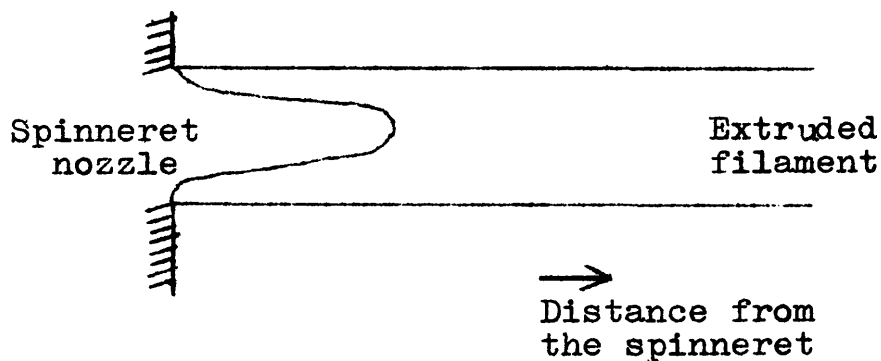
Stübner and George (27) carried out some experiments on the diffusion of zinc ions into tyre cord filaments, and claimed that during spinning, zinc ions penetrated, shortly after the spinneret, into the primary gel. Some Zn ions then formed ZnS and the excess took part in the formation of zinc-cellulose-xanthate intermediate, from which a skin structure resulted. Providing the acid-alkali conditions of the spin bath allowed the existence of zinc-cellulose-xanthate, the formation of the latter could proceed towards the centre of filaments and result in an all-skin structure.

In a later publication Klare and Gröbe (28) altered their conditions of spinning due to criticism and spun tyre cord filaments of 70-80 μ diameter from a spin bath of lower acid concentration. They opposed the idea of Stübner and George and confirmed the reaction zone of the zinc ions in the regenerated cellulose filaments as being only at the periphery of the filaments. From autoradiographic, electron and optical microscopical observations they measured the reaction zone of the penetrated Zn^{++} ions to be around 18-20 μ . This value is the total depth of Zn^{++} ions in the filament cross-section, i.e., almost twice as the thickness of annulus penetrated by the Zn^{++} ions. This still appears to be a depth greater than that of the cuticle region, while Klare and Gröbe

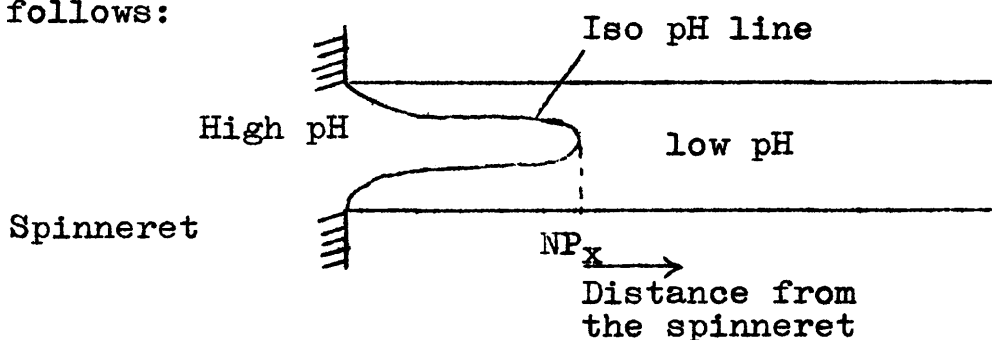
maintain that zinc-cellulose-xanthate is only formed in the cuticle.

Vermaas (15) agreed with Van de Ven and Stübner and George on the formation of zinc-cellulose-xanthate as being the first step in the formation of skin structure, but from his diffusion studies claimed that metal-cellulose-xanthate complex formation alone was not sufficient in bringing about the skin structure. He suggested that high swelling of sodium-cellulose-xanthate primary gel was needed for the formation of skin structure, which would facilitate the ion-exchange process between the zinc and the sodium ions. In other words, the time lapse between the formation of the sodium-cellulose-xanthate gel and the zinc-cellulose-xanthate formation should be as short as possible. Another condition put down by Vermaas for the formation of skin structure was that the life-time of the zinc-cellulose-xanthate should be as long as possible. This condition would be achieved by maintaining the pH of viscose between 9 and 2 for as long as possible, and Vermaas considered that the buffering-action of the viscose salts played an important part.

Vroom (2) concluded that the diffusion of the spin-bath components into the filament agreed with the conditions of a cylindrical diffusion process, i.e., equiconcentration points in the filament lay on a "bell-shaped" surface of rings, which had their centres on the longitudinal axis of the filaments. This is illustrated as follows:

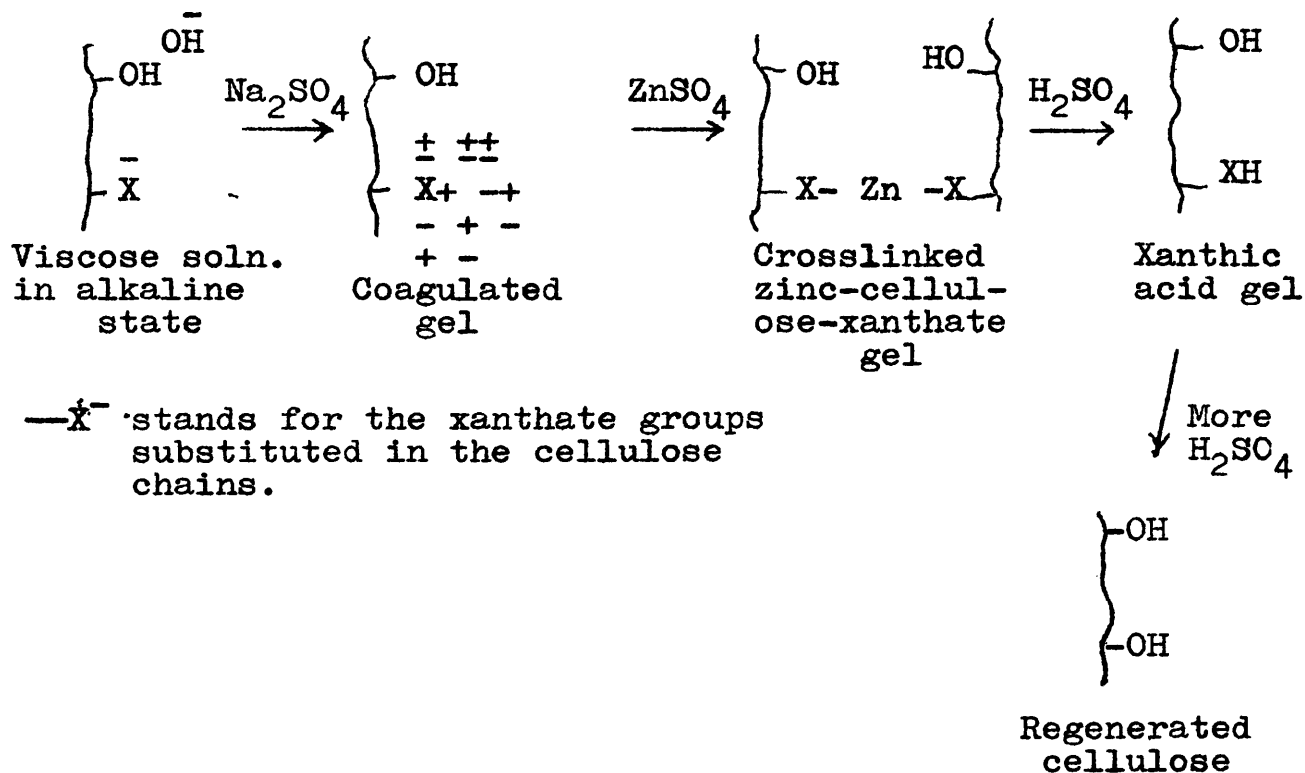


when the course of the spinning was followed by the addition of an indicator the picture then would become as follows:

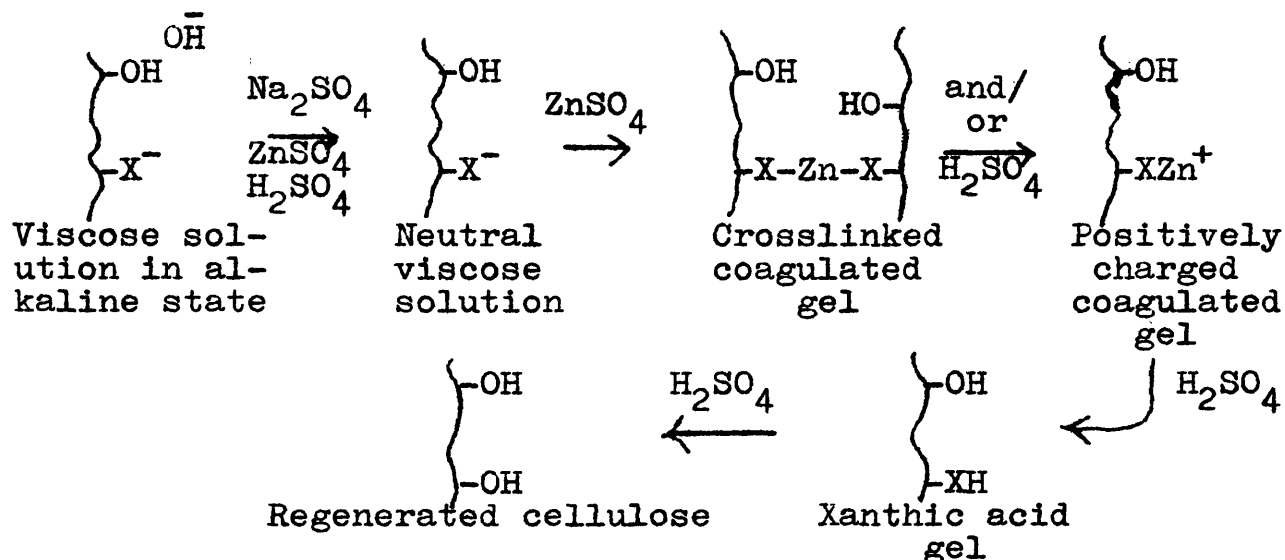


NP_x = the neutralisation point

Taking the above statement as his basis, Vroom studied the diffusion into the filaments and formulated the reaction schemes given below:



This reaction is considered to lead to the formation of a thin skin structure (e.g. the spinning of ordinary textile rayon). Vroom claimed that spinning of viscose of high γ -number into a bath of low acid concentration, containing an increased amount of Zn^{++} ions resulted in the formation of a thicker skin structure. (e.g., tyre cord spinning). The reaction scheme he proposed is as follows:

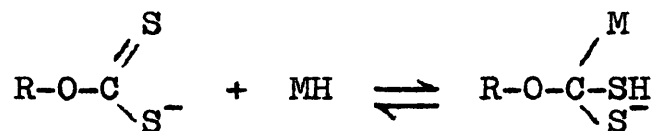


The intermediate ZnX^+ state which was claimed to be responsible for the increased skin structure was stabilised by the viscose salts providing counterions. The stabilised forms of ZnX^+ state were given as $\text{ZnX}^+\text{HCS}_3^-$ and ZnX^+SH^- .

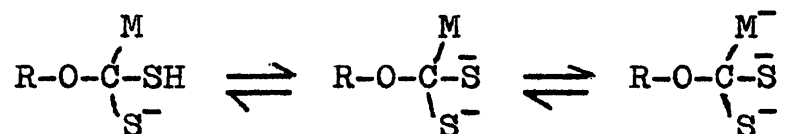
In the presence of a modifier, spinning into the same bath involved the ZnX^+ state. Vroom, however, did not accept the hypothesis put forward by Sisson (29) that the modifiers exerted their action by interfering with the diffusion of H^+ , OH^- , Zn^{++} ions, but suggested that the modifiers might be acting as plasticisers. He also suggested that modifiers might exert their action during the transition to the ZnX^+ state by one of the following possibilities:

- (1) By keeping the chains in the ZnX_2 state far enough apart to permit newly-arriving Zn^{++} ions to result in a ZnX^+ formation.
- (2) By increasing the susceptibility of the gel to undergo structural reorganisation to the ZnX^+ state.
- (3) By complex formation between the xanthate group, modifier and Zn^{++} ions, in the form of modifier $-\text{Zn}-\text{X}$ which was believed to be a competing partner for the ZnX^+ state.

The third possibility was supported by Toms (30) who concluded that xanthate groups reacted with compounds with an active hydrogen atom to form an ortho-ion as follows:



MH could be an amine or H_2S . In an alkaline media these ions were said to dissociate further as shown below:



1.3. Conclusions.

There is considerable agreement to the effect that the presence of zinc sulphate in the spin bath and the presence of modifiers in either the viscose or spin bath delays regeneration of the cellulose and thereby allows deswelling to proceed to a greater extent before regeneration is completed. At a low degree of swelling the number of polymer contacts is relatively high and following regeneration these points of contact are the nuclei for crystallisation. In this way skin structure consisting of many small crystalline regions is produced.

There is no doubt that the slowing down of regeneration results from the presence of zinc sulphate and that its function is enhanced by the presence of modifiers, but there is little, if any, agreement on how these substances function. Some workers are of the opinion that their action is to interfere with structure formation and others that they function by interfering with the diffusion processes. Reactions between zinc sulphate, modifiers, and cellulose xanthate are frequently reported but it is not clear whether they have any direct effect or whether they are simply parallel phenomena.

Two schools of thought may be distinguished in relation to the function of zinc ions. Vermaas (15), Vroom (2), Van de Ven (24), George and Stübner (27), Cichowski (31), and Serkov, are of the opinion that skin formation requires the presence of zinc ions at least within the regions in which skin structure forms. The second school of thought, supported by Klare and Gröbe (25) (28), Cumberbirch and co-workers (9) (22), and McGarry and Priest (32), claim that the skin structure area is not necessarily the whole of the area penetrated by zinc ions. These workers are of the opinion that the presence of zinc ions is essential for cuticle formation and that the cuticle acts as a membrane to accelerate deswelling.

1.4. The Present Work.

Two aspects of skin formation have been investigated. The first investigation was to provide experimental data to substantiate the claim made by Vermaas (15) that even when modifiers are present skin structure cannot be obtained unless viscose salts are also present. It should be

clear from the above review of the subject that skin formation is dependent on nucleation conditions, hence the second investigation was an attempt to influence the nucleation process by chemical modification of the cellulose prior to xanthation. The approach used was to partially methylate the cellulose.

SECTION 2.

THE EFFECT OF VISCOSE IMPURITIES

ON TYRE CORD RAYON FIBRES

2.1. Introduction.

Vermaas (15) made an extensive study of the diffusion of spin bath components into the extruded filaments during the spinning of viscose rayon filaments. Viscose impurities, also known as "viscose salts", were found to play an important part in the formation of skin structure. He claimed that when viscose, purified from its usual impurities, but containing a certain amount of sodium zincate, was spun into an acid bath of 1.5 N H_2SO_4 , very little skin structure was observed, whereas an all-skin structure was obtained when spun into a bath of 6N acetic acid. The sulphur by-products were considered to exert a buffering action, which was found to be operating at pH values from 9 to 2 during fibre formation. A detailed mechanism of fibre formation was given, but the properties of the fibres so obtained were not determined.

It was considered desirable to investigate the claims of Vermaas by spinning viscoses containing various amounts of viscose salts. The different viscoses were obtained by completely freeing one sample of viscose from impurities and mixing this viscose in various proportions with the original sample. The investigation differed from that of Vermaas in several ways. Firstly, the viscose system was investigated, that is no artificial buffering system

was resorted to. Secondly, the proportions of skin and core structures were quantitatively determined by a differential staining technique. Thirdly, the effect of varying proportions of pure and impure viscoses on the morphology of the filaments was investigated, namely by

(i) gel swelling value,

(ii) crystalline content,

(iii) crystallite size from levelling-off DP,

as the skin content decreased very weak filaments were obtained and so no attempt was made to determine load-extension properties.

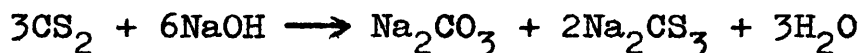
2.2. Experimental.

2.2.1. Filtration and Deaeration of Tyre Cord Viscose.

The spinning experiments were carried out with tyre-cord viscose, containing 1.5% Polyoxyethylene 1500 as a modifier. The viscose supplied by Courtaulds Limited, Preston, was in an unripe and unfiltered state. It was transferred into small polythene bottles which were then stored in deep-freeze at about -20°C . Before the spinning process, one bottle, containing enough viscose for one spinning, was allowed to defrost at room temperature and then filtered through the stainless steel apparatus shown in Figure 2.1. The necessary pressure of 3-5 p.s.i. was supplied by a hydraulic press. Filtered viscose was then allowed to ripen for 16-18 hours at room temperature to a salt-figure or salt-index of 6. The ripe viscose was centrifuged in polythene containers at 3000 r.p.m. for 10-15 minutes. Centrifuging deaerated the viscose and permitted any particles that had escaped the filtering process to settle at the bottom of the container. These particles, if not removed, would block the spinneret holes.

2.2.2. Purification of Viscose from Impurities.

During the conversion of alkali cellulose into xanthate an unavoidable secondary reaction occurs in which sodium hydroxide and carbon disulphide react according to the reaction scheme suggested by Cherkasskaya (33):



In addition to sodium trithiocarbonate, sulphide and

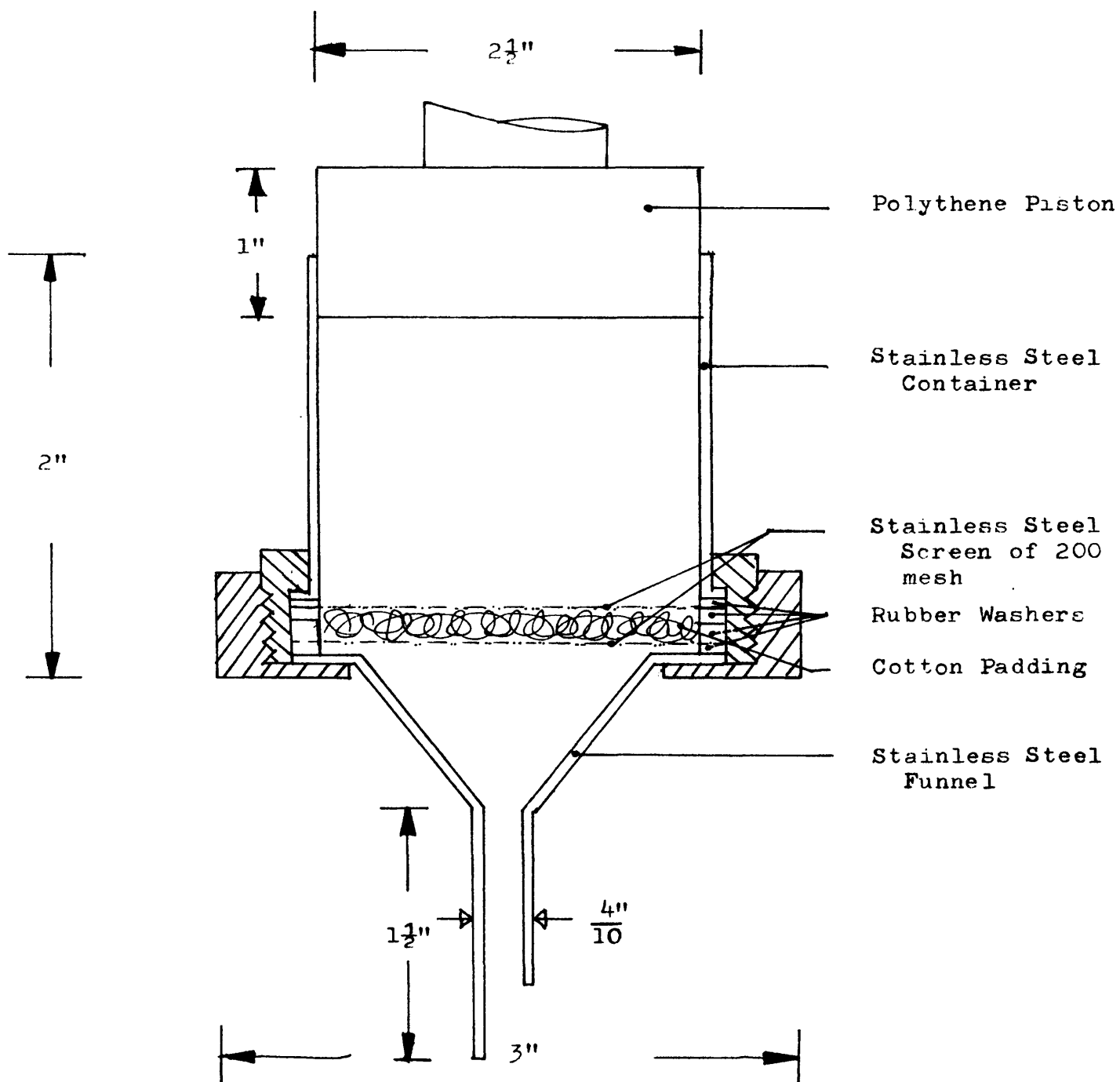


FIGURE 2.1. THE FILTER FUNNEL.

perthiocarbonates are considered to be present (34). These sulphur-containing products, the so-called impurities or viscose salts, correspond, for practical purposes, to the carbon disulphide not bound as xanthate. These sulphur by-products are known to be responsible for the deep orange colour of viscoses.

Viscose can be purified from these by-products by an ion-exchange process using a strongly basic anion exchange resin, Permutit De-Acidite FF-IP (manufactured in its chloride form by Permutit Company Limited). The hydroxyl form of the resin is required in order to avoid the chloride ions in viscose. The method of purification depends on the fact that when viscose is passed through a column of anionic exchange resin in its hydroxyl form, the small by-product anions such as CS_3^- , CS_4^- and CO_3^- are retained by the resin and replaced in the solution by hydroxyl ions. The large cellulose xanthate ions pass through the column. The resin was converted to the hydroxyl form by steeping it in a 6% w/v solution of sodium hydroxide for at least one hour before use.

A bed of resin was obtained in a stainless steel exchange column constructed similar to the design given by Dux Phifer (35) who used this technique to determine the γ -number of viscose. The apparatus is shown in Figure 2.2. The slurry of the resin was poured into the column and the excess alkali washed away with distilled water until the effluent gave a very pale pink colour with phenolphthalein. Washing the resin in the column ensured that the resin column was uniformly packed. After washing in this manner the column was filled with the viscose

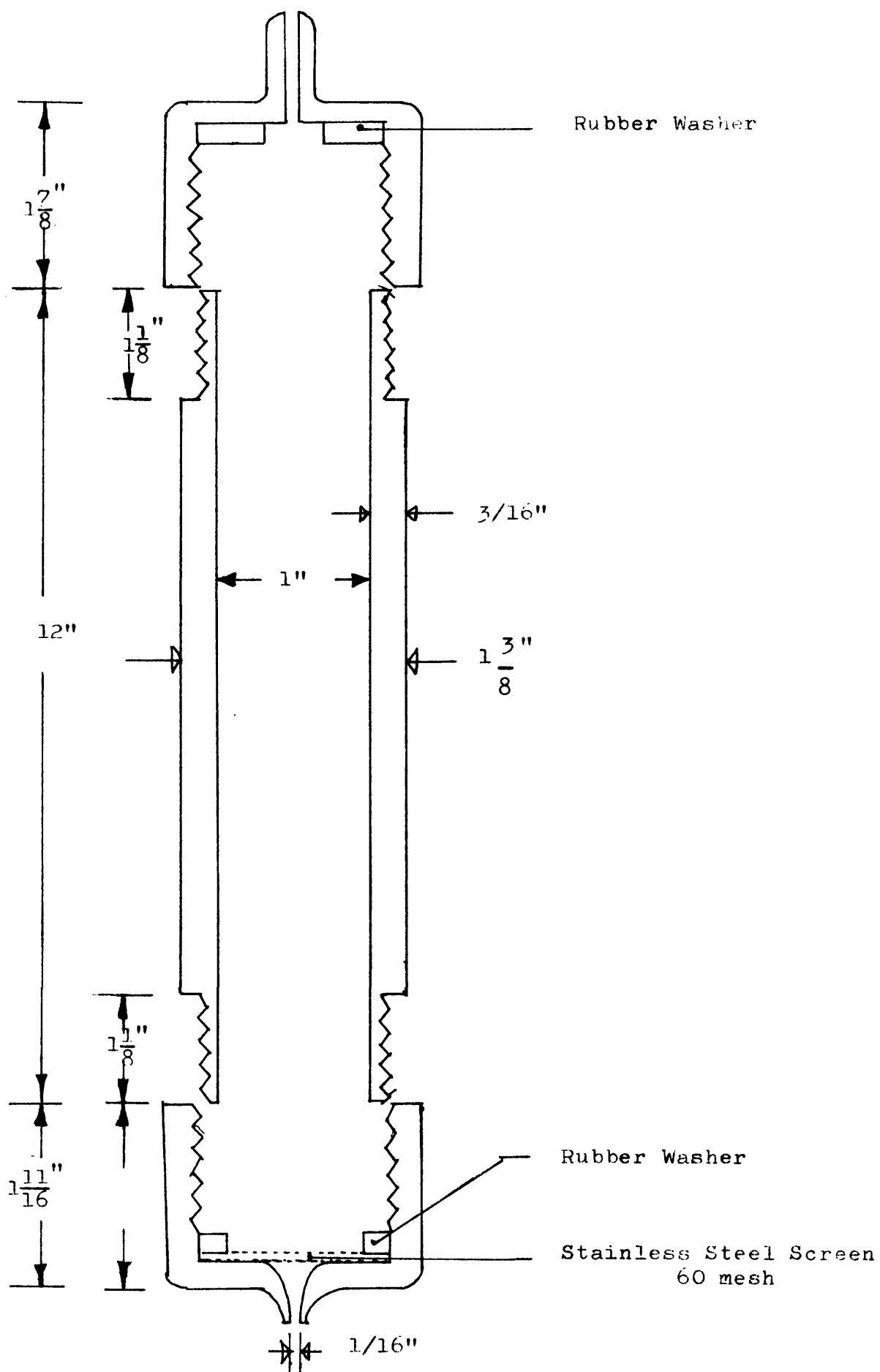


FIGURE 2.2. STAINLESS STEEL ION-EXCHANGE COLUMN FOR THE PURIFICATION OF VISCOSE.

to be purified. The top end of the column was screwed on and a pressure of 25-30 p.s.i. was applied by means of a cylinder of nitrogen. The first 50-70 ml of pure viscose contained some water from the column and were discarded. Subsequently, "white" viscose was collected in a polythene bottle partially immersed in a flask containing acetone/solid carbon dioxide mixture to prevent ripening. The bottles were then transferred into a deep-freeze at -20°C and kept until required for spinning.

Before spinning, "white" viscose was allowed to defrost and then filtered. Ripening was then effected by leaving the viscose at room temperature until the salt-figure decreased to 6.

2.2.3. The Analysis of Viscose. (See Appendix Table I)

2.2.3.1. The Alkali Content of Viscose.

The total alkali content of viscose was measured by weighing 4.00 ± 0.01 g of viscose and dissolving it in about 30 ml hot distilled water. The solution was then diluted with 150 ml cold distilled water. After dilution 15 ml 1 N sulphuric acid were added to the solution. The mixture was allowed to stand 15 minutes, and then titrated with 1 N caustic soda solution, with methylorange as indicator.

The percentage alkali content was calculated from the following expression:

$$\% \text{ Alkali Content} = \text{ml of 1 N H}_2\text{SO}_4.$$

2.2.3.2. The Cellulose Content of Viscose.

About 3.5 ± 0.01 g of viscose were spread as a thin film on a previously weighed glass plate, and then allowed to dry in an oven at 60°C for one hour.

The partially dried film was soaked in a saturated solution of common salt for 5 hours, the cellulose regenerated by soaking in a bath of 5% HCl for 10 minutes, and the acid removed by washing in water. The film of regenerated cellulose was dried in an oven at 105°C for at least 12 hours between sheets of dry wood pulp of 4x3 inches dimensions. The percentage cellulose content was calculated from the weight of the dry film.

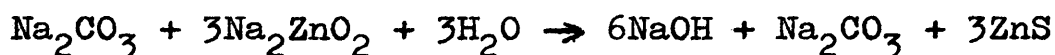
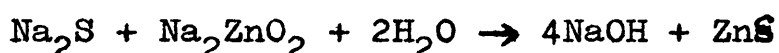
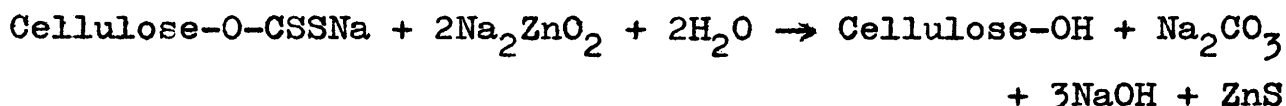
2.2.3.3. The Total Sulphur Content of Viscose.

The total sulphur was determined by a method which depends on the fact that if a dilute solution is boiled with sodium zincate the sulphur compounds are converted to zinc sulphide, which may be determined iodometrically.

25 g of viscose were weighed into a 50-ml beaker and dissolved in some distilled water. The solution was then made up to 250 ml in a graduated flask and shaken to obtain a uniform solution. To a 500-ml conical flask were added 100 ml distilled water, 10 ml of 10% sodium zincate (10 g ZnO in 1000 ml of 10% NaOH), and 10 ml of diluted viscose solution. The flask was allowed to boil gently for half-an-hour. The contents were then cooled and flushed into a 600-ml beaker containing 50 ml cold 2 N H_2SO_4 and 20 ml 0.1 N iodine solution. The contents of the beaker were

transferred back to the conical flask and allowed to stand for 20 minutes to ensure decomposition of zinc sulphide. The excess iodine was titrated with 0.1 N sodium thiosulphate solution using starch solution as an indicator. A blank determination using 10 ml distilled water in place of viscose was also carried out.

The reaction scheme is given below:



The percentage total sulphur was calculated from the following expression:

$$\% \text{ Total Sulphur} = 0.16 \times \text{ml of 0.1 N iodine}$$

2.2.3.4. The Degree of Substitution (the χ -number or value) and the Xanthate Sulphur Determination.

The χ -number was determined by an ion-exchange process which was based on the same system as that used for the purification of viscose. (See 2.2.2.) The only difference between the two systems was in the construction of the columns. For the present purpose the column was made of glass, and a resin column of about 4 inches high was used. (See Figure 2.3.) Ice-cold water at 0-5°C was circulated through the outer jacket of the column.

About 2.000 \pm 0.001 g viscose were dissolved in 50 ml ice-cold water at 0-5°C, the solution was run through the resin column with the capillary fully opened and the

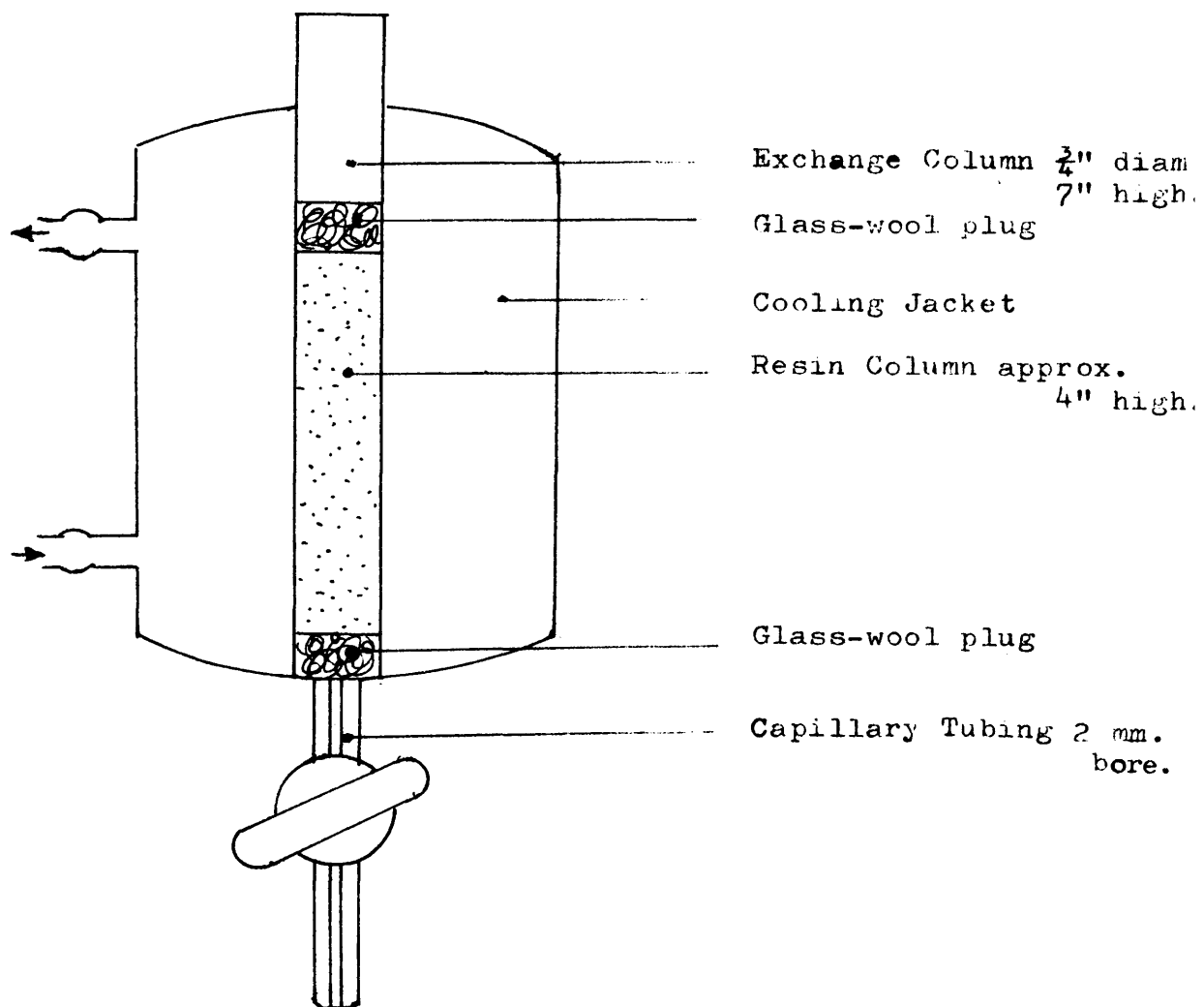
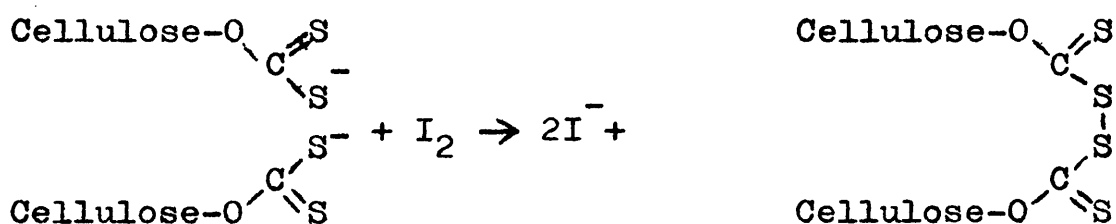


FIGURE 2.3. THE ION-EXCHANGE COLUMN FOR THE γ -NUMBER DETERMINATIONS.

effluent was collected in a 250-ml conical flask. The column was washed with 100 ml of ice-cold distilled water, and the washing effluent was also collected in the same flask. The contents of the flask were neutralised with 0.5 N acetic acid using phenolphthalein as indicator, and were then immediately titrated with 0.005 N iodine solution with starch as indicator.

The reaction scheme is shown in the following:



The γ -number was obtained from the following expression:

$$\gamma\text{-number} = 20.26 \times F \times \frac{V}{C}$$

where F is the normality of the iodine solution, V is the volume of iodine solution, C is the cellulose content of viscose.

Xanthate sulphur was obtained from the following:

$$\% \text{ xanthate sulphur} = 0.08 \times F \times V$$

where F and V have the same significance as in the above expression.

2.2.3.5. The Determination of the Degree of Ripeness.

The salt index, or salt figure, was used as a measure of viscose ripeness. It is related to the γ -number of viscose. The method used to determine the salt index is based on the minimum volume of 15% NaCl solution which when added to a dilute viscose solution gives the first

signs of permanent flocculation. Standard timing and stirring conditions are also required.

Three stirrers of the same dimensions were attached to a stirrer motor running at 350 r.p.m. See Figure 2.4. 20 ml, (20 + 0.6) and (20-0.6)ml portions of 15% NaCl solution were run into three 50-ml graduated flasks and diluted to the mark with distilled water. The solutions were transferred into three 100-ml tall-form beakers and three drops of viscose were added to each beaker from a capillary tube 6 inches long and 4 mm internal diameter. The stirring was continued for 1.5 minutes and the temperatures of the solutions were taken. The volume of NaCl solution was varied in ± 0.6 ml intervals and the minimum volume of salt solution required just to produce a distinct and flocculent precipitate in the solution was taken as the end-point.

The salt index was obtained from the following expression:

$$\text{Salt index} = (\text{Volume of 15\% NaCl solution}) \times 0.3 \pm \begin{matrix} \text{temperature} \\ \text{correction} \\ \text{factor} \end{matrix}$$

where 0.3 is a constant.

Temperature correction factors are given in the following table:

TABLE IV

Dependence of Correction Factor on Temperature

The temperature of solution ($^{\circ}\text{C}$)	The correction factor
16	-0.2
17	-0.1
18	0
19	+0.1
20	+0.2

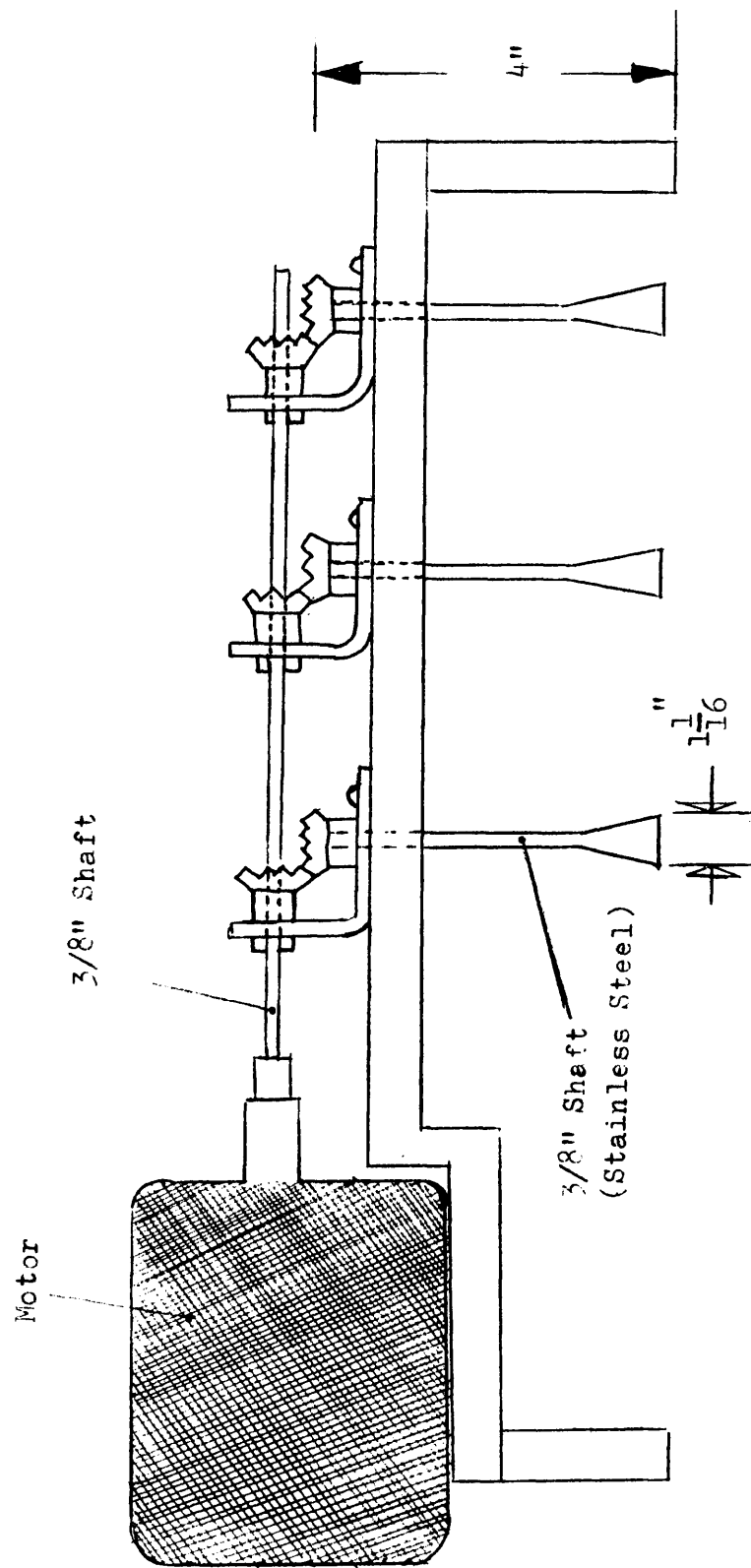


FIGURE 2.4. THE STIRRER UNIT FOR THE SALT-INDEX MEASUREMENTS.

2.2.4. Mixing of the Pure and the Impure Viscoscs.

Viscoscs with various amounts of sulphur by-products were prepared by mixing pure and impure viscoscs in certain proportions in stainless steel or polythene containers, which prevent contamination of viscose with unwanted ions. The mixtures were stirred vigorously for 10-15 minutes and then centrifuged for 20 minutes at 3000 r.p.m. They were then frozen and stored in the deep-freeze until required for spinning.

2.2.5. The Spinning of Viscoscs.

2.2.5.1. The Design and Arrangement of the Spinning Apparatus.

The small-scale viscose spinning apparatus shown in Figure 2.5. was a modification of a model designed by Mr. R. J. E. Cumberbirch of the Shirley Institute, Manchester, and was built in the U.M.I.S.T. workshops.

The unit consisted of three parts:

- (1) An extrusion unit.
- (2) Take-up and stretch rollers.
- (3) Wind-up unit.

The extrusion unit consisted of a stainless steel piston, travelling within a precision-bore glass tube of 15 mm diameter, fitted with a rubber piston ring of circular cross section, and was driven through a three-speed gearbox, capable of giving linear speeds of 0.011, 0.022, 0.044 cm/sec. The unit was powered by a synchronous motor running at 60 r.p.m. The extrusion unit was fitted with a microswitch, in order to limit travel at desired points in both directions, and also a clamp to hold the tube containing the viscose.

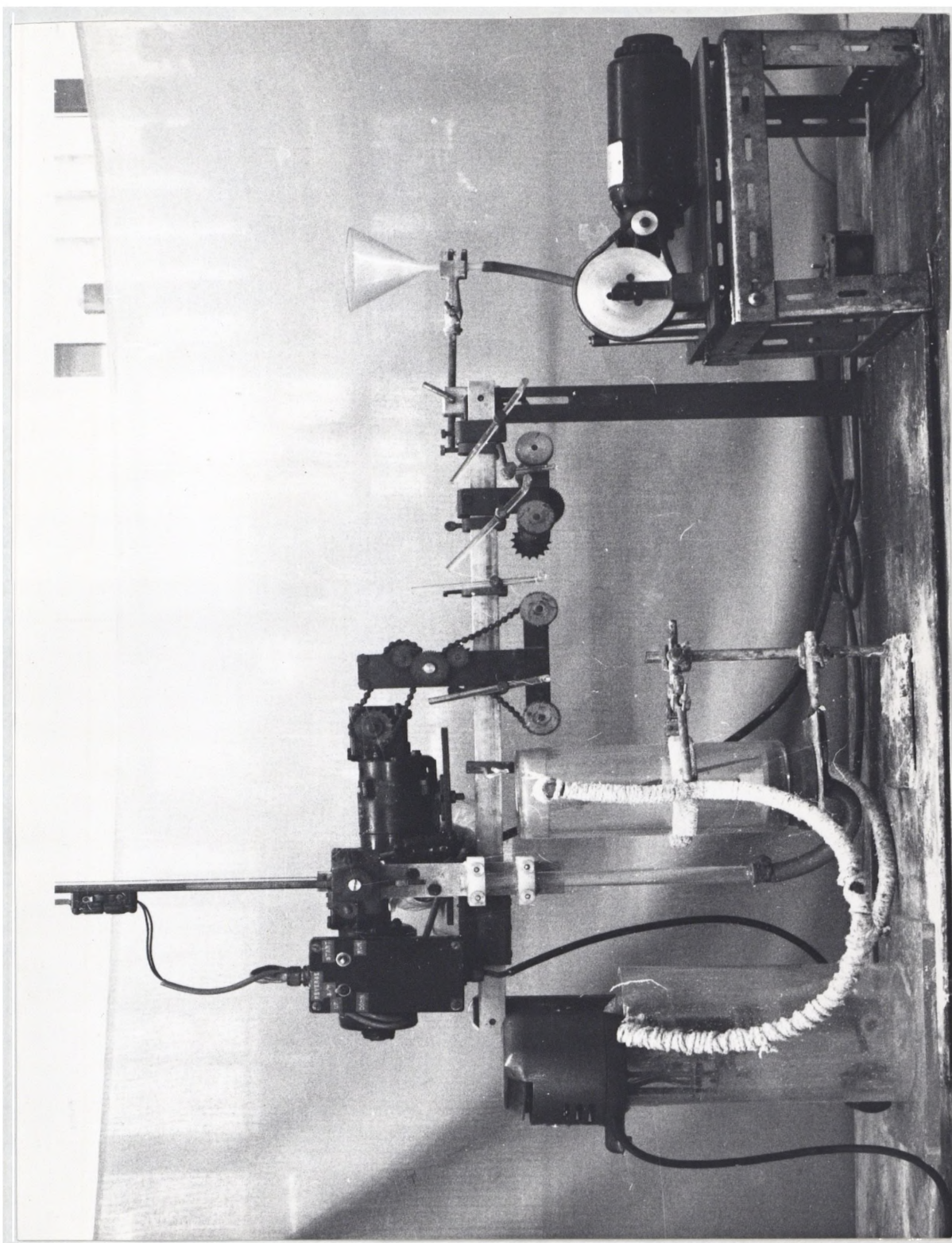


FIGURE 2.5. THE SMALL SCALE VISCOSE RAYON SPINNING APPARATUS.

The take-up and the stretch rollers were made of stainless steel. They are all of the same diameter, 41 mm and measured 20 mm across the face. The face was cut like a pinion wheel with flattened teeth so that liquid carried forward by the filaments could flow away; this helped to prevent slippage of the filaments and ensured that yarn motion was equal to the surface speed of the rollers. The speed of the take-up rollers was constant, while the speed of the stretch rollers could be varied by a second gearbox fitted within the frame of the unit. Both sets of rollers, generally called "godet wheels", were driven by a second synchronous motor running at 60 r.p.m.

A further requirement to prevent yarn slippage on the take-up and stretch rollers was that the yarns had to lap each roller several times. In order to prevent entanglement, the yarns were passed alternately round a particular roller and then round a stationary glass rod inclined at a slight angle to the axis of the roller. In this way the individual laps were kept separate.

Stretch was applied to the yarns between the take-up and stretch rollers while the yarn was submerged in a dilute acid bath at about 95°C. The yarn was deflected in and out of the bath by means of suitably supported glass rods.

The winding unit was powered by a small variable-speed electric motor. The extended driving shaft carried a stainless steel bobbin which was free to rotate. Motion was imparted to the bobbin by pressure between the face of the bobbin nearest the motor and a plate of similar diameter secured to the shaft. A PTFE washer was placed between the two and pressure was applied by a spring on the shaft

pressing on a second PTFE washer contacting the other face of the bobbin. The spring was compressed so that a tension of 5 g was applied to the yarn being wound.

A thread-guiding device was also incorporated within the winding unit to traverse the bobbin as the filaments were wound on. A jet made of glass tubing, fitted to the traverse guide, sprayed dilute acid directly on to the bobbin during spinning and winding.

Subsequent to the spinning process the wind-up unit could be used to rewind and spray the yarn with sodium bicarbonate to neutralise acid, and in the second rewind with water. In these operations the yarn was taken over the end of a stationary bobbin to the wind-up unit.

2.2.5.2. The Viscose Delivery Tube and the Spinneret Mounting.

The original viscose delivery tube is shown in Figure 2.6. The tube was made of precision bore glass tubing. The assembly of the spinneret mounting is shown in Figure 2.7., and was made of stainless steel.

The original arrangement was such that the delivery tube was placed directly in the hot spin bath at 60°C and not surprisingly it was observed that the temperature of viscose in the tube had risen to that of the bath within 20 minutes. See the following Table:

TABLE V

Rate of Increase in Temperature of
Viscose in the Extrusion Tube

<u>Time (Mins.)</u>	<u>Temperature (°C)</u>
0	20.5
5	29.0
7	31.5
10	39.0
15	48.0
20	59.1

It was known that rate of ripening is accelerated by the increase in temperature of viscose, (see Figure 2.8. and Appendix Table II), and that the properties of viscose rayon fibres are very much dependent on the degree of ripeness prior to spinning. It was, therefore, necessary to prevent significant changes during the period of spinning. After attempts to insulate the viscose from the spin bath in a variety of ways it was found necessary to extrude the viscose from an external tube via the bottom of the bath. The arrangement is shown in Figure 2.9.

The bath temperature was maintained constant at 60°C by circulating hot water through the jacket of the bath as shown in Figure 2.9. A new spinneret holder was made of polypropylene since the stainless steel holder gassed during spinning.

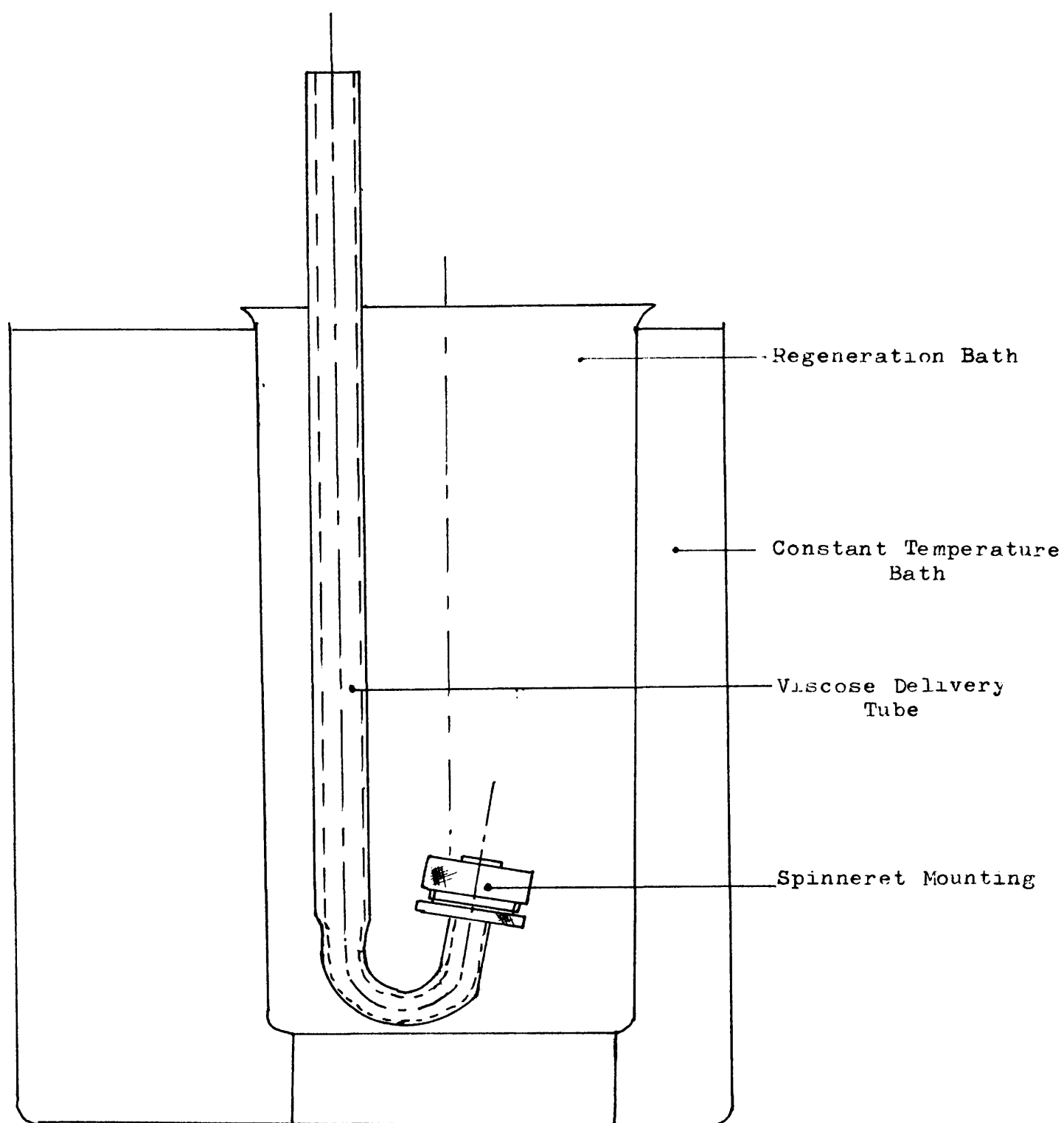


FIGURE 2.6. THE ORIGINAL SPINNERET MOUNTING AND THE VISCOSE DELIVERY TUBE. (Scale $\frac{1}{2}$).

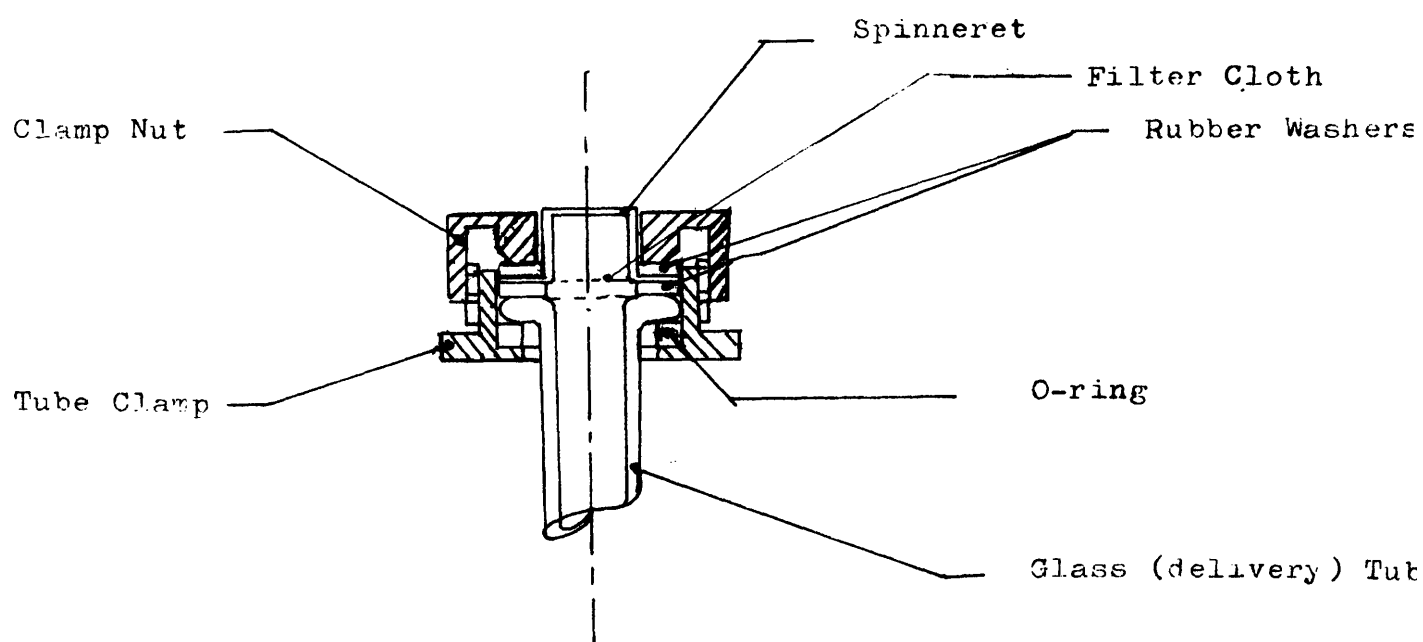


FIGURE 2.7. THE ORIGINAL ASSEMBLY OF SPINNERET MOUNTING.
(Actual Size.)

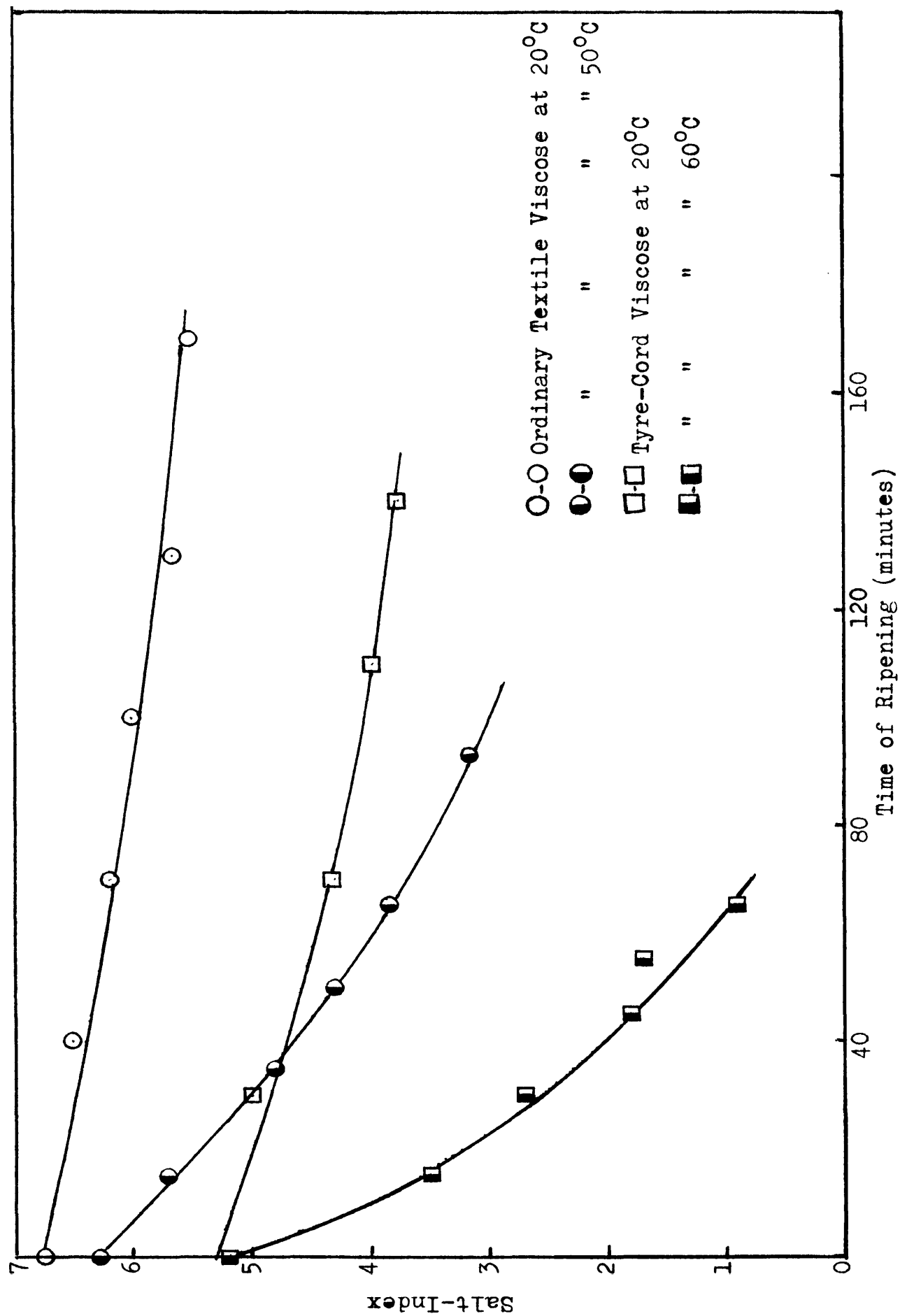


FIGURE 2.8. THE EFFECT OF TEMPERATURE ON THE RIPENING OF VISCOSE.

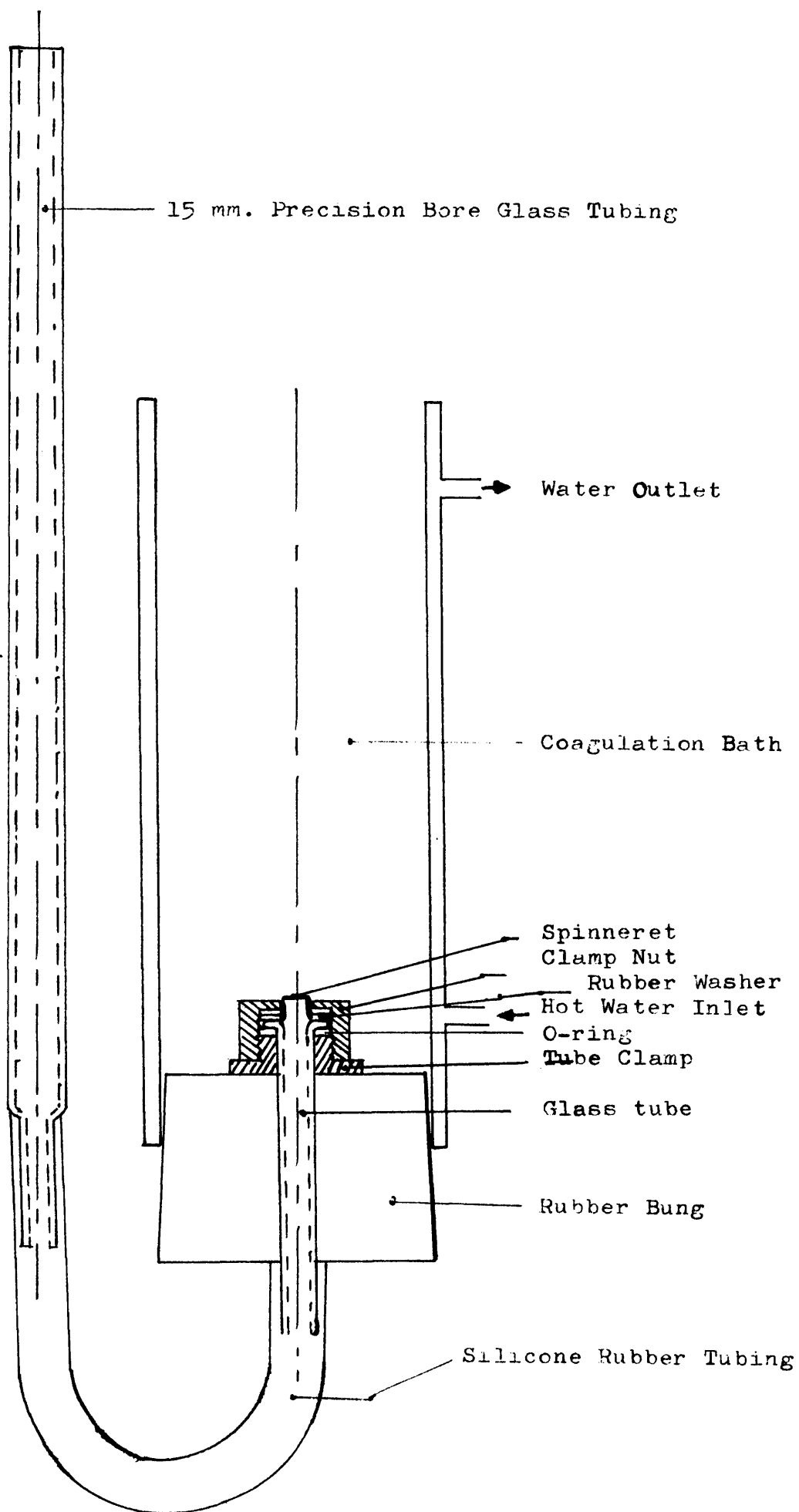


FIGURE 2.9. NEW VISCOSE DELIVERY TUBE AND THE SPINNERET MOUNTING. (Scale approx. $\frac{1}{2}$).

2.2.5.3. The Spinning of Viscose by the Two-Bath Process.

The set-up of a two-bath spinning process is shown in Figure 2.10. Viscose samples containing various amounts of sulphur by-products were prepared as described previously, ripened to the desired salt index, and then centrifuged at 3000 r.p.m. for 15 minutes to remove air bubbles.

The delivery tube was carefully filled with viscose, avoiding the introduction of any air bubbles, and secured to the clamp on the extrusion unit. The piston drive was started, and viscose exuded from the spinneret. As soon as the surface of the spinneret was covered with viscose, the spin bath solution previously adjusted to 60°C was poured into the bath to a level of 12 cm from the surface of the spinneret. By starting up in this way regeneration behind the spinneret was prevented.

The lump of partially regenerated viscose on the surface of the spinneret was then carefully pulled upwards by means of a pair of stainless steel tongs, and passed over the guide rollers on to the take-up rollers. The filaments were highly swollen and yellowish as they came out of the bath. They were then passed over the glass guides in the hot stretch bath which is generally called the "regeneration bath". Threading-up was done with the hot-stretch bath lowered, which was then raised to cover the running yarn. The regeneration bath more or less completed the regeneration while a 100% stretch was applied to the filaments.

After passing over the stretch rollers the filaments were guided on to the wind-up bobbin. Spraying with dilute acid of 3.5% H_2SO_4 was continued as long as the spinning and

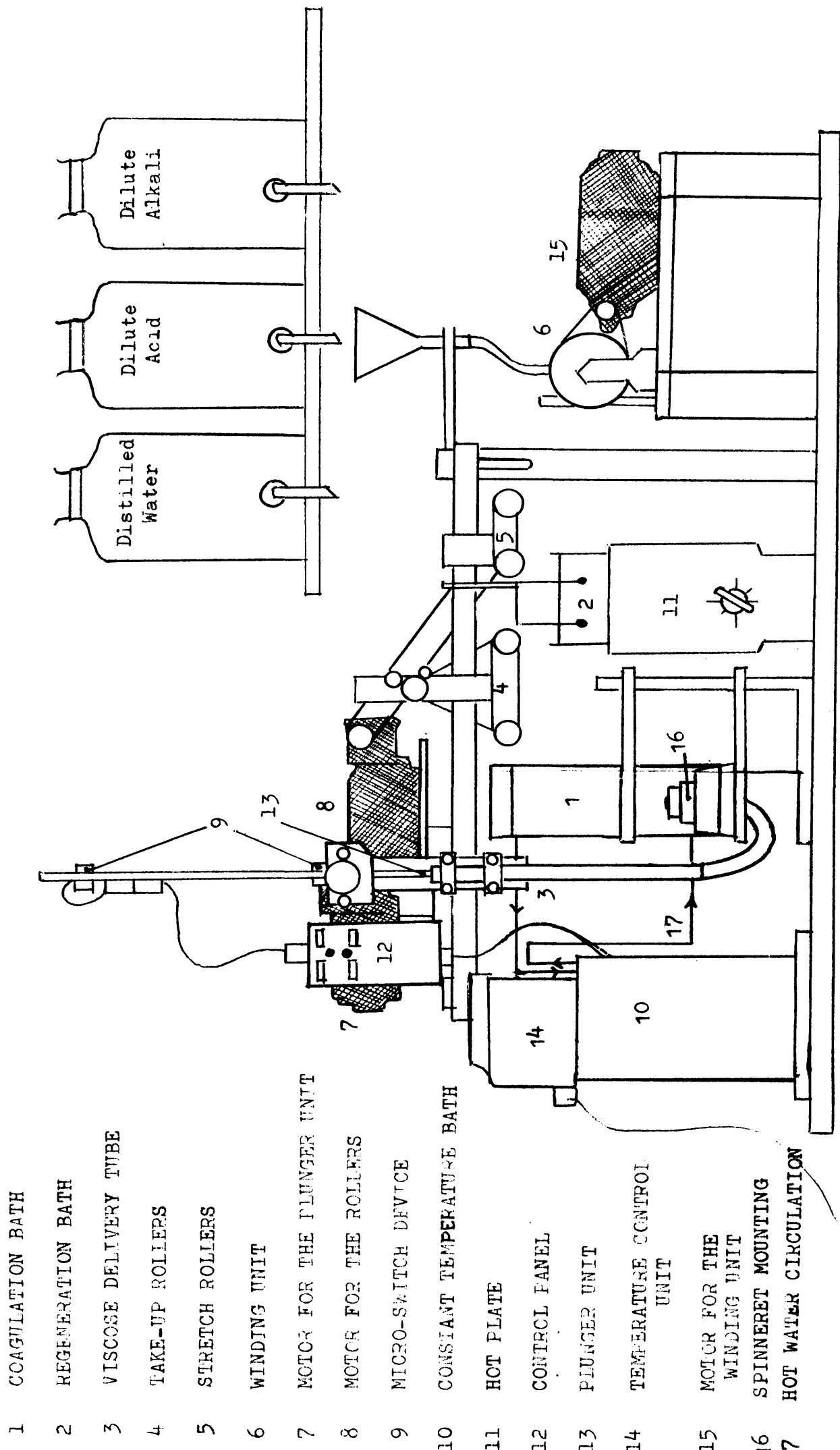


FIGURE 2.10. THE SET-UP OF THE TWO-BATH SPINNING PROCESS.

winding operations lasted. Spraying with dilute acid ensured complete regeneration and prevented stickiness of the filaments. The bobbin was then placed in a hot distilled water bath and the yarn was rewound on to another bobbin and sprayed with dilute sodium bicarbonate solution (14 g/l). The procedure was repeated but distilled water was sprayed on to the yarn. Finally, bobbin and yarn were put in a vacuum oven at 68.5°C and allowed to dry for 3-4 hours.

The technical data for the spinning process are given in the following Table. (See also Appendix Table 1).

TABLE VI
Composition of the Viscoses.

Contents	Impure Viscose	"White Viscose"
Alkali Content (%)	5.44	5.40
Cellulose Content (%)	6.20	6.20
Total Sulphur (%)	2.17	0.97
Y-number	39.1	39.00
Xanthate Sulphur (%)	0.96	0.95
Salt-index	5.75	5.71
*Polyoxyethylene 1500 (%)	1.5	1.5

* based on the weight of cellulose, the others are based on the total composition.

The spin bath, generally referred to as "coagulating bath", was made up as follows:

5.7%	H ₂ SO ₄
7.0%	ZnSO ₄ (anhydrous)
11.5%	Na ₂ SO ₄ (anhydrous)

The regeneration bath consisted of:

3.5% H_2SO_4

1.5% ZnSO_4 (anhydrous)

at 90-92°C. All percentages are on the weight-to-weight basis in aqueous baths.

TABLE VII
The Spinning Variables

No. of viscose samples						
	1	2	3	4	5	6
Spinning variables						
% Pure viscose in the mixture	0	19.70	36.84	59.62	76.37	100
The depth of immersion, cm.	8	12	12	12	12	12
Spinnerets						
No. of holes	168	36	36	36	36	36
Diam. of holes	1.6 mils	0.10 mm	0.10 mm	0.10 mm	0.10 mm	0.10 mm
The speed of spinning, m/min.	3.2	3.2	3.2	3.2	3.2	3.2
The rate of viscose delivery ml/min.	2.37	2.37	2.37	2.37	2.37	2.37
*Extrusion ratio	.30	.38	.38	.38	.38	.38
**Rate of extrusion m/min.	10.8	8.5	8.5	8.5	8.5	8.5
Stretch applied (%)	100	100	100	100	100	100

* is defined as the ratio of speed of spinning to the rate of extrusion.

** is defined as the length of filament spun in one minute.

Difficulty was experienced in the spinning of the viscose mixtures with a 168-hole spinneret. Logically it was desirable to spin the impure viscose with a 36-hole spinneret, but

the cessation of viscose supplies prevented this from being done. To compensate for the difference the depth of the spin bath was increased from 8 to 12 cm when using the 36-hole spinneret.

2.2.5.4. Titration of Buffered Viscose.

In order to produce some evidence to support the hypothesis put forward by Vermaas (15) that viscose impurities act as a buffering agent during the fibre formation, two approaches were made. One approach was the titration of 10% (W/w) solutions of impure, white and buffered white viscoses in distilled water with the acid solution from the coagulation bath of the following composition:

5.7% H_2SO_4 (conc.) (W/w)
7.0% ZnSO_4 (anhydrous) (W/w)
11.5% Na_2SO_4 (anhydrous) (W/w)

The buffering agent selected to function between pH values of 10-3 was a mixture of a solution containing 12.369 grams H_3BO_3 and 14.911 grams KCl per litre plus 43.96 ml 0.2 M NaOH and 50 ml 0.2 M potassium hydrogen phthalate plus 47.00 ml 0.2 M NaOH solution diluted to 200 ml.

During the titration of the above viscose solutions, 5 ml of acid solution were added at a time and the mixture was stirred for 30 seconds before the addition of a second 5 ml of acid solution. The pH values were measured with a pH-meter with a glass electrode.

2.2.5.5. Spinning of Buffered Viscose.

As a second approach, spinning of buffered pure viscose was carried out. "White" viscose was freeze-dried to a

known weight to allow the addition of a buffer solution without diluting the viscose. A buffer solution containing 0.511 gram potassium hydrogen phthalate, 0.182 gram potassium chloride and 0.152 gram boric acid in 22.1 grams distilled water was prepared.

The weight of the distilled water was equal to the differences in weights of pure viscose before and after the freeze-drying.

The buffer solution was then mixed with the pure viscose at a salt-index of 5.7. Mixing was aided by stirring for 10-15 minutes. The spinning of buffered viscose was carried out by the technique described in section 2.2.5.3., using a spinneret of 0.10 mm diameter and 36 holes.

2.2.6. The Analysis of the Filaments.

The following are the analytical treatments to which the tyre-cord fibres spun under the conditions described were subjected.

2.2.6.1. Gel Swelling Determination.

Unstretched yarn taken from the last two-minutes of spinning were successively immersed for a few minutes in 3.5% sulphuric acid solution, water, sodium bicarbonate solution (14 g/l), and finally water for 15 minutes.

About 2 grams of fibres were cut into small lengths and placed in a polythene tube fitted with a bottom of fine-mesh stainless-steel wire, and centrifuged for exactly 20 minutes at 4500 r.p.m. The centrifuged samples were weighed, and then dried overnight in an oven set at 105°C, cooled and reweighed. Gel swelling was expressed in grams of water taken up by 100 grams of dry cellulose.

2.2.6.2. Moisture Regain, Accessibility and Crystallinity.

Mann and Marrinan (36) have shown how infra-red spectroscopy in conjunction with the deuterium isotopic exchange reaction may be used to measure the accessibility and the crystallinity of different celluloses. The method is based on the fact that the shape of the absorption band of the hydroxyl groups in the amorphous regions is different from that of the hydroxyl groups in the crystalline regions, and the infra-red spectrum can be used to determine when all the hydroxyl groups in the amorphous regions have been deuterated, hence an accurate measurement of crystallinity can be made.

Frillette, Hainle and Mark (37) have shown that the relation between percentage crystallinity (α) and percentage accessibility (A) may be expressed by

$$\alpha = \frac{100-A}{1-\sigma}$$

where σ is the fraction of a crystallite accessible to a particular reagent. This fraction is most probably associated with the surfaces of individual crystallites, and if certain assumptions are made about the shape of these regions a rough estimate may be made of its value. Knowing this value and measuring accessibility one can then arrive at a value for the percentage crystallinity. The values of percentage crystallinity derived in this way are useful for comparing different samples of cellulose, but too much significance should not be attached to the actual values obtained.

The value of σ used in the present investigation was taken to be 0.28 (38) and was obtained on the following

assumptions:

- (i) the ratio of length to breadth of crystallites is high enough to neglect end effects,
- (ii) the crystallites are of square cross section.

Moisture regain was calculated as follows:

Samples weighing approximately 0.5 g were conditioned at 65% relative humidity and $20 \pm 1^{\circ}\text{C}$ for 24 hours. A desiccator containing a saturated solution of ammonium nitrate was used for the purpose of conditioning. The conditioned samples were then accurately weighed, completely dried, and reweighed. The percentage moisture regain was then calculated.

Accessibility to water was measured in terms of moisture regain on the assumptions that the crystal lattice of cellulose II is not penetrated by the water molecules, and that there is a linear relationship between the moisture regain and accessibility. At 65% relative humidity and 20°C this relationship is as follows:

$$A = \text{Moisture Regain} \times \frac{43.5}{B}$$

where B is the moisture regain of cotton cellulose and measured to be 7.95% at 65% R.H. and 20°C , and 43.5 is an average value of percentage accessibility of cotton cellulose measured by deuteration technique (39).

2.2.6.3. Acid Hydrolysis, Crystalline Content and Limiting-Degree of Polymerisation.

It is possible to hydrolyse the acid accessible regions of cellulose to soluble products. The loss in weight, which is initially relatively rapid, eventually becomes more or less independent of treatment time (40). It is usual to regard the insoluble material as the crystalline phase and

to estimate it by weighing (41). By measuring the intrinsic viscosity of the residue and calculating the degree of polymerisation it is possible to arrive at an estimate of the length of the crystalline regions (42). The estimates of percentage crystalline matter and crystallite size are by no means absolute since it is well known that further crystallisation occurs during the acid treatment (43), but the methods are useful for purposes of comparison.

About 2 grams of finely chopped filaments were dried and weighed, refluxed in 200 ml of distilled water for 15-20 minutes, and then 100 ml of 3 N HCl were added; refluxing was continued for 1 hour (22). The hydrolysate was quickly filtered through a sintered funnel of porosity 2. The residue was washed with 100 ml of 1 N ammonia solution followed by distilled water until free from alkali. The residue was finally washed with acetone to remove the water and dried in a vacuum oven at 68.5°C for 3-4 hours. The weight of the dried residue expressed as a percentage of the weight of the original cellulose is a measure of the crystalline content.

Dried hydrolysed samples (app. 0.4 g) were weighed accurately in small weighing funnels and introduced into long-tail Shirley viscometers. The fluidity measurements were then carried out in cuprammonium hydroxide at 20°C. (42). Fluidity of solvent was also measured and found to be 72.60.

The limiting degrees of polymerisation were obtained from the knowledge of intrinsic viscosities. Fluidities were first converted to relative viscosities. Intrinsic viscosities were then obtained from Baker's equation (42):

$$\eta_R = \left[\frac{1 + [\eta]_x C}{3.5} \right]^{3.5}$$

where η_R is the relative viscosity

$[\eta]$ is the intrinsic viscosity (dl/g)

C is the concentration of the solution (g/dl)

3.5 is the Baker's constant and said to be valid for relative viscosities up to 10.

Finally, levelling-off degrees of polymerisation were obtained from the following expression:

$$\overline{DP} = 175 [\eta]$$

2.2.6.4. Skin-Core Ratio by Differential Staining of Cross-Sections.

This method is based on the observation that certain dyes preferentially stain the skin structure (19). After staining the whole cross-section the dye within the core may be removed by a suitable solvent. The skin-core ratio is obtained by measuring the stained and unstained areas in photomicrographs.

The staining was carried out by dyeing the filaments in a 5% solution of Chlorazol Sky Blue FF 200, without any addition of sodium chloride, at the boil for 2 hours (44). The dyed samples were then embedded in an acrylic cement called "Tensol No. 7", manufactured by I.C.I. Plastics Ltd.

The filaments were first passed through the two halves of a gelatin capsule, using a needle, and then stretched across a U-shaped copper wire. The capsule was then filled with the cement, making sure that no air bubbles were introduced. The cement was allowed to set

at room temperature overnight.

A square pyramid was cut out from the capsules and then sections of 7 microns thick were cut on a rotary microtome.

The sections were placed on microscope slides and the dye within the core regions removed by treatment with a 20% aqueous solution of pyridine. The time of stripping was 10 minutes.

The stripped sections were permanently mounted on Canada Balsam dissolved in xylene. The photographs of the sections were taken on an Ilford HP4 film using a Vickers Photomicroscope fitted with an automatic exposuremeter. The amounts of skin and core structures were obtained by outlining the relevant areas on tracing paper, cutting them out and weighing them.

2.3. Results and Discussions.

2.3.1. Gel Swelling Values.

The gel swelling values, defined as the amount of water retained by 100 grams of dry cellulose, are given in Appendix Table III, and plotted in Figure 2.11. They relate to the swelling of unstretched "never-dried" filaments.

Gel swelling values are significant in that they are a measure of the extent of dehydration of filaments prior to complete regeneration. A high gel swelling value is indicative of relatively little dehydration before regeneration; complete regeneration of such a filament therefore leads to a fibre with a coarse, open structure, i.e., core-type structure. A low gel swelling value corresponds to a higher degree of dehydration and ultimately to a finer and more uniform structure referred to as skin. Gel swelling values are thus in present context an indirect measure of rate of regeneration.

It may be seen from Figure 2.11. that there is a more or less linear relation between gel swelling values and percent of pure viscose in the mixture. At 100 per cent pure viscose the gel swelling value is very much lower than that of even the 100 per cent impure viscose; this second observation is not considered to be spurious. There are reasons for this conclusion; it should be noted that a viscose containing as much as 80 per cent pure viscose has a skin content as high as 55 per cent (Figure 2.15.) but 100 per cent pure viscose gives a filament of zero skin content. Observation of the latter filaments showed that

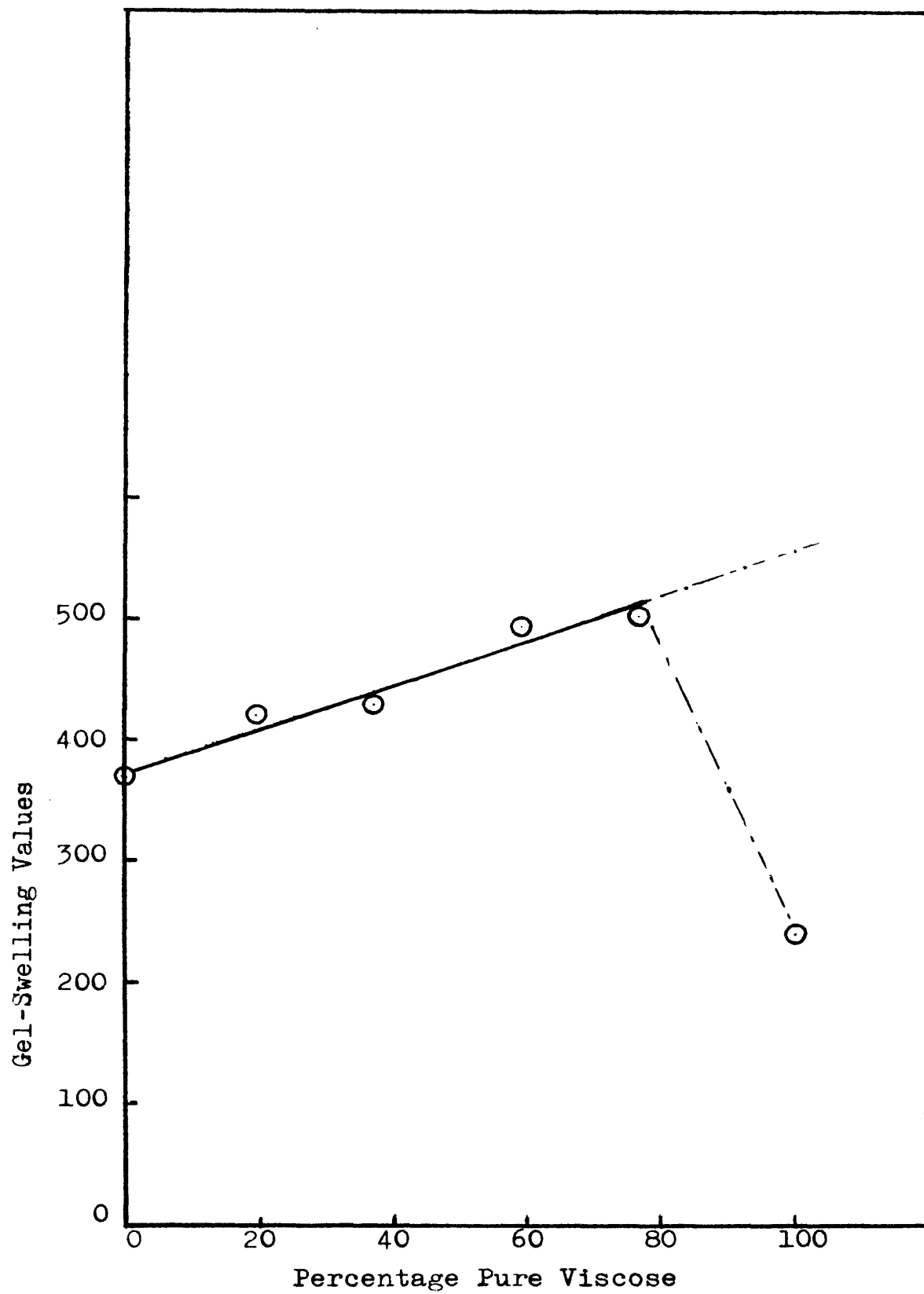


FIGURE 2.11. EFFECT OF IMPURITIES ON GEL-SWELLING.

they were very highly swollen prior to being centrifuged and it is concluded that the relatively high loss of water, which leads to a low gel swelling value, is related to the complete absence of skin structure; in other words, the method of measuring gel swelling fails.

The increase of swelling value up to 80 per cent pure viscose corresponds to a decrease in extent of dehydration prior to complete regeneration and therefore to an increase in rate of regeneration. This conclusion agrees with the contention of Vermaas (15) that the viscose salts exert buffering action and slow down regeneration.

2.3.2. Crystallinity from Moisture Regain.

Percentage crystallinities obtained from moisture regain are given in Appendix Table IV and plotted in Figure 2.12.

It may be seen from Figure 2.12 that the effect of increasing the proportion of purified viscose is mainly to increase the percentage crystallinity. A possible explanation is that when regeneration, and therefore crystallisation occur under conditions of relatively high gel swelling, nuclei density is low and the chain molecules have a relatively high degree of freedom, and may therefore crystallise to a greater extent. This difference may be seen between ordinary viscose rayon and tyre cord rayon. The former are regenerated under conditions of relatively high gel swelling and have an appreciably higher crystalline content (39).

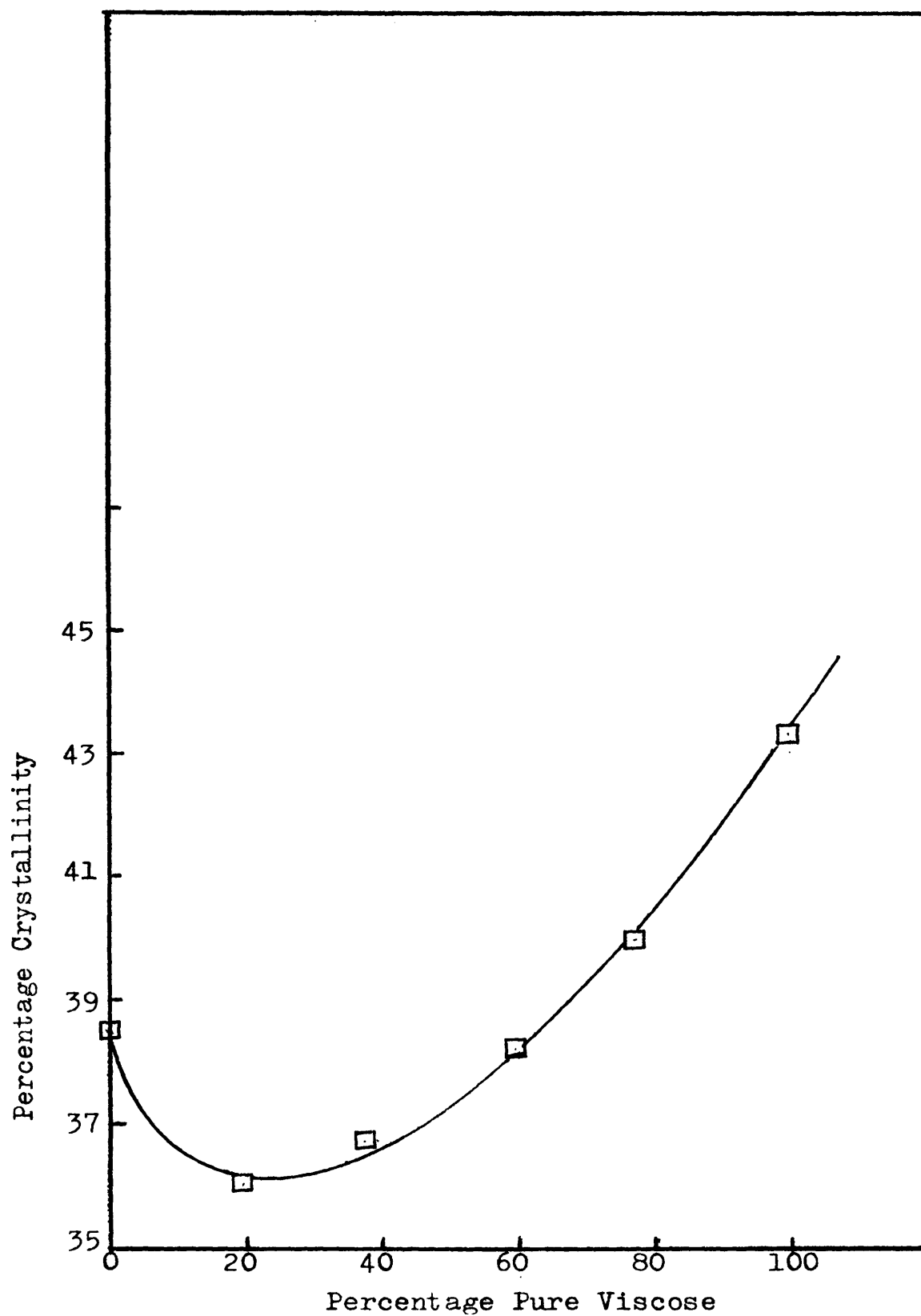


FIGURE 2.12. EFFECT OF IMPURITIES ON CRYSTALLINITY (MOISTURE REGAIN METHOD)

A second feature of the relation between crystallinity and per cent pure viscose is that it passes through a minimum at about 30 per cent of the latter. It will be seen later (section 2.3.3.) that a similar relation is obtained when percentage crystallinity is derived from acid hydrolysis experiments, though the minimum is even more marked. It is difficult to believe that the upswing in the relation at low contents of pure viscose is real. It will be recalled that the calculation of crystallinity from moisture regain accessibility measurements involved a constant, σ , which is used to correct for the contribution made by the surface of crystallites to the estimate of amorphous content. Since crystallite length decreases with decrease in pure viscose content (section 2.3.3.) the value of σ is likely to increase; a change which will increase the calculated degree of crystallinity.

2.3.3. Acid Hydrolysis, Crystallinity and Limiting-Degree of Polymerisation.

The percentage crystallinities determined from the weights of residues after hydrolysis are given as a function of the percentage of pure viscose in the spinning mixture, Figure 2.13. (See also Appendix Table V.) It will be seen that the relation is similar to that obtained by estimating crystallinity from moisture regain (section 2.3.2.), although the values for the crystalline content are much higher. The higher values undoubtedly arise because further crystallisation occurs during acid hydrolysis.

The minimum in the relation is again thought to be spurious in the sense that it cannot be explained as a direct

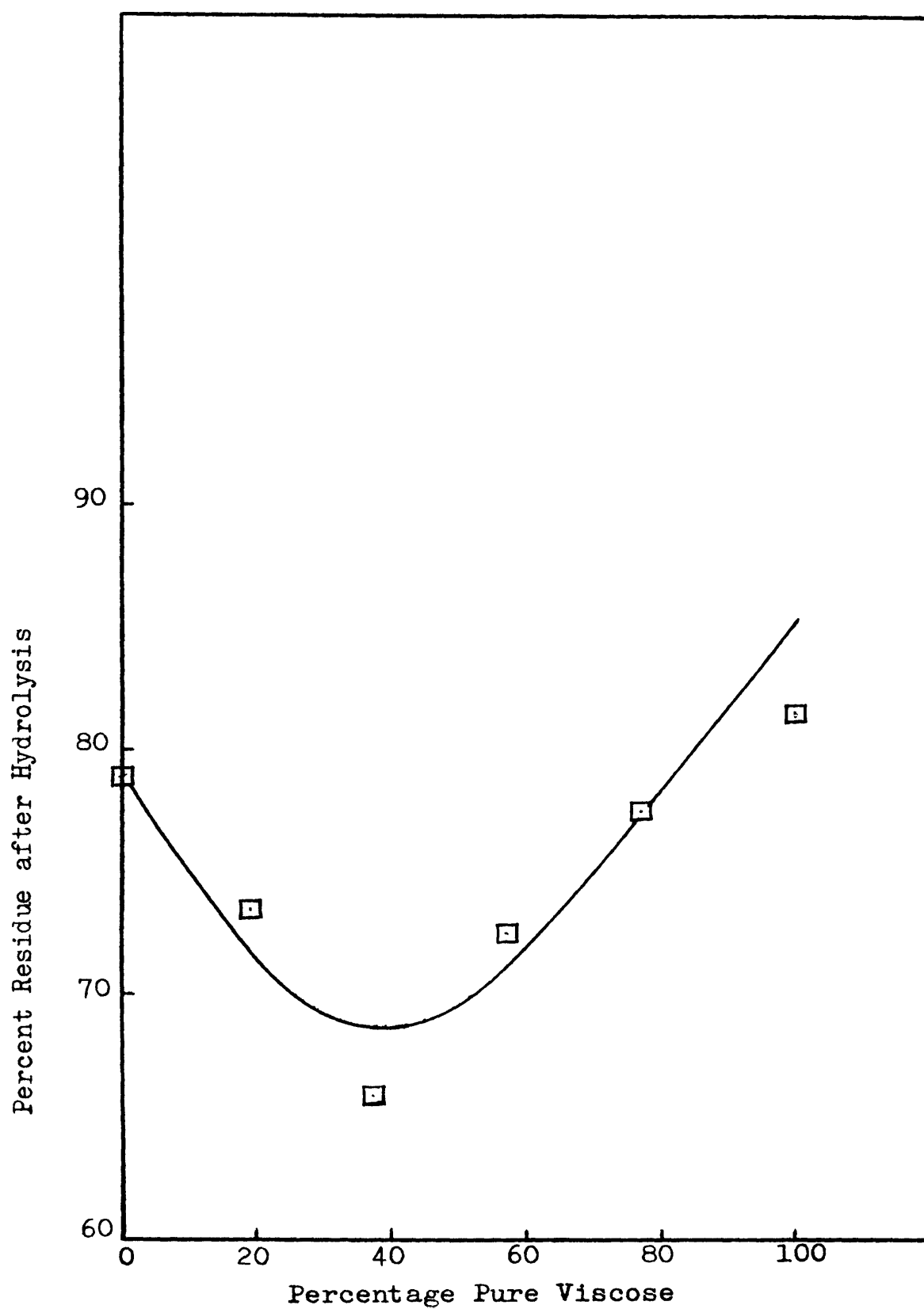


FIGURE 2.13. EFFECT OF IMPURITIES ON CRYSTALLINITY (ACID-HYDROLYSIS METHOD).

consequence of varying the proportion of white viscose. The minimum is probably caused by further crystallisation during acid hydrolysis, the amount occurring increasing with increase in the crystallite population. Relatively small and relatively numerous crystallites are characteristic of skin structure compared to core structure, and the former is increasing with decrease in the white viscose content of the spinning mixture (cf. Figure 2.15).

Regardless whether the rayon structure is named as fringed-micellar or fringed-fibrillar an increase in the crystallite population implies a decrease in the average length of the portions of molecules lying within the amorphous or accessible regions. Chain scission by acid hydrolysis will therefore lead to relatively short chain molecules protruding from crystalline regions or relatively short chain molecules existing separately. In either case a higher degree of crystallinity will result than if the chain lengths were greater, since the greater the chain length, the greater is the restriction by chain entanglement on the segmental mobility required for crystallisation.

The relation between limiting or levelling-off degree of polymerisation and composition of the viscose is shown in Figure 2.14. (See Appendix Table VI.) With decrease in the percentage of pure viscose there is a steady decrease in limiting-degree of polymerisation, the slope of the curve diminishes as the percentage of pure viscose decreases. If the varying extents of recrystallisation postulated above are correct, then the changes of slope would not be expected to be so marked; in other words, fibres prepared from

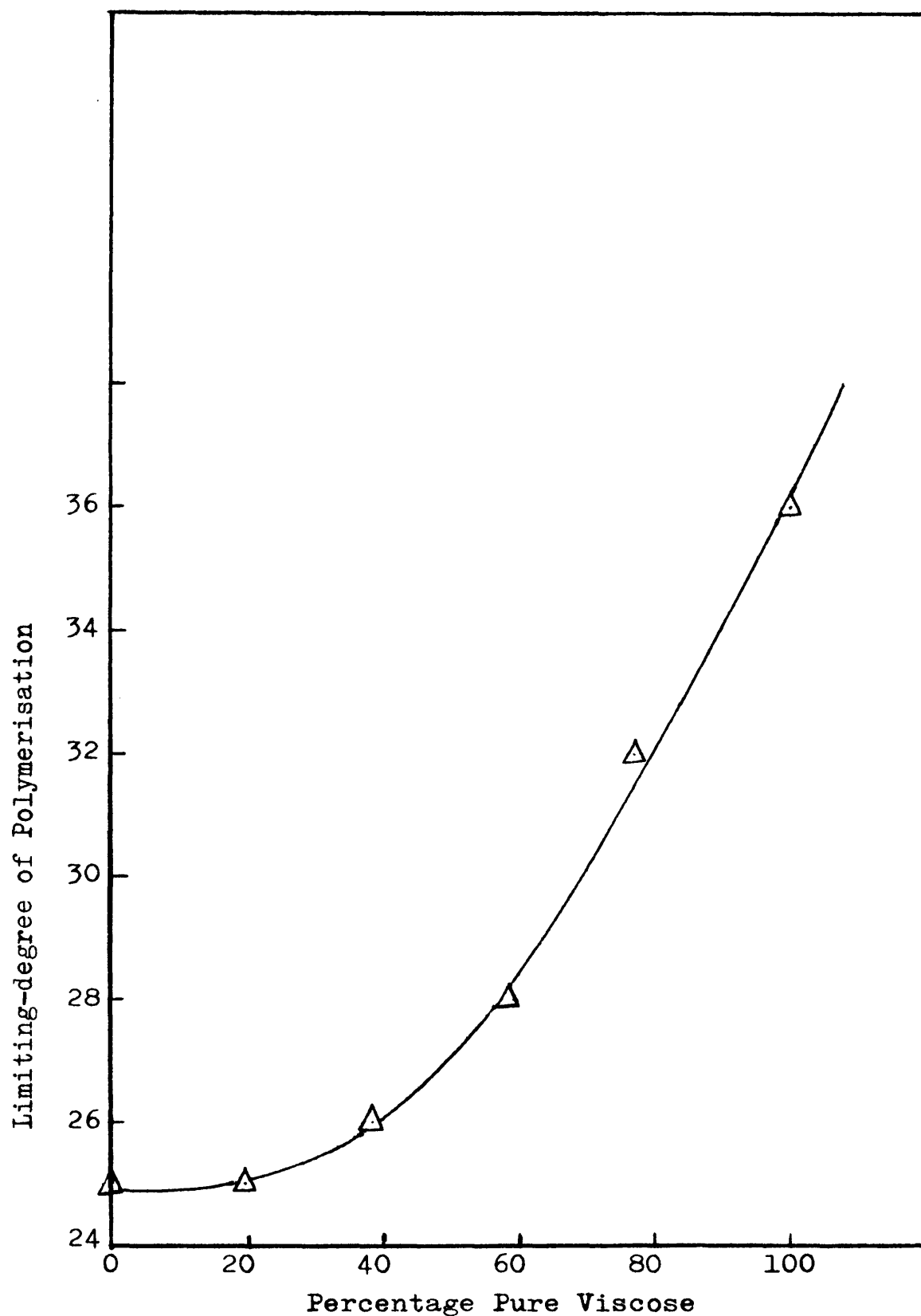


FIGURE 2.14. EFFECT OF IMPURITIES ON THE LIMITING-DEGREE OF POLYMERISATION.

viscose containing less than about 30 per cent white viscose would have a lower limiting-degree of polymerisation than found.

2.3.4. Skin Structure and Shape of Filament Cross Section.

An all-skin structure is obtained from impure viscose and an all-core type structure results from white viscose. The proportion of skin structure obtained when spinning mixtures of the two is shown in Figure 2.15. (See Appendix Table VII)..

Photomicrographs of typical cross sections are shown in Figure 2.16. Where the structure is entirely of the skin type the cross sections are circular and smooth, and as the proportion of core structure increases the cross sections become more irregularly shaped and are serrated. It has been long accepted that an irregular and serrated cross section arises when surface regeneration of cellulose occurs before the inner regions are sufficiently dehydrated, subsequent de-swelling causes the regenerated surface to buckle as it encloses a decreasing volume. Consequently the increasing irregularity of the cross sections with increasing proportions of white viscose point to an increase in rate of regeneration of the cellulose which accords with the views of Vermaas (15) that the by-products in impure viscose exert a buffering action and delay regeneration. The same conclusion was reached earlier (section 2.3.1.) in terms of gel swelling values.

2.3.5. Buffered White Viscose.

Vermaas (15) has claimed that buffered white viscose will give fibres with a proportion of skin structure, but since he did not give any analytical data his work was repeated but

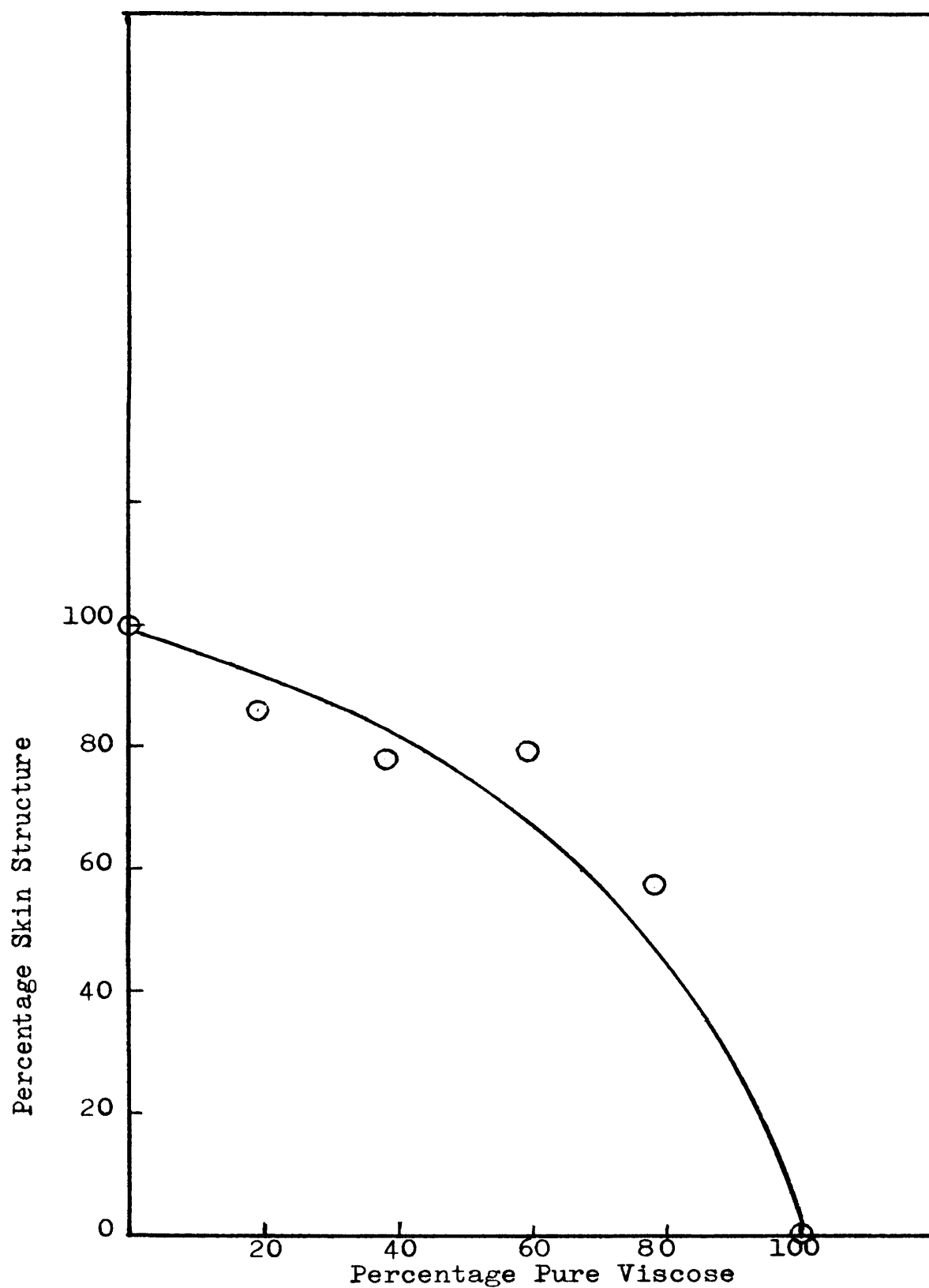
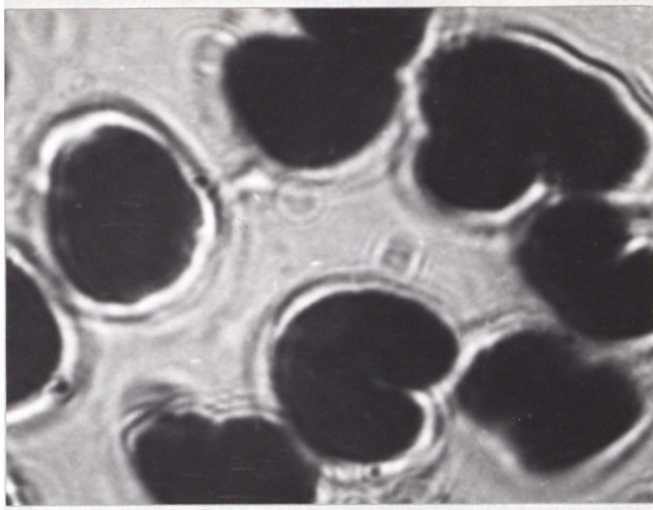


FIGURE 2.15. EFFECT OF IMPURITIES ON THE AMOUNT OF SKIN STRUCTURE.

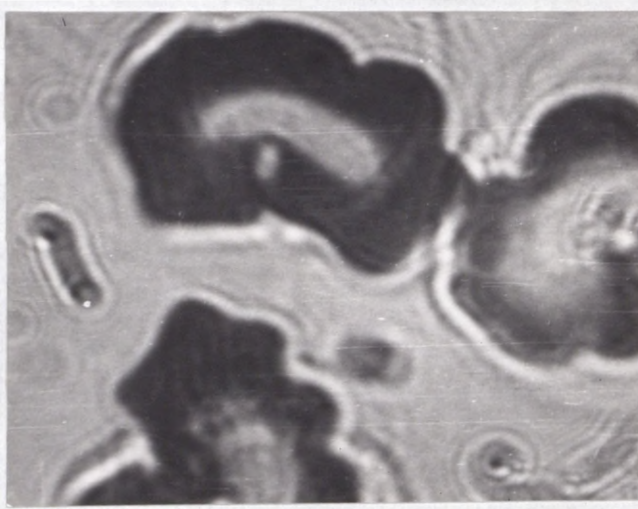
Magnification

Fibres spun
from:



Ca. 1200 X

impure viscose,



Ca. 1200 X

viscose
mixture
containing
19.7% pure
viscose,



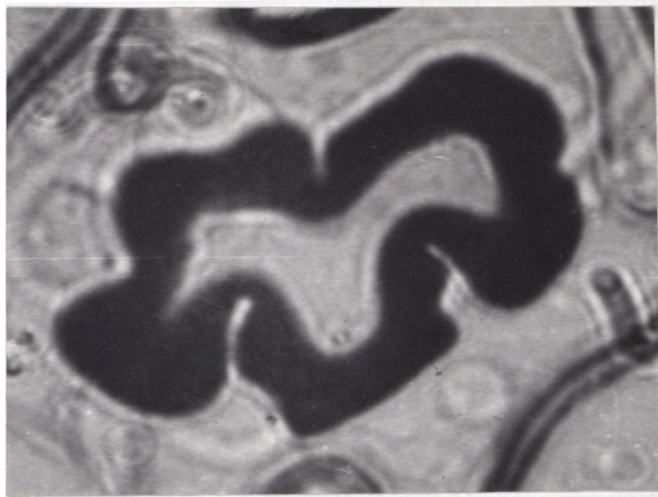
Ca. 1200 X

viscose
mixture
containing
36.84% pure
viscose,

FIGURE 2.16. PHOTOMICROGRAPHS OF CROSS-SECTIONS OF TYRE CORD FIBRES.

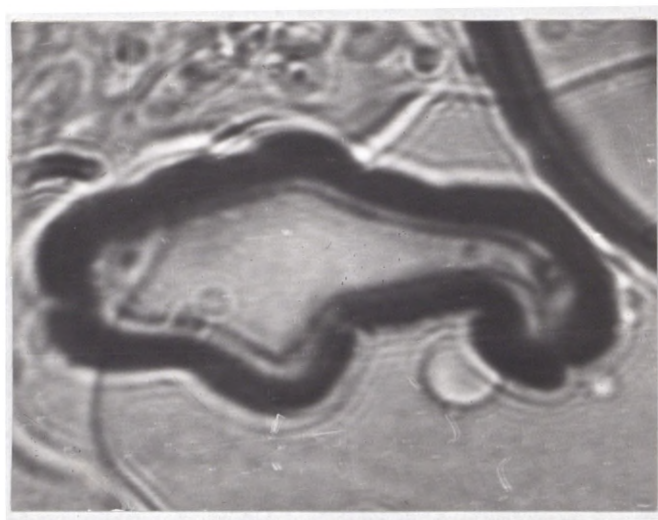
Magnification

Fibres spun
from:



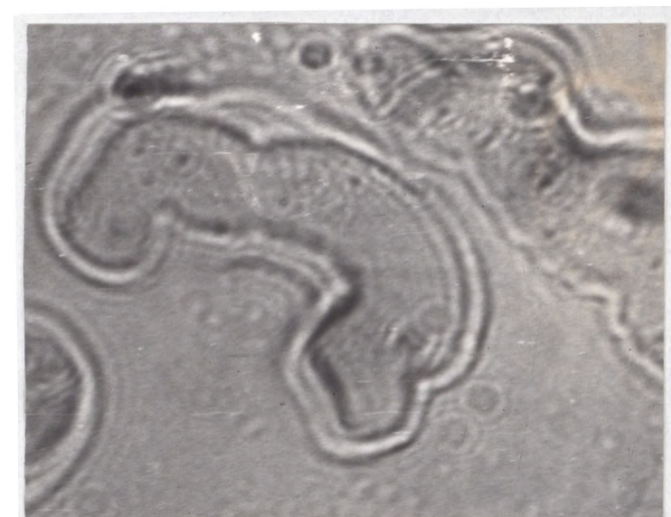
Ca. 2000 X

viscose
mixture
containing
59.62% pure
viscose,



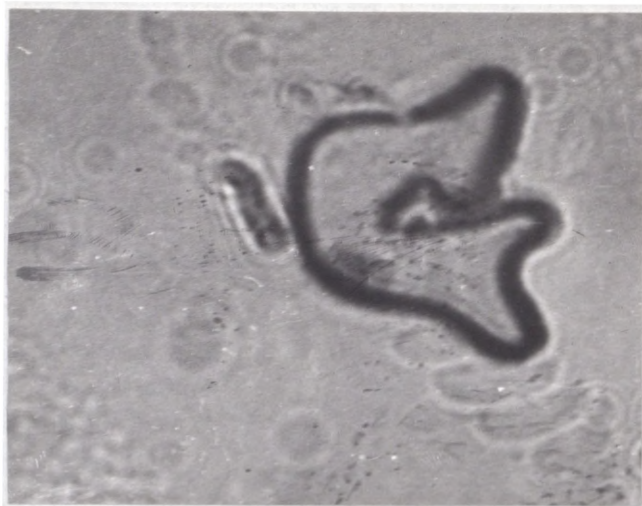
Ca. 2000 X

viscose
mixture
containing
76.37% pure
viscose,



Ca. 2000 X

pure viscose,



Magnification

Fibres spun
from:

Ca. 1200 X

buffered pure
viscose.

with a different buffering medium; he used sodium zincate. In the present work the buffering action has been investigated both by titrating buffered viscose with the contents of the spin bath and by spinning fibres from the buffered viscose.

Figure 2.17 shows titration curves for white viscose, white viscose containing buffer solution, and impure viscose. (See Appendix Table VIII). It will be seen that for a given volume of spin bath added, and at all pH values between 10-3, the pH of the buffered white viscose is greater than that of impure viscose, and both are greater than that for the unbuffered white viscose.

Table VIII gives a comparison of fibre properties for filaments spun from buffered and unbuffered white viscose.

TABLE VIII
Comparison of Filaments Spun from Buffered and
Unbuffered White Viscose.

	Buffered	Unbuffered
Gel swelling	701.0	241.1
Moisture regain (%)	13.7	12.6
Accessibility (%)	75.1	68.7
Crystallinity (%)	34.6	43.4
% residue on hydrolysis	73.3	81.9
Intrinsic viscosity (dl/g)	.163	.205
Limiting-DP	28	36
% Skin structure	49.4	0

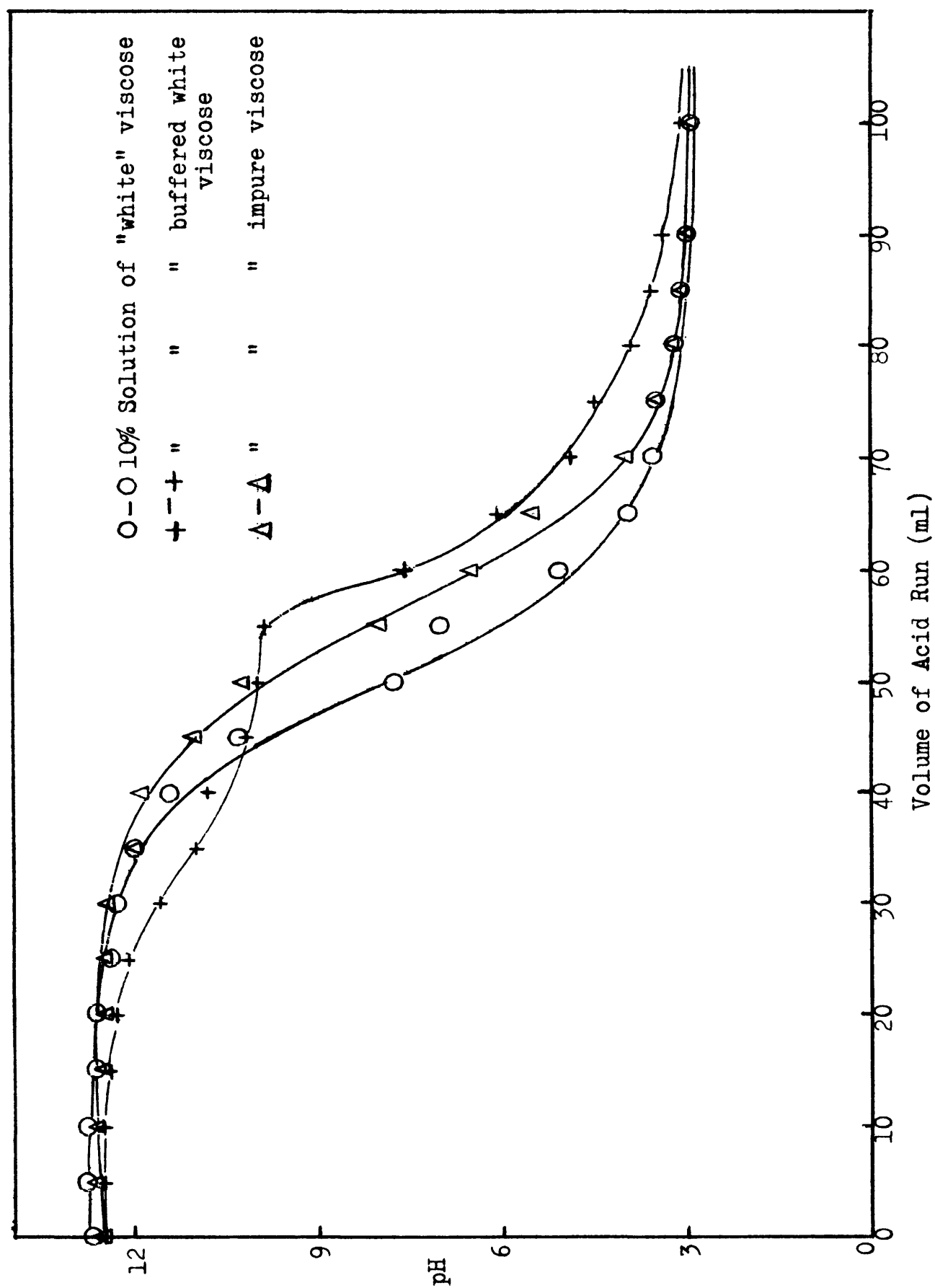


FIGURE 2.17. THE TITRATION OF VISCOSE SOLUTIONS WITH THE SPINNING BATH SOLUTION.

2.4. Conclusions.

It was the contention of Vermaas (15) that the impurities in viscose, the so-called viscose salts, exerted a buffering action on the process of regeneration. In consequence regeneration was delayed which permitted regeneration to occur at a lower gel swelling value. A low gel swelling value corresponds to a relatively high polymer content which in turn leads to a relatively large number of nuclei during regeneration and hence small crystallites or skin-type structure. Vermaas patented the spinning of cellulose xanthate solution containing sodium zincate as buffering agent (45).

The results of the present investigation in which mixtures of impure and purified viscoses have been spun into filaments entirely supports the conclusions of Vermaas. There is a well-defined relation between the percentage of skin structure and the percentage of pure or impure viscose; gel swelling increases with percentage of pure viscose, and so does the estimate of crystallite length. The percentage of crystalline material also increases with increase in the content of pure viscose. The conclusions have been further confirmed by adding a buffering agent to pure viscose which when spun produced filaments containing some skin structure.

It is interesting to note, too, that there is a more or less linear relation between levelling-off degree of polymerisation (crystallite length) and the percentage of skin structure (Figure 2.18.) A similar relation was observed by Cumberbirch (22) even though percentage skin structure was changed by altering other parameters of the spinning process.

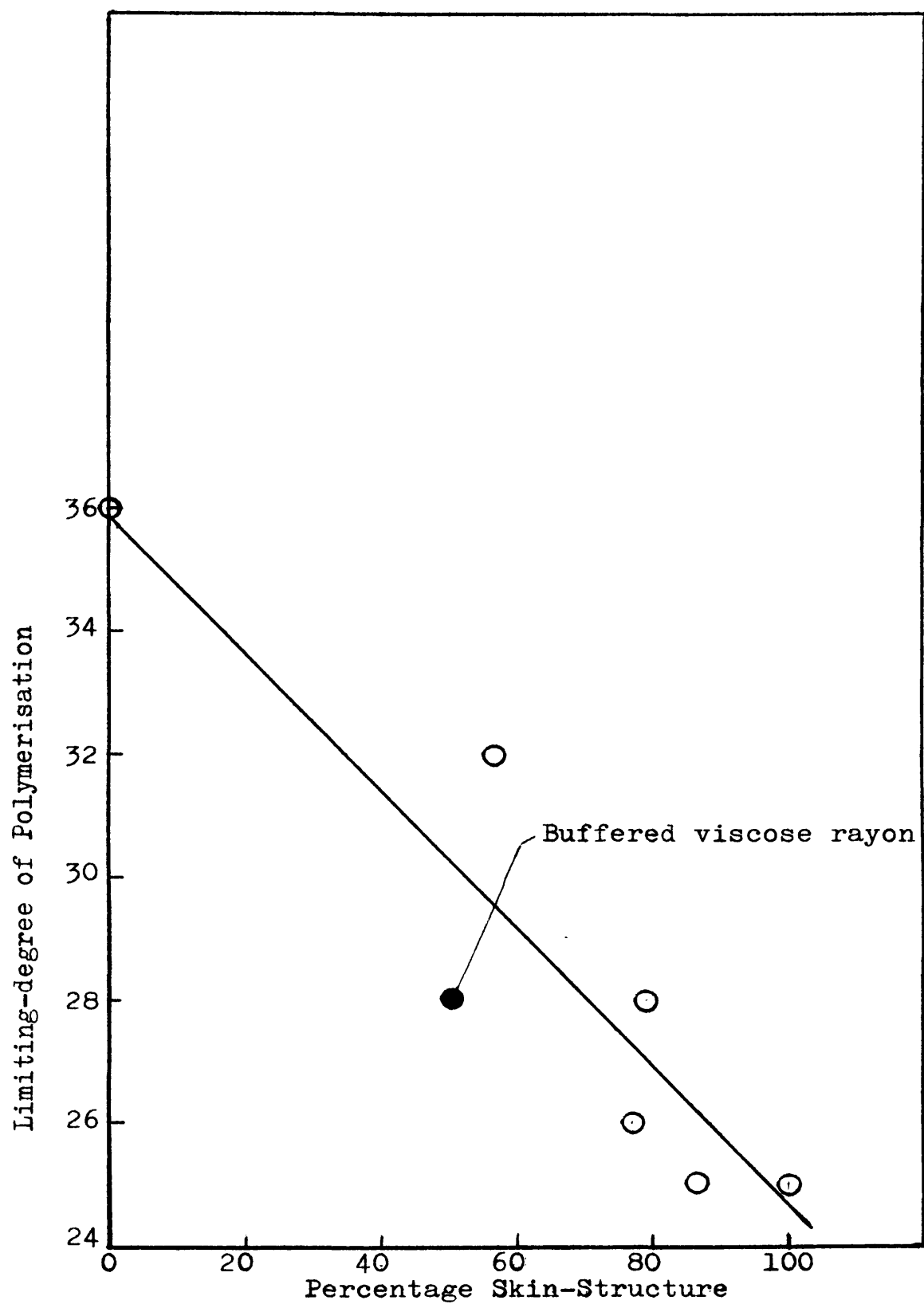


FIGURE 2.18. RELATION BETWEEN THE CRYSTALLITE LENGTH AND THE AMOUNT OF SKIN STRUCTURE.

SECTION 3.

EFFECT OF PARTIAL METHYLATION OF CELLULOSE ON THE PROPERTIES OF VISCOSE AND VISCOSE RAYONS

3.1. Introduction.

It should be clear from sections 1 and 2 that the formation of skin structure is highly dependent on nucleation and crystallisation conditions, the principal objectives being to ensure a large number of nuclei. A possible alternative method of achieving the same end would be to convert cellulose prior to xanthation into a block copolymer of the type where only the cellulose blocks could crystallise. This type of structure should at least reduce the formation of relatively large crystallites. However, at the same time, it would be expected that the total crystalline content would fall.

Block copolymers normally have to be synthesised, but since this is impossible in the case of cellulose, an attempt has been made to methylate the accessible regions of cotton cellulose in order to create something akin to a block copolymer. Whether one names the structure of cellulose as a fringed-micellar, fringed-fibrillar, or as an array of crystalline fibrils containing imperfections or voids, there exist possibilities for block copolymer formation. Different products may also be obtained by pre-swelling the cellulose in caustic soda prior to methylation.

Some consideration was given to the possibility of achieving the same end by using mixtures of cellulose and methyl celluloses of varying degrees of substitution, but

the idea was abandoned on the grounds that such materials would be more likely to be rejected during crystallite formation and would exist solely in the amorphous regions of regenerated cellulose. Mikami and Ellefsen (46) made modified polynosic rayons by a similar method in which they incorporated 10 per cent of two hydroxyethyl celluloses into viscose. Small changes only were observed in the wet modulus of the resulting filaments and there were also small changes in the fine structure reported (47). Perhaps no significant changes were observed for the reasons given above.

The preparation of the methylated celluloses presented many problems. Cotton linters were used as starting material and one of the main difficulties was to prepare a series of methylated products all with the same degree of polymerisation. To be economical methylation was by the use of dimethyl sulphate rather than diazomethane but it had the disadvantage of degrading cellulose and there was also a loss in weight of low molecular weight material during alkali swelling. These difficulties were largely overcome by ageing alkali cellulose to different extents prior to methylation.

Unlike the investigation in the first part of this thesis, viscose had to be made in the laboratory and the necessary equipment for all stages of the process had to be designed and made. Furthermore, since the viscoses were being made from methylated celluloses, rates of ripening had to be studied, and it was also necessary to see what influence methylation had on the viscosity of the viscose.

Since the primary object of the work was to study skin formation, it would have been logical to spin with a two-bath process, but since difficulty was experienced with this system in the work described in the first part of this thesis, a one-bath process was used. Spinnings were done at several levels of acid concentration and in one case with and without the presence of a modifier.

The methods used to investigate the properties and structure of the filaments obtained were those used for the work in the first part of the thesis, namely:

- (i) gel swelling value,
- (ii) crystalline content by moisture regain and acid hydrolysis,
- (iii) limiting-degree of polymerisation,
- (iv) skin/core ratio by differential staining.

In addition to the above methods, stress-strain measurements, both in the wet and dry states, were also made.

3.2. Methylation of Cellulose.

3.2.1. Introduction.

The starting material for the preparation of partially methylated celluloses was in all cases cotton linters. Since the DP of this material is much higher than required for viscose rayon spinning, the DP was first reduced to a DP of about 600 by acid hydrolysis. A standard acid concentration and temperature were used and the relation between time of treatment and DP estimated from viscosity measurements was derived for the cotton linters.

For the purpose of producing methyl celluloses with suitable degrees of substitution for xanthation and spinning, dimethyl sulphate was used as methylating agent and the effects of dimethyl sulphate concentration, alkali concentration, and time were studied. The extent of reaction is very dependent on the accessibility of the cellulose used and the effect of pre-swelling the cellulose with caustic soda of various concentrations was also investigated. The extent of pre-swelling was intended to be a means of varying the dimensions of the cellulose and methyl cellulose blocks.

The reaction with dimethyl sulphate and the subsequent and necessary washing operations are likely to remove some undegraded and degraded methyl celluloses. For this reason it was also necessary to follow weight changes and to compare these with the theoretical increases in weight for given degrees of substitution. Within certain ranges of extent of reaction there were noticeable weight losses, the most serious consequence being that they resulted in an increase in the average DP of the product. Variations in DP produced

in this way would lead to the spinning of rayon fibres differing in DP and make comparisons of fibre properties of doubtful value. It was decided to ignore these losses and compensate for variations in average DP by ageing soda cellulose to different extents prior to methylation. In this way fibres of the same average DP would be produced but they probably differed slightly in DP distribution.

3.2.2. Prehydrolysis of Cotton Linters.

Since the degree of polymerisation of cotton linters is much higher than required for viscose rayon spinning, the DP was reduced to about 600 by acid hydrolysis. Prior to hydrolysis, the cotton linters were scoured in a solution containing:

Lissapol N	1 g/l
Na ₂ CO ₃	0.5 g/l

at the boil for one hour, followed by rinsing and drying.

Acid hydrolysis was carried out for different extents of time in 4.96 N HCl at $24.2 \pm 0.1^{\circ}\text{C}$. Hydrolysed samples were neutralised in 5 N ammonia solution followed by washing with hot and cold distilled water until free from acid. Finally, samples were rinsed with acetone to remove water and then dried.

Chain lengths were determined from fluidity measurements made at $20 \pm 0.1^{\circ}\text{C}$ using cuprammonium hydroxide as solvent and Shirley Institute-type short-tail viscometers (48). The fluidities were converted to intrinsic viscosities using the J.K.M. equation given below. This equation is said to be valid for relative viscosities up to 100 (42):

$$\frac{\eta_{R-1}}{C} = \log [\eta] + 0.14 [\eta] C$$

where,

η_R is the relative viscosity of solutions,
 $[\eta]$ is the intrinsic viscosity of " (dl/g),
 C is the polymer concentration of " (g/dl).

The degrees of polymerisation were calculated from the measured intrinsic viscosities using Harland's equation (49):

$$[\eta] = 0.0319 (\text{DP})^{0.657}$$

When values of DP are plotted against the time of hydrolysis a hyperbolic curve is obtained, Figure 3.1., see also Appendix Table 1X, from which it may be seen that in order to obtain a sample of DP of around 600, a hydrolysis time of 8.5 hours is needed under the conditions used.

3.2.3. Methylation of Cellulose with Dimethyl Sulphate.

3.2.3.1. Method of Methylation.

The method used for the methylation of hydrocellulose was similar to that of Croon's (50), that is, reaction of alkali cellulose with dimethyl sulphate in toluene.

One gram of cellulose was pre-swollen (steeped) in 50 ml of various concentrations of caustic soda solution for one hour under a nitrogen atmosphere at 23°C. Following steeping, excess alkali was squeezed out by means of a polypropylene piston, and by the use of a water suction pump, until the weight was 3 grams. Pressed alkali cellulose was shredded with tweezers and then transferred into a 3-neck round-bottom flask fitted with a stirrer. The flask contained 50 ml of toluene at $20 \pm 0.5^\circ\text{C}$. The stirring was started and allowed to continue for 10 minutes before the addition of the required volume of dimethyl sulphate from a dropping funnel. The rate of dropping was controlled at around 5 ml per hour. An atmosphere of nitrogen was supplied from a commercial cylinder fitted with a reducing valve. The arrangement of the apparatus is shown in Figure 3.2.

After stirring for a given time, the contents of the flask were filtered through a sintered funnel of porosity 3,

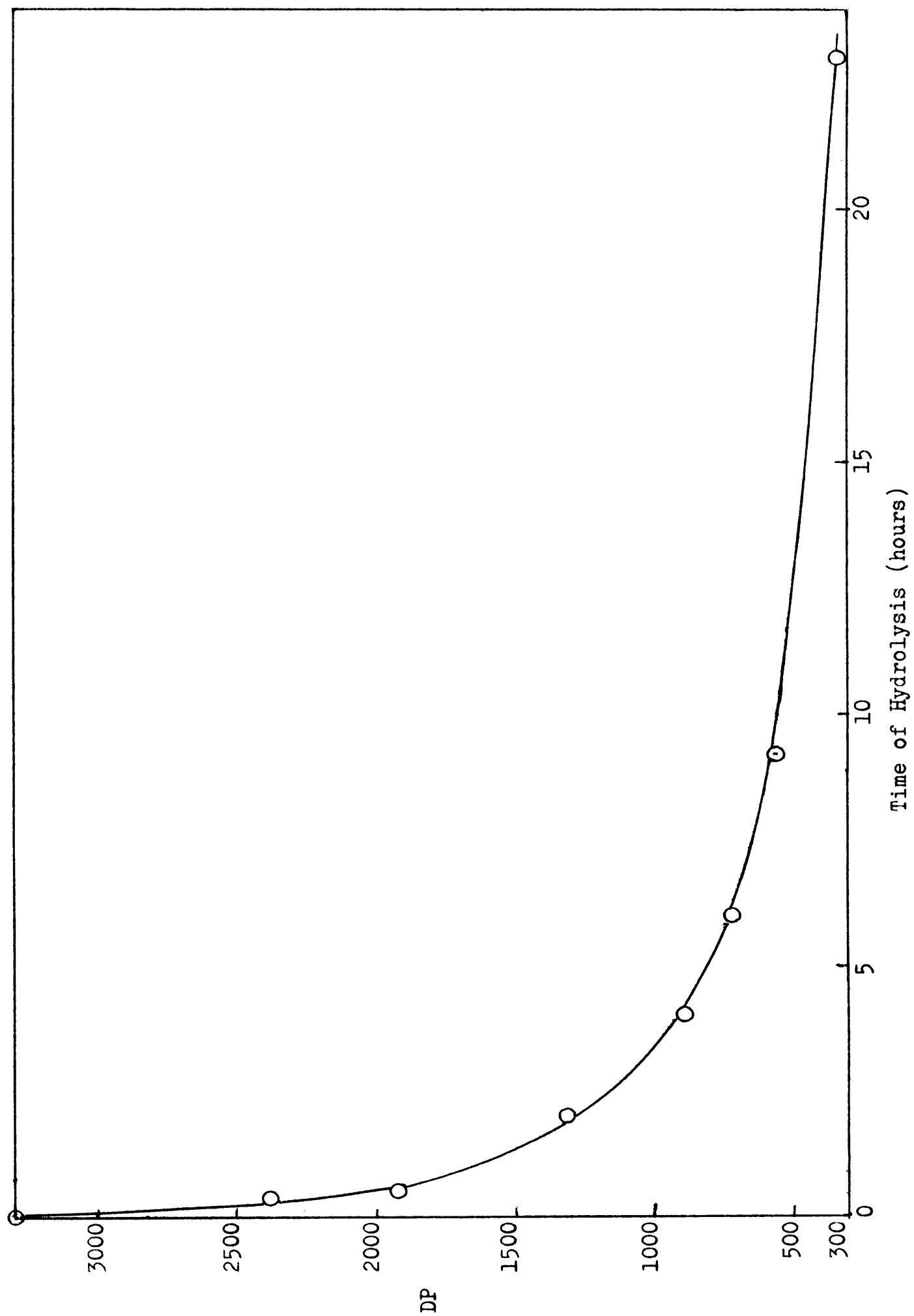


FIGURE 3.1. ACID HYDROLYSIS OF COTTON LINTERS.

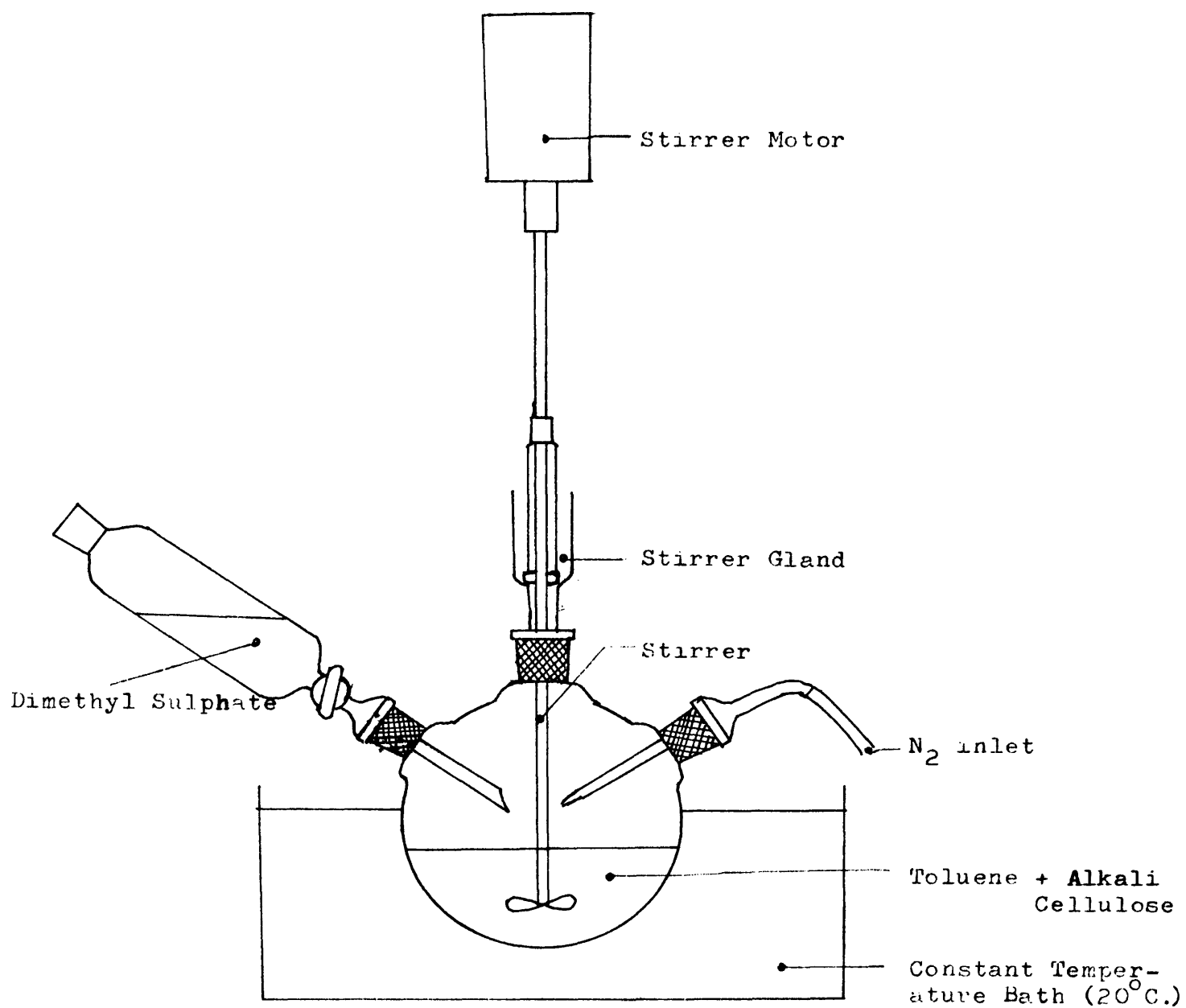
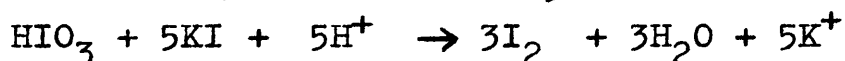
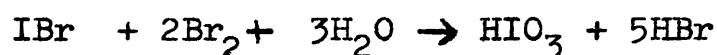
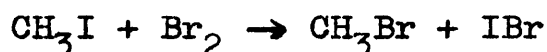


FIGURE 3.2. THE METHYLATION APPARATUS.

and washed with 25 ml of 10% acetic acid and 100 ml of methanol in portions of 10 ml. Methyl celluloses were collected and dried in a vacuum oven at 68.5°C.

3.2.3.2. Estimation of Methoxyl Content.

Determinations of methoxyl content were carried out by a technique devised by Vieböck and Brecker (51), which is based on the original method of Zeisel's (52). This method is based on iodometric estimation of HIO_3 produced during the reaction between cellulose ether and HI, see the following reaction scheme:



The apparatus used is shown in Figure 3.3., and the reagents are given as follows:

- (1) Potassium acetate in acetic acid. 100 g of A.R. anhydrous potassium acetate were dissolved in one litre of solution containing 900 ml of glacial acetic acid and 100 ml of acetic anhydride.
- (2) 5 ml of bromine were dissolved in 145 ml of 10% solution of potassium acetate in acetic acid. A fresh solution was used every week.
- (3) KI, analytical reagent grade, (A.R.).
- (4) NaOAc solution. 250 g of A.R. anhydrous sodium acetate were dissolved in one litre of distilled water.
- (5) Formic acid. Analytical reagent grade, 90% solution, specific gravity 1.20.

- (6) Hydroiodic acid, HI. Analytical reagent, constant boiling mixture, specific gravity 1.7. Boiling point 126-127°C. Pure samples were obtained from the British Drug Houses Ltd., Poole.
- (7) Approximately 0.1 N sodium thiosulphate solution, standardised against 0.1 N iodine solution which in turn was standardised against 0.1 N arsenious oxide.
- (8) Approximately 10% solution of sulphuric acid, prepared by adding 60 ml of concentrated H_2SO_4 to 940 ml of distilled water.
- (9) An aqueous suspension of red phosphorus, prepared by adding about 32 g of A.R. red phosphorus to 50 ml of distilled water.
- (10) CO_2 gas, supplied from a commercial cylinder fitted with a reducing valve.

Finely divided methyl cellulose samples, previously dried in a vacuum oven, were filled into gelatin capsules of known weight and then weighed. The trap of the micro determination apparatus (Figure 3.3.) was filled with a suspension of red phosphorus through the cup. The trap was rinsed with a little distilled water until half full, then closed with a cork. 6-7 ml of bromine-potassium acetate-acetic acid mixture were added to the first absorption tube and 10-12.5 ml to the second one. The gelatin capsule containing the methyl cellulose sample was dropped into the boiling flask containing a few chips of porous tile. 6 ml of hydroiodic acid were run into the flask which was immediately attached to the air condenser with a spring. The glass joint was sealed off by means of a few drops of HI. Throughout the operation, CO_2 gas was allowed to issue

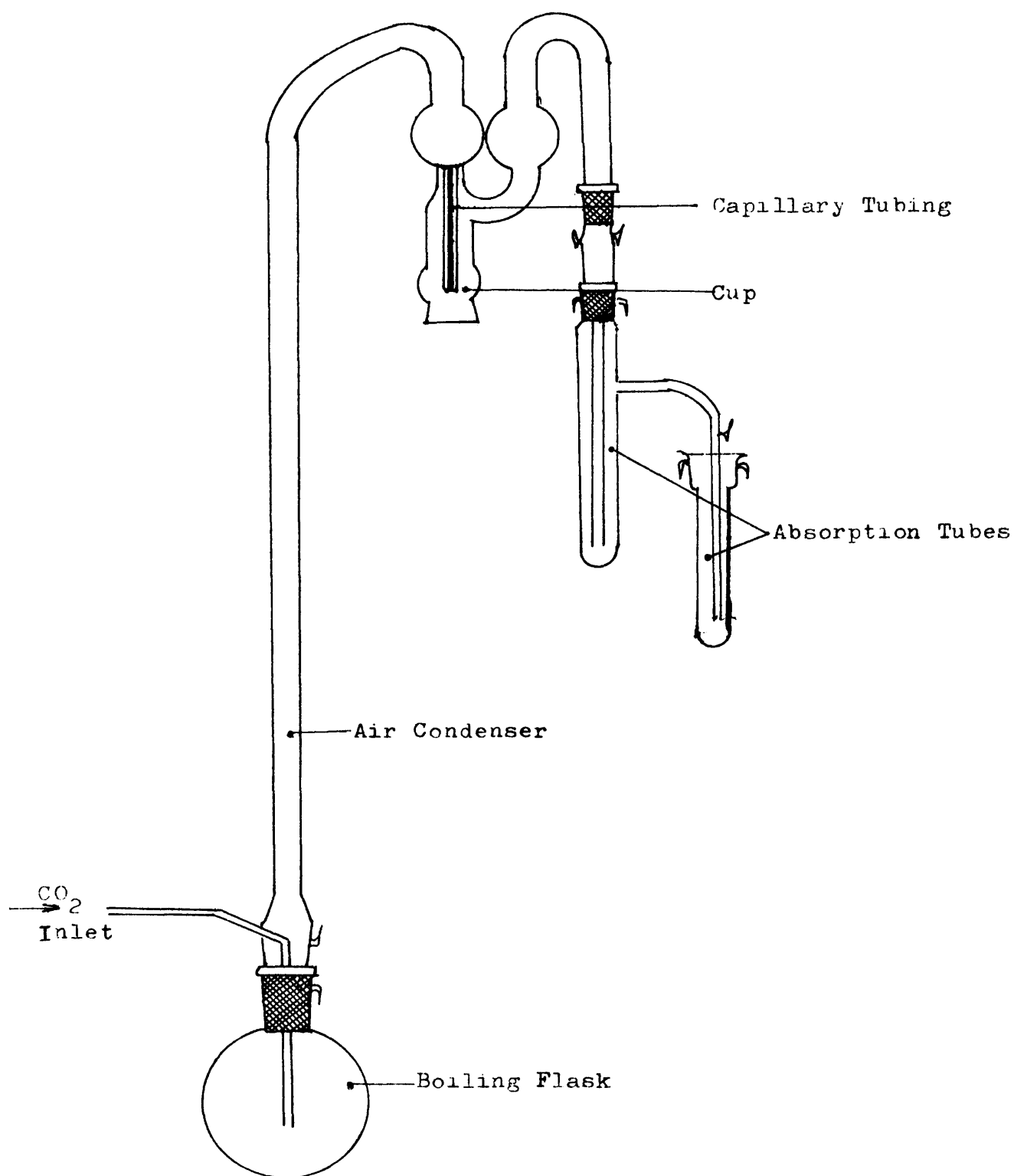


FIGURE 3.3. APPARATUS FOR THE METHOXYL DETERMINATION.

from the cylinder at a rate of approximately 2 bubbles per second; boiling was continued for 40 minutes.

The contents of the absorption tubes were transferred into 500-ml conical flasks containing 10 ml of sodium acetate solution. The contents were then diluted to 125 ml with distilled water, and formic acid was added dropwise with swirling until the colour of bromine disappeared. Three more drops of formic acid were added and the conical flasks, with the contents, were allowed to stand for three minutes. Afterwards three grams of KI and 15 ml of 10% H_2SO_4 were added to the flasks. Liberated iodine was titrated with the standardised thiosulphate solution using fresh starch solution as indicator. A blank determination without the ether was also carried out.

Percentage methoxyl content was calculated from the following equation:

$$\% \text{ OMe} = \frac{517.2 \times a \times n}{w}$$

where,


n is the normality of thiosulphate solution,

a is the volume of thiosulphate solution (ml),

w is the dry weight of methyl cellulose (mg).

The corresponding values of degree of substitution were calculated from the following:

$$\text{D.S.} = \frac{1.62 \times \% \text{ OMe}}{31 - 0.14 \times \% \text{ OMe}}$$

To check the accuracy of the measurements the methoxyl content of pure vanillin, , was determined and compared with the theoretical value. The methoxyl content of this substance is 20.39%, whereas a measured value was 20.27% (Appendix Table X).

3.2.3.3. Results and Discussions.

3.2.3.3.1. Effects of Pre-swelling, Methylating Reagent Concentration and Time on Degree of Substitution.

The object of the work was to survey the effects of these variables so that a hydrocellulose could be methylated quickly and reproducibly to a suitable extent.

The effect of varying the time of methylation when the ratio of cellulose to dimethyl sulphate is 1 g: 5 ml is shown in Figure 3.4. (See Appendix Table XI) for various concentrations of alkali used in the initial alkali steep. It will be seen that for different alkali concentrations reaction is substantially complete in four hours. The extent of reaction is seen to be strongly dependent on the alkali concentration which may be interpreted as due either to an increase in accessibility of the cellulose, or to the partial exhaustion of the alkali during the course of the reaction, or both.

The effect of varying the concentration of dimethyl sulphate at one level of alkali concentration (2.5 N) is shown in Figure 3.5 for the hydrocellulose and for mercerised hydrocellulose. (See also Appendix Table XI.) It may be seen that maximum extent of reaction is attained when the ratio of cellulose to dimethyl sulphate is 1 g: 5 ml in 50 ml . toluene. In addition the mercerised hydrocellulose has a final extent of reaction more than twice that of the straight hydrocellulose. It would appear, therefore, that the effect of varying the concentration of the alkali for steeping (Figure 3.4.) is largely the result of changes in accessibility rather than decrease in alkali concentration during methylation.

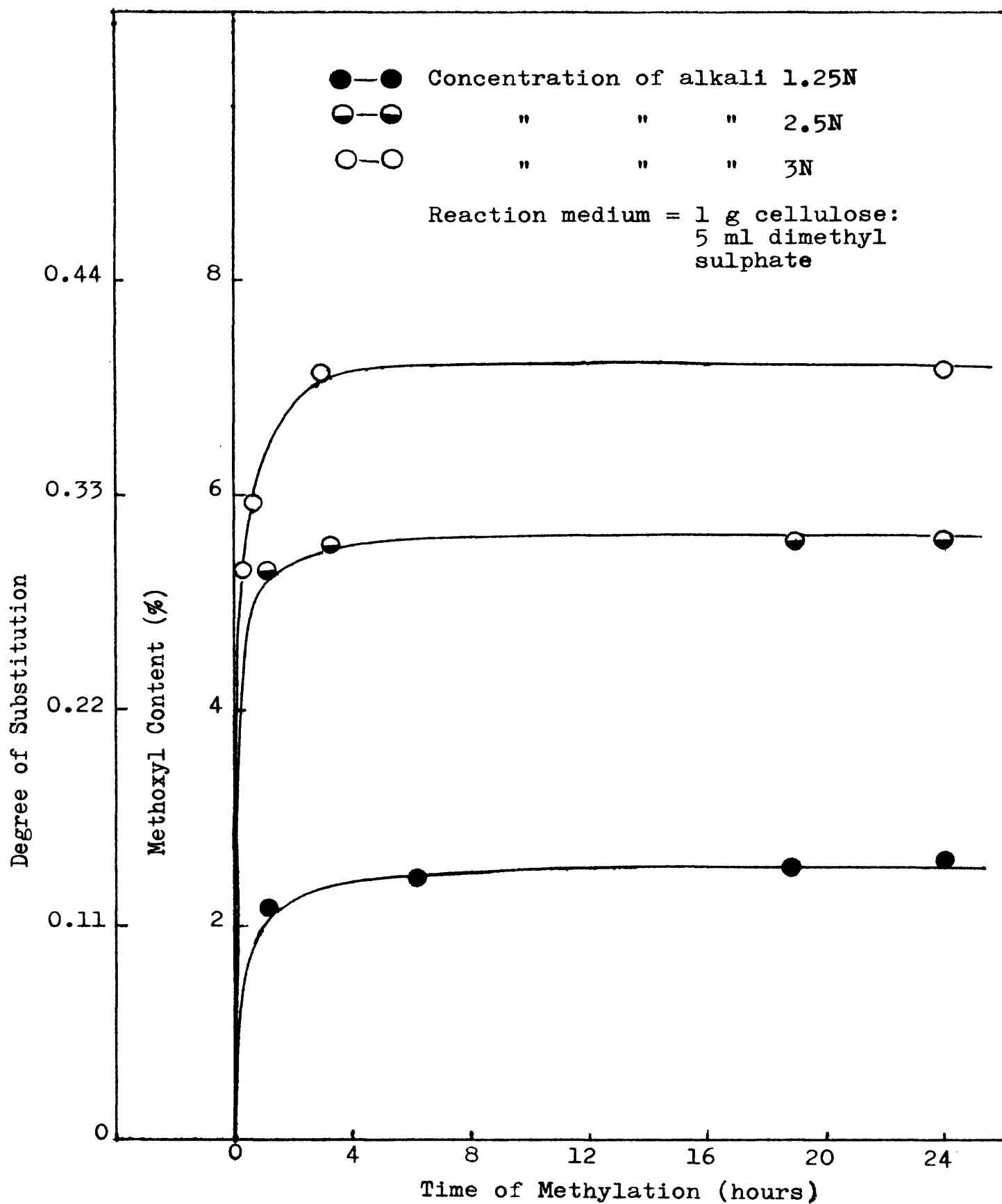


FIGURE 3.4. RATES OF METHYLATION OF HYDROCELLULOSE.

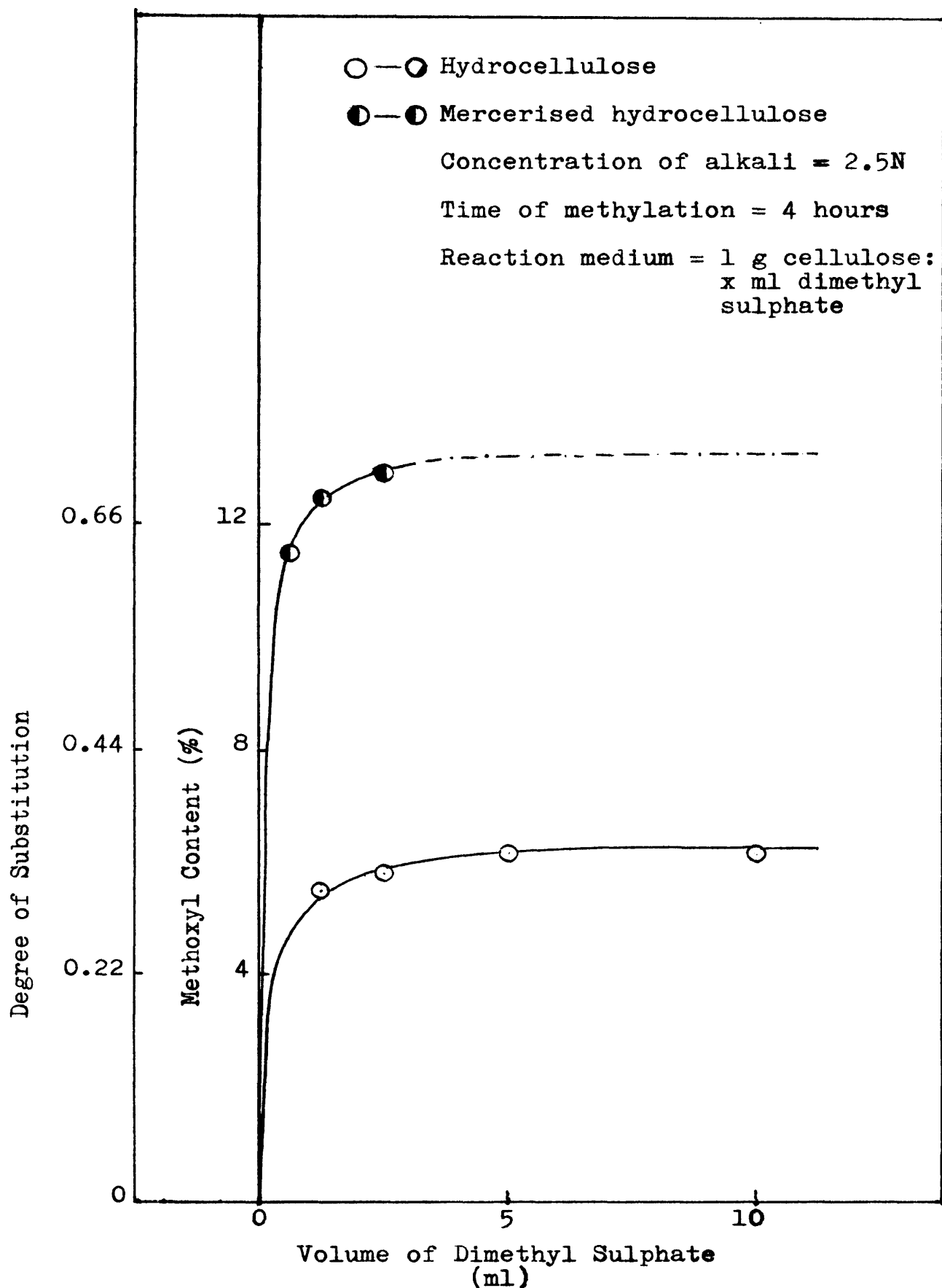


FIGURE 3.5. EFFECT OF DIMETHYL SULPHATE CONCENTRATION ON METHYLATION.

It was decided to investigate the effect of the alkali concentration used for steeping in greater detail, keeping the time of reaction and concentrations of reacting species constant. The results are shown in Figure 3.6., and Appendix Table X, for cotton linters, hydrocellulose and mercerised hydrocellulose. Comparing the mercerised and unmercerised hydrocelluloses it may be seen that the methoxyl contents of the unmercerised hydrocellulose rise relatively sharply when the alkali concentration is between 3 and 4 normal, hence it would be difficult to reproduce a given degree of substitution in this range. This sudden change is not found for the mercerised hydrocellulose since it has previously been subjected to alkali of a higher concentration. There is seen to be no appreciable difference between the cotton linters and the hydrocellulose which suggests that acid treatment does not seriously change the morphology of the cellulose.

From these results it was decided that for the purpose of preparing methylated hydrocellulose for viscose rayon spinning, the accessibility of the hydrocellulose should be varied by pre-swelling in caustic soda in the concentration range up to 3.125 N; that the ratio of dimethyl sulphate to cellulose should be 5 ml: 1 g in 50 ml toluene; and that the time for reaction should be four hours. The details of these samples are given in the following table:

TABLE 1X

Partially Methylated Hydrocellulose Samples

Alkali used in steeping (N)	Methoxyl content (%)	Degree of Substitution D.S.
1.25	2.78	0.14
2.5	5.77	0.31
3.125	7.87	0.43

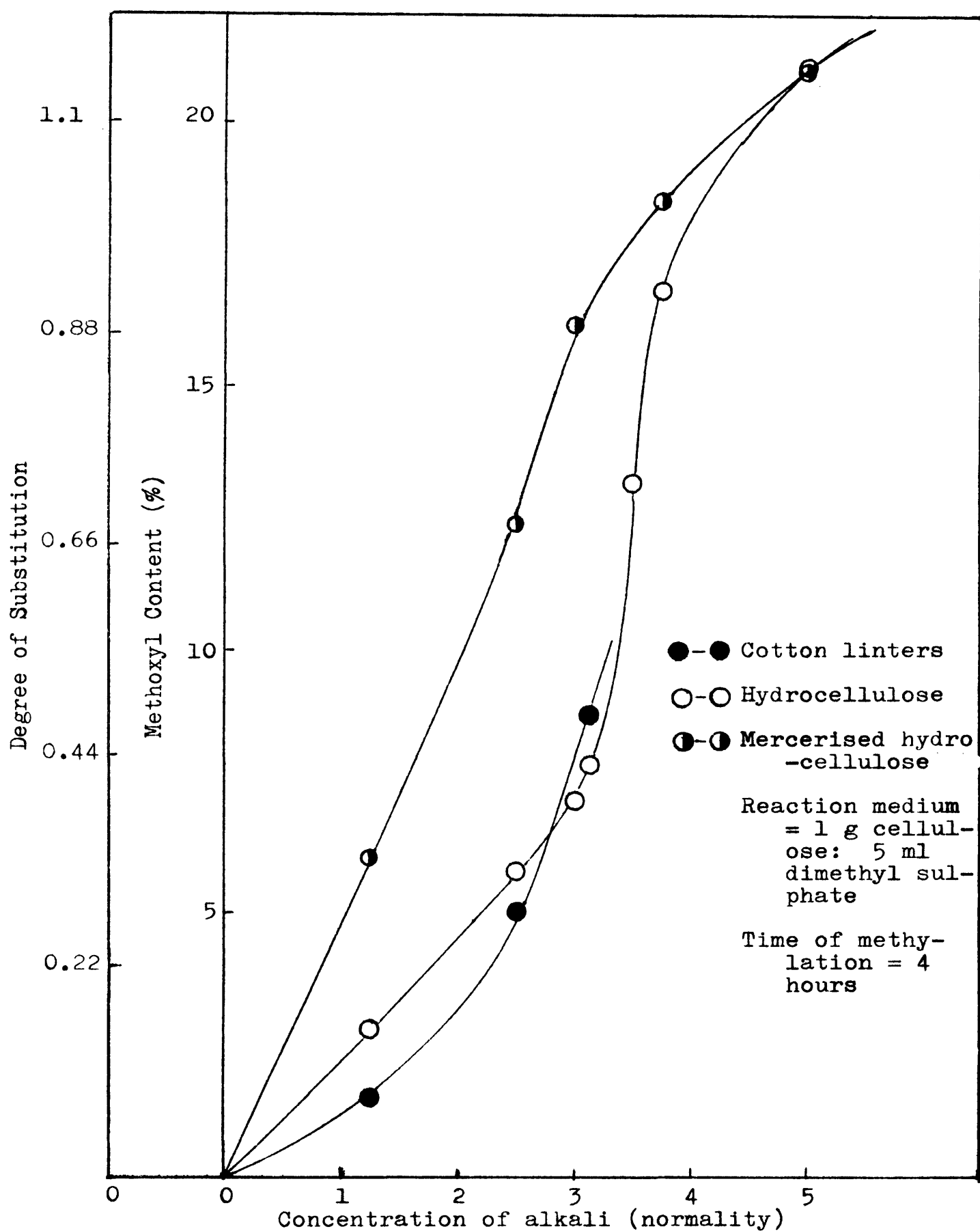


FIGURE 3.6. EFFECT OF ALKALI CONCENTRATION ON METHYLATION.

3.2.3.3.2. Changes in Weight and Fluidity During Methylation.

When hydrocellulose and cotton linters were methylated the weight of cellulose used and the weight of product were determined. The weight increases plotted as a function of methoxyl content are shown in Figure 3.7. (Appendix Table XIII.) together with the theoretical relation. It will be seen that there is a loss in weight which can only be attributed to either solution of some cellulose during the pre-swelling step or solution of degradation products produced during methylation, particularly during purification after methylation.

The problem was investigated further by determining the weight losses during the alkali steeping process only. Figures are given in Table X and are seen to be comparable in magnitude with losses incurred in the complete methylation procedure.

TABLE X
Weight Losses During Alkali Steeping

Concentration of alkali (N)	Methoxyl content after methylation (%)	Weight loss during steeping (%)	Weight loss from Figure 3.4.
1.25	2.78	.12	0
2.5	5.77	.84	2.0
3.125	7.87	1.92	2.3

The weight losses are most serious from the point of view of changing the degree of polymerisation of the hydrocellulose. For this reason changes in cuprammonium hydroxide fluidity were looked for. Fluidities of the methyl celluloses as a function of concentration of alkali used in pre-swelling are shown in Figure 3.8. (Appendix Table XIV) for methylated celluloses derived from hydrocellulose, mercerised hydrocellulose, and

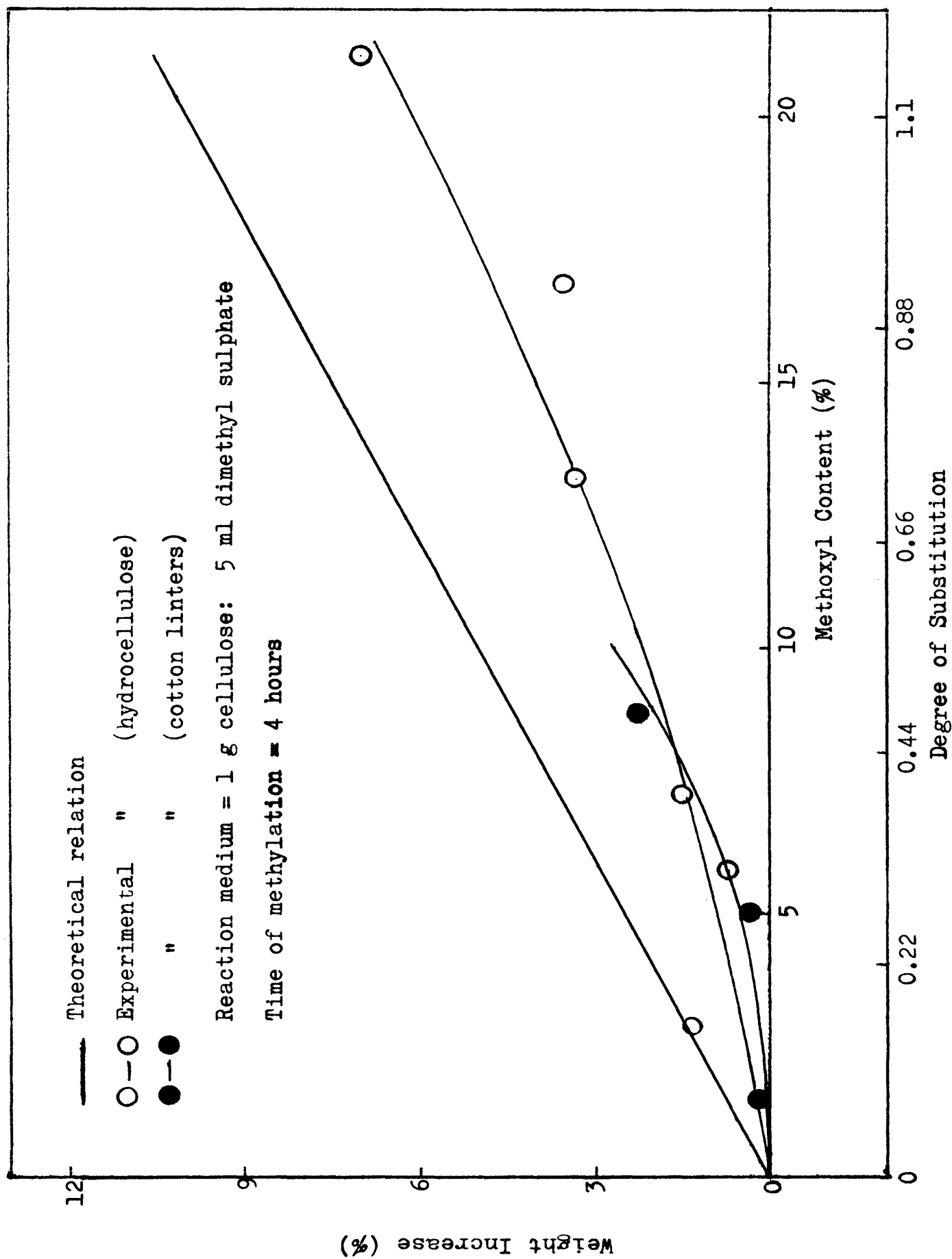


FIGURE 3.7. PERCENTAGE WEIGHT INCREASE DURING METHYLATION.

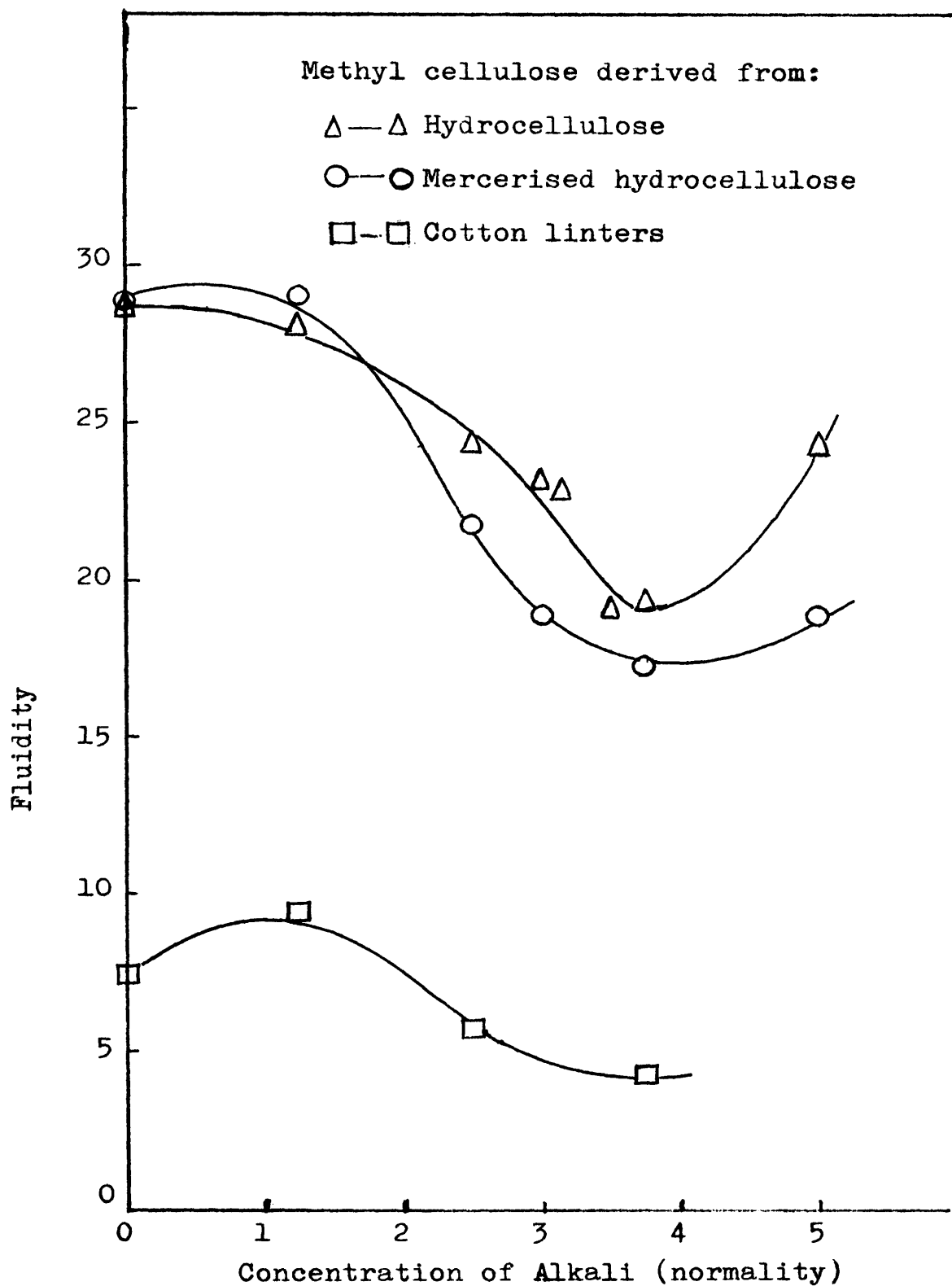


FIGURE 3.8. EFFECT OF ALKALI CONCENTRATION ON FLUIDITIES OF METHYL CELLULOSES.

cotton linters. All three sources of cellulose are seen to give a similar relation with a minimum at about 3.5 N caustic soda, that is the region where maximum change occurs in accessibility. The characteristic shapes of the curves may be interpreted in terms of a small rise in fluidity owing to the rapid rate of oxidative degradation at low alkali concentrations (cf. Figure 3.9.) during hand shredding of the alkali cellulose prior to methylation, followed by a decrease in fluidity resulting from loss of low DP material at higher alkali concentrations. The subsequent rise in fluidity at still higher alkali concentrations, which it should be noted is determined by one experimental observation, cannot be explained.

3.2.3.3.3. Control of Fluidity of Methylated Hydrocellulose.

From the above experimental data it is clear that the fluidities of methylated celluloses vary according to the concentration of alkali used in their preparation. For the purpose of comparing the properties of rayons spun from these products it is necessary to ensure that the fluidity and hence the DP is reasonably constant. In order to achieve this end the alkali celluloses prepared for methylation were aged in air until their fluidities after methylation rose to 29, which is equivalent to a DP of 600 (49).

The results of studying rates of ageing at different alkali concentrations and two temperatures are shown in Figures 3.9 and 3.10 respectively. See also Appendix Table XV. The rate of ageing is seen to be strongly dependent on alkali concentration, being most rapid at low concentrations. The time of ageing required to achieve a fluidity is experimentally

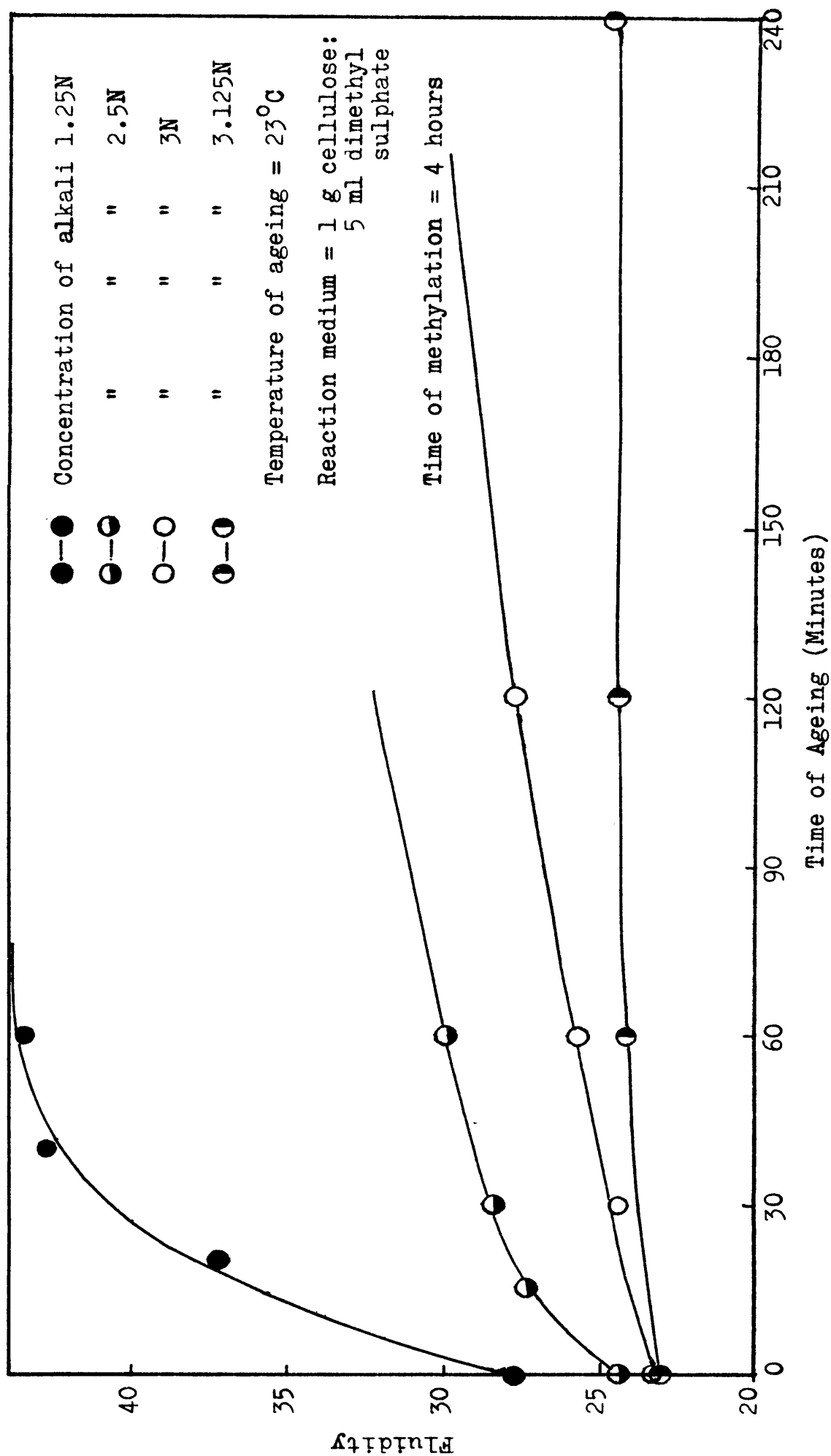


FIGURE 3.9. EFFECT OF AGEING OF ALKALI CELLULOSE ON FLUIDITIES OF METHYL CELLULOSES.

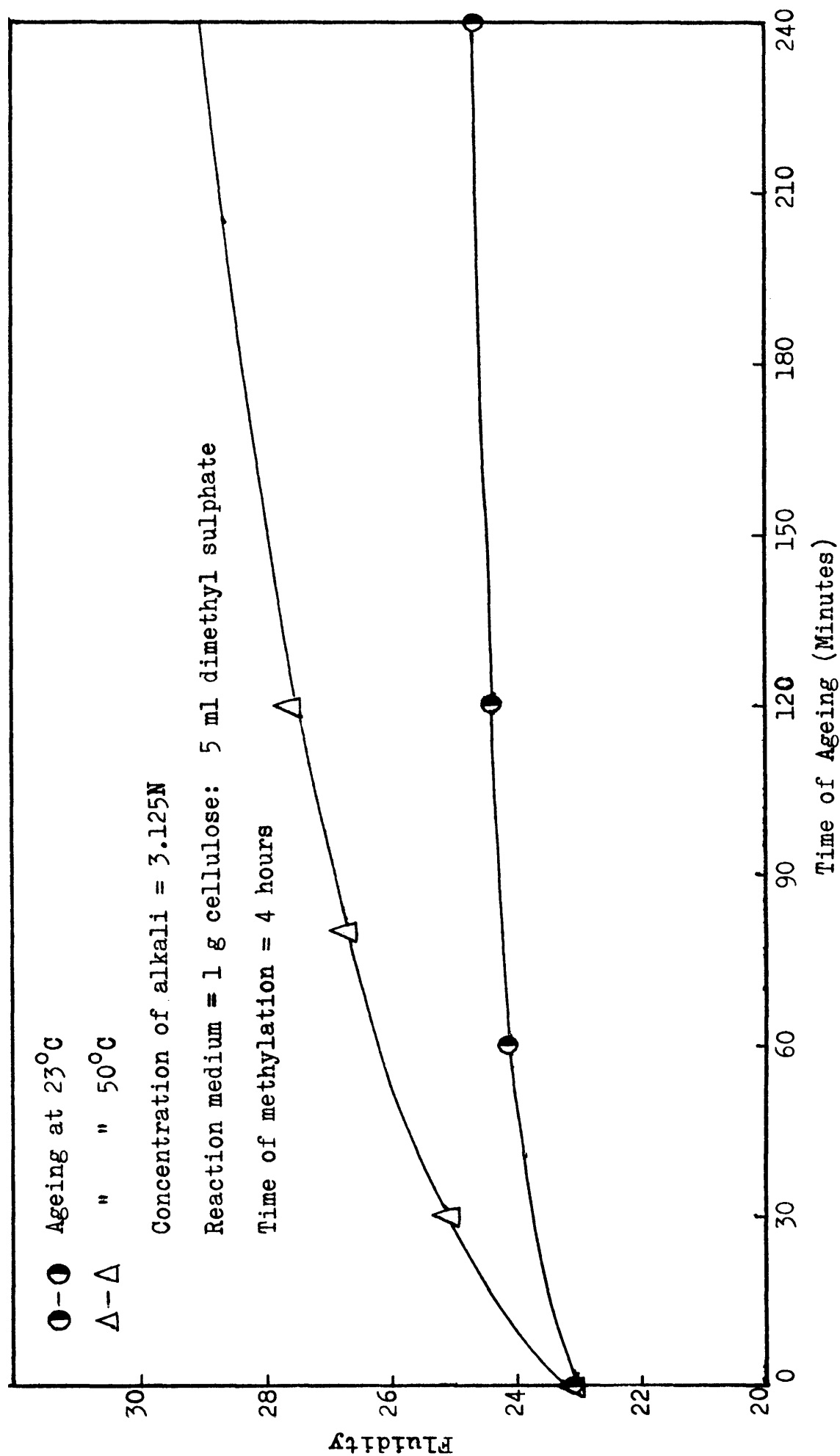


FIGURE 3.10. EFFECT OF TEMPERATURE ON THE DURATION OF AGEING OF ALKALI CELLULOSE USED IN METHYLATION.

convenient at 23°C for alkali concentration up to 3.125 N (Figure 3.9.), but above this concentration it was found convenient to increase the temperature to 50°C. (Figure 3.10).

3.2.3.3.4. Structure of Partially Methylated Hydrocellulose.

Since the hydrocellulose has only been partially methylated the fine structure of the derivatives will be dependent on the structure of the initial hydrocellulose and the extent of swelling prior to methylation.

Theories on the fine structure of cotton have ranged from Nageli's (53) theory of micelles built into a structure like bricks in a wall to micelles with entangled fringes, to the fringed-micellar theory to a fringed-fibrillar, and finally to the crystalline-fibrillar theory. The fringed-micellar theory held sway for many years and is still generally considered to be adequate for regenerated cellulose. But as early as 1938 Frey-Wyssling (and Farr before him) (54) began to doubt the validity of this concept for native cellulose until at this date the general concensus of opinion is that native cellulose is composed of crystalline fibrils. In this type of structure there is no cellulose that can be considered as non-crystalline in the manner of the amorphous cellulose in the fringed-micellar theory. There may, however, be some 5-10 per cent of the cellulose which is in a para-crystalline state, that is derivating only slightly from the crystalline lattice, on the surface of the fibrils and in small regions along the length of the fibrils. A further feature of the structure, repeatedly emphasised by Frey-Wyssling, is the system of voids bounded by fibrillar surfaces, to which Ambronn (54) drew attention to as early as 1896. Many reactions attributed to

the amorphous regions on the basis of the fringed-micellar theory are equally well explained in terms of long narrow voids of varying width. These coarse voids are accessible to large molecules and particles; in addition a finer system of voids seems to exist after swelling.

One of the basic concepts of the fringed-micellar theory is that molecules pass through several crystalline regions, hence alternate portions of the lengths of same molecules are accessible to methylation. If one accepts the fringed-fibrillar model with branching fibrils then some molecules are within crystalline regions for part of their length and therefore inaccessible to methylation but become accessible when they subsequently lie on the surface of a branching fibril. A structure based on the theory of crystalline fibrils with long narrow voids and intermittent regions of para-crystalline cellulose also offers an opportunity for the formation of a block copolymer type of structure following partial methylation. Methylation may occur in the para-crystalline regions, which are considered to be short zones along the length of the fibrils, and particularly on the fibrillar surfaces bounding the voids. Since there is no reason to suppose that any one void will run the entire length of a fibril, and since molecules may begin and end on a fibril surface, there will be an opportunity for part of the length of a surface molecule to be methylated while the following portion remains inaccessible. The extent of block copolymer formation will also be influenced by the extent of swelling in caustic soda to produce alkali cellulose for reaction with dimethyl sulphate, since such swelling is known to open up an additional series of fine voids in the structure.

It is very difficult if not impossible at the present time to prove positively that the postulated copolymer-type structure exists in some molecules following partial methylation, or to deduce the lengths of the blocks. If one accepts that cellulose consists of molecules aggregated into fibrils then it is only the surfaces of these fibrils that are methylated and become accessible to acid hydrolysis, in other words only a fraction of the cellulose will be methylated. The limiting DP of the methylated celluloses after acid hydrolysis should therefore be largely independent of the extent of methylation. Values for three methylated hydrocelluloses shown in Table XI confirm this expectation. (See also Appendix Table XVlll.)

TABLE XI
Limiting-Degree of Polymerisation of Methyl Cellulose

Concentration of alkali used in steeping (N)	Methoxyl content (%)	Limiting-degree of polymerisation (DP)
0	0	138 (Hydro- cellulose)
1.25	2.78	137
2.5	5.77	137
3.125	7.87	130

Weight and methoxyl content losses during acid hydrolysis with 2 N HCl at 100°C are shown in Figures 3.11 and 3.12 respectively and in Table Xll. (See Appendix Table XVl). Weight loss increases with increase of alkali concentration used in methylation, in other words originally inaccessible regions, are penetrated by the alkali used during methylation and maintained in the accessible state by the introduction of

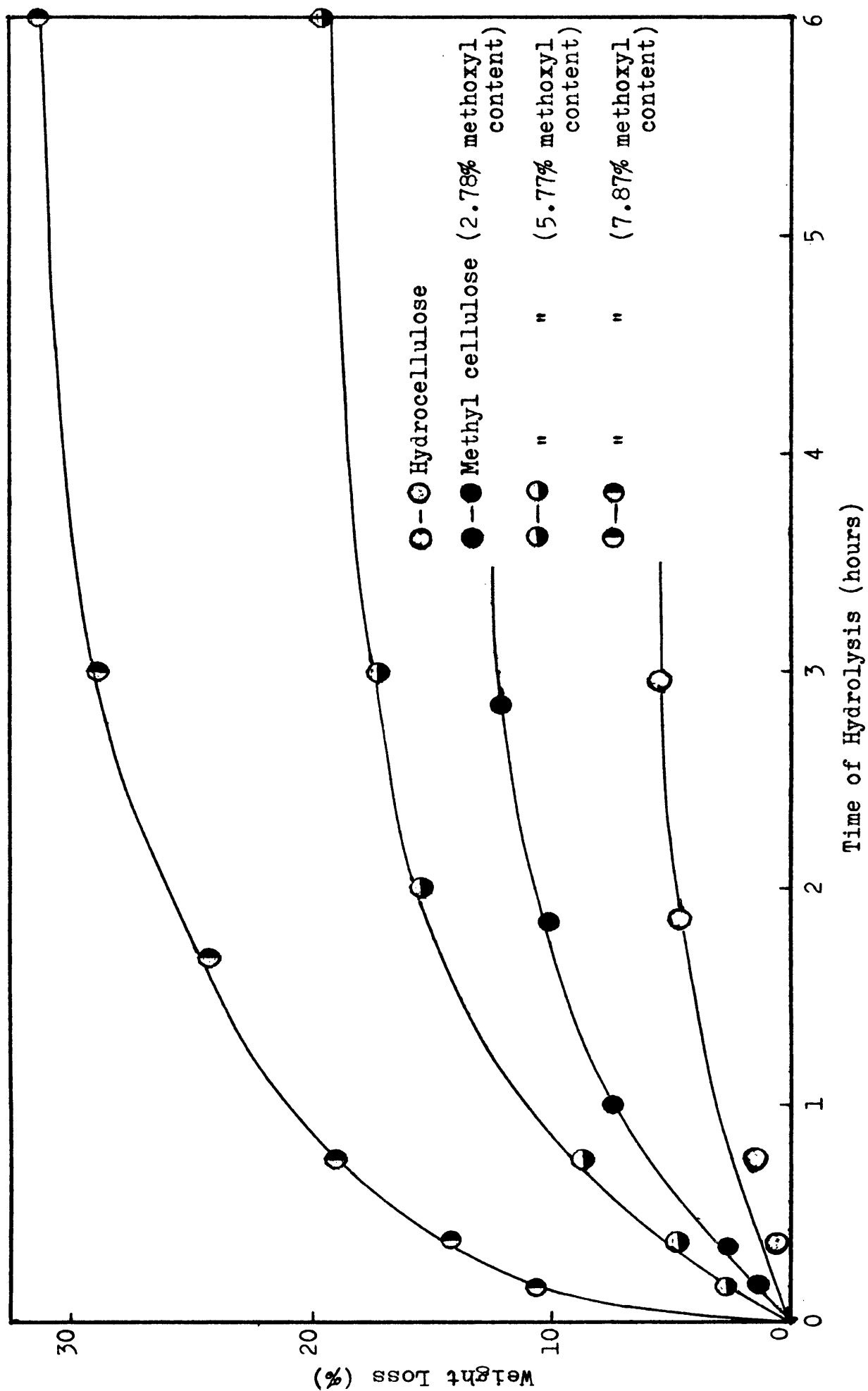


FIGURE 3.11. EFFECT OF ACID HYDROLYSIS ON THE PERCENTAGE WEIGHT LOSS.

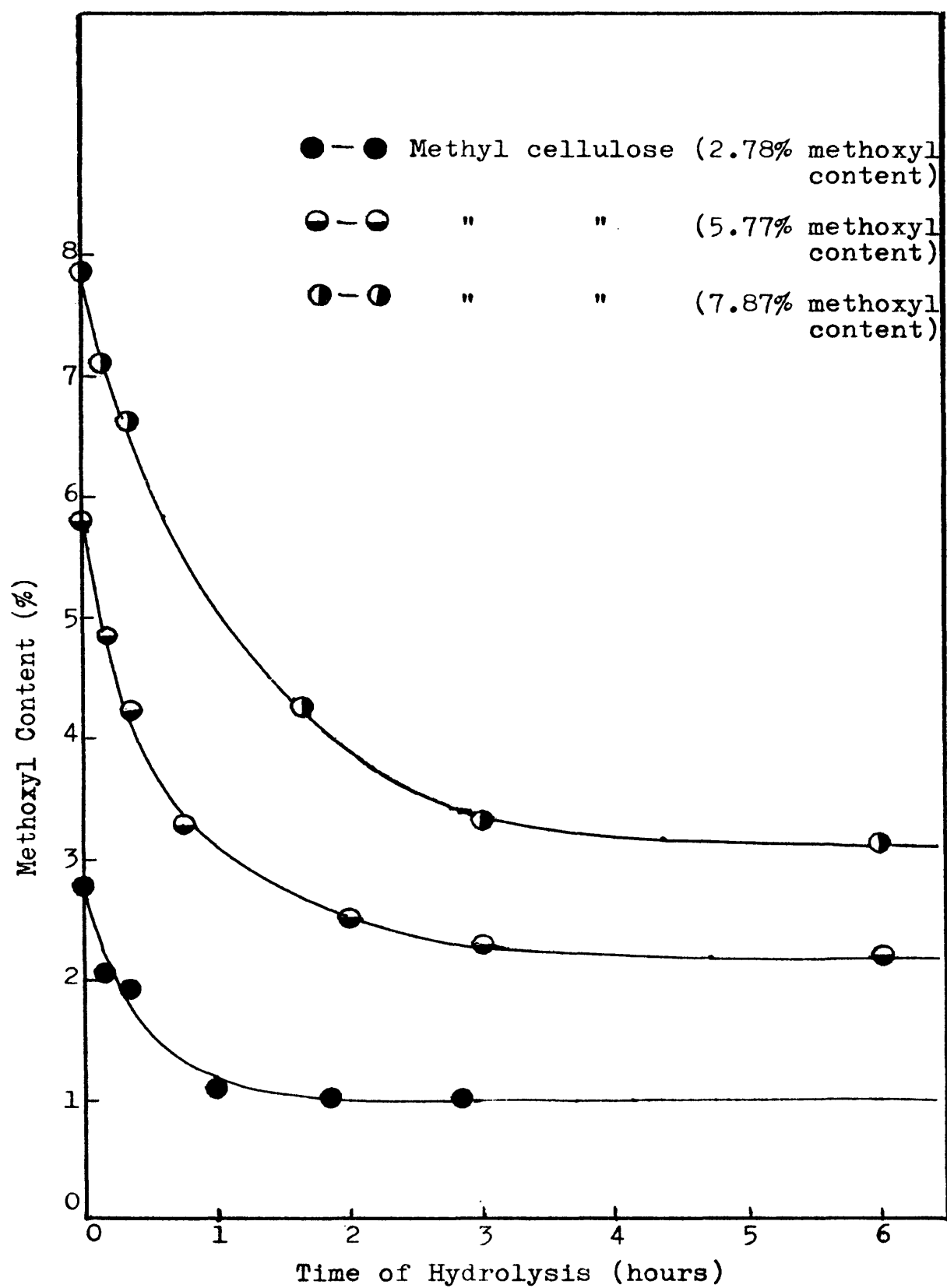


FIGURE 3.12. EFFECT OF ACID HYDROLYSIS ON THE METHOXYL CONTENTS OF METHYL CELLULOSES.

methoxyl groups. However since the methoxyl contents do not fall to zero, but very approximately to one-third of the initial values, some of the methylated anhydro-glucose units lose their accessibility to acid. From a private communication (55) it has been learned that this resistance to hydrolysis is found with some units methylated in the 2 and 6 positions only, apparently owing to hydrogen bonding of the remaining free hydroxyl groups. It is noticeable, too, that the time for both weight and methoxyl losses to reach a minimum level increases with increase of initial methoxyl content. This may be related to the removal of an increasing mass of material or it may point to methylation having occurred in decreasingly accessible regions.

TABLE XI1
Effect of Acid Hydrolysis on Methyl Celluloses

Original methoxyl content (%)	Time for weight loss to reach equilibrium (hours)	Levelling-off methoxyl content (%)	Levelling-off weight loss (%)	*Ratio of accessible to inaccessible cellulose
0	3	0	5.6	.06
2.78	3.5	1.1	12.0	.11
5.77	6	2.2	19.5	.19
7.87	12	3.1	34.4	.45

*This ratio is obtained from the percentage weight losses during acid hydrolysis by making an allowance for the weight of methoxyl groups both in residues and the hydrolysates.

Figures 3.13 and 3.14 compare weight and methoxy losses respectively during hydrolysis in 2 N HCl at 100°C for the methylated hydrocellulose containing 7.87% methoxyl before

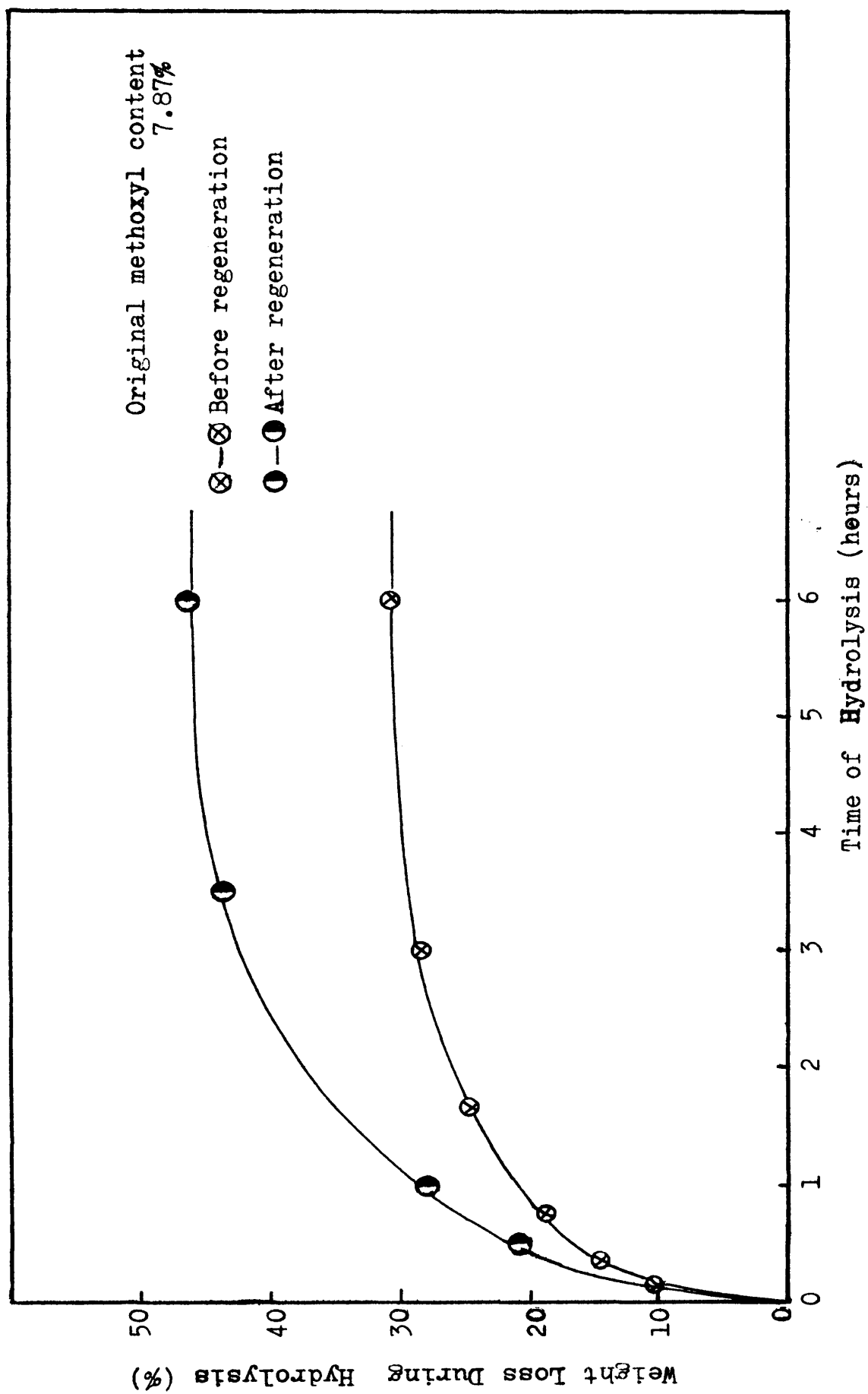


FIGURE 3.13. EFFECT OF REGENERATION ON THE WEIGHT LOSS DURING ACID HYDROLYSIS.

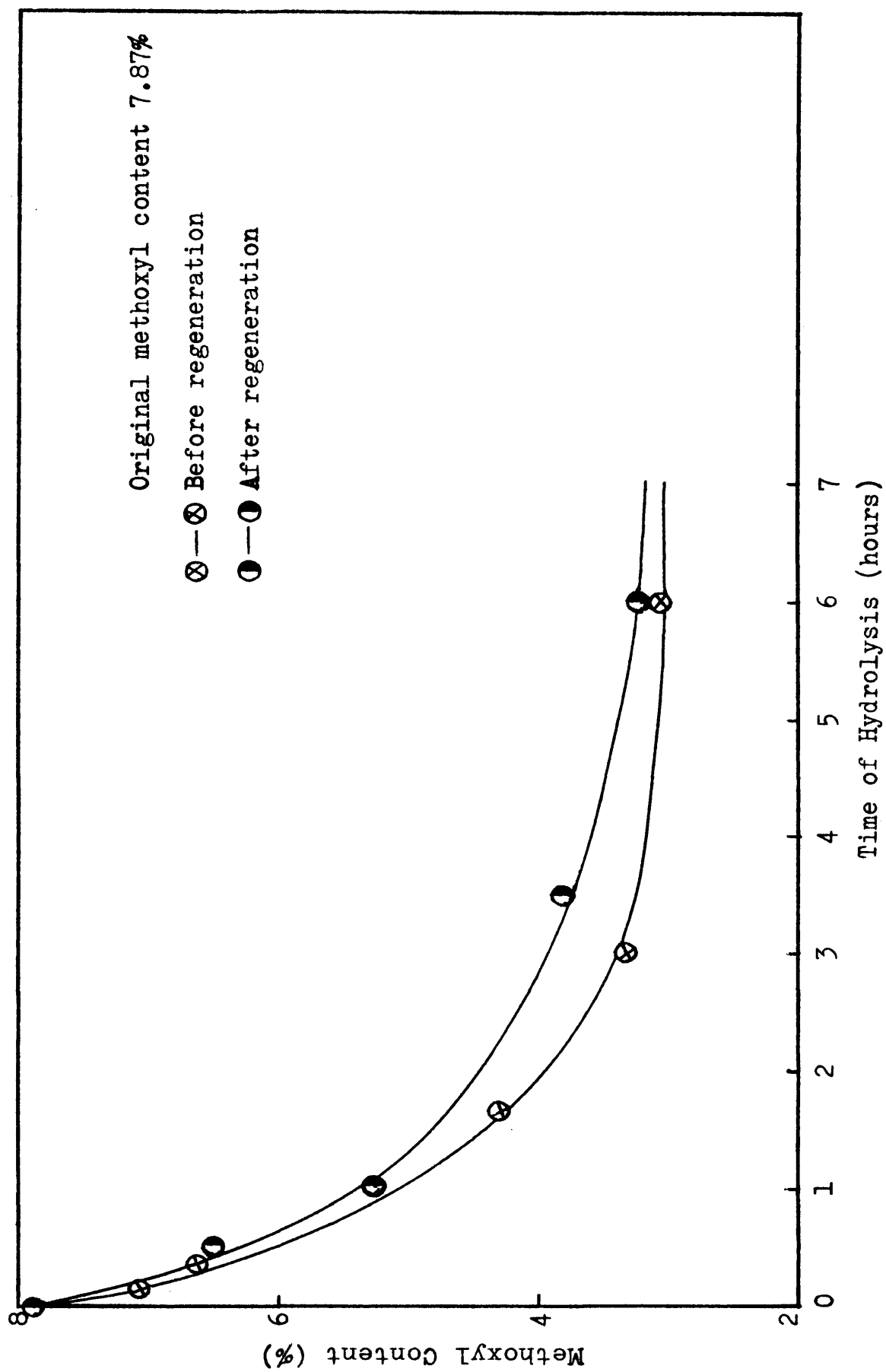


FIGURE 3.14. EFFECT OF REGENERATION ON THE LOSS OF METHOXYL GROUPS DURING ACID HYDROLYSIS.

before and after regeneration from cuprammonium hydroxide solution. (See Appendix Table XVll). The higher weight loss after regeneration is to be expected since the proportions of crystalline material will have decreased appreciably. On the other hand the similarity of the curves showing changes in per cent methoxyl content with time of hydrolysis are surprising since they suggest a similarity of structure for the original and regenerated products.

3.3. The Effect of Partial Methylation of Cellulose on the Properties of Viscose.

3.3.1. Introduction.

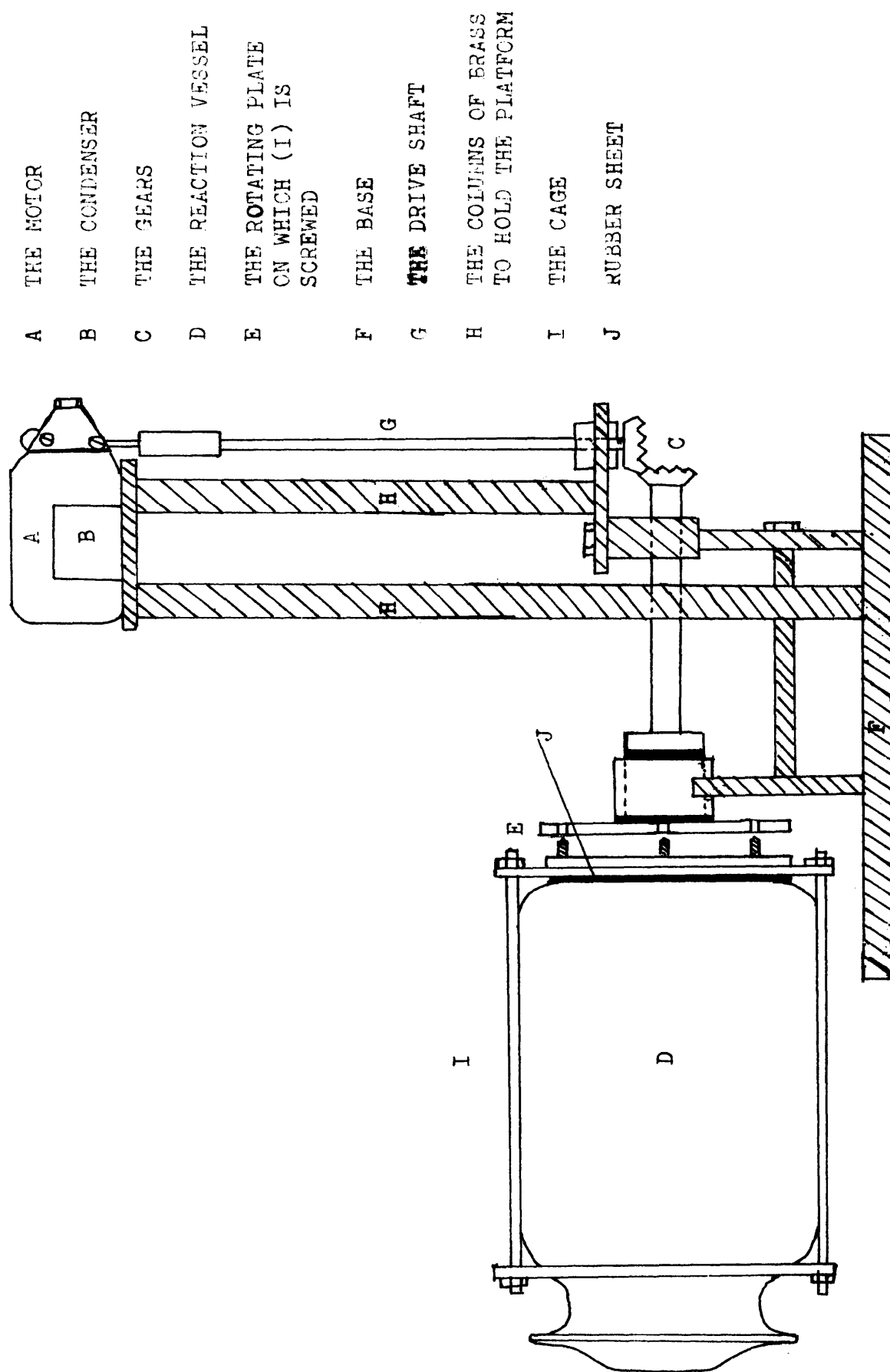
Viscoses were prepared from hydrocellulose (DP = 600) derived from cotton linters and from the same hydrocellulose which had been partially methylated. Products with methoxyl contents of 2.78, 5.77, and 7.87 per cent were used. The degrees of polymerisation of these products were adjusted to be approximately 600. The effects of varying the methoxyl contents on rates of ripening and on the viscosities of the viscoses were examined.

3.3.2. Experimental.

3.3.2.1. Preparation of Viscose.

The preparation of viscose requires the impregnation of cellulose with caustic soda solution of mercerising strength at a fixed temperature; the removal of excess caustic soda by pressing; the addition of the required amount of carbon disulphide; slow churning of the reaction mass at constant temperature to produce sodium cellulose xanthate; removal of excess CS₂ by vacuum; and the dissolution of the product with the aid of stirring in dilute caustic soda.

Most of these steps were done in a 2-litre reaction flask with flanged top and ground glass lid clamped in a metal cage, which could be mounted vertically or revolved at 4 r.p.m. about a horizontal axis while submerged in a thermostat bath. The equipment is shown in Figure 3.15. The pressing out of excess caustic soda was done by means of a piston and cylinder made of polypropylene; pressure was applied by means of a hand-operated



A THE MOTOR

B THE CONDENSER

C THE GEARS

D THE REACTION VESSEL

E THE ROTATING PLATE
ON WHICH (I) IS
SCREWED

F THE BASE

G THE DRIVE SHAFT

H THE COLUMNS OF BRASS
TO HOLD THE PLATFORM

I THE CAGE

J RUBBER SHEET

FIGURE 3.15. VISCOSITY-MAKING APPARATUS.

hydraulic press. The polypropylene cylinder had numerous small holes (diameter about 3 mm) bored radially through its wall to allow solution to escape. To prevent the plastic cylinder bursting it was contained within a metal cylinder also constructed with numerous escape routes for the caustic solution.

The actual preparation was as follows. Dry hydro-cellulose or methylated cellulose (60 g) were steeped in 1 litre of 18% ^w/w caustic soda solution containing 1% ^v/w Mercerol wetting agent. Steeping was for one hour at 21°C under nitrogen. Mercerol was added because otherwise the methylated products were difficult to wet out. Subsequently, the contents of the flask were emptied into a large sintered funnel and excess alkali solution quickly removed with a water pump. Removal of alkali solution to the desired extent was achieved by pressing as described above to a press factor of 3.

The alkali cellulose was then transferred to another 2-litre flask with flanged neck and shredded as far as possible with a glass rod. Carbon disulphide (15 ml) was added and the flask closed. The contents of the flask were then churned on a horizontal axis within the thermostat bath for 3 hours at 21°C. Subsequently excess CS₂ was removed by applying vacuum to the flask.

The orange-coloured cellulose xanthate crumbs were then added to a stirred solution of caustic soda containing 101.4 g of 18% NaOH solution and 458.4 g of water maintained at 21°C. Stirring was continued and samples were removed for analysis at intervals from 2 hours onwards. The samples were kept in polythene bottles at -20°C until the analysis could be done.

3.3.2.2. Cellulose and Alkali Contents of Viscoscs.

These analyses were according to the methods given in section 2.2.3. See also Appendix Table XLX.

3.3.2.3. Viscosity Measurements.

It is usual to measure the viscosity of viscose by means of the falling-sphere method. Since this method requires about 300 ml of viscose, measurements were made with the Ferranti-Shirley cone and plate viscometer which only requires a few drops of liquid. Measurements were made at 25°C over a range of rates of shear of 167 to 1670 sec⁻¹.

3.3.2.4. Degree of Ripeness - Hottenroth-Number.

The so-called Hottenroth-number is measured in terms of the volume (ml) of a 10% ^w/v solution of ammonium chloride required to gel a solution of 20 g viscose in 30 ml water. During the addition of the NH₄Cl solution the viscose is stirred at a constant rate with an L-shaped glass rod of 7 mm diameter. The end point is judged to be at the stage when the stirrer is removed and no viscose drips from it. The ammonium chloride solution must be added at a constant rate of about 1 ml per 15 seconds.

During ripening there are changes in the extent and distribution of xanthate groups which affect the susceptibility of the viscose to coagulate. This susceptibility is measured by the Hottenroth-number which, despite the apparent crudeness of the method, is remarkably reproducible.

3.3.3. Results and Discussions.

3.3.3.1. Ripening.

The ripening behaviour of viscoses derived from hydrocellulose and methylated hydrocelluloses is shown in Figure 3.16 (Appendix Table XX) for viscoses of the same cellulose and alkali content. It is clear that the rate of ripening is very little affected by the presence of varying quantities of methoxyl groups. The curves are displaced on the time axis because the methoxyl contents of the viscoses differ.

The variation of χ -number with methoxyl content is shown in Figure 3.17 (Appendix Table XXI), the χ -numbers having been determined immediately after the viscoses were prepared. It will be seen that the points for the three methylated products lie on a curve while the χ -number for viscose derived from the hydrocellulose lies below the curve. This same difference is reflected in the rate curves shown in Figure 3.16. The higher χ -numbers of the methylated products are little surprising since there are fewer hydroxyl groups available for xanthation. It can only be concluded that the methoxyl groups reduce the amount of association between hydroxyl groups and thereby increase xanthate formation.

3.3.3.2. Viscosity of Viscos.

The relations between viscosity at 1670 sec^{-1} and times of ripening are shown in Figure 3.18. (See Appendix Table XXI). The curves have the characteristic shape usually found, namely an initial fall in viscosity followed by a slow rise. This change with time is usually attributed to the simultaneous redistribution of the xanthate groups and some loss of xanthate

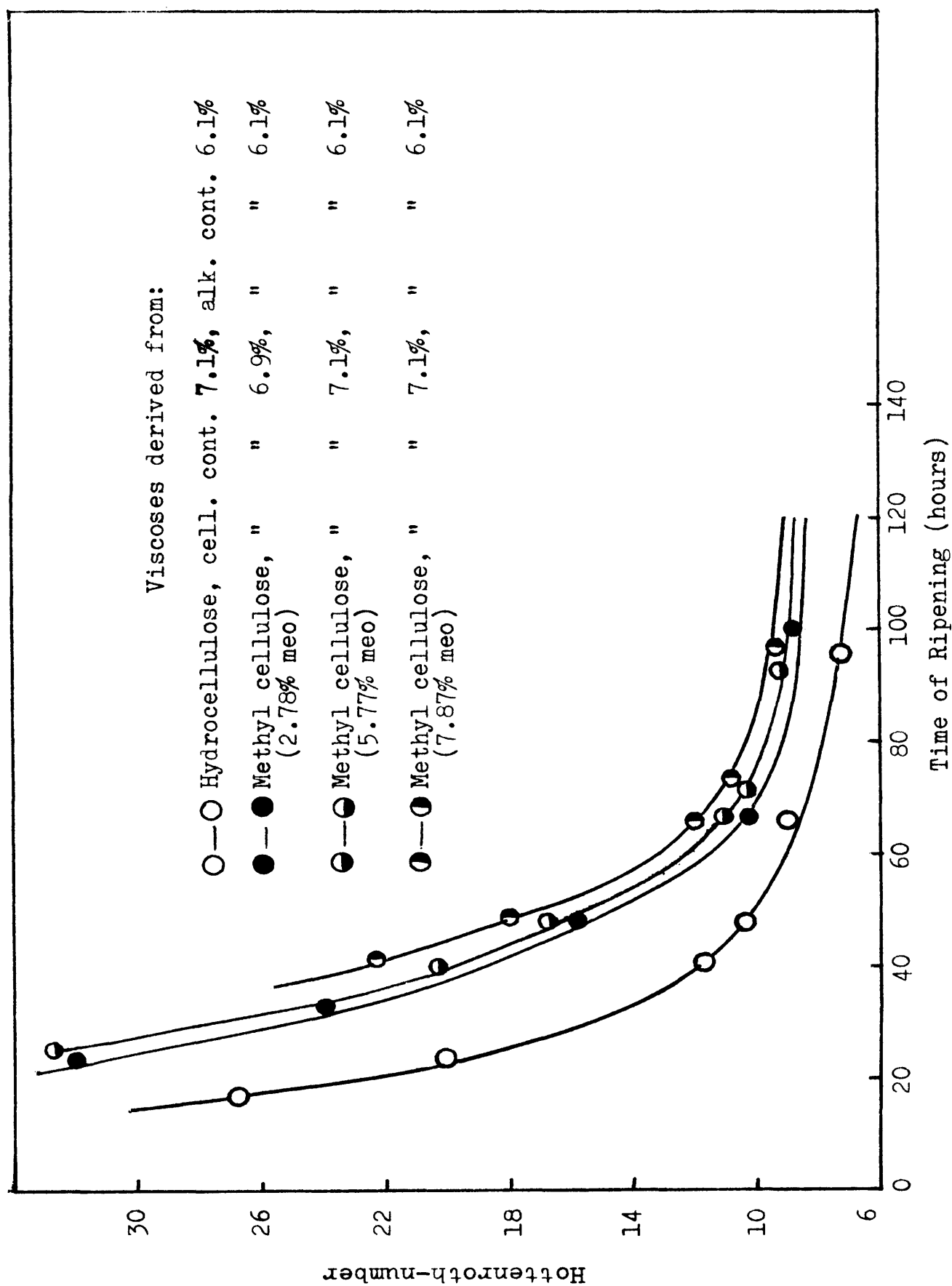


FIGURE 3.16. THE EFFECT OF METHYLATION ON RIPENING.

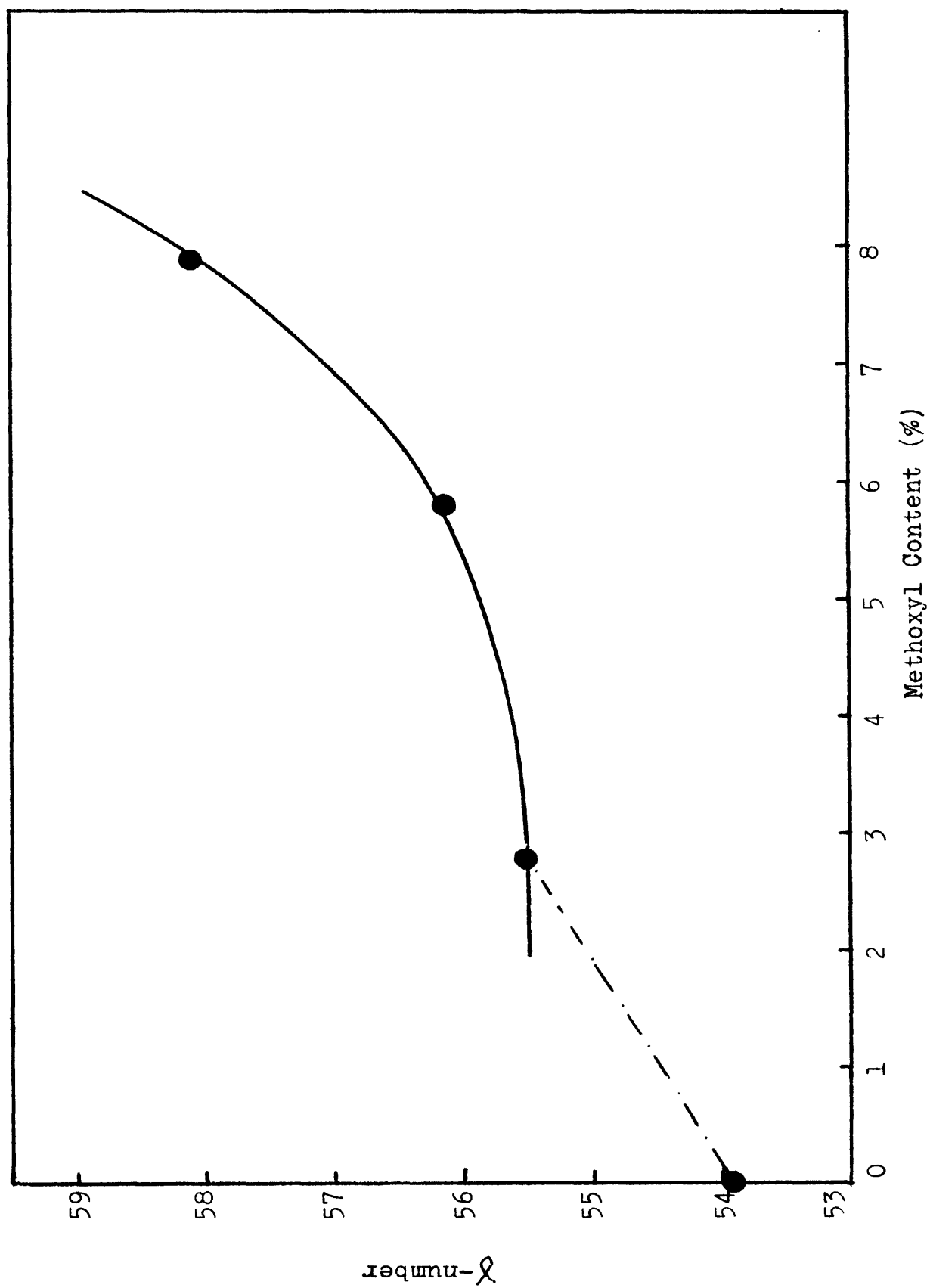


FIGURE 3.17. DEPENDENCE OF X-NUMBER ON METHOXYL CONTENT.

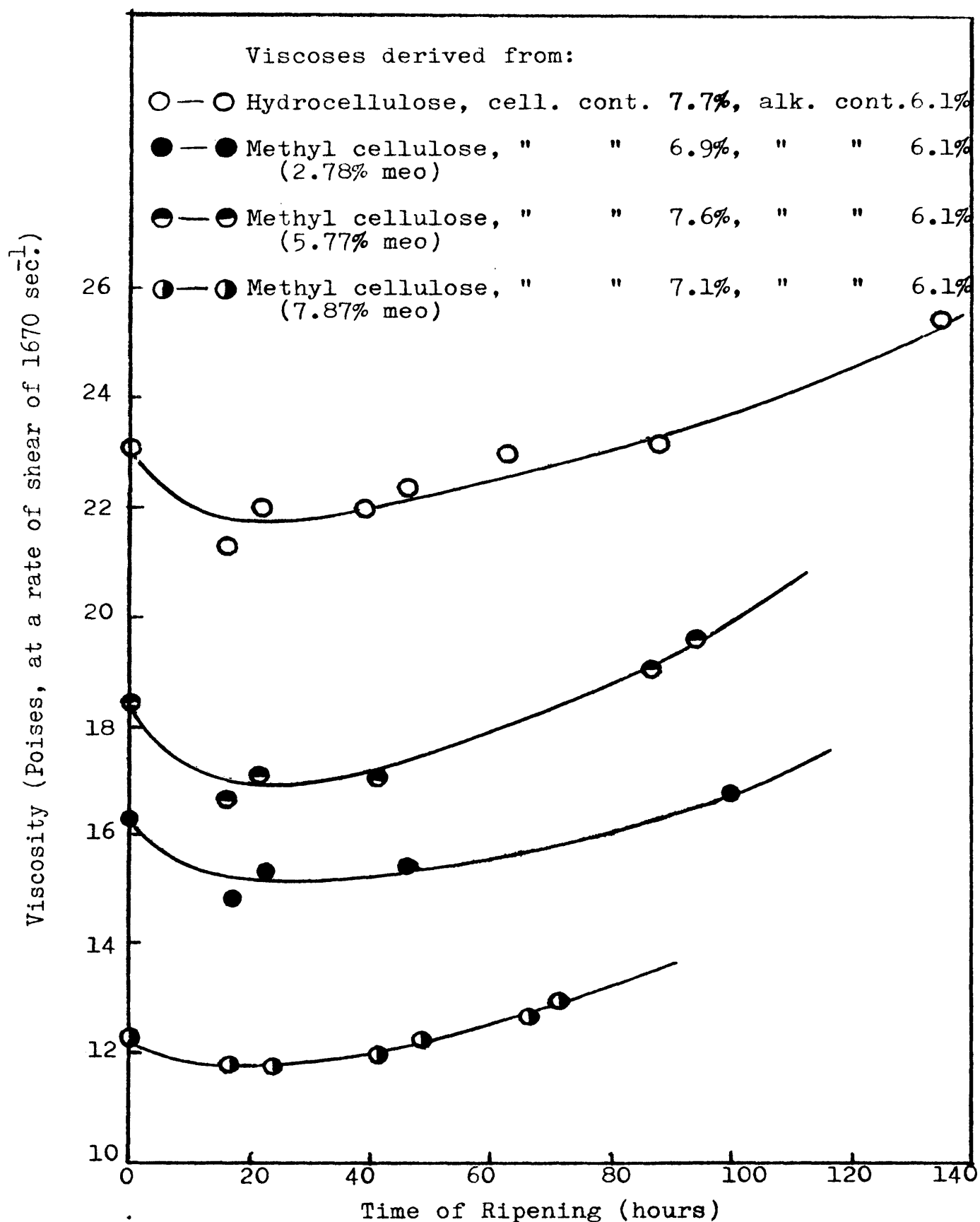


FIGURE 3.18. EFFECT OF METHYLATION ON VISCOSITY CHANGES DURING RIPENING.

groups by hydrolysis, the former change reducing the viscosity and the latter increasing it. Redistribution reaches an equilibrium whereas hydrolysis continues, hence the minima in the curves.

It will be noted that the general levels of viscosity for the different products are out of order with respect to the methoxyl contents. This is because the comparison is made at somewhat different cellulose concentrations, particularly so in the case of viscose made from methyl cellulose of 2.78% methoxyl content. Figure 3.19 (see Appendix Table XXII) shows that the influence of cellulose concentration is quite marked, as would be expected, and Table XIII gives a comparison of the viscosities of the different viscoses at a cellulose concentration of 7 per cent.

TABLE XIII
Effect of Methoxyl Groups on the Viscosity of Viscose

<u>% Methoxyl content of starting material</u>	<u>Viscosity of viscose (poise)</u>
0	17.5
2.78	16.5
5.77	15.6
7.87	12.2

This comparison is still, however, not strictly valid since the comparison is made at slightly different extents of ripening (different Hottenroth-number); this is particularly so in relation to viscose from methyl cellulose of 7.87% methoxyl content. However, it may be deduced from Figures 3.16 and 3.18-3.19 that if this viscose had a Hottenroth-number of about 10 its viscosity could still be less than

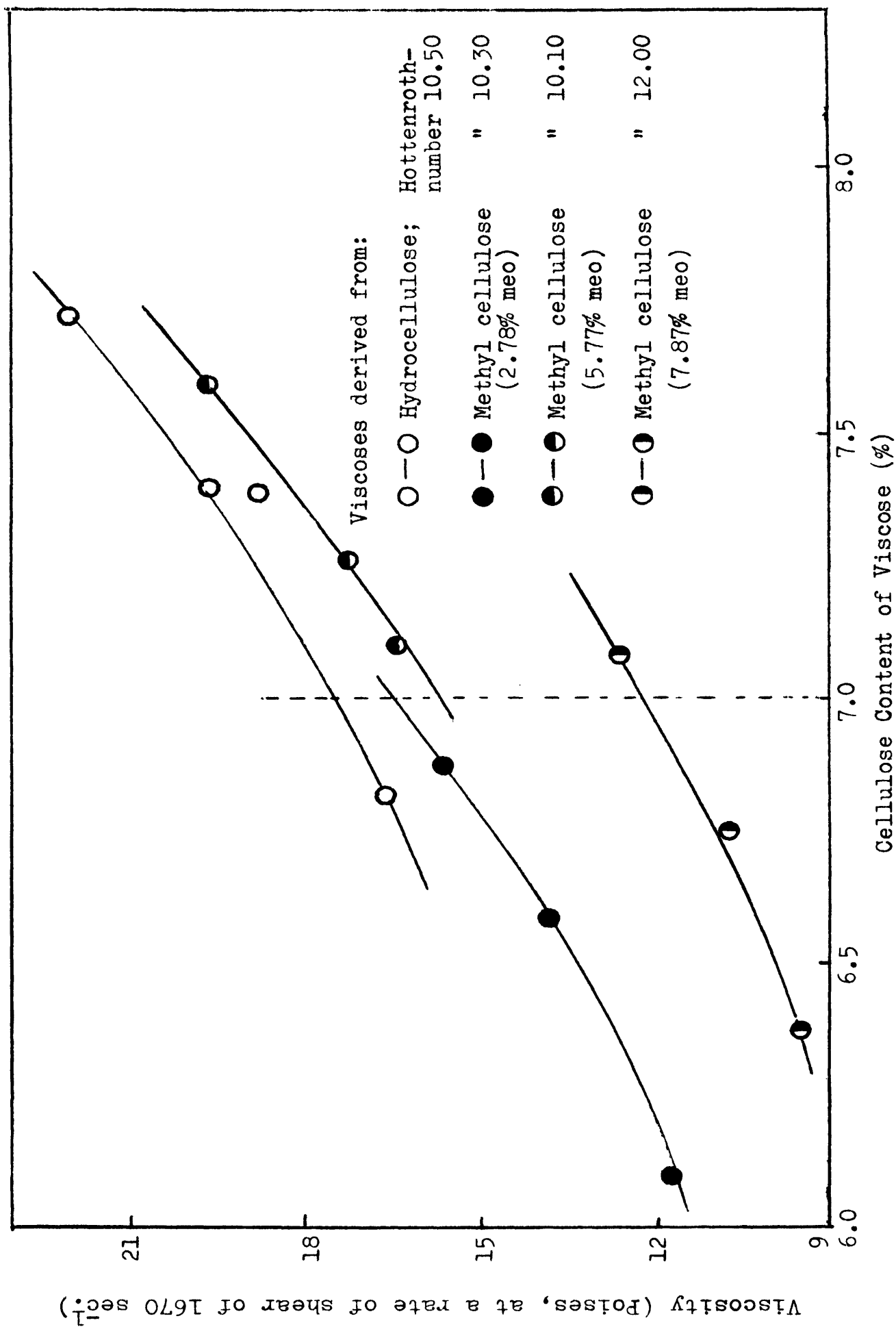


FIGURE 3.19. EFFECT OF CELLULOSE CONCENTRATION ON VISCOSITY OF VISCOSE AT A GIVEN DEGREE OF RIPENESS.

13 poises. Hence it may be concluded that increasing methoxyl content in the range investigated progressively decreases the viscosity of viscose.

The change in viscosity with methoxyl content may be interpreted on the basis of the influence of solvent-polymer interaction. High solvent-polymer interaction usually leads to relatively high viscosities, whereas high polymer-polymer interaction gives relatively low viscosities. Since the methoxyl groups have no affinity for aqueous caustic soda, an increasing proportion will tend to decrease polymer-solvent interaction and therefore to decrease the viscosity.

3.4. The Properties of Viscose Rayon Derived from Partially Methylated Hydrocellulose.

3.4.1. Introduction.

The purpose of the work described in this section has been given in the introduction to section 3.

The viscoses used for the work described here were prepared and analysed by methods previously described. The results of the analyses are summarised in Table XIV below. (See Appendix Table XXIII).

TABLE XIV
Analysis of Viscoscs Used in the Spinning

Methoxyl content of material (%)	0	2.78	5.77	7.87
Cellulose content %	7.5	7.0	7.6	7.1
Alkali content %	6.1	6.1	6.1	6.1
Y-number	53.4	55.6	56.0	58.7
Xanthate sulphur %	1.61	1.54	1.70	1.64
Total sul- phur %	1.77	1.76	1.80	1.81
Hottenroth- number	11.00	11.10	11.20	11.00

The equipment used for spinning was essentially the same as that used in section 2.2.5, except that a one-bath process was used; see Figure 2.5. The details of the spinning process are given in Table XV.

TABLE XV
Spinning Variables

The composition of the acid bath	x% sulphuric acid w/w 3% anhydrous zinc sulphate w/w 20% anhydrous sodium sulphate w/w x = 6, 9, 12 and 15%. (6% acid was found to give very weak fibres, therefore it was not used again.)
The amount of modifier (cyclohexylamine)	3% on the weight of cellulose
The temperature of the spinning bath	50 ± 0.5°C
The spinneret used	36 holes, 0.12 mm diameter
Percentage stretch applied	20%
The rate of viscose delivery	2.37 ml/min.
The speed of spinning	5.88 m/min.
The rate of extrusion	5.82 m/min
The extrusion ratio *	1.00
The depth of immersion	20 cm
The composition of the spraying baths:	
a. The acid bath	2% concentrated H ₂ SO ₄ ^{v/v}
b. The neutralisation bath	14 g/l NaHCO ₃

* is defined as the ratio of the speed of spinning (m/min.) to the rate of extrusion (m/min.)

Modifier was only included in the viscoses when spinning into a bath containing 12 per cent sulphuric acid. The 12 per cent bath was also used to spin viscoses free from modifier.

3.4.2. Analysis of Spun Filaments.

The rayons were analysed for methoxyl content (3.2.3.2.); degree of polymerisation, obtained from fluidities measured at

at 0.5% polymer concentration using cuprammonium hydroxide as solvent and Shirley Institute-type of short-tail viscometers. Fluidities were measured at concentrations of $\pm 10\%$ of 0.5% and converted to fluidities at 0.5% using the expression given by Clibbens (42):

$$F_x - F_{0.5} = \frac{F_o \text{ (Solvent)}}{1.44} \log \frac{C_{0.5}}{C_x}$$

where F_x is the fluidity of a concentration of $x\%$, $F_o = 72.60$ at $20 \pm 0.1^\circ\text{C}$ and 1.44 is a constant from Baker's equation (42).

Degrees of polymerisation were obtained from the conversion tables of fluidity vs. DP, given by Harland (49); gel-swelling value (2.2.6.1); moisture regain, accessibility and crystallinity (2.2.6.2); skin and core structure and cross-sectional shape (2.2.6.4.); and by the method of acid hydrolysis to yield limiting-DP values and a second estimation of accessibility (2.2.6.3.) The figures in the brackets refer to the earlier sections in which the experimental details may be found.

*The methoxyl contents of the rayons and their degrees of polymerisation obtained are compared in Table XVI with values for the parent hydrocellulose and methylated hydrocelluloses. It will be seen that there is no change in methoxyl contents during regeneration, but the degrees of polymerisation fall by about 50 units. The change in DP is not considered to be significant in so far as this work is concerned.

* See also Appendix Tables XXIV and XXV.

TABLE XVI
Methoxyl Content and Degree of Polymerisation
of Parent Material and Spun Filaments

Methoxyl Content %					Degree of Polymerisation				
Parent mater- ial	Fibres spun from				Parent mater- ial	Fibres spun from			
	9% acid	12% acid	15% acid	12% acid + modifier		9% acid	12% acid	15% acid	12% acid + modifier
0	0	0	0	0	610	568	575	563	570
2.78	2.69	2.66	2.67	2.68	620	572	576	577	570
5.77	5.67	5.74	5.75	5.78	617	579	578	576	571
7.87	7.87	7.87	7.87	7.88	609	579	583	585	594

Although the determination of accessibility from moisture regain has been dealt with earlier in connection with the influence of viscose salts on skin/core formation, it is now necessary to take into account the effects of substitution of methoxyl groups. According to Valentine (56) percentage accessibility to water vapour is given by the expression:

$$\frac{100 (M.R. + 0.323 D.S.)}{1.53}$$

where M.R. is moles of water per glucose ring,

D.S. is degree of substitution,

1.53 is the number of moles of water per glucose ring for fully accessible polymer,

0.323 is a constant, generally known as Valentine's value. It is used to correct for the hydrophobic effect of the methoxyl groups on the moisture regain per methoxyl substituent group.

The tensile properties of the rayons were measured on an Instron machine. The specimen length was 5 cm, the cross-head

speed 5 cm/minute, and the chart speed 20 cm/minute. Dry tests were carried out after conditioning the filaments at 65% relative humidity and 20°C for 24 hours. Load-extension curves were also obtained with the rayons completely immersed in water at 20°C. In all cases 10 specimens were examined and the average taken and standard deviations were calculated. Fibre denier was measured by weighing 27 metres of yarn which had been conditioned at 65% relative humidity and 20°C for 24 hours. (See Appendix Table XXXI).

3.4.3. Results and Discussions.

3.4.3.1. Gel Swelling Values.

The gel swelling values of the rayons are given in Appendix Table XXVI and are plotted in Figure 3.20 as a function of methoxyl content. The data include the results of using spin baths of different acid content and also show the effect of the presence of modifier in the viscoses, in this case 3 per cent of cyclohexylamine.

The general effect of increasing methoxyl content may be seen to be to increase the gel swelling value, particularly at the highest acid concentration (15%), although in this case there is an initial decrease between the value for hydro-cellulose and methylated cellulose containing 2.78% methoxyl groups. The increase of gel swelling value with increasing methoxyl content can be ascribed to the increasing size of disordered regions in the primary gel state, an effect which is paralleled by the increasing accessibility of the ultimate rayon filaments (see section 3.4.3.2.)

With modifier present gel swelling values also increase with increase of methoxyl content, but it should be noted that below a methoxyl content of about 5% gel swelling values are lower than when modifier is not present, while above this methoxyl content they are appreciably greater.

The effect of increasing concentration of acid in the spin bath is seen to increase the gel swelling values. Since the gel swelling value is a measure of the extent of deswelling prior to complete regeneration of the cellulose (or methylated cellulose), increasing the acid concentration will

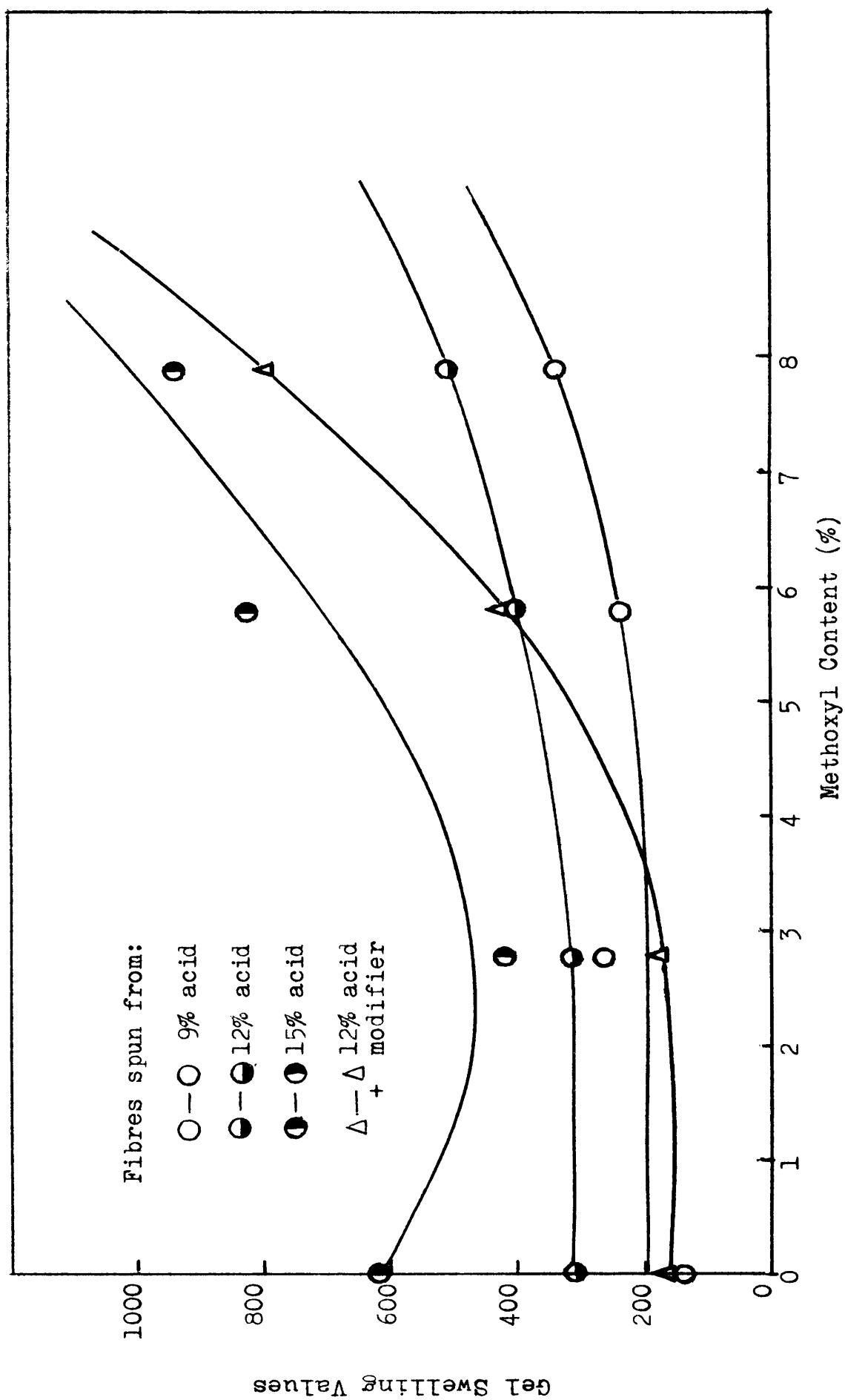


FIGURE 3.20. EFFECT OF METHYLATION ON THE GEL SWELLING OF FILAMENTS.

speed up regeneration and reduce the time available for deswelling, hence the data are as might be expected.

The part played by the modifier is difficult to interpret since the mechanism for a cellulose viscose is not yet fully understood. In the case of the hydrocellulose and for low extents of methylation it plays its usual role of decreasing gel swelling. The mechanisms suggested for modifier action have been discussed earlier (section 1.2.2.) and it will be recalled that they are considered either to involve semipermeable membrane formation in the cuticle region or to have a plasticising action which influences the formation of the ZnX^{+} -state. The most that may be deduced from the present data is that the presence of methoxyl groups could conceivably interfere with semipermeable membrane formation, but not with a plasticising action. In fact the methoxyl groups present should maintain a relatively extended structure themselves and therefore contribute to any plasticising mechanism.

3.4.3.2. Accessibility, Crystallinity, and Limiting-Degree of Polymerisation.

Accessibility both to aqueous acid and water vapour has been determined and values for the latter have been used to calculate percentage crystallinity. Accessibilities to aqueous acid and water vapour as a function of methoxyl content are shown in Figures 3.21 and 3.22 respectively. (See also Appendix Tables XXVlll and XXVll). It may be seen that in both cases accessibility increases with increasing methoxyl content. There are, however, some notable differences. Firstly, percentage accessibility derived from moisture regain

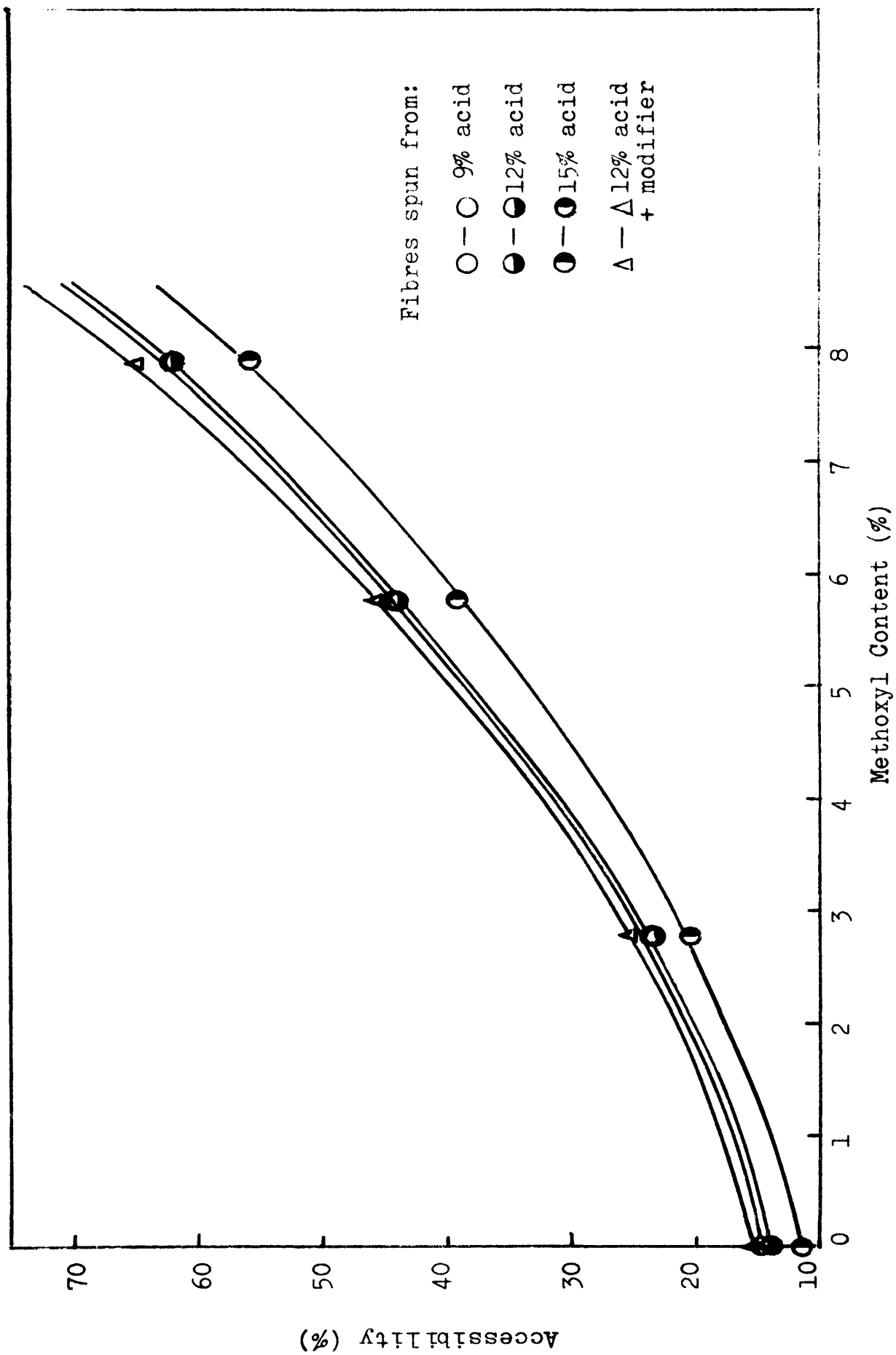


FIGURE 3.21. EFFECT OF METHYLATION ON ACCESSIBILITY OF FILAMENTS (ACID HYDROLYSIS METHOD).

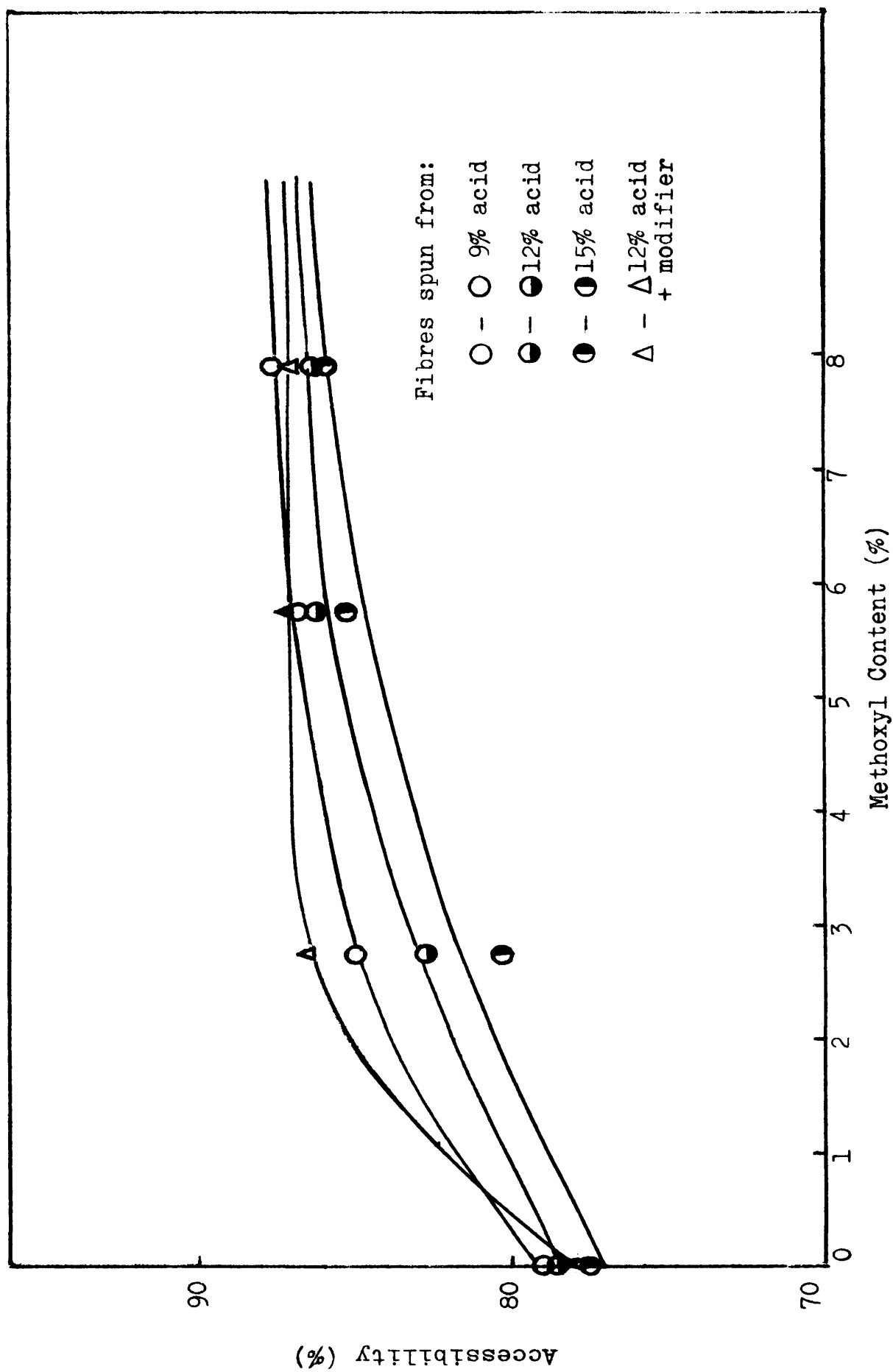


FIGURE 3.22. EFFECT OF METHYLATION ON ACCESSIBILITY OF FILAMENTS (MOISTURE REGAIN METHOD).

is much higher than accessibility derived from loss in weight during acid hydrolysis, a feature which has been observed by others(57). Secondly, accessibilities derived from acid hydrolysis continue to increase with increasing methoxyl content, whereas values derived from moisture regain tend toward a limiting value. With regard to accessibilities from acid hydrolysis it should be remembered that they are based on weight losses and that the fraction lost contains most of the methoxyl groups, hence the estimation of accessibility becomes increasingly too high as methoxyl content increases. This fact can only partly account for the different types of relations given by the two methods of measuring accessibility. It is also clear from Figures 3.21 and 3.22 that the relation between accessibilities measured by the two methods is non-linear. Another disturbing feature is that the accessibility figures derived from acid hydrolysis for the regenerated hydro-cellulose are abnormally low at around 15-10 per cent; 30 per cent is a commonly reported level for regenerated cellulose (54). It can only be concluded that structural parameters are having unknown effects.

Figure 3.23 (see Appendix Table XXVII) shows plots of crystallinity derived from moisture regain as a function of methoxyl content for the viscoses spun into baths of varying acid concentration, and at 12 per cent acid concentration with and without modifier present. Similar data in terms of limiting-degree of polymerisation derived from acid hydrolysis residues are shown in Figure 3.24 (see Appendix Table XXIX). It will be seen that as the acid concentration decreases so does the percentage crystallinity and the crystallite size as

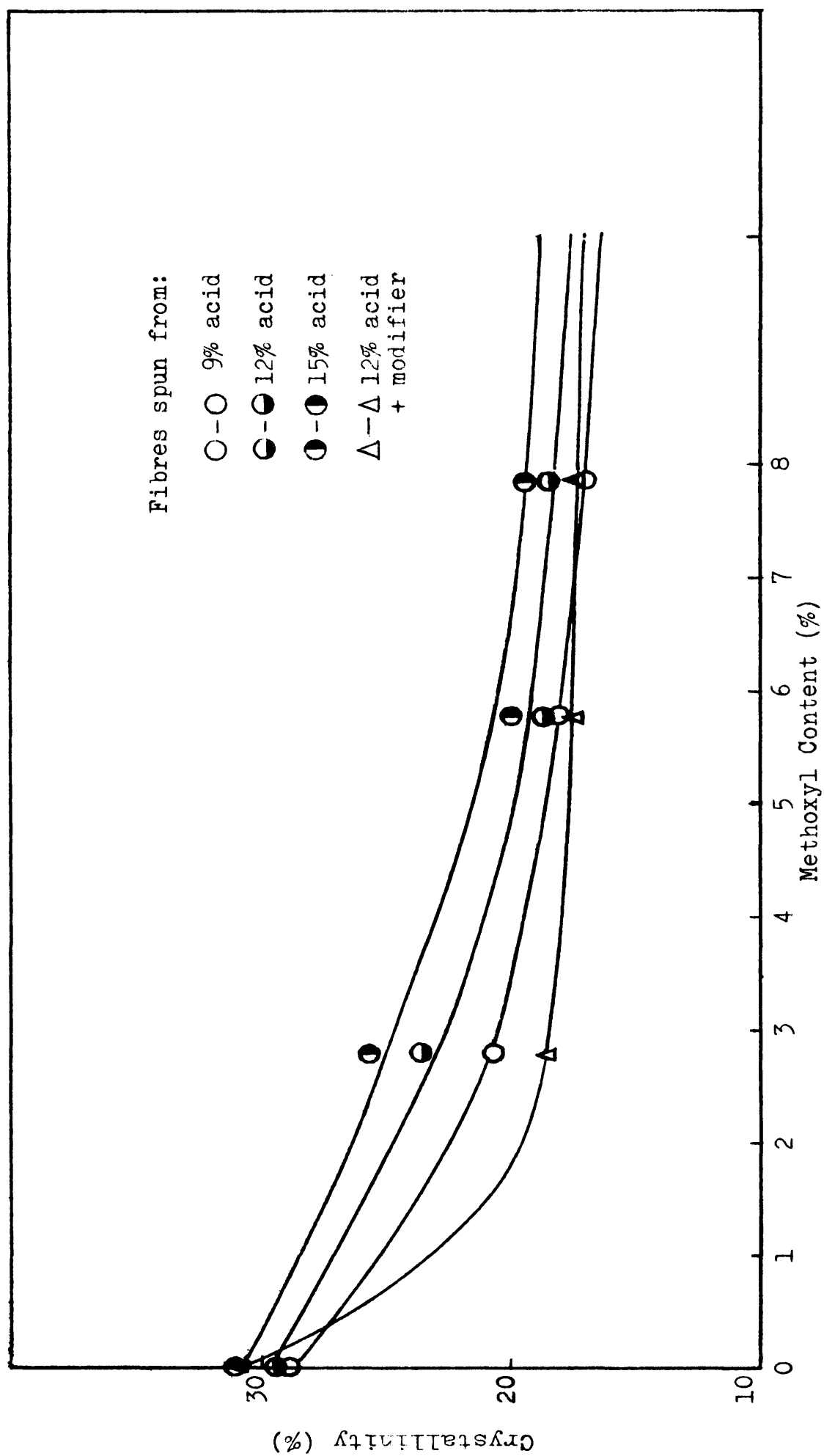


FIGURE 3.23. EFFECT OF METHYLATION ON CRYSTALLINITY OF FILAMENTS (MOISTURE REGAIN METHOD).

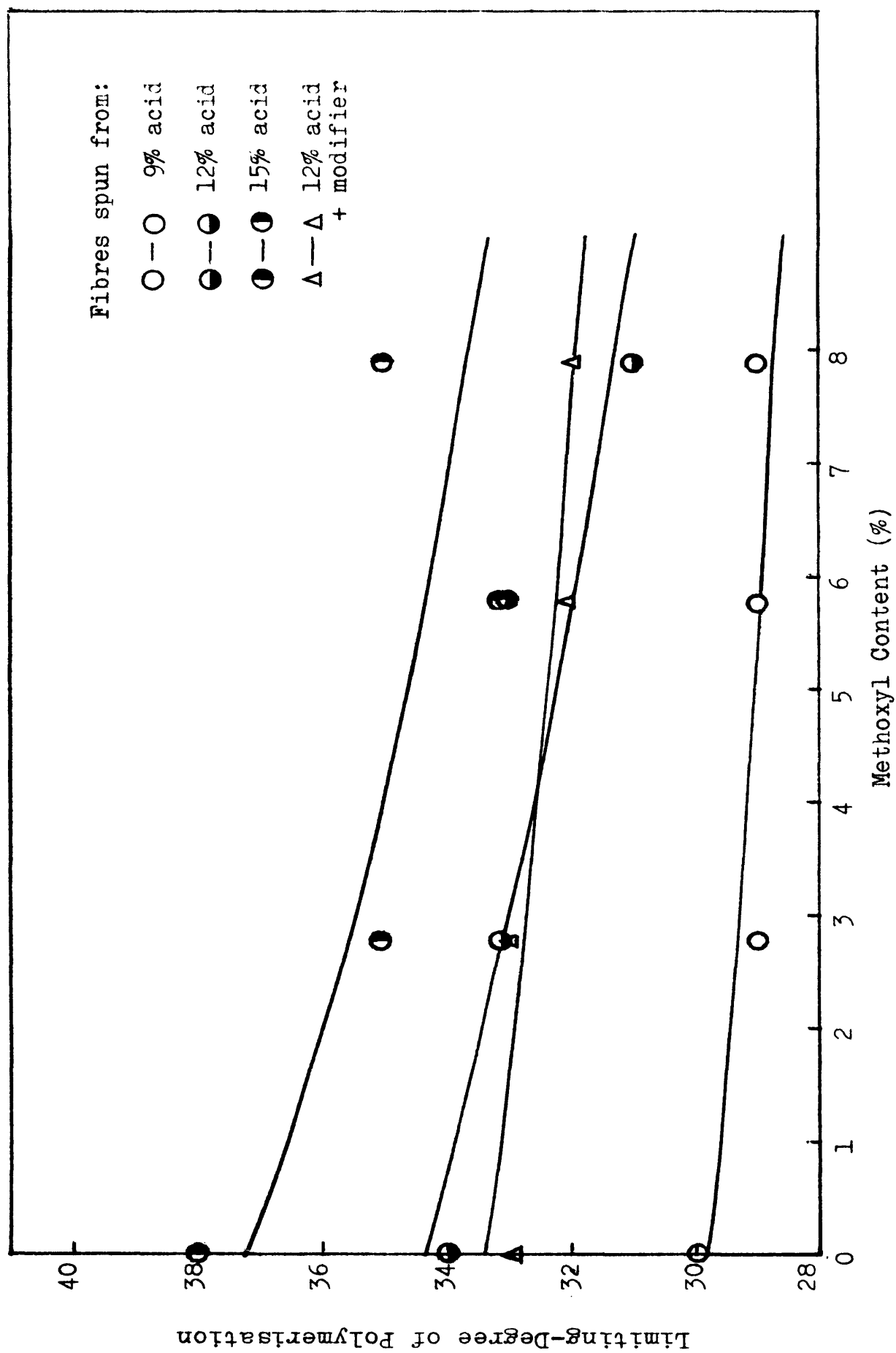


FIGURE 3.24. EFFECT OF METHYLATION ON LIMITING-DEGREE OF POLYMERISATION.

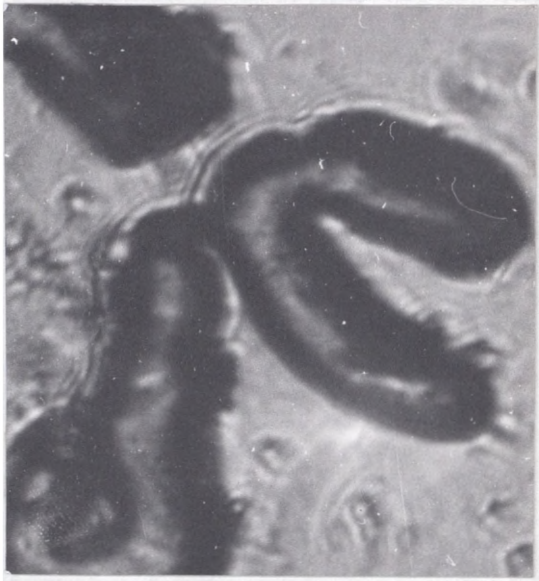
measured by limiting-degree of polymerisation, and both decrease with increasing methoxyl content. The presence of modifier has little effect on limiting-degree of polymerisation, but as with gel swelling values (Figure 3.20), there is evidence of it producing the expected effect (here of reducing limiting-DP) at methoxyl contents less than 5 per cent. The presence of modifier in the viscose does, however, produce methylated rayons of lowest crystallinity.

The object of using methylated cellulose in viscose was to influence crystallite size and the fine structure of rayon as is done by the use of modifiers. It was expected that partial methylation would reduce crystallite size and therefore limiting-degree of polymerisation. To a small degree the object has been achieved, particularly at the higher concentration (15%) of spin bath acid used. The results are not as striking as was hoped for but this may be because a tyre cord process of spinning could not be used. In this connection it should be noted that the effect of the presence of modifier on the limiting-degree of polymerisation of the rayon derived from the unmethylated cellulose is very small.

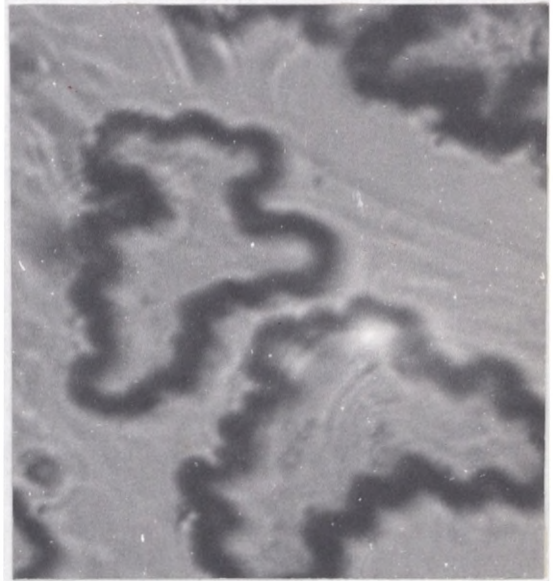
3.4.3.3. Skin-Core Structure and Filament Shape.

The percentage of skin structure was calculated from the photomicrographs shown in Figure 3.25 (see also Appendix Table XXX). The results are compiled in Table XVll.

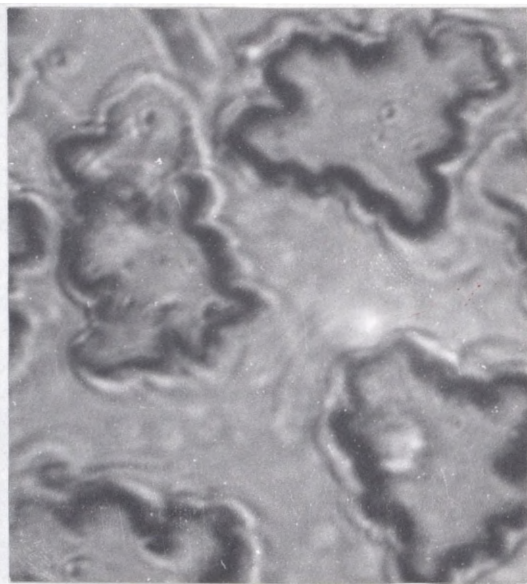
(1) Fibres from Hydrocellulose



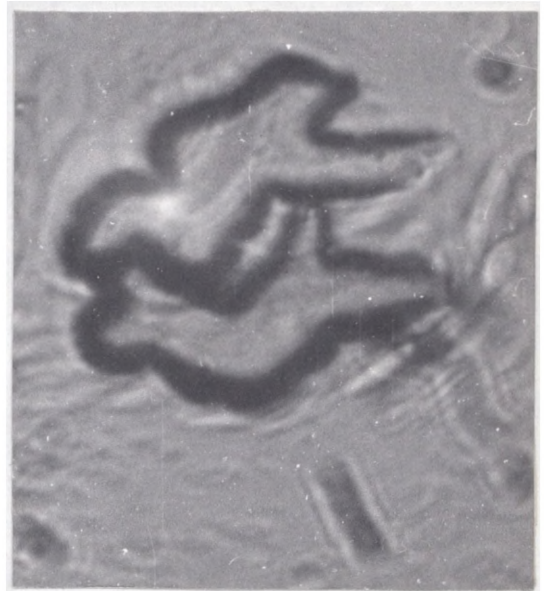
Acid Concentration 9%
Magnification 1000X



Acid Concentration 12%
Magnification 1000X



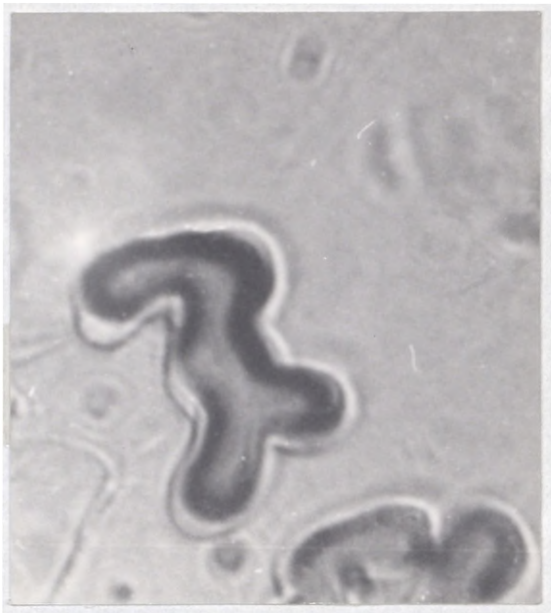
Acid Concentration 15%
Magnification 1000X



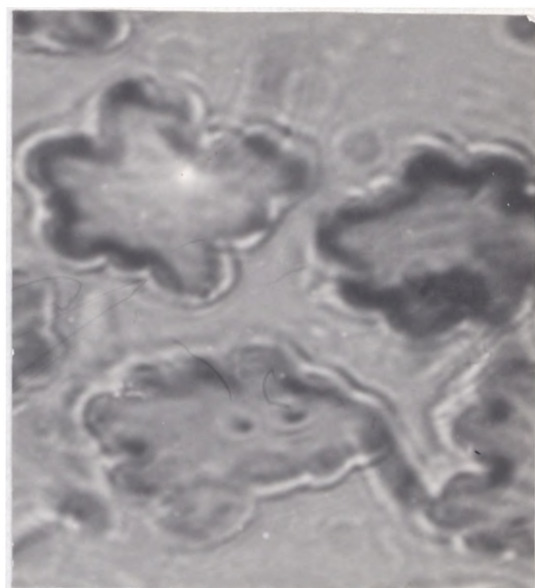
Acid Concentration 12%
+ modifier
Magnification 1000X

FIGURE 3.25. PHOTOMICROGRAPHS OF VISCOSE RAYON FIBRES.

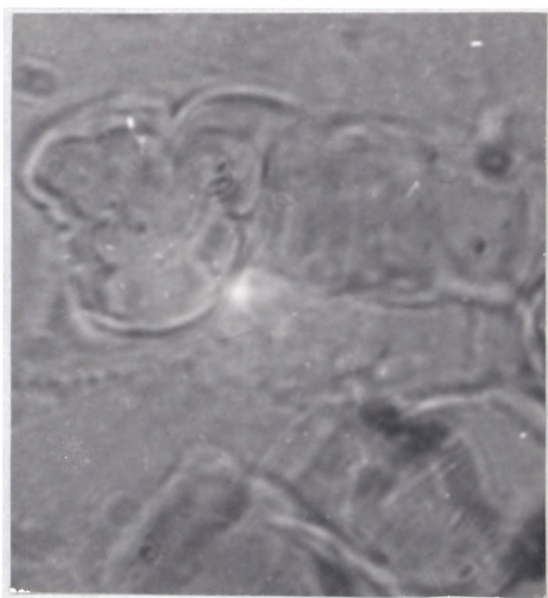
(2) Fibres from Methylated Cellulose (Methoxyl Content 2.78%)



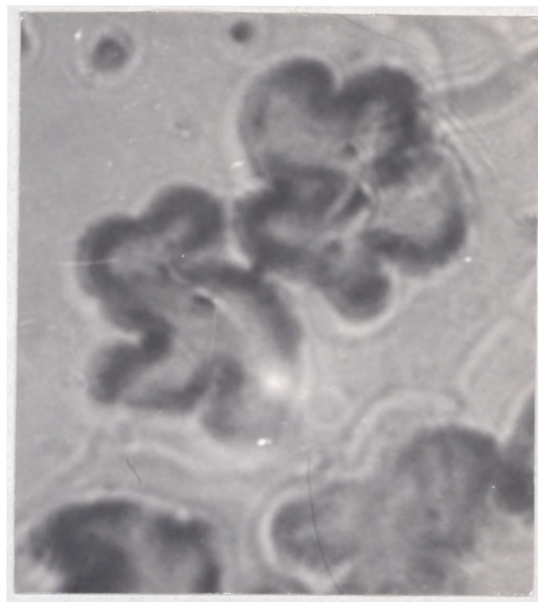
Acid Concentration 9%
Magnification 1000X



Acid Concentration 12%
Magnification 1000X

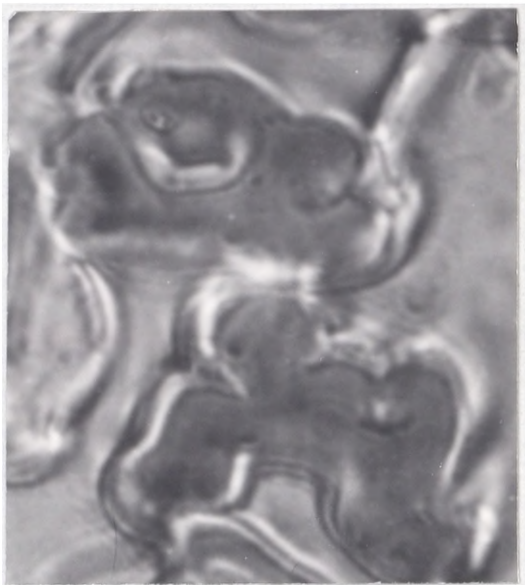


Acid Concentration 15%
Magnification 1000X

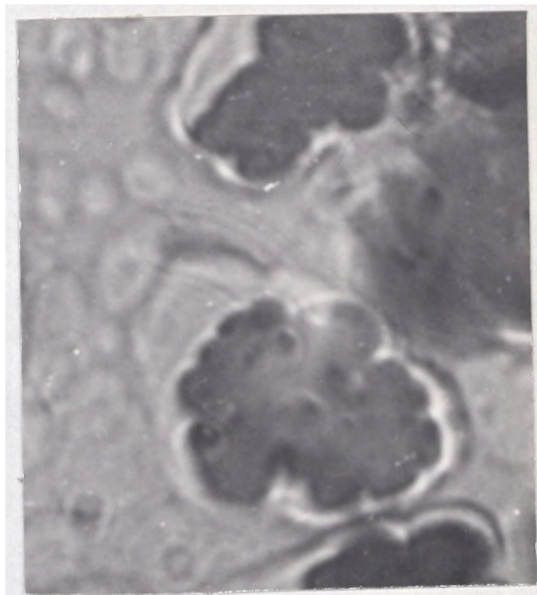


Acid Concentration 12%
+ modifier
Magnification 1000X

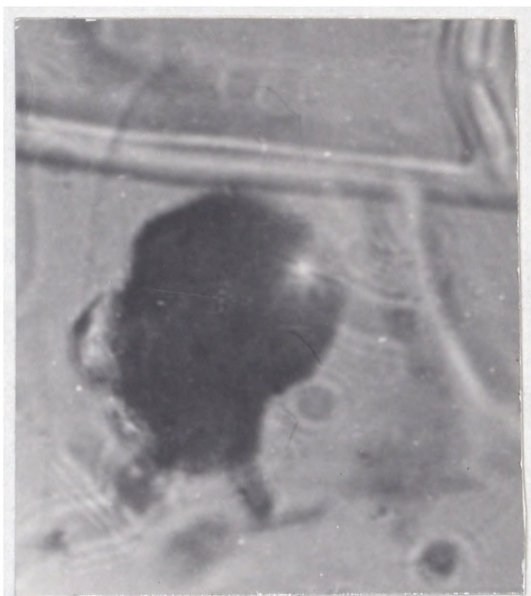
(3) Fibres from Methylated Cellulose (Methoxyl Content 5.77%)



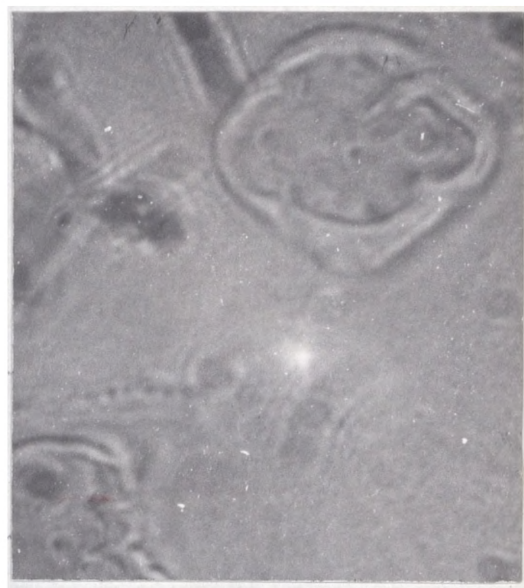
Acid Concentration 9%
Magnification 1000X



Acid Concentration 12%
Magnification 1000X

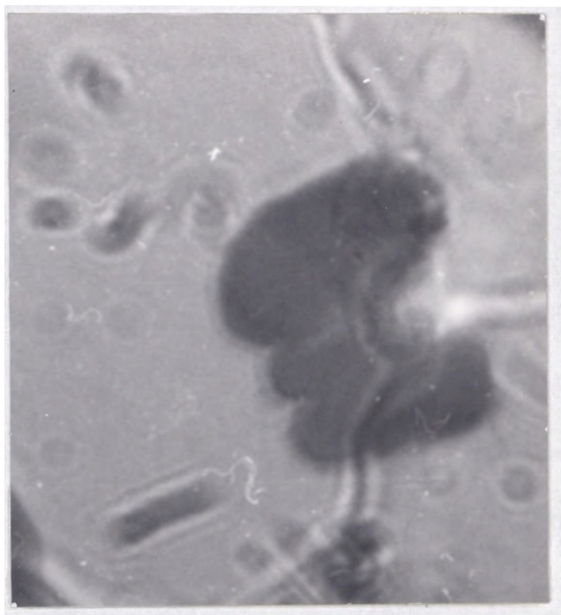


Acid Concentration 15%
Magnification 1000X

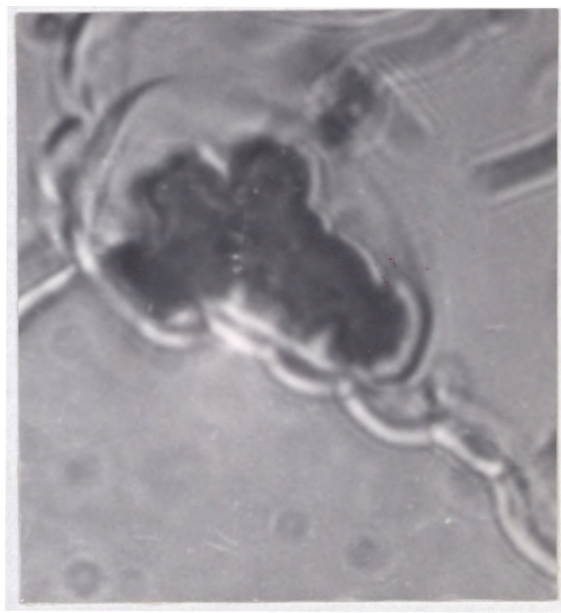


Acid Concentration 12%
+ modifier
Magnification 1000X

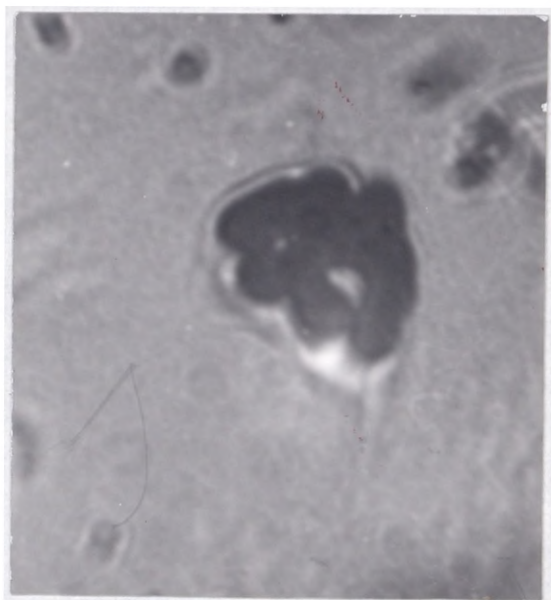
(4) Fibres from Methylated Cellulose (Methoxyl Content 7.87%)



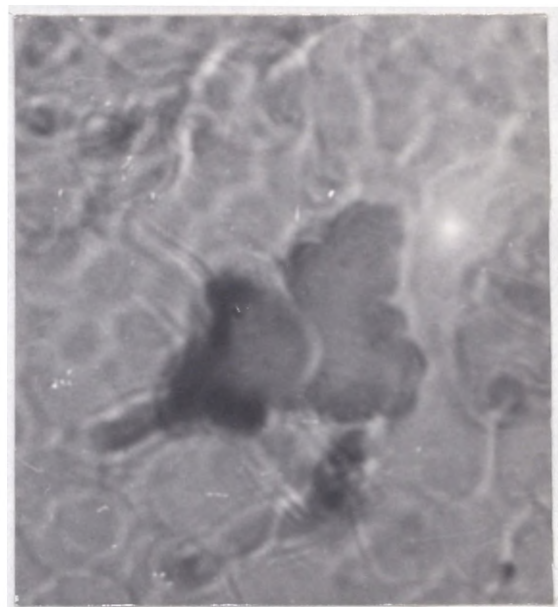
Acid Concentration 9%
Magnification 1000X



Acid Concentration 12%
Magnification 1000X



Acid Concentration 15%
Magnification 1000X



Acid Concentration 12%
+ modifier
Magnification 1000X

TABLE XV11
Skin/Core Structure of Spun Filaments

Methoxyl content %	Percentage acid used in spinning	Percentage skin structure
0	9	75.1
	12	50.1
	15	38.7
	12+ modifier	55.6
2.78	9	68.6
	12	45.8
	15	All core
	12+ modifier	55.7
5.77	9	All skin
	12	All skin
	15	All skin
	12+ modifier	All core
7.87	9	All skin
	12	All skin
	15	All skin
	12+ modifier	All core

Various trends may be detected among these results. In the products with zero and 2.78 per cent methoxyl content an increase in spin bath acid concentration lowers the amount of skin structure and the presence of modifier increases it.

In the products with a higher methoxyl content the structure is all skin at all acid concentrations provided that modifier is not present. When modifier is present it is surprising to find that the structure is entirely core type.

In general delaying regeneration to permit adequate deswelling of the primary gel is essential for the formation of skin-type structure, but as Vroom (2) has pointed out, filaments containing an entirety of skin structure are not obtained even in the most dilute acid baths, instead the filaments tend to have an all-core structure. It is unlikely, therefore, if acid concentrations below 9 per cent had been used, an all-skin structure would have resulted from celluloses with zero or lowest methoxyl content.

In so far as the presence or absence of modifier is concerned, the pattern of results bears some similarity to the results obtained for gel swelling values and limiting-degrees of polymerisation in that there is a "cross-over effect" as the methoxyl content rises from 2.78-5.77 per cent. (cf Table XVll and Figures 3.20 and 3.24). These correlations substantiate the data but do not permit a mechanism to be postulated. As commented earlier, an explanation will require a more positive understanding of the usual modifier action.

It may be seen from Figure 3.25 that the shapes of the cross-sections also depend on both acid concentration, methoxyl content, and presence or absence of modifier. In general the sections have a more regular shape as the acid concentration and methoxyl content increase. As is usually found, sections from filaments with either an all

skin or all core-type structures tend towards a smooth circular shape. The presence of modifier makes the cross-section shape more regular for products with methoxyl contents of zero or 2.78 per cent, but it is difficult to distinguish the shapes from modified and unmodified viscoses of higher methoxyl content, even though the modified ones have an all core structure and the unmodified an all skin structure.

3.4.3.4. Tensile Properties.

Tenacities and per cent ultimate elongation for yarns measured at 65 per cent R.H. and 20°C and for yarns immersed in water at 20°C are shown in Table XVlll in relation to the concentration of the spin bath acid and the methoxyl contents of the yarns. The same data are given in graphical form in Figures 3.26, 3.27, 3.28 and 3.29 (see also Appendix Table XXXll).

TABLE XVlll
Tensile Properties of Fibres

% Acid used in spinning	% Methoxyl content	Tenacity (g/den.)		Ratio of tenacities Dry/Wet	% Elongation	
		Dry	Wet		Dry	Wet
9	0	1.4	0.8	1.8	21.2	41.9
	2.78	1.4	0.6	2.3	18.8	32.7
	5.77	1.5	0.6	2.5	17.6	48.1
	7.87	1.4	0.4	3.5	18.1	52.2
12	0	1.8	0.9	2.0	23.9	43.0
	2.78	1.8	0.8	2.3	26.2	43.9
	5.77	1.6	0.7	2.3	21.8	52.3
	7.87	1.8	0.5	3.6	12.2	33.9
15	0	1.5	0.8	1.9	15.7	25.6
	2.78	1.6	0.7	2.3	12.8	26.9
	5.77	1.5	0.7	2.1	10.2	19.9
	7.87	1.4	0.3	4.7	15.3	46.4
12+ modifier	0	2.0	1.1	1.8	20.0	31.8
	2.78	1.9	0.9	2.1	24.9	47.4
	5.77	1.6	0.7	2.3	17.4	46.6
	7.87	1.6	0.4	4.0	10.2	17.5

Unfortunately the relations between the ultimate properties and methoxyl content are not always well defined. In general the "wet" and "dry" tenacities, particularly the former, decrease with increasing methoxyl content. This is not surprising since the crystalline content of the yarns is also decreasing (cf Figure 3.23). The ratio of dry/wet tenacities is seen to increase markedly with

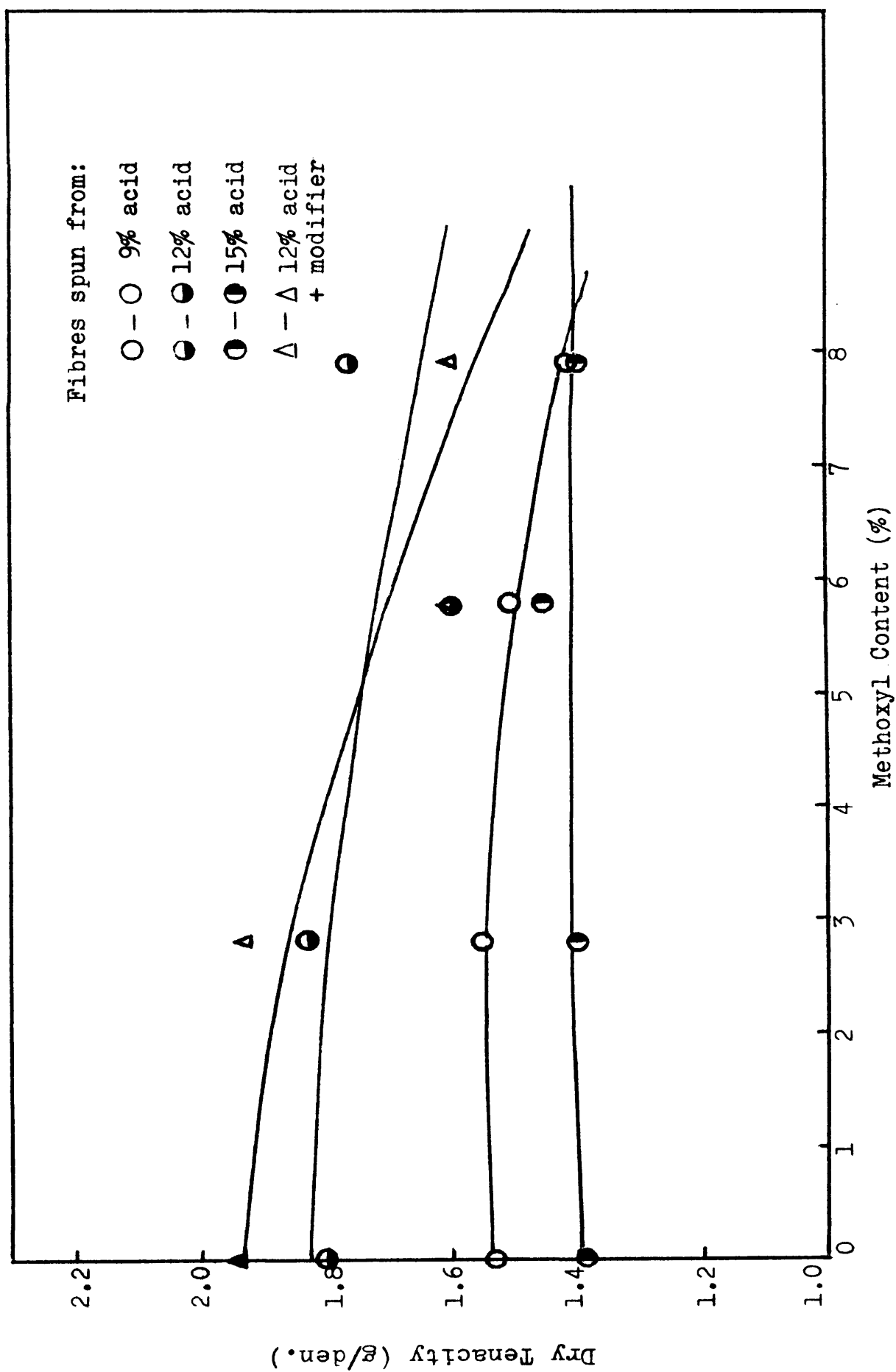


FIGURE 3.26. EFFECT OF METHYLATION ON DRY TENACITIES OF FILAMENTS.

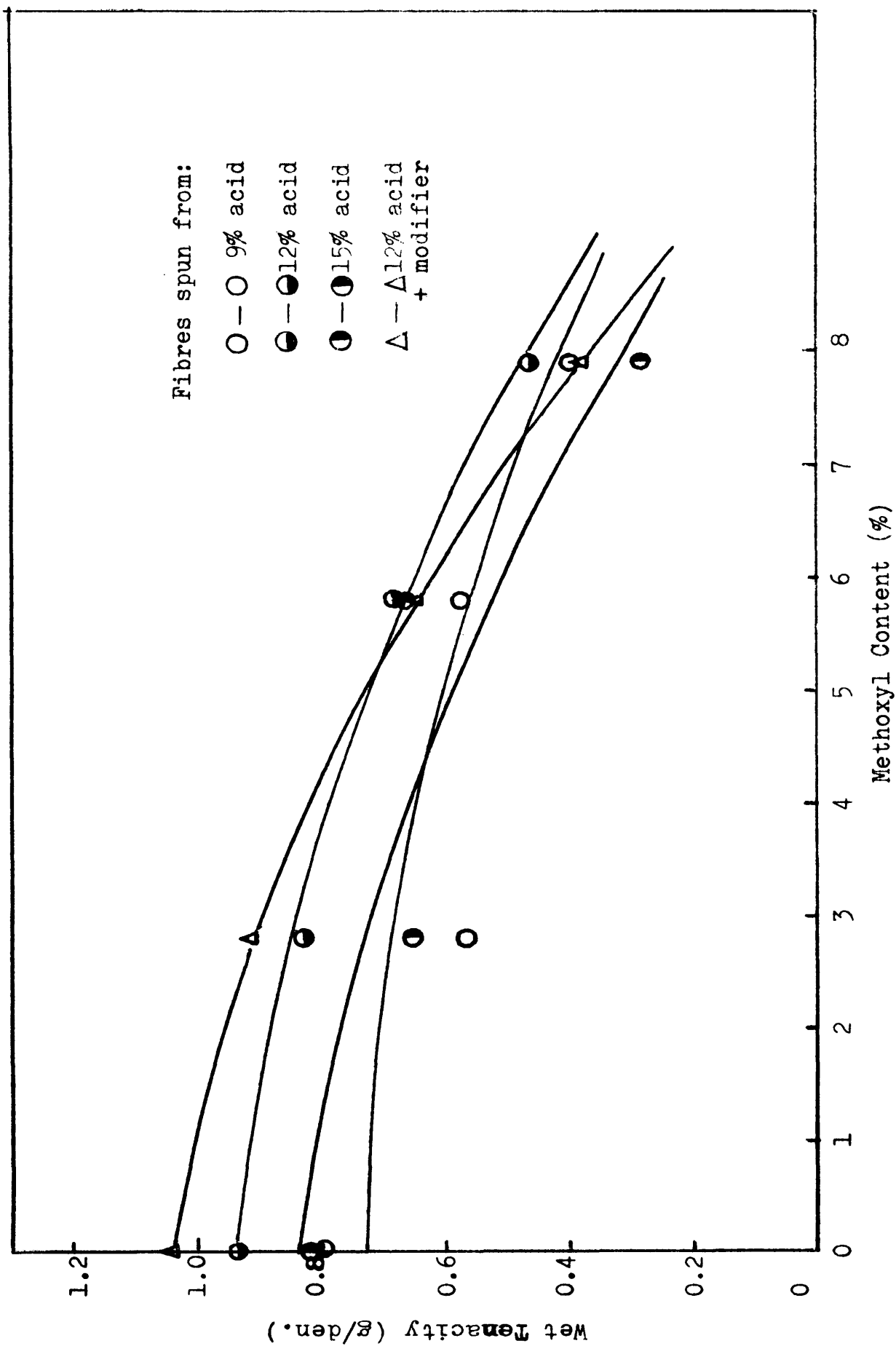


FIGURE 3.27. EFFECT OF METHYLATION ON WET TENACITIES OF FILAMENTS.

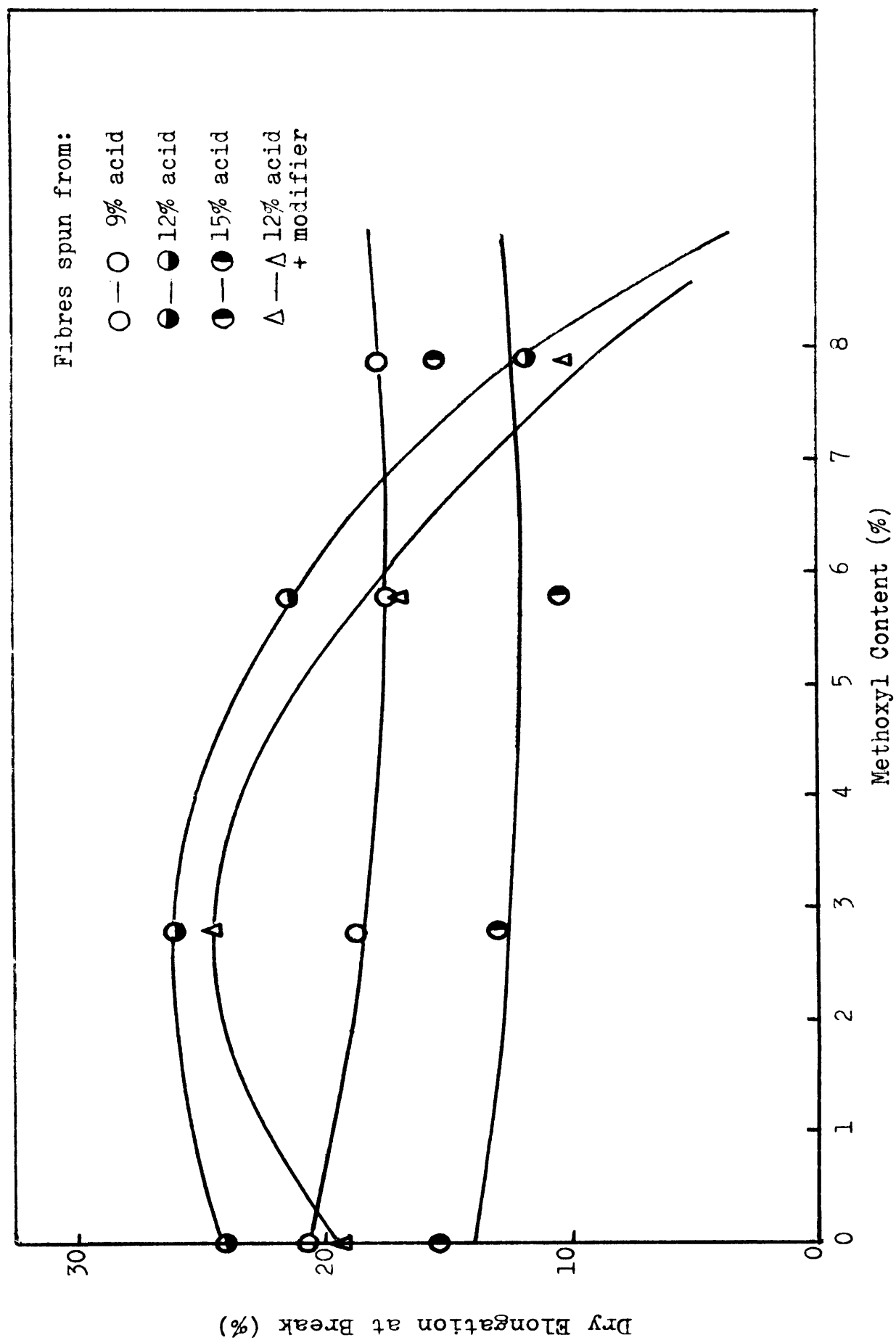


FIGURE 3.28. EFFECT OF METHYLATION ON THE DRY ELONGATION OF FILAMENTS.

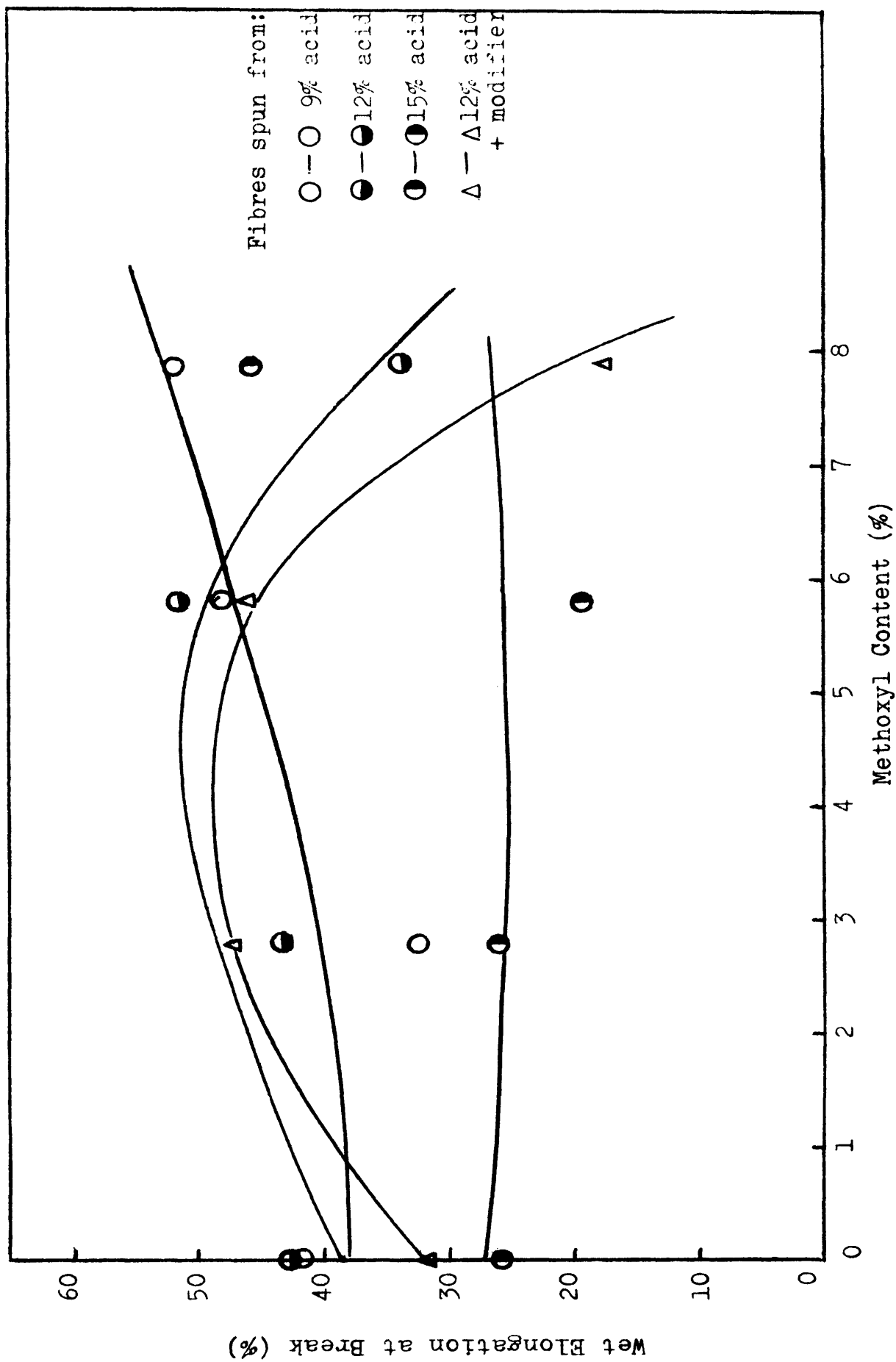


FIGURE 3.29. EFFECT OF METHYLATION ON THE WET ELONGATION OF FILAMENTS.

increase of methoxyl content. The effect of acid concentration in the spin bath is not very marked though a concentration of 12 per cent gives the highest tenacities and slight improvement at this concentration results from the presence of modifier in the viscose.

The relations between ultimate elongation and methoxyl content are less well defined, though relations for "wet" and "dry" elongation have a similar pattern. At acid concentrations of 9 and 15 per cent measurements made on "dry" filaments show a slight fall in elongation at break with increasing methoxyl content, whereas the values for the "wet" filaments increase with increasing methoxyl content. In contrast, with a spin-bath acid concentration of 12 per cent the relations have fairly well-defined maxima regardless of whether modifier is present or not; in the presence of modifier lower values are obtained over the whole range of methoxyl contents.

It is, however, surprising that the tensile data are not sensitive to changes in type of structure. For example, the viscoses spun into 15 per cent acid have structures ranging from skin/core, all core, all skin, all skin structures, in the same order of increasing methoxyl contents, and yet there is no very apparent discontinuity in a tensile property plotted as a function of methoxyl content.

It was thought that initial moduli would be more sensitive to structure but the values and type of structure present, which are given in Table XLX, do not appear to correlate one with the other.

TABLE XIX
* Initial Moduli of Filaments

Methoxyl content %		0		2.78		5.77		7.87	
Acid concentration in spin bath	Initial modulus g/den.	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
9		60.9 (S/C)	2.57	36.5 (S/C)	2.38	42.3 (S)	1.95	38.8 (S)	1.44
12		44.2 (S/C)	3.03	40.3 (S/C)	2.60	32.7 (S)	2.12	43.5 (S)	2.50
15		53.0 (S/C)	4.21	64.5 (C)	3.47	42.1 (S)	5.37	37.1 (S)	0.82
12+ modifier		52.2 (S/C)	3.90	36.2 (S/C)	2.41	41.9 (C)	2.17	49.3 (C)	3.06

where S/C is skin/core structure,

S is all skin "

C is all core "

It was the object of this work to vary the skin-core structure of viscose rayon by partial methylation of the parent cellulose as opposed to the commercial methods of varying spin-bath composition. It has been shown that this object has been achieved (cf section 3.4.3.3.) However, the advantages gained by the commercial methods, namely higher tenacities with conservation of ultimate elongation, and higher "wet" strength, have not been realised. The reason for this would appear to be due to the decreasing crystallinity with increasing methoxyl content. The introduction of this additional variable makes the interpretation

* See also Appendix Table XXXIII.

of the tensile data in terms of the fine structure more or less impossible. In addition, it should be emphasised that the commercial methods referred to use a two-bath spinning process which is essential to achieve the advantages mentioned.

3.5. Suggestions for Further Work.

Further work needs to be done to elucidate the composition of partially methylated cellulose and similar investigations to those reported here could be attempted with hydroxyethyl cellulose. At the same time it would be desirable to make comparisons with viscoses prepared from mixtures of cellulose and the partially etherified derivatives, and the latter should be randomly substituted.

It is equally desirable to spin the viscoses so obtained using spin baths of a wider range of composition, in particular varying the zinc and sodium sulphate concentrations, using a two-bath process, and methods for the preparation of the so-called Polynosic rayons.

APPENDIX TABLE I

Analysis of tyre cord viscoses.

A. Impure Viscose.

1. The alkali content.

- a. Standardisation of alkali solution with a solution of potassium hydrogen phthalate (2.0430 g.in 100 cc. = .1000N).

The alkali solution was first diluted ten times and titrated with the potassium hydrogen phthalate solution.

$$25 \text{ cc. } \frac{x}{10} \text{ N NaOH} = 24.50 \text{ cc. } 0.1 \text{ N KHP.}$$

then
$$x = 0.9800 \text{ N}$$

- b. Standardisation of the acid solution (H_2SO_4) with a standard alkali solution:

$$25 \text{ cc. } 0.9800 \text{ N NaOH} = 24.35 \text{ cc. } y \text{ N } \text{H}_2\text{SO}_4$$

then
$$y = 1.0061 \text{ N}$$

- c. Titration of viscoses:

	I	II
cc. of 0.98 N NaOH run	10.10	10.00
cc. of 1.00 N NaOH equiv.	9.90	9.80
cc. of acid equivalent	9.64	9.54
cc. of acid used up by the alkali in viscose	5.36	5.46
The alkali content (%)	5.39	5.49
Mean alkali content (%)	5.44	

2. The cellulose content.

Weight of viscose taken (g)	Weight of dry film (g)	% Cellulose content	Mean
1.546	0.0941	6.08	6.3
1.857	0.1133	6.10	
2.089	0.1364	6.53	

3. Y-Number and the xanthate sulphur content.

The normality of the iodine solution = 0.0250 N		
cc. iodine used	12.10	11.80
Y-number	39.55	38.57
Xanthate sulphur (%)	0.97	0.94

4. Salt-index.

cc. 15 % NaCl solution run	17.5	18.0	18.5
Flocc. ppt. observed	nil	nil	yes
Temperature of solution	20°C	20°C	20°C
Salt-index	-	-	5.75

5. Total sulphur content.

Concentration of viscose soln.	4.9967 g/50 cc.	
Concentration of ZnO soln.	0.5014 g/50 cc.	
Normality of sodium thiosulphate soln.	0.1	
cc. thiosulphate needed		total sulphur (%)
Blank	19.90	0.01
1	7.40	2.17
2	7.20	2.19

B. Pure (white) Viscose.

1. The alkali content.

cc. alkali run	9.95	10.05
cc. 1N alkali	9.75	9.85
cc. acid equiv.	9.56	9.65
cc. acid used by viscose	5.44	5.39
The alkali content (%)	5.47	5.42

2. The Y-number and xanthate sulphur.

cc. 0.025 N iodine soln. used	11.95	11.90
Y-number	39.04	38.89
Xanthate sulphur (%)	0.96	0.95

3. Total sulphur content.

cc. thiosulphate soln. (0.1N)	14.05	13.85
Total sulphur (%)	0.96	0.98

4. Salt-index.

cc. 15% NaCl soln.	17.5	18.0	18.3
Flocc. ppt. formed	nil	nil	yes
Salt-index.	-	-	5.71
Temperature of the solution	20°C	20°C	20°C

A P P E N D I X T A B L E I I .

Ripening of Ordinary Textile and Tyre Cord Viscoses.

1. Tyre Cord Viscose. (Temperature of NaCl Solution 19°C).

Ripening at 20°C			Ripening at 60°C		
Time of Ripening (min.)	Volume of NaCl soln. (cc.)	Salt index	Time of Ripening (min.)	Volume of NaCl soln. (cc.)	Salt index
0	17.4	5.3	0	17.4	5.3
30	16.0	4.9	15	11.3	3.49
70	14.0	4.3	30	9.0	2.8
110	12.5	3.85	45	6.0	1.9
140	12.0	3.7	55	5.5	1.75

2. Ordinary Textile Viscose. (Temperature of NaCl Solution 20°C).

Ripening at 20°C			Ripening at 50°C		
Time of Ripening (min.)	Volume of NaCl soln. (cc.)	Salt index	Time of Ripening (min.)	Volume of NaCl soln. (cc.)	Salt index
0	22.0	6.8	0	21.0	6.3
40	21.0	6.5	15	18.3	5.69
70	20.5	6.15	35	15.5	4.85
100	19.5	6.05	50	14.0	4.40
130	18.5	5.65	65	9.3	3.15
160	18.0	5.55			

A P P E N D I X T A B L E I I I .

Gel Swelling Values of Tyre Cord Fibres.

Sample No.	% Pure Viscose in the mixture	Gel Swelling Values	Mean Swelling Values
1	0	392.3 376.5 352.6	373.8
2	19.70	412.3 424.5 429.0	421.9
3	36.84	451.4 428.4 410.1	429.9
4	59.62	522.3 479.1 481.3	494.2
5	76.37	505.4 517.7 489.4	504.2
6	100	248.5 231.2 243.8	241.1
7	100% Pure Viscose + Buffers	721.2 700.9 -	701.0

A P P E N D I X T A B L E I V .

Moisture Regain and Accessibilities of Fibres.

% Pure Viscose in the mixture	Weight of dry fibres taken (g)	Weight of con- ditioned fibres (g)	Moisture Regain (%)	Mean Moisture Regain (%)	Acces- sibility (%)	Crystal- linity (%)
0	.5545 .6240	.6291 .7050	13.45 12.98	13.2	72.3	38.5
19.70	.4882 .4731	.5536 .5378	13.40 13.68	13.5	74.1	36.0
36.84	.4616 .4371	.5238 .4961	13.48 13.50	13.5	73.8	36.7
59.62	.4097 .5997	.4654 .6769	13.60 12.89	13.3	72.4	38.4
76.37	.5517 .5596	.6234 .6325	13.00 13.03	13.0	71.2	40.1
100	.5312 .5786	.5984 .6508	12.65 12.48	12.6	68.7	43.4
Buffered 100% pure viscose	.5677 .5164	.6457 .5873	13.74 13.73	13.7	75.1	34.6

A P P E N D I X T A B L E V.

Acid Hydrolysis of Fibres.

<u>% Pure Viscose in mixture</u>	<u>Weight of Dry Fibres (g)</u>	<u>Weight of Dry Residue (g)</u>	<u>% Residue on Hydrolysis</u>
0	1.9413	1.5313	78.87
19.70	1.9157	1.4072	73.46
36.84	1.8852	1.2498	66.30
59.62	1.8637	1.3592	72.96
76.37	1.8140	1.3641	75.20
100	1.9265	1.5782	81.93
Buffered 100% pure Viscose	1.8918	1.4811	78.30

A P P E N D I X T A B L E V I .

Limiting-degrees of Polymerisation.

% Pure Vis- cose in the Mixture	Concentration of solution (g/100 cc.)	Fluidity (F)	Relative Viscosity (η_R)	Intrinsic Viscosity $[\eta]$	Limiting Degree of Polymeri- sation	Mean Limiting DP.
0	2.416	52.06	1.388	.142	24.84	25
	2.823	47.75	1.506	.158	26.30	
	2.806	50.60	1.434	.136	23.79	
19.70	1.644	56.73	1.276	.155	27.14	25
	2.829	50.16	1.438	.135	23.60	
36.84	2.581	50.39	1.441	.149	26.10	26
	2.512	51.22	1.418	.146	25.61	
	2.366	52.55	1.381	.142	24.85	
59.62	3.800	38.76	1.874	.169	29.47	28
	2.314	51.92	1.392	.153	26.80	
76.37	3.058	42.53	1.707	.189	33.06	32
	2.743	46.16	1.572	.176	30.77	
100	3.195	40.35	1.799	.199	34.89	36
	3.579	37.28	1.947	.204	35.76	
	3.414	37.54	1.934	.212	37.12	
Buffered 100% pure Viscose	3.118	45.32	1.602	.162	28.49	28
	2.759	47.41	1.531	.164	28.19	
	2.887	46.41	1.564	.165	28.25	

A P P E N D I X T A B L E V I I .

The Amount of Skin Structure.

% Pure Viscose in the Mixture	1	2	3	4	5	6	Mean % Skin Structure
0	100	100	100	100	100	100	100
19.70	86.48	85.86	87.66	87.08	86.72	86.84	86.7
36.84	78.65	78.03	79.82	78.12	78.79	77.62	78.5
59.62	79.52	79.62	79.69	79.84	79.66	79.21	79.5
76.37	60.29	56.03	57.29	56.56	60.39	55.76	57.7
100	0	0	0	0	0	0	0
Buffered 100% Pure Viscose	48.91	48.69	48.07	50.07	49.77	50.79	49.4

A P P E N D I X T A B L E V I I I .

The Titration of Solutions of Viscoscs.

10% Solution of 100% Pure Viscose		10% Solution of Buffered 100% Pure Viscose		10% Solution of Impure Viscose	
cc. acid added	pH	cc. acid added	pH	cc. acid added	pH
0	12.70	0	12.58	0	12.50
5	12.80	5	12.58	5	12.65
10	12.78	10	12.48	10	12.68
15	12.72	15	12.40	15	12.68
20	12.66	20	12.30	20	12.59
25	12.40	25	12.10	25	12.50
30	12.30	30	11.60	30	12.43
35	12.04	35	11.05	35	12.10
40	11.40	40	10.80	40	11.90
45	10.30	45	10.25	45	11.00
50	7.80	50	10.00	50	10.25
55	7.10	55	9.85	55	8.05
60	5.10	60	7.58	60	6.50
65	3.95	65	6.10	65	5.55
70	3.60	70	4.85	70	4.00
75	3.38	75	4.50	75	3.55
80	3.20	80	3.90	80	3.29
85	3.08	85	3.60	85	3.15
90	3.00	90	3.45	90	3.08
100	2.88	100	3.10	100	2.85

A P P E N D I X T A B L E I X .

Prehydrolysis of Cotton Linters Cellulose.

- 1 -

Time of Hydrolysis (Hours)	Viscometer Constant (C)	K	Volume of Solution (cc.)	Flow Times (Secs.)	Weight of Cellulose (g)
0	2205	480	19.2	468.1	0.1203
0	2100	460	20.0	442.4	0.1192
.25	2155	470	19.3	325.5	0.1224
.25	2090	460	19.3	253.4	0.1086
.50	2190	475	19.2	244.0	0.1186
.50	2165	475	20.1	304.6	0.1410
2.0	2040	450	20.2	132.9	0.1087
2.0	2100	460	20.0	184.2	0.1362
4.0	2090	460	19.3	161.7	0.1566
4.0	2155	470	20.2	140.8	0.1446
6.0	2190	475	19.2	192.2	0.1968
6.0	2165	475	20.1	208.1	0.2137
9.16	2050	455	19.1	172.3	0.2200
9.16	2090	460	19.3	200.4	0.2410
23.0	2205	480	19.2	132.1	0.2404
23.0	2155	470	19.3	132.5	0.2425

Time of Hydrolysis (hours)	Fluidity (F)	Relative Viscosity (η_R)	Concn. of Solution (g/100 cc.)	Intrinsic Viscosity $[\eta]$	Degree of Polymerization	Mean DP
0	4.721	15.38	0.6265	6.446	3229	3310
0	4.758	15.25	0.5961	6.656	3390	
.25	6.651	10.91	0.6342	5.293	2392	2388
.25	8.294	8.752	0.5627	5.283	2384	
.50	9.042	8.028	0.6176	4.572	1914	1926
.50	7.147	10.16	0.7015	4.608	1937	
2.0	15.75	4.609	0.5381	3.592	1326	1324
2.0	11.55	6.281	0.6750	3.584	1321	
4.0	13.15	5.518	0.8114	2.727	871.9	891
4.0	15.45	4.697	0.7158	2.740	909.7	
6.0	11.53	6.291	1.0250	2.362	700.6	724
6.0	10.52	6.901	1.0630	2.419	726.3	
9.16	12.09	6.008	1.1520	2.039	560.1	567
9.16	10.54	6.890	1.2480	2.059	574.0	
23.0	17.46	4.230	1.2520	1.442	330.6	336
23.0	16.70	4.345	1.2560	1.469	340.0	

$[\eta]$'s were obtained from $\frac{\eta_{R-1}}{c} = \log [\eta] + 0.14 [\eta] c$

DP's were obtained from $[\eta] = 0.0319(\text{DP})^{.657}$

A P P E N D I X T A B L E X.

The Methylation of Prehydrolysed Cellulose.

Effect of NaOH Concentration.

1. Methoxyl Content of Vanillin.

Weight of Vanillin (mg)	Volume of Sodium Thiosul- phate solution (.1017N) (cc.)	Thiosulphate solution used for the blank (cc.)	% Methoxyl content after the blank
57.5	22.45	0.41	20.16
67.1	26.50	0.41	20.45
78.4	30.55	0.41	20.22

2. Methoxyl Content of Sodium Thiosulphate Solution = 0.1074N.

Concentration of NaOH solution	Weight of Substance (mg)	Thiosul- phate run (after blank) (cc.)	% Methoxyl Content	Mean % Methoxyl Content	Degree of Substitu- tion (DS)
1.25 N	70.3	3.49	2.76	2.78	.14
	68.4	3.44	2.79		
2.50 N	70.8	7.39	5.79	5.77	.31
	75.2	7.79	5.75		
3.00 N	69.7	8.79	7.00	7.13	.39
	73.7	9.64	7.26		
3.125 N	78.3	11.09	7.86	7.87	.43
	81.0	11.49	7.88		
3.50 N	78.2	18.79	13.34	13.20	.73
	60.5	14.24	13.06		
3.75 N	58.0	17.79	17.02	16.82	.95
	59.7	17.89	16.63		
5.00 N	71.1	26.49	20.67	21.13	1.22
	63.6	24.74	21.59		

3. Methoxyl Content of Mercerised Methyl Celluloses.

Concentration of NaOH solution	Weight of Substance (mg)	Thiosul- phate run (after blank) (cc.)	% Methoxyl Content	Mean % Methoxyl Content	Degree of Substitu- tion (DS)
1.25 N	64.6	7.19	6.18	6.16	.33
	62.5	6.74	6.13		
2.5 N	71.0	16.69	13.05	12.90	.71
	61.1	14.04	12.76		
3 N	80.0	23.39	16.25	16.19	.91
	63.4	18.19	16.12		
3.75 N	74.0	24.59	18.50	18.54	1.06
	72.0	24.09	18.59		
5 N	68.8	25.59	20.65	20.95	1.21
	72.6	27.79	21.26		

4. Methoxyl Content of Unhydrolysed Cotton Linters Cellulose.

1.25 N	80.8	2.24	1.54	1.53	.08
	76.3	2.09	1.52		
2.5 N	83.2	7.49	5.00	5.07	.27
	71.2	6.59	5.14		
3.125 N	69.0	10.99	8.85	8.83	.47
	71.2	11.29	8.81		
Vanillin	68.3	24.99	20.33	20.32	1.10
	70.6	25.79	20.31		

APPENDIX TABLE XI.

Methylation of Prehydrolysed Cellulose

Effect of Time on Methylation.

Concentration of NaOH soln.		1.25 N			
Time of Methylation (hours)	Weight of Substance (mg)	Thiosul- phate run (after blank) (cc.)	% Methoxyl Content	Mean (%) Methoxyl Content	Degree of Substitu- tion (DS)
1.25	80.1 66.0	3.75 2.54	2.31 2.14	2.23	.12
6.25	67.1 66.2	2.94 2.92	2.43 2.45	2.44	.13
19.0	60.3 68.1	2.71 3.21	2.50 2.62	2.56	.14
24.25	68.1 79.5	3.69 3.29	2.64 2.68	2.66	.14
2.5 N					
1.25	59.5 75.6	5.69 7.29	5.31 5.35	5.33	.29
3.25	67.7 68.0	6.79 6.79	5.57 5.54	5.56	.30
19.0	61.3 71.5	6.29 7.04	5.70 5.42	5.58	.30
24.25	66.1 71.1	6.59 6.99	5.53 5.64	5.58	.30
3 N					
.25	76.8 77.4	7.49 7.39	5.42 5.30	5.36	.29
.50	72.4 71.9	7.74 7.69	5.94 5.94	5.94	.32
3.0	76.1 61.3	10.09 7.89	7.36 7.13	7.25	.39
24.0	66.0 67.0	8.65 8.84	7.30 7.20	7.25	.39
Vanillin	64.9 71.1	23.76 26.00	20.32 20.30	20.31	1.10

APPENDIX TABLE XII.

Methylation of Prehydrolysed Cellulose.

Effect of Concentration of dimethyl-sulphate.

1. Non-mercerised prehydrolysed cellulose: steeping solution = 2.5 N NaOH.

Concentration of dimethyl-sulphate (molar)	Weight of Substance (mg)	Thiosulphate run (after blank) (cc.)	% Methoxyl Content	Mean (%) Methoxyl Content	Degree of Substitution (DS)
.53 M	80.9	7.94	5.45	5.50	.30
	91.6	9.14	5.55		
1.06 M	78.0	7.39	5.79	5.77	.31
	75.2	7.79	5.75		
2.12 M	64.9	7.19	6.15	6.21	.33
	74.2	8.39	6.28		
4.24 M	72.2	7.99	6.14	6.12	.33
	77.0	8.39	6.09		

2. Mercerised cellulose: steeping solution = 2.5 N NaOH.

.21 M	83.4	17.09	11.38	11.49	.63
	68.9	14.39	11.60		
.53 M	69.1	15.24	12.75	12.50	.69
	76.2	17.49	12.25		
1.06 M	71.0	16.69	13.05	12.91	.71
	61.1	14.04	12.76		

A P P E N D I X T A B L E X I I I .

Methylation of Cellulose.

Weight Increase During Methylation.

1. Methylation of Unhydrolysed Cotton.

Concentra- tion of NaOH soln.	DS of Methyl Cellulose	Weight of dry Cellulose taken (g)	Weight of dry Methyl Cell. (g)	% Weight increase (Experimental)	% Weight increase (Theoretical)
1.25 N	.08	1.3291	1.3294	.02	.68
2.5 N	.27	1.4643	1.4699	.38	2.29
3.125 N	.47	1.4268	1.4609	2.32	4.00

2. Methylation of Prehydrolysed Cellulose.

1.25 N	.14	1.1547	1.1701	1.30	1.24
2.5 N	.31	1.1721	1.1806	0.73	2.68
3 N	.39	1.1423	1.1594	1.49	3.33
3.5 N	.73	1.1475	1.1859	3.35	6.34
3.75 N	.95	1.0814	1.1187	3.45	8.21
5 N	1.22	1.4574	1.5590	6.97	10.55

APPENDIX TABLE XIV.

Methylation of Cellulose².

Fluidity of Methyl Celluloses.

1. Non-mercerised Cellulose.

% Methoxyl Content	Weight (x) of Substance (g)	Flow times (secs.)	Visco- meter Constant (c)	K	Volume of soln. (cc.)	Weight of dry cel- lulose (g)	Fluidity at xg/dl	Fluidity at 0.5g/dl	Mean Fluidity
0	.1079	88.8	2205	480	19.2	.09588	26.44	29.02	28.76
	.1028	81.9	2050	455	19.1	.09539	26.86	28.50	
2.78	.0958	76.6	2165	475	20.1	.1075	30.75	28.08	27.90
	.1049	81.0	2125	470	20.2	.1075	28.26	27.73	
5.77	.1003	95.1	2205	480	19.2	.09588	24.49	25.47	24.46
	.0955	96.0	2155	470	19.3	.09634	23.65	23.46	
7.13	.0964	93.9	2050	455	19.1	.09539	23.02	23.30	23.30
	.1077	104.6	2090	460	19.3	.09634	20.85	23.29	
7.87	.1037	104.6	2155	470	19.3	.09634	21.53	23.14	23.10
	.1028	110.7	2090	460	19.3	.09634	21.65	23.07	
13.20	.0944	103.1	2165	475	20.1	.1070	21.99	19.25	19.23
	.1032	110.0	2125	470	20.2	.1075	20.10	19.21	
16.82	.1054	114.4	2040	450	20.2	.1075	18.47	19.48	19.46
	.1001	122.3	2190	475	19.2	.09588	18.49	19.43	
21.13	.0906	86.3	2155	470	19.3	.09634	26.65	25.30	24.45
	.0973	84.4	2040	450	20.2	.1025	25.80	23.60	

2. Mercerised Cellulose.

% Methoxyl Content	Weight (x) of Substance (g)	Flow times (secs)	Visco- meter Constant (c)	K	Volume of soln. (cc.)	Weight of dry cel- lulose (g)	Fluidity at xg/dl	Fluidity at 0.5g/dl	Mean Fluidity
0	.0963	80.3	2155	470	19.3	.09634	28.93	28.92	28.77
	.1024	86.1	2190	475	19.2	.09588	27.67	28.62	
6.16	.1006	80.2	2050	455	19.1	.09539	27.51	28.77	29.14
	.1034	83.0	2155	470	19.3	.09634	27.86	29.51	
12.90	.1043	118.2	2090	460	19.3	.09634	19.17	21.48	21.69
	.1066	108.0	2190	475	19.2	.09588	20.15	21.89	
16.19	.1103	132.4	2090	460	19.3	.09634	16.21	19.17	18.88
	.1046	127.4	2050	455	19.1	.09539	16.56	18.58	
18.54	.1003	125.2	2050	455	19.1	.09539	16.87	17.97	17.29
	.0984	137.0	2155	470	19.3	.09634	16.14	16.61	
20.95	.0986	118.7	2090	460	19.3	.09634	18.20	18.71	18.82
	.0993	124.4	2190	475	19.2	.09588	18.17	18.93	

3. Unhydrolysed Cotton Linters Cellulose.

% Methoxyl Content	Weight of Substance (g)	Flow times (secs.)	Visco- meter Constant (C)	K	Volume of soln. (cc.)	Weight of dry cel- lulose (g)	Fluidity at 1g/dl	Fluidity at 0.5g/dl	Mean Fluidity
0	.0983	324.8	2270	495	19.4	.09680	7.22	7.66	7.72
	.0997	316.0	2180	475	19.2	.09588	6.93	7.78	
1.53	.0978	235.7	2320	505	19.4	.09680	9.93	10.15	9.87
	.0966	232.9	2195	480	19.3	.09634	9.51	9.59	
5.07	.0977	395.6	2095	460	19.3	.09634	5.31	5.64	5.61
	.0976	407.2	2205	485	19.4	.09680	5.43	5.58	
8.83	.0998	551.0	2100	460	19.3	.09634	3.82	4.11	4.35
	.0968	531.8	2155	470	19.3	.09634	3.99	4.59	

A P P E N D I X T A B L E X V .

Methylation of Cellulose.

Effect of Ageing on the Fluidities of Methyl Celluloses.

1. Concentration of steeping solution = 1.25 N; Temperature = 23°C.

Time of Ageing (mins.)	Weight of dry substance taken (g)	Flow times (secs.)	Visco-meter Constant (c)	K	Weight of dry cellulose (g)	Fluidity at x g/dl	Fluidity at 0.5 g/dl	Mean Fluidity
0	.0958	76.6	2165	475	.1070	30.75	28.08	27.90
	.1049	81.0	2125	470	.1075	28.26	27.73	
20	.0959	66.2	2205	480	.09588	37.40	37.40	37.50
	.1031	66.7	2155	470	.09634	36.12	37.60	
40	.0984	59.7	2190	475	.09588	42.41	42.99	42.79
	.1065	61.0	2155	470	.09634	40.42	42.66	
60	.1099	62.6	2205	480	.09588	42.05	43.57	43.35
	.1023	56.8	2050	455	.09539	40.15	43.13	

2. Concentration of steeping solution = 2.5 N; Temperature = 23°C.

Time of Ageing (mins.)	Weight of dry substance taken (g)	Flow times (secs.)	Visco-meter Constant (c)	K	Weight of dry cellulose	Fluidity at x g/dl	Fluidity at 0.5 g/dl	Mean Fluidity
0	.1003 .0955	95.1 96.0	2205 2155	480 470	.09588 .09634	24.49 23.65	25.47 23.46	24.46
15	.1080 .1033	93.3 87.2	2155 2050	470 455	.09634 .09539	24.41 25.01	27.91 26.72	27.33
30	.1032 .1051	88.0 89.3	2190 2205	475 480	.09588 .09588	26.51 26.26	28.11 28.27	28.19
60	.1078 .1088	86.5 84.7	2205 2155	480 470	.09588 .09634	27.26 27.22	29.80 29.88	29.84

3. Concentration of steeping solution = 3 N; Temperature = 23°C.

0	.0964 .1077	93.9 104.6	2050 2090	455 460	.09539 .09634	23.02 20.85	23.30 23.29	23.30
30	.1023 .1034	99.3 95.6	2190 2050	475 455	.09588 .09539	23.12 22.57	24.54 24.33	24.43
60	.0995 .1019	93.5 92.3	2205 2155	480 470	.09588 .09634	24.96 24.42	25.77 25.65	25.71
120	.1045 .1027	86.7 87.3	2050 2190	455 475	.09539 .09588	25.17 26.75	27.27 28.25	27.76

4. Concentration of steeping solution = 3.125 N: Temperature = 23°C.

Time of Ageing (mins.)	Weight of dry substance taken (g)	Flow times (secs.)	Visco-meter Constant (c)	K	Weight of dry cellulose	Fluidity at x g/dl	Fluidity at 0.5 g/dl	Mean Fluidity
0	.1037	104.6	2155	470	.09634	21.53	23.14	23.10
	.1028	110.7	2090	460	.09634	21.65	23.07	
60	.1029	99.7	2190	475	.09588	23.05	24.59	24.21
	.0995	98.0	2155	470	.09634	23.12	23.88	
150	.1061	102.3	2190	475	.09588	22.41	24.62	24.47
	.1022	94.7	2050	455	.09539	22.81	24.32	
240	.1023	95.6	2090	460	.09634	23.02	24.35	24.62
	.1041	97.7	2155	470	.09634	23.20	24.89	

5. Concentration of steeping solution = 3.125 N: Temperature = 50°C.

0	.1037	104.6	2155	470	.09634	21.53	23.14	23.10
	.1028	110.7	2090	460	.09634	21.65	23.07	
30	.1013	95.2	2155	470	.09634	23.87	24.97	25.18
	.1020	96.0	2190	475	.09588	24.03	25.38	
80	.1034	87.9	2050	455	.09539	24.78	26.54	26.66
	.1020	91.3	2190	475	.09588	25.43	26.78	
120	.1024	85.8	2090	460	.09634	25.98	27.32	27.60
	.1010	82.5	2050	455	.09539	26.63	27.88	

APPENDIX TABLE XVI.

Acid Hydrolysis of Methylcelluloses.

1. Percentage weight loss during Acid Hydrolysis.

* Sample	Time of Hydrolysis (mins.)	Weight of substance taken (g)	Weight of residue (g)	Weight loss during Hydrolysis (%)
C.1	20	1.1468	1.1407	0.53
	45	1.5080	1.4820	1.72
	110	1.2584	1.1959	4.90
	175	1.6054	1.5154	5.60
M.C.1	10	1.2103	1.1920	1.50
	20	1.0996	1.0657	3.10
	60	1.1269	1.0426	7.50
	110	1.2584	1.1293	10.27
	170	1.1427	1.0053	12.02
M.C.2	10	1.1301	1.0970	2.90
	20	1.1280	1.0758	4.60
	45	1.2257	1.1155	8.99
	120	1.1654	0.9846	15.51
	180	1.2222	1.0098	17.37
	360	1.4464	1.1640	19.52
M.C.3	10	1.0033	0.8911	10.71
	20	1.1361	0.9715	14.48
	45	1.0892	0.8736	19.33
	100	1.0650	0.8029	24.61
	180	1.0197	0.7231	29.08
	360	1.8050	1.2434	31.11
	720	1.9482	1.2774	34.43

*

C.1 = Prehydrolysed Cellulose.

M.C.1 = Methylated Prehydrolysed Cellulose of 2.78% Methoxyl Content.

M.C.2 = Methylated Prehydrolysed Cellulose of 5.77% Methoxyl Content.

M.C.3 = Methylated Prehydrolysed Cellulose of 7.87% Methoxyl Content.

2. Methoxyl Content of Hydrocellulose residues.

Sample	Time of Hydrolysis (mins.)	Weight of substance taken (mg)	cc. of Thio- sulphate used after blank (.1074 N)	% Methoxyl Content	Mean % Methoxyl Content
M.C.1	10	92.4	3.39	2.05	2.06
		84.8	3.19	2.09	
	20	101.1	3.49	1.92	1.95
		93.4	3.34	1.98	
	60	144.2	2.94	1.13	1.09
		113.8	2.14	1.04	
	110	136.0	2.59	1.06	1.12
		148.7	3.19	1.19	
	170	175.7	3.79	1.20	1.12
		168.9	3.19	1.04	
M.C.2	10	95.0	8.24	4.82	4.86
		79.2	6.99	4.90	
	20	70.1	6.69	4.35	4.28
		88.1	6.29	4.22	
	45	105.0	6.29	3.33	3.29
		110.4	6.49	3.26	
	120	148.7	6.69	2.56	2.64
		137.7	6.49	2.74	
	180	193.9	8.04	2.30	2.31
		154.1	6.44	2.31	
	360	168.5	6.69	2.17	2.18
		149.2	5.89	2.19	

2. Methoxyl Content of Hydrocellulose residues. (continued)

Sample	Time of Hydrolysis (mins.)	Weight of substance taken (mg)	cc. of Thio- sulphate used after blank (.1074 N)	% Methoxyl Content	Mean % Methoxyl Content
M.C.3	10	67.0	8.59	7.12	7.11
		73.1	9.34	7.10	
	20	93.2	11.59	6.79	6.67
		102.6	12.09	6.55	
	100	135.1	10.49	4.31	4.31
		144.6	11.19	4.30	
	180	185.1	11.39	3.42	3.37
		149.4	8.94	3.32	
	360	155.4	8.69	3.11	3.11
		153.2	8.59	3.11	
	720	160.0	8.74	3.04	3.04
		158.5	8.64	3.03	
Vanillin		59.3	21.69	20.32	20.29
		67.0	21.84	20.26	

A P P E N D I X T A B L E XVll.

Acid Hydrolysis of Regenerated Methylcellulose
(7.87 % Methoxyl Content).

1. % Weight loss during Acid Hydrolysis.

Time of Hydrolysis (mins.)	Weight of dry Methylcellulose (g)	Weight of residue (g)	Weight Loss (%)
30	1.0242	0.8098	20.93
60	1.2149	0.8594	28.43
210	1.1677	0.6538	44.00
360	1.2121	0.6477	46.56

2. Methoxyl Content of Hydrocellulose residues.

Time of Hydrolysis (mins.)	Weight of substance (mg)	cc. of Thiosulphate used after blank (.1074 N)	% Methoxyl Content	Mean % Methoxyl Content
30	111.1	12.99	6.50	6.52
	121.8	14.34	6.54	
60	110.3	10.49	5.28	5.24
	131.4	12.29	5.20	
210	129.0	8.74	3.76	3.83
	114.2	7.99	3.89	
360	173.2	9.94	3.20	3.21
	148.0	8.59	3.22	

APPENDIX TABLE XVII.

The Limiting degrees of Polymerization.

Sample	Weight of substance	Flow times (secs.)	Visco-meter Constant	Volume of solution	K	Fluidity	* Relative Viscosity	Log $[\eta]_C$	$[\eta]$	Limiting degree of Polymeri-sation	Mean limiting degree of Polymeri-sation
	(g)		(c)	(cc.)		(F)	(R)				
C.1	.2142 .2811	359.4 439.1	9523 9074	13.99 14.41	275 275	26.56 20.69	2.734 3.509	0.0860 0.1854	0.796 0.786	139.3 137.5	138
M.C.1	.2658 .3193	435.5 544.1	9212 9512	14.08 14.02	275 275	21.20 17.58	3.423 4.130	0.1754 0.2482	0.793 0.778	138.8 136.0	137
M.C.2	.2539 .2046	403.4 335.5	9286 9337	14.50 14.23	275 275	23.04 27.90	3.149 2.602	0.1384 0.0484	0.786 0.778	137.5 136.0	137
M.C.3	.2515 .2014	380.7 198.2	9055 9292	14.07 14.12	275 275	23.82 29.28	3.047 2.479	0.1239 0.0223	0.744 0.738	130.2 129.1	130
Rege-nerated M.C.3	.3227 .2968	188.0 186.7	9093 9512	14.15 14.02	275 275	48.75 51.35	1.489 1.414	1.6280 -	0.186 0.170	32.58 29.80	31

* Obtained from Baker's equation

$$\eta_R = \left[\left(1 + \frac{[\eta]_C}{3.5} \right) \right]^{3.5}$$

APPENDIX TABLE XIX.

The Analysis of Viscos.

1. Viscos made from Prehydrolysed Cellulose (Denoted as V.C.1).

a. Cellulose Content (1).

Weight of Viscose (g)	Weight of Films (g)	% Cellulose Content	Mean % Cellulose Content
2.569	.1987	7.73	7.7
2.873	.2219	7.71	

b. Alkali Content (1).

Normality of Alkali used	Normality of Acid used	Volume of Alkali used (cc.)	% Alkali Content	Mean % Alkali Content
.9444 N	.9634 N	8.85	6.10	6.1
		8.85	6.10	

a. Cellulose Content (2).

Weight of Viscose (g)	Weight of Films (g)	% Cellulose Content	Mean % Cellulose Content
1.413	.0999	7.07	7.1
1.405	.0986	7.02	
2.118	.1500	7.10	

b. Alkali Content (2).

Normality of Alkali used	Normality of Acid used	Volume of Alkali used (cc.)	% Alkali Content	Mean % Alkali Content
.9444 N	.9634 N	8.80	6.14	6.1
		8.90	6.04	

2. Viscoses made from partially Methylated Cellulose (2.78 % Methoxyl Content) (Denoted as V.M.C.1).

a. Cellulose Content.

Weight of Viscose (g)	Weight of Films (g)	% Cellulose Content	Mean % Cellulose Content
3.245	.2033	6.88	6.9
2.941	.1996	6.96	
2.730	.1866	6.78	

b. Alkali Content.

Normality of Alkali used	Normality of Acid used	Volume of Alkali used (cc.)	% Alkali Content	Mean % Alkali Content
.9748 N	.9614 N	8.60	6.12	6.1
		8.55	6.06	

3. Viscoses made from partially Methylated Cellulose (5.77 % Methoxyl Content) (Denoted as V.M.C.2).

a. Cellulose Content (1).

Weight of Viscose (g)	Weight of Films (g)	% Cellulose Content	Mean % Cellulose Content
2.742	.2083	7.59	7.6
1.799	.1376	7.59	

b. Alkali Content (1).

Normality of Alkali used	Normality of Acid used	Volume of Alkali used (cc.)	% Alkali Content	Mean % Alkali Content
.9486 N	.9799 N	9.05 9.10	6.12 6.06	6.1

a. Cellulose Content (2).

Weight of Viscose (g)	Weight of Films (g)	% Cellulose Content	Mean % Cellulose Content
2.100	.1481	7.05	7.1
2.228	.1573	7.05	
2.794	.1983	7.09	

b. Alkali Content (2).

Normality of Alkali used	Normality of Acid used	Volume of Alkali used (cc.)	% Alkali Content	Mean % Alkali Content
.9444 N	.9634 N	8.90 8.85	6.04 6.08	6.1

4. Viscose made from partially Methylated Cellulose (7.87 % Methoxyl Content) (Denoted as V.M.C.3).

a. Cellulose Content.

Weight of Viscose (g)	Weight of Films (g)	% Cellulose Content	Mean % Cellulose Content
2.843	.2011	7.07	7.1
2.881	.2047	7.08	
3.104	.2199	7.08	

b. Alkali Content.

Normality of Alkali used	Normality of Acid used	Volume of Alkali used (cc.)	% Alkali Content	Mean % Alkali Content
.9581 N	.9816 N	8.90	6.19	6.1
		9.10	6.10	

A P P E N D I X T A B L E XX.

Effect of Partial Methylation on Ripening.

Cellulose Content = 7.1 % Alkali Content = 6.1 % (V.C.2)		Cellulose Content = 6.9 % Alkali Content = 6.1 % (V.M.C.1)	
Time of Ripening (hours)	Hottenroth-number (cc. of NH_3Cl soln.)	Time of Ripening (hours)	Hottenroth-number (cc. of NH_3Cl soln.)
17.25	26.80	24.25	32.00
24.25	20.25	32.50	24.00
40.75	11.80	47.50	15.80
48.00	10.40	66.50	10.30
65.50	9.10	100.00	8.95
95.25	7.30		

Cellulose Content = 7.1 % Alkali Content = 6.1 % (V.M.C.2)		Cellulose Content = 7.1 % Alkali Content = 6.1 % (V.M.C.3)	
Time of Ripening (hours)	Hottenroth-number (cc. of NH_3Cl soln.)	Time of Ripening (hours)	Hottenroth-number (cc. of NH_3Cl soln.)
25.00	32.80	42.00	22.40
40.00	20.00	48.50	17.90
48.00	16.60	66.00	12.00
65.50	11.00	72.50	10.50
71.00	10.10	96.50	9.30
93.00	9.00		

A P P E N D I X T A B L E X X I .

Effect of Partial Methylation on Viscosity of Viscose.

Cellulose Content = 7.7 % Alkali Content = 6.1 % (V.C.1)			Cellulose Content = 7.6 % Alkali Content = 6.1 % (V.M.C.2)		
Time of Ripening (hours)	Galva- nometer Scale	Viscosity (poise)	Time of Ripening (hours)	Galva- nometer Scale	Viscosity (poise)
0	294	23.14	0	236	18.57
15.50	276	21.72	15.50	212	16.68
22.30	280	22.04	22.50	216	17.10
39.50	280	22.04	41.00	218	17.16
46.25	290	22.75	87.00	242	19.05
63.00	294	23.04	94.50	250	19.68
88.50	296	23.19			
135.00	324	25.50			

Cellulose Content = 6.9 % Alkali Content = 6.1 % (V.M.C.1)			Cellulose Content = 7.1 % Alkali Content = 6.1 % (V.M.C.3)		
Time of Ripening (hours)	Galva- nometer Scale	Viscosity (poise)	Time of Ripening (hours)	Galva- nometer Scale	Viscosity (poise)
0	208	16.37	0	156	12.28
17.45	188	14.80	17.50	150	11.81
24.00	195	15.35	24.00	150	11.81
45.75	196	15.43	41.50	152	11.96
66.25	199	15.66	47.75	155	12.20
100.00	213	16.80	65.50	160	12.59
			71.25	164	12.90

APPENDIX TABLE XXII.

Effect of Cellulose Concentration on the Viscosities of Viscos.

V.C.1 Hottenroth-number = 10.50			V.M.C.1 Hottenroth-number = 10.30		
Cellulose Content (%)	Galva- nometer Scale	Viscosity (poise)	Cellulose Content (%)	Galva- nometer Scale	Viscosity (poise)
7.72	280	22.04	6.87	199	15.66
7.40	262	20.63	6.59	176	13.85
7.39	252	19.84	6.09	150	11.78
6.83	210	16.53			

V.M.C.2 Hottenroth-number = 10.10			V.M.C.3 Hottenroth-number = 12.00		
Cellulose Content (%)	Galva- nometer Scale	Viscosity (poise)	Cellulose Content (%)	Galva- nometer Scale	Viscosity (poise)
7.59	250	19.68	7.08	160	12.59
7.26	220	17.32	6.75	137	10.78
7.10	208	16.38	6.37	121	9.52

A P P E N D I X T A B L E X X I I I .

Analysis of Viscoscs used in Spinning.

1. Cellulose Content.

Sample	Weight of Viscose (g)	Weight of dry Films (g)	% Cellulose Content	Mean % Cellulose Content
V.C.1	1.853	.1396	7.54	7.5
	1.827	.1364	7.46	
V.M.C.1	2.388	.1670	6.99	7.0
	2.096	.1464	6.99	
V.M.C.2	1.450	.1108	7.64	7.7
	1.428	.1095	7.66	
V.M.C.3	2.843	.2011	7.07	7.1
	2.889	.2047	7.08	
	3.104	.2199	7.08	

2. Alkali Content.

Sample	Normality of Alkali used	Normality of Acid used	Volume of Alkali run (cc.)	% Alkali Content	Mean % Alkali Content
V.C.1	.9581 N	.9816 N	9.00	6.06	6.1
			9.05	6.07	
V.M.C.1	.9581 N	.9816 N	9.00	6.10	6.1
			9.05	6.06	
V.M.C.2	.9444 N	.9634 N	9.10	6.08	6.1
			9.10	6.08	
V.M.C.3	.9581 N	.9816 N	8.90	6.19	6.1
			9.00	6.09	

3. χ -number and Xanthate Sulphur Content.

Sample	Normality of Thiosulphate Solution	Normality of Iodine Solution	Volume of Iodine Solution run (cc.)	χ -number	Xanthate Sulphur %
V.C.1	.02438 N	.9752 N	20.30	53.5	1.61
V.M.C.1	.02485 N	.9942 N	19.30	55.6	1.54
V.M.C.2	.02438 N	.9752 N	21.70	56.0	1.69
V.M.C.3	.02485 N	.9942 N	20.65	58.8	1.64

4. Total Sulphur Content.

Sample	Normality of Thio-sulphate Solution	Normality of Iodine Solution	Volume of Thiosul-phate run (cc.)	Volume of Iodine Solution left (cc.)	Volume of Iodine Solution used up (cc.)	Total Sulphur %
V.C.1	.1074 N	.9752 N	7.70	8.48	11.23	1.80
V.M.C.1	.1074 N	.9940 N	8.25	8.91	11.03	1.76
V.M.C.2	.1074 N	.9752 N	7.55	8.39	11.22	1.80
V.M.C.3	.1074 N	.9940 N	8.00	8.64	11.29	1.80

APPENDIX TABLE XLV.

Fluidities of Spun Filaments.

* Sample	% Acid used in the bath	Weight of Substance (g)	Flow times (secs.)	Visco- meter Constant (c)	K	Weight of dry cel- lulose (g)	Fluidity at x g/dl	Fluidity at 0.5 g/dl	Mean Fluidity
F.C.1	9	.0999	78.0	2095	460	.09634	29.06	29.86	29.97
		.0975	78.5	2155	470	.09588	29.72	30.08	
	12	.0991	80.2	2180	475	.09588	29.35	30.07	29.77
		.0981	80.9	2205	485	.09680	29.43	29.46	
	12+ Modifier	.1000	84.4	2270	495	.09680	29.27	29.98	29.91
		.0986	77.5	2100	460	.09634	29.34	29.85	
	15	.1021	80.8	2170	475	.09727	28.97	30.03	30.04
		.1023	78.8	2110	465	.09727	28.95	30.05	
	9	.0997	80.8	2205	485	.09680	29.56	30.20	29.84
		.1052	89.2	2320	505	.09680	27.77	29.49	
F.M.C.1	12	.0967	72.4	2100	460	.09634	29.39	29.47	29.74
		.1009	79.9	2170	475	.09727	29.35	30.01	
	12+ Modifier	.1003	82.0	2100	460	.09634	28.80	29.68	29.90
		.0992	84.4	2320	505	.09680	29.59	30.12	
	15	.1000	81.8	2180	475	.09588	28.69	29.61	29.69
		.0993	81.3	2195	480	.09634	29.11	29.78	

Fluidities of Spun Filaments (Continued).

* Sample	% Acid used in the bath	Weight of Substance (g)	Flow times (secs.)	Visco- meter Constant	K	Weight of dry cel- lulose	Fluidity at x g/dl	Fluidity at 0.5 g/dl	Mean Fluidity
(c)									
F.M.C.2	9	.1032	80.6	2095	460	.09634	27.98	29.48	29.62
		.0997	79.9	2155	470	.09588	29.12	29.77	
	12	.0974	81.2	2210	485	.09727	29.38	29.41	29.66
		.1059	80.0	2110	465	.09727	28.04	29.90	
F.M.C.3	12+	.0977	80.6	2155	470	.09634	29.49	29.80	29.88
	Modifier	.1003	83.7	2270	495	.09680	29.18	29.96	
	15	.1022	84.0	2210	485	.09727	28.25	29.33	29.72
		.1007	76.8	2155	470	.09634	29.16	30.12	
F.M.C.3	9	.1011	84.9	2270	495	.09680	28.71	29.66	29.62
		.0999	81.8	2180	475	.09588	28.69	29.59	
	12	.0995	78.8	2110	465	.09727	28.95	29.44	29.50
		.1009	82.7	2210	485	.09727	28.76	29.56	
F.M.C.3	12+	.0977	80.4	2155	470	.09588	28.89	29.30	29.17
	Modifier	.0979	79.1	2100	460	.09634	28.70	29.05	
	15	.1020	82.9	2195	480	.09634	28.45	29.70	29.45
		.1008	87.7	2320	505	.09680	28.31	29.21	

* F.C.1 is the filaments obtained from the spinning of Viscose made from Prehydrolysed Cellulose.
 F.M.C.1 is the filaments obtained from the spinning of Viscose made from Methyl Cellulose of 2.78% Methoxyl Content.
 F.M.C.2 is the filaments obtained from the spinning of Viscose made from Methyl Cellulose of 5.77% Methoxyl Content.
 F.M.C.3 is the filaments obtained from the spinning of Viscose made from Methyl Cellulose of 7.87% Methoxyl Content.

A P P E N D I X T A B L E XXV.

Methoxyl Content of the Spun Filaments.

* Sample	% Acid used in Spinning	Weight of Substance (mg)	cc. of Thio- sulphate run after blank (.1074 N)	% Methoxyl Content	Mean % Methoxyl Content
F.M.C.1	9	85.0	4.14	2.71	2.69
		73.5	3.54	2.68	
	12	88.8	4.20	2.67	2.66
		80.6	3.84	2.64	
	12+ Modifier	81.1	3.84	2.63	2.63
		75.4	3.69	2.72	
	15	59.7	2.89	2.69	2.67
		69.8	3.49	2.64	
F.M.C.2	9	87.4	9.29	5.67	5.67
		91.1	8.89	5.66	
	12	54.1	5.59	5.74	5.74
		50.7	5.24	5.74	
	12+ Modifier	55.8	5.79	5.77	5.78
		72.9	7.59	5.79	
	15	55.6	5.69	5.68	5.75
		73.2	7.69	5.84	
F.M.C.3	9	61.1	8.64	7.86	7.87
		73.9	11.19	7.88	
	12	57.3	8.09	7.84	7.87
		61.8	8.79	7.90	
	12+ Modifier	64.1	9.14	7.92	7.88
		61.5	8.69	7.85	
	15	65.0	9.24	7.90	7.87
		66.5	9.39	7.85	
	Vanillin	50.5	18.39	20.23	20.24
		62.4	22.74	20.24	

* F.M.C.1 stands for the fibres spun from Viscoscs made from Methyl Cellulose of 2.78% Methoxyl Content.

F.M.C.2 stands for the fibres spun from Viscoscs made from Methyl Cellulose of 5.77% Methoxyl Content.

F.M.C.3 stands for the fibres spun from Viscoscs made from Methyl Cellulose of 7.87% Methoxyl Content.

A P P E N D I X T A B L E XXVI.

Gel-swelling Values of Spun Filaments.

Sample	% Acid used in Spinning	Gel-swelling Values			Mean % Gel-swelling
		1	2	3	
F.C.1	9	154.7	144.6	142.6	147.3
	12	365.8	329.4	322.6	339.2
	15	668.7	578.9	609.8	619.1
	12+ Modifier	169.6	186.3	170.9	175.6
F.M.C.1	9	255.2	292.5	262.1	269.9
	12	349.1	318.5	289.1	318.9
	15	444.8	407.0	429.0	426.9
	12+ Modifier	156.9	231.9	195.1	194.6
F.M.C.2	9	250.2	225.5	254.0	243.2
	12	419.8	400.3	405.3	408.4
	15	855.3	851.6	816.1	841.1
	12+ Modifier	440.7	436.1	426.3	434.4
F.M.C.3	9	317.5	365.2	360.6	344.4
	12	520.1	500.7	556.6	529.1
	15	941.8	955.0	937.9	944.6
	12+ Modifier	800.0	757.7	849.0	802.2

A P P E N D I X T A B L E XXVII.

Moisture Regain and Accessibilities of Spun Filaments.

Sample	% Acid used in Spinning	Weight of dry Substance (g)	Weight of cond. Substance (g)	% Moisture Regain	Mean % Moisture Regain	% Accessibility	% Crystallinity
F.C.1 Weight of Repeating Unit = 162 g.	9	.3400	.3851	13.27	13.45	79.1	29.0
		.3061	.3478	13.62			
	12	.3420	.3872	13.22	13.38	78.7	29.6
		.3036	.3448	13.57			
	15	.2336	.2654	13.19	13.20	77.6	31.1
		.3038	.3450	13.22			
F.N.C.1 Weight of Repeating Unit = 164 g. (average)	12+ Modifier	.3628	.4117	13.48	13.32	78.3	30.8
		.3444	.3897	13.15			
	9	.3383	.3843	13.63	13.79	85.0	20.8
		.3683	.4197	13.95			
	12	.3787	.4293	13.36	13.40	82.7	24.0
		.4285	.4862	13.44			
F.N.C.1 Weight of Repeating Unit = 164 g. (average)	15	.2768	.3140	13.43	13.18	81.4	25.9
		.3827	.4322	12.93			
	12+ Modifier	.3935	.4488	14.05	14.05	86.6	18.7
		.3309	.3774	14.05			

Moisture Regain and Accessibilities of Spun Filaments (Continued).

Sample	% Acid used in Spinning	Weight of dry Substance (g)	Weight of cond. Substance (g)	% Moisture Regain	Mean % Moisture Regain	% Accessibility	% Crystallinity
F.M.C.2 Weight of Repeating Unit = 166.3 g. (average)	9	.3496 .3878	.3962 .4393	13.33 13.29	13.31	86.9	18.1
	12	.3597 .3202	.4078 .3629	13.09 13.33	13.21	86.3	19.0
	15	.4351 .2844	.4911 .3220	12.84 13.22	13.06	85.4	20.3
	12+ Modifier	.3225 .5140	.3656 .5826	13.37 13.34	13.35	87.2	17.8
F.M.C.3 Weight of Repeating Unit = 168 g. (average)	9	.3924 .5423	.4433 .6117	12.97 12.79	12.88	87.6	17.3
	12	.3882 .4619	.4372 .5207	12.62 12.73	12.68	86.4	18.9
	15	.4122 .3788	.4646 .4263	12.71 12.51	12.61	86.0	19.4
	12+ Modifier	.4405 .3939	.5627 .4449	12.67 12.94	12.80	87.1	17.9

A P P E N D I X T A B L E XXVII.

Acid Hydrolysis of Spun Filaments.

Sample	% Acid used in Spinning	Weight of Substance taken (g)	Weight of the residue (g)	Weight loss during Hydrolysis (%)	% Residue
F.C.1	9	1.4663	1.2448	15.10	84.9
	12	1.5845	1.3534	14.54	85.5
	15	1.1460	1.0126	11.64	88.4
	12+				
	Modifier	1.3514	1.1458	15.21	84.8
F.M.C.1	9	1.3090	0.9985	23.60	76.4
	12	1.3015	0.9942	23.61	76.4
	15	1.1803	0.9365	20.65	79.4
	12+				
	Modifier	1.4105	1.0545	25.23	74.8
F.M.C.2	9	1.4514	0.7991	44.44	55.6
	12	1.6770	0.9355	44.21	55.8
	15	0.8738	0.5344	38.84	61.2
	12+				
	Modifier	1.5180	0.8232	45.78	54.2
F.M.C.3	9	1.6444	0.6177	62.43	37.6
	12	1.0375	0.3905	62.36	37.6
	15	1.1235	0.5009	55.41	44.6
	12+				
	Modifier	1.1213	0.3925	64.99	35.0

APPENDIX TABLE XXX.

Limiting degree of Polymerisation (1).

Sample	% Acid used in Spinning	Weight of Substance taken (g)	Flow times (secs.)	Visco- meter Constant (c)	Volume of Solution (cc.)	K
F.C.1	9	.2820	181.5	9512	14.02	275
		.4380	209.3	9286	14.50	275
	12	.3337	210.3	9523	13.99	275
		.3842	201.9	9055	14.07	275
	15	.2701	185.7	9212	14.08	275
		.2962	193.5	9074	14.41	275
	12+ Modifier	.4451	225.0	9293	14.14	275
		.4697	229.9	9337	14.23	275
	9	.4062	220.9	9523	13.99	275
		.4207	214.1	9286	14.50	275
F.M.C.1	12	.3198	193.5	9293	14.12	275
		.4052	215.9	9512	14.02	275
	15	.3645	207.7	9337	14.23	275
		.3690	209.9	9055	14.07	275
	12+ Modifier	.3967	204.1	9074	14.41	275
		.4043	211.4	9212	14.08	275
	9	.1825	162.1	9512	14.02	275
		.2013	165.5	9337	14.22	275
	12	.3653	201.4	9212	14.08	275
		.3409	203.6	9523	13.99	275
F.M.C.2	15	.1986	164.7	9286	14.50	275
		.1819	160.9	9055	14.07	275
	12+ Modifier	.2847	180.0	9286	14.50	275
		.3551	197.1	9074	14.41	275
	9	.1936	158.3	9074	14.41	275
		.1920	163.5	9523	13.99	275
	12	.1945	163.0	9212	14.08	275
		.1268	151.6	9293	14.12	275
	15	.1620	162.1	9337	14.22	275
		.1945	168.2	9293	14.12	275
F.M.C.3	12+ Modifier	.2074	162.1	9074	14.41	275
		.2783	177.4	9055	14.07	275

Limiting degree of Polymerisation (2).

Sample	% Acid used in Spinning	Concn. of Solution (g/dl)	Relative Viscosity (η_R)	Intrinsic Viscosity [η]	Limiting degree of Polymeri- sation	Mean degree of Polymeri- sation
F.C.1	9	3.021	1.627	1.727	30.21	30
		2.011	1.413	1.653	28.93	
	12	2.731	1.610	1.872	32.75	34
		2.441	1.609	2.036	35.63	
	15	1.919	1.450	2.043	35.75	38
		2.055	1.533	2.214	38.75	
	12+ Modifier	3.301	1.778	1.898	33.21	33
		3.153	1.748	1.921	33.60	
F.M.C.1	9	2.562	1.639	1.639	28.68	29
		2.623	1.673	1.675	29.31	
	12	2.263	1.497	1.918	33.56	33
		2.892	1.638	1.840	32.19	
	15	2.902	1.676	1.917	33.55	35
		2.900	1.702	1.979	34.62	
	12+ Modifier	2.753	1.622	1.881	32.94	33
		2.872	1.655	1.889	33.06	
F.M.C.2	9	1.302	1.224	1.586	27.74	29
		1.416	1.276	1.700	29.76	
	12	2.436	1.546	1.897	33.19	33
		2.595	1.576	1.875	32.80	
	15	1.370	1.282	1.891	33.09	33
		1.293	1.255	1.813	31.70	
	12+ Modifier	2.463	1.566	1.946	32.53	32
		1.963	1.395	1.782	31.20	
F.M.C.3	9	1.344	1.253	1.746	30.55	29
		1.372	1.233	1.581	27.68	
	12	1.381	1.271	1.799	31.48	31
		0.979	1.170	1.792	31.34	
	15	1.377	1.302	1.983	34.73	35
		1.139	1.248	1.997	34.94	
	12+ Modifier	1.439	1.282	1.800	31.50	32
		1.987	1.409	1.797	31.40	

APPENDIX TABLE XXX

Amount of Skin Structure of Spun Filaments.

Sample	% Acid used in Spinning	% Skin Structure					Mean
		1	2	3	4	5	
F.C.1	9	78.2	79.0	77.1	69.9	71.2	75.1
	12	53.9	53.8	46.5	47.8	50.1	50.0
	15	39.4	41.4	40.4	36.8	35.4	38.7
	12+ Modifier	55.9	58.0	53.2	56.9	53.9	55.6
F.M.C.1	9	69.4	68.9	70.2	66.2	68.3	68.6
	12	46.4	41.7	47.2	45.9	47.7	45.8
	15	0	0	0	0	0	0
	12+ Modifier	50.7	50.9	59.9	60.7	56.5	55.7
F.M.C.2	9	100	100	100	100	100	100
	12	100	100	100	100	100	100
	15	100	100	100	100	100	100
	12+ Modifier	0	0	0	0	0	0
F.M.C.3	9	100	100	100	100	100	100
	12	100	100	100	100	100	100
	15	100	100	100	100	100	100
	12+ Modifier	0	0	0	0	0	0

A P P E N D I X T A B L E X X I

The Filament Deniers.

Sample	% Acid used in Spinning	Weight in grams of 27 metres of conditioned filaments					Mean	Fibre Denier
		1	2	3	4	5		
F.C.1	9	.4896	.4871	.4705	.4822	.4570	.4773	159.1
	12	.4771	.4574	.4672	.4882	.4780	.4736	157.9
	15	.4406	.4323	.4305	.4343	.4348	.4345	144.8
	12+							
	Modifier	.4008	.3996	.3898	.4118	.4092	.4021	134.0
F.M.C.1	9	.3603	.3651	.3610	.3649	.3607	.3624	120.8
	12	.3910	.3930	.3941	.3926	.3883	.3918	130.6
	15	.3731	.3646	.3566	.3599	.3542	.3617	120.6
	12+							
	Modifier	.3800	.3796	.3871	.3863	.3799	.3826	127.5
F.M.C.2	9	.4333	.4420	-	-	-	.4372	145.7
	12	.4498	.4346	.4286	.4271	-	.4350	145.0
	15	.4710	.4620	.4705	.4600	.4506	.4628	154.1
	12+							
	Modifier	.4534	.4120	.4435	.4201	.4252	.4326	144.2
F.M.C.3	9	.4500	.4506	.4478	.4501	-	.4484	149.5
	12	.4136	.4117	.4195	.4240	.4205	.4179	139.3
	15	.3540	.3660	.3420	-	-	.3540	118.0
	12+							
	Modifier	.3785	.3808	.3768	.3668	.3895	.3785	126.1

APPENDIX TABLE XXXI.

Dry and Wet Tenacities and Elongations of Spun Filaments.

Sample	% Acid used in Spinning	Tenacity (g/den.)			Elongation (%)						
		Dry tests		Wet tests	Dry tests		Wet tests		Standard Devia- tion		
		Breaking load (g)	Standard Devia- tion	Breaking load (g)	Standard Devia- tion	% Elon- gation	Standard Devia- tion	% Elon- gation			
F.C.1	9	220.7	12.75	127.8	5.73	1.39	0.80	21.20	1.68	41.85	4.54
	12	287.0	12.95	148.6	12.27	1.81	0.94	23.90	1.84	43.00	3.45
	15	223.0	13.62	119.0	12.12	1.54	0.82	15.70	1.05	25.61	3.09
	12+										
	Modifier	261.5	5.29	140.9	6.87	1.95	1.05	19.97	1.06	31.80	2.97
F.M.C.1	9	169.3	13.99	68.3	7.57	1.40	0.57	18.80	1.56	32.70	5.60
	12	241.1	11.39	109.6	8.50	1.84	0.84	26.23	2.32	43.85	5.56
	15	189.2	10.89	80.0	7.83	1.57	0.66	12.80	1.34	26.85	2.71
	12+										
	Modifier	247.4	13.36	117.1	8.53	1.94	0.92	24.88	2.62	47.40	4.17
F.M.C.2	9	211.9	14.87	85.4	6.48	1.46	0.58	17.55	1.90	48.10	2.65
	12	231.0	7.45	98.7	7.05	1.59	0.68	21.77	1.97	52.30	5.29
	15	232.1	20.83	104.6	7.36	1.50	0.68	10.22	2.03	19.90	3.60
	12+										
	Modifier	229.1	7.04	92.5	6.15	1.59	0.65	17.39	2.06	46.63	3.96
F.M.C.3	9	209.1	20.08	60.0	6.16	1.39	0.40	18.11	2.68	52.21	6.45
	12	248.3	25.14	66.4	2.50	1.77	0.47	12.15	1.56	33.90	3.37
	15	163.1	20.51	32.9	5.87	1.40	0.28	15.30	2.86	46.35	8.06
	12+										
	Modifier	203.9	17.70	49.9	4.48	1.61	0.39	10.20	1.14	17.50	3.14

A P P E N D I X T A B L E XXXIII.

Initial Moduli of Filaments.

1. Dry Modulus.

	Meth- oxyl con- tent (%)	Acid used in spin- ning (%)	Initial modulus g/den.										Mean mod- ulus g/den.
			1	2	3	4	5	6	7	8	9	10	
0		9	62.9	59.7	52.4	62.9	40.9	78.6	62.9	62.9	62.9	62.9	60.9
		12	34.8	55.4	42.2	36.9	31.7	42.2	52.8	39.1	34.8	63.3	44.2
		15	60.4	55.2	46.0	48.3	50.6	50.6	62.2	46.0	41.4	69.1	53.0
		12+ modifier	49.7	74.6	69.0	56.0	56.0	41.0	43.5	43.5	42.2	46.0	52.2
2.78		9	53.8	45.5	20.7	31.7	31.7	41.4	31.0	41.4	31.7	35.8	36.5
		12	46.9	34.5	34.5	40.8	38.3	38.3	57.4	38.3	40.8	33.5	40.3
		15	62.2	44.2	72.6	58.0	70.1	44.2	55.2	66.4	92.9	78.8	64.5
		12+ modifier	35.3	34.4	28.2	34.4	35.3	33.3	33.3	44.4	44.4	39.2	36.2
5.77		9	44.6	41.2	44.6	58.4	36.6	39.5	48.0	36.6	36.6	36.6	42.3
		12	31.0	34.6	29.9	36.8	41.4	30.3	32.8	39.0	28.3	22.8	32.7
		15	40.6	48.7	51.9	24.3	37.9	32.4	34.3	58.5	40.0	51.9	42.1
		12+ modifier	40.4	43.9	55.5	37.3	40.4	31.2	48.5	34.7	46.2	40.4	41.9
7.87		9	50.2	34.6	48.0	36.8	44.5	30.1	39.0	35.7	39.0	30.1	38.8
		12	53.9	57.4	47.9	43.1	50.3	37.7	35.9	35.9	37.1	35.9	43.5
		15	23.3	33.1	42.4	45.2	38.1	29.7	33.9	31.8	47.7	45.6	37.1
		12+ modifier	63.5	49.0	52.1	44.6	44.6	44.9	52.1	52.1	52.1	37.7	49.3

2. Wet modulus.

Meth- oxyl con- tent (%)	Acid used in spin- ning (%)	Initial modulus g/den.										Mean mod- ulus g/den.
		1	2	3	4	5	6	7	8	9	10	
0	9	2.42	2.90	2.18	3.78	1.89	2.36	3.59	1.84	2.68	2.06	2.57
	12	3.90	2.82	2.76	2.96	3.12	2.79	2.96	2.92	2.98	3.12	3.03
	15	3.69	4.70	4.27	4.25	4.15	4.15	3.90	4.15	4.26	4.56	4.21
	12+ modifier	3.92	3.79	3.68	4.08	3.81	4.06	3.68	3.91	4.48	3.58	3.90
2.78	9	2.37	2.06	2.44	2.79	2.92	1.95	2.88	1.90	2.01	2.45	2.38
	12	2.38	2.35	2.46	2.65	2.58	2.41	2.88	3.07	2.49	2.73	2.60
	15	4.31	3.83	3.46	3.32	2.40	3.43	3.45	3.92	3.43	3.12	3.47
	12+ modifier	2.38	2.11	2.19	2.51	2.51	2.64	2.54	2.55	2.20	2.51	2.41
5.77	9	1.99	1.89	1.88	1.89	2.06	1.85	1.91	1.93	1.97	2.16	1.95
	12	1.97	2.07	2.76	2.19	2.21	2.13	1.91	1.95	1.90	2.11	2.12
	15	4.29	5.41	4.72	4.15	5.98	6.17	4.87	5.31	7.52	5.00	5.37
	12+ modifier	2.47	2.22	2.09	2.03	1.96	1.97	1.97	1.95	2.50	2.50	2.17
7.87	9	1.67	1.53	1.55	1.38	1.40	1.54	1.23	1.18	1.52	1.34	1.44
	12	2.76	2.99	2.40	2.21	2.28	2.70	2.45	2.40	2.59	2.20	2.50
	15	0.85	0.88	0.99	0.89	0.81	1.06	0.85	0.67	0.56	0.67	0.82
	12+ modifier	2.91	3.18	3.18	3.30	2.65	2.98	2.58	2.75	3.18	3.86	3.06

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