THESIS

on

SOME PROPERTIES OF RESIN TREATED VISCOSE RAYON

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ABSTRACT

A study has been made of some physical and chemical properties of viscose rayon, and the modifications in these properties resulting from the addition of a resin.

Methods of stripping a resin from a fabric have been studied and it has been shown that chemical degradation may result, but the use of 0.1N hydrochloric acid at 60° C for 20 minutes for urea-formaldehyde and methylatedurea-formaldehyde finishes, and of 1.5% phosphoric acid in 5% urea solution at 60° C for 20 minutes for melamine-formaldehyde and ethyleneurea-formaldehyde, has been recommended. Fluidity measurements, made to determine the degree of chemical degradation, have shown that any change in the physical properties of the present materials was not due to chemical degradation of the material either as a result of resin impregnation or removal. The Kjeldahl method of nitrogen determination has been used to estimate the original resin content of the material and to follow the rate of resin removal during the stripping process. This method was preferred because measurement of loss in weight does not give any indication of the amount of resin which might still be present in the fibre after stripping and in case the loss in weight was not due solely to

removal of resin. It has been shown that the last traces of resin were extremely difficult to remove but played no part in modifying the mechanical properties of the resin treated sample.

A study of the kinetics of acid hydrolysis of urea-formaldehyde treated viscose rayon in hydrochloric acid failed to separate the fast, and the slow, first order reactions of hydrolysis of resin polymerized in the fibre at the temperatures, and concentrations, of hydrochloric acid investigated, and further trials using lower concentrations and buffered solutions have been suggested.

Tests on fabrics and yarns before and after resin treatments, and after resin removal, have shown that the physical properties have been altered or modified but tend to revert to those of the untreated sample on stripping.

A study of the effect of additives showed that they reduced strength and extension but improved tear and abrasion properties in one case, and recovery properties in the other.

The study of abrasion resistance, and correlation with mechanical properties, carried out on the second batch of samples containing four different types of resins, and two different concentrations, showed that the results from the Bocking tester correlated with yarn extensibility, energy for rupture, and total stiffness; whereas those from the Accelerotor correlated with initial modulus and yield stress. It has been shown that correlation exists between extensibility, energy for rupture and total stiffness and between initial modulus and yield stress but no correlation was obtained between these two sets of properties and therefore no correlation has been observed between Bocking Abrader and the Accelerotor. The reasons why the two abraders correlate with different mechanical properties have been discussed on grounds of difference in mechanisms of abrasion and forms of frictional wear, the magnitudes of strain during abrasion, and the end points of the test methods, and the importance of shear properties.

Stress-relaxation of fibres in water and in acid solutions has been carried out using resistance wire strain gauges which were designed and constructed for the purpose; the sensitivity, the stability over long periods of time, and reproducibility have been shown to be satisfactory.

Viscose rayon, cuprammonium rayon, silk, nylon 66, and polyvinyl alcohol showed the same relative rate of relaxation in water while cellulose acetate and polypropylene showed different relative rates. These anomalies have been explained. Resin treated viscose rayon samples exhibited different relative rates of relaxation and it has been suggested that these may be due to alterations in physical structure and as chemical effects.

Stress-relaxation in acid solutions exhibited a change in slope at a point near the completion of resin hydrolysis. The time at which the change occurs has been shown to be different for different resins and to be a measure of the susceptibility of the various resins to acid hydrolysis.

Finally, the use of stress-relaxation as a means of measuring the relative accessibility of a modified material has been further illustrated using Fibro, Strong Fibro, Vincel and Durafil fibres.

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A study of the effect of additives showed that they reduced strength and extension but improved tear and abrasion properties in one case, and recovery properties in the other.

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of samples containing four different types of resins, and two different concentrations, showed that the results from the Bocking tester correlated with yarn extensibility, energy for rupture, and total stiffness; whereas those from the Accelerotor correlated with initial modulus and yield stress. It has been shown that correlation exists between extensibility energy for rupture and total stiffness and between initial modulus and yield stress but no correlation was obtained between these two sets of properties and therefore no correlation has been observed between Bocking Abrader and the Accelerotor. The reasons why the two abraders correlate with different mechanical properties have been discussed on grounds of difference in mechanisms of abrasion and forms of frictional wear, the magnitudes of strain during abrasion, and the end points of the test methods, and the importance of shear properties.

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Stress-relaxation in acid solutions exhibited a change in slope at a point near the completion of resin hydrolysis. The time at which the change occurs has been shown to be different for different resins and to be a measure of the susceptibility of the various resins to acid hydrolysis.

Finally, the use of stress-relaxation as a means of measuring the relative accessibility of a modified material has been DISCUSSED

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CHAPTER 1

INTRODUCTION

The present investigation was undertaken to further the study and understanding of the effects of treatment with resin compounds upon the properties of a cellulosic fibre. The particular cellulosic fibre chosen was viscose rayon and as the material may be used in the form of fibre, yarn, or fabric it was decided to obtain the material in fabric form from which yarn and fibres could be chosen as required. It was decided to restrict the investigation to one particular fabric construction, a plain weave, and lengths of this were obtained which were representative of a pure finish, for control purposes, and of various types of common commercial resin finish.

The work fell into three parts, and these have been retained although some matter may be found that is common to more than one part.

In Part 1, the main concern was to investigate chemical damage caused by resin treatment. The measurement of such damage required that the finish be stripped from the fabric, and hence the study was extended to cover methods of stripping which had to remove the finish without causing degradation. A brief study of the kinetics of acid hydrolysis and the mechanism of the reaction between cellulose and resins has also been made.

Although originally the main reason for applying a resin finish to a cellulosic fibre was to improve the property of crease recovery, it is now known that many other properties are also affected and tests have been carried out to measure the changes in some of these properties and relate them to the material and resin finish.

For Part 2, another batch of the fabric was obtained in which the finish was restricted to resins only, as difficulty had been found in Part 1 in separating effects which could be attributed solely to a specific resin rather than to resin and other additives.

Two wear testers were used, a Bocking Abrader (B.F.T. Mark IV) and an Accelerotor, and the results of the abrasion studies have been compared with mechanical properties of the yarn to try and find some correlation between these properties and the performance or service values.

In Part 3, the stress-relaxation behaviour of resin treated viscose rayon fibres in water, and in acid solutions, has been studied and consideration given to the hypothesis that the relative accessibility of viscose rayon could be measured from a knowledge of the rate of stress-relaxation in acid solutions. Studies of the stress-relaxation in water of different viscose rayons; Durafil, Strong Fibre 48, Bright Fibre, and Vincel and of different fibres; cuprammonium rayon, cellulose acetate, silk, nylon 66, polypropylene and polyvinyl alcohol, have been included.

It may be mentioned, to clarify, that the tensile tests reported in Part 1 were carried out on fabric and on yarn but in Part 2, for experimental convenience, tests were restricted to yarn only; whereas in Part 3, single fibre tests were made. The reason for the use of either the fibre or the yarn or the fabric tests has been given in the appropriate sections. Comparison of fibre, yarn and fabric tests have been reported in survey of literature and the yarn and the fibre tests have been correlated in Chapter 6.

In order to simplify the legend and to distinguish between the fabrics used in Part 1 and Parts 2 and 3, the fabrics have been numbered (Table 1), the table being included at this point for ease of reference.

Table 1

Key to Resin Treated Fabrics

	Fabric	Resin Treatment	Percentage Resin Content
	i	Melamine-formaldehyde	6.2
	ii	Ethyleneurea-formaldehyde	7.0
Part 1	iii	Methylatedurea-formaldehyde	10.3
	iv	Urea-formaldehyde	7.3
	v	Urea-formaldehyde plus Additive 'A'	-
	vi	Urea-formaldehyde plus Additive 'B'	-
	1	Melamine-formaldehyde	7.2
	2	Melamine-formaldehyde	9.5
	3	Ethyleneurea-formaldehyde	10.5
Part 2	4	Ethyleneurea-formaldehyde	14.7
and	5	Methylatedurea-formaldehyde	11.0
Part 3	6	Methylatedurea-formaldehyde	15.5
	7	Urea-formaldehyde	13.5
	8	Urea-formaldehyde	6.5
	B	Pure finish (untreated)	0

PART 1

CHEMICAL PROPERTIES AND PRELIMINARY STUDY OF RESIN TREATED VISCOSE RAYON

CHAPTER 2

SURVEY OF LITERATURE

Survey of Resin Chemistry

Methods of Investigation

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Survey of Resin Chemistry

History

It was as early as 1900 A.D. that it was observed (186) that a bone dry cellulosic fabric showed better wrinkle resistance than a conditioned fabric, a factor which was later proved to be due to the formation of more physical crosslinkages (hydrogen bonds) within the fibre. The search for compounds that would give chemical crosslinkages between the cellulose chains was obviously the next proposition, and formaldehyde, in the presence of an acid, had the distinction of being the first compound known to form chemical crosslinkages or methylene bridges between the cellulose macromolecules. Unfortunately, it was not possible to develope the process commercially due to the volatile nature of formaldehyde and the difficulty of obtaining uniform fibre modification. A large number of compounds have since been synthesized for achieving the same effect as that produced by formaldehyde (279, 305, 306) and in the first chemical crease proofing process fabrics were impregnated with resin precondensates, dried and finally cured at elevated temperatures (96).

The mechanisms through which an improvement in wrinkle recovery was obtained were not understood because the structure of neither textile fibre nor synthetic resin was clear at that time (186). Considerable study of both has since been made. (1,2,3,4,8,14,17,41,52,77, 91,95,100,101,104,105,106,118,124,157,173,201,202,212, 214,218,223,228,234,240,244,256,258,259,265,266,270,277, 288,341,368,380). The advent of synthetic fibres drew attention to the so called non-iron properties of textile materials and in 1954, the conventional wrinkle resistance process was extended to allow cellulosic materials to compete in this field (196,279) while other applications of resin treatment now include shrink proofing, water repellancy, and the improvement of dyeing techniques (197, 306,343). The fundamental process is still the thermo-fixation of a suitable molecular block within a fibre but only those aspects likely to be used in the present work have been discussed below, although further information may be obtained from a number of general reviews of resin and fibre chemistry (196,197,297,303,304,305,306,343).

Commercial resins

Methylolurea compounds

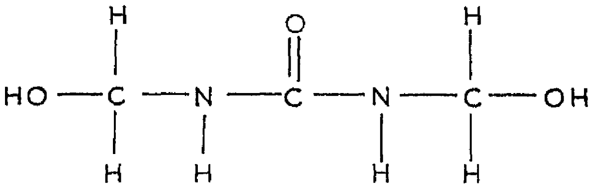

Figure 1. Dimethylolurea or urea-formaldehyde.

Methylolurea compounds, Figure 1, products of the reaction between urea and formaldehyde, were the first resin precondensates used commercially for improving the wrinkle resistence of cotton (96). These compounds are believed to react with the hydroxyl groups on cellulose through their N-methylol groups, though some resin polymer formation also takes place and some polymerization occurs both inside and on the surface of the fibres. Methylolureas react readily with cellulose, the catalytic agents and the conditions required need not be severe, and the reaction is easily controlled. However, the bonds between cellulose and urea compounds are easily hydrolysed; the efficiency depends largely on the urea to formaldehyde ratio and the reaction product is unstable in storage (125,302).

Substituted methylolurea compounds

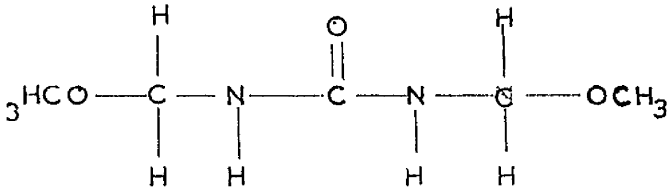

Figure 2. Methylated urea-formaldehyde.

The storage property of methylolurea compounds is improved if the reactive hydroxyl groups are replaced by nonreactive groups like methyl groups. These compounds hydrolyse in the presence of acid to give methylolurea.

Cyclic methylolurea compounds

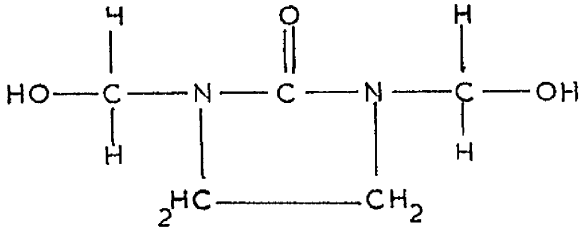

Figure 3. Dimethylolethyleneurea or cyclic urea-formaldehyde.

Cyclic methylolurea compounds are tetra-substituted derivatives of urea in which the two nitrogen atoms are connected by a carbon chain (100,188) the most widely used of these compounds being dimethylolethyleneurea (DMEU) or cyclic urea-formaldehyde. This compound is claimed not to form an insoluble resin, is stable in storage and in the treating bath, does not form surface resin, but is susceptible to acid hydrolysis.

Methylol melamine compounds

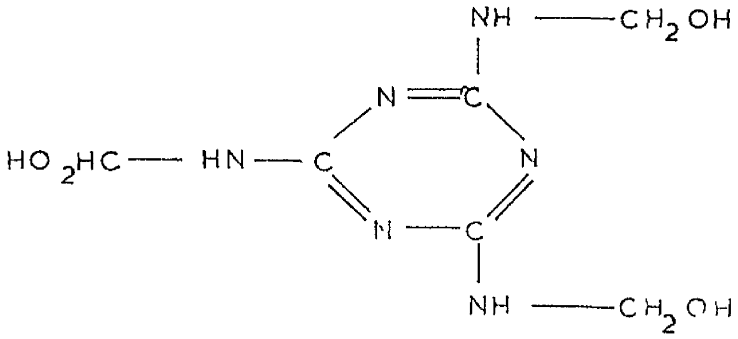

Figure 4. Trimethylol melamine or melamine-formaldehyde.

Methylol melamines are prepared by reacting melamine with formaldehyde and by varying the ratio of reagents the degree of substitution, the number of methylol groups in the final product, may also be varied. Methylol melamines are comparatively large molecules and are capable of resin formation and although their efficiency on weight basis is not as high as that of cyclic ureas they produce comparable wrinkle recovery with lower strength losses. They also give a more durable finish, possibly because of the tertiary nitrogen atoms present in their molecules.

Other creaseproofing compounds which may be mentioned but which have not been considered in the present work, include epoxides and related compounds, triazones, and reaction products of formaldehyde with acetone, with phenol, with polymerised methacryl amides, with alkaline oxides, with polyurethane, with glyoxal and urea and many more.

Cellulose

Before further consideration of the effects of resin treatment on cellulose, some mention may be made of cellulose itself.

It has been generally agreed that cellulose consists of long chain molecules of cellobiose; some of the molecular chains are straight and parallel, being grouped together into a regular crystallite with hydrogen bonds between the individual chains, whereas other molecular chains are neither straight nor parallel but exist in an amorphous chaos. Between the two extremes there is a whole range of intermediate variations. It has been shown by Hearle (133) that most, but not all, of the amorphous molecular chains pass through more than one crystallite holding them together but in addition to the connector chains there are also chain fragments. The combination of orderly and disorderly molecular arrangement has a bearing on the visco-elastic properties of the fibre.

From the standpoint of textile chemistry, the amorphous region is very important for this is the accessible part of the cellulose structure, and it has been estimated that about 60% of the structure of viscose rayon is amorphous. The individual molecular chains in the disorderly region have some mobility so that they may come sufficiently close together, here and there, for hydrogen bonding to occur. It is important to appreciate that there is a network in the amorphous region itself for where the individual chain molecules do come sufficiently close together they may form junction points as suggested by Hermans (139). The hydrogen bonding forces between the molecules are of two types. Between the molecular chains in the crystallite there are regular interlocking forces, whilst the bonds in the amorphous regions are random interchain forces of cohesion. When an external stress is applied to the system some of the interchain bonds break, allowing fibre deformation and then form new bonds with a new equilibrium; these interchain bonds may not be sufficiently strong to restore the fibre to its original position so that the fibre has poor recovery from deformation.

Resin application

The crease proofing of a cotton or rayon fabric usually consists of impregnating the fabric with a solution of suitable resin former of cofunctional reactants, squeezing out the excess liquor, and then drying and curing at an elevated temperature. The fabric should be clean and absorbent and in the case of cotton, may be premercerised. The resin may be any of a large number of monomeric reagents of small enough size to permit penetration into the cellulose and capable of reacting with itself and/or with the cellulose. A suitable catalyst is added to facilitate reactivity and subsequent washing to remove unreacted resin is a common practice (39).

Modes of cellulose-resin interactions

Two major theories have been advanced to explain the effects of resin precondensates on cellulose, the resin deposition theory and the cross-link theory.

The resin deposition theory was suggested by the fact that the original agents used were resin precondensates which could form three dimensional polymers within the fibre under the conditions used in treating cellulose. However, it was found that many resin formers which were known to be capable of reaction with cellulose did not improve wrinkle recovery when polymerized with the fibre (132,227,231). Moreover, acetylated cotton, which cannot be cross-linked because the hydroxyl groups are blocked, showed no improvement in wrinkle resistance on treatment with either resin precondensates or non-resin forming agents (245). Another arguement was based on the comparative ease with which some precondensates could be stripped from treated fabrics whereas formaldehyde, acknowledged to cross-link cellulose, cannot be hydrolysed as easily. However, susceptibility to hydrolysis depends on the chemical nature of the bond, and the bonds formed between N-methylol precondensates and cellulose are easier to hydrolyse than those formed by formaldehyde (27,54,85,120).

The resin deposition theory has the support of some experimental evidence (53,83,108,147,206,231). Certain precondensates believed to be incapable of cross-linking cellulose when applied with an alkaline catalyst have been found to improve the crease recovery of the material, although the improvement obtained with the alkaline catalyst was generally limited in amount and duration. Resin particles, presumed to form within the fibre under these conditions, may, in fact, be hydrogen bonded to adjacent cellulose chains and thus act as cross-linkages as long as the fibre is dry and the lack of wash fastness can perhaps be attributed to rupture of these bonds by water (343). It has been reported that no evidence of reaction of cellulose with urea- and melamine-formaldehyde precondensates was found when the infra-red spectra of treated cellulose films were examined, whereas the spectra of films treated with epoxy reagents, and with formaldehyde, indicated ether formation (28). The recovery of all four films was increased by the treatment but those which showed no evidence of ether formation lost the improvement on washing. Other workers have reported spectroscopic evidence of ether formation in cellulose treated with urea- and melamine-formaldehyde precondensates (66,179), and fabric treated commercially with these compounds did not lose wrinkle recovery on washing, so that whether it is possible to improve wrinkle recovery of cellulose by simple deposition remains in some doubt.

The cross-link theory is supported by an impressive amount of evidence (109). Treatment with compounds, which give water soluble materials when polymerized by themselves, gave fabrics which did not lose their improved recovery upon prolonged laundering (360). The recovery of cellulose can be improved by treatment with compounds which do not form resins (74,137,257). Polymerization of ethyl acrilate in allylated cotton fibres improved recovery, but polymerization within untreated fibres which cannot be cross-linked by acrilate, did not produce an improvement (88,342). The treated fabrics were insoluble in solvents (264,296) and they resisted microbiological degradation, indicating that hydroxyl groups on cellulose chains in the treated fabrics were blocked (65,113). While insolubility in cellulose solvents and resistance to microbiological degradation can be obtained by means other than cross-linking (33,283,284,285), these means are not effective on ultra thin sections of fibres investigated by electron microscopic technique (280,348). Unlike cotton treated with monomethylolurea, which cannot cross-link cellulose, dimethylol urea treated fibres do not disintegrate into thin sheets of microfibrils upon beating in water in a blender, but break into short, thick chunks of cellulose several layers thick, suggesting the presence of both interfibril and interlayer cross-linkages. Cellulose, treated with many crease-proofing agents, has been found to exhibit an increased absorption in the 11μ region, which indicates new ether groups and thus chemical linkages (66,236,312). Furthermore, the absorption decreased rapidly upon acid hydrolysis, at a rate correlating with decrease in wrinkle recovery but faster than that for the removal of the agents (179). Thus it may be surmised that it is the extent of bonding of the reagent with cellulose that is important in improving wrinkle recovery and not the mere presence of the reagent in the fibre (343).

Mechanism of improved recovery

Whatever the mode of action may be, it is believed (343) to depend on a decrease in the stress-induced slippage between the structural elements of the fibre. According to the proponents of the deposition theory, resin particles inside the fibre exert the effect mechanically simply by their presence. Also since water cannot be absorbed on resin bonded hydroxyl groups the resulting decrease in internal lubrication provides additional improvement in recovery. According to the proponents of the cross-link theory, the decreased slippage is due to the restraining action of covalent cross-linkages, formed between structural elements of the fibre.

Structure and size of crosslink~~ing~~s

A long cross-linkage is likely to be somewhat less effective than a short one in preventing chain and fibril slippage. It has been suggested that if cellulose chains in the fibre were bridged by long molecules, the fibre would not lose much strength. The long cross-linkages would permit molecular slippage and hence better load distribution and higher elongation. The experimental evidence is contradictory (107,311) where it has been shown that the longer the molecules of cross-linking agent, the lower the loss in strength for a given level of wrinkle recovery, whereas according to others (223,304), the strength loss due to crease proofing is always directly proportional to the degree of recovery, regardless of the type of the reagent used or the degree of cure.

A part of the tensile loss due to crease proofing may be the result of the hydrolysis of cellulose by acid catalysts, it having been reported that, with cyclic ethyleneurea, as much as one half of the total loss is due to factors other than cross-linking (100). The hydrolytic damage is lower in the case of triazone or melamine treated cotton, apparently because the basic nitrogen atoms in these compounds act as buffers.

Distribution of resin polymer

Monomeric treating agents penetrate the amorphous regions of a fibre more or less completely, but do not enter into the crystalline lattice of the cellulose. The first has been indicated by electron microscope photomicrographs of fibre surfaces, and by evidence from metal reduction, dye staining and radiographic evidences (80,81,201,202,345, 347,360), while the latter has been indicated by studies of X-ray diffraction patterns (66).

It has been suggested that the size of reagent, and the degree of swelling at the time of treatment, control the location of reaction sites (191,267,321). In the conventional process the fabric is impregnated, dried and cured. The reaction is believed to take place in the dried, collapsed fibres, and cross-linkages are likely to form primarily in the highly disordered regions. In the 'wet' process, however, the impregnated fabrics are not cured at high temperatures and the reaction takes place in the swollen or distorted fibres, and cross-links in the region of moderate lateral order. It must be noted that reagents can react with single cellulose molecules and intramolecular cross-linking is possible particularly in the distended regions.

This leads to the concept of dual function of cross-linkages. Linkages formed in dry fibres in highly disordered regions have primarily a restrictive effect. They bind molecules and macrofibrils together, hinder slippage, and reduce swelling, moisture absorption, and dye penetration. Linkages formed in regions of greater lateral order are likely to have a disruptive effect. Such cross-linkages decrease the amount of hydrogen bonding in the dry fibre, increase chain slippage, increase regain, swelling and dye absorption and generally increase the accessibility of the fibre (172,254,317).

Dry and wet wrinkle resistance

The deformation recovery of cellulose fibres depends largely on hydrogen bonding between the structural elements. Heating, which removes moisture and increases hydrogen bonding, improves wrinkle recovery. Conventional methods which introduce cross-linkages into the fibre, improve both dry and wet recovery, but the recovery in the wet state is generally lower than in the dry state. Making cotton more accessible to moisture appears to improve its recovery in the wet but not in the dry state (149). The wet recovery obtained may depend on the internal pressure generated by swelling forces. It has been suggested that the cross-linkages produced by the wet reaction process impose no restrain on chain slippage in dry fibres. However, these cross-linkages stabilise the swollen structure and restrain slippage when the fibres are wet (234,257,280,318,348). Cross-linking at an intermediate state of distension yields better properties for most normal uses than treatments at either extremes (54,267). High wrinkle recovery (wet and dry) has also been obtained by conventional resin treatment of fabrics previously treated in the swollen state (266).

Methods of Investigations

A number of methods have been proposed by various workers to assist in measuring the mode and effect of resin finish.

Cuprammonium hydroxide insolubility

Cuprammonium hydroxide insolubility as a means of detecting cross-linkages in chemically modified cellulose has been elaborated by Reeves, et al. (264). Cellulose dissolves in cuprammonium hydroxide by first becoming solvated and swollen before the long chain molecular units are separated and dispersed, but if these chains were cross-linked separation would be restricted.

In a conventional crease proofing treatment formaldehyde is evolved during curing and the reaction between cellulose and free formaldehyde has been proposed by Gagliardi and Nuessle (106) and experimentally demonstrated by Best-Gordon (35) and Alvaeaker and Turner (9).

Mehta, et al.(206,207) found that even after removal of the resin by acid hydrolysis, some formaldehyde remained fixed and as little as 0.02% rendered cellulose insoluble in cuprammonium hydroxide, an amount supported by Best-Gordon (35). Mehta also showed that treatment with 0.5N alkali hydrolysed the methylene ether bonds between cellulose and the resin and that the reaction was practically complete in 24 hours. The insolubility of the cellulose in cuprammonium hydroxide, which is highly alkaline, cannot be due to the presence of resin cross-linkages as these are no longer present.

Water imbibition

When cellulose is immersed in water a considerable volume of water is imbibed and this is accompanied by a large increase in the volume of the fibre, due to the internal pressure. However, the amount of water remaining after centrifuging is usually dependent upon the chemical and physical characteristics of the fibre, but can be altered by modifying or by altering the nature of the accessible region (178). Thus chemical modification, cross-linking, or mercerisation alter the amount of water imbibed. Cameron and Morton (52) were the first to suggest from the data on water imbibition that at least part of the resin was involved in covalent cross-links with cellulose. Welo, et al.(374) and some others (190) have also published data on water imbibition.

Modified resins

To differentiate between covalent cross-linkages and physical cross-linkages in a crease-proofed fabric it should be possible to adjust the conditions of treatment so that one or the other would be favoured. Many such experiments have been carried out by various workers. Nuessle, et al.(231) used monofunctional resins such as mono-methylolurea, thereby eliminating the chance of cross-linking so that the effect would be mainly due to physical bonds; however, mono-methylolurea has been shown by deJung and deJonge (158,159,160) to contain free urea, formaldehyde, and di-methylolurea besides mono-methylolurea. Recently, Gagliardi and Shippee (109) using resins with different reactive sites, have shown that those with higher reactivity had higher wrinkle resistance. Again, the reaction with cellulose is necessarily a heterogenous reaction, with the density of crosslinks very high in the amorphous regions and practically nil in the crystalline regions. Because of these physical limitations imposed by the state of cellulose during processing, and because of the various side reactions which would occur, it has been concluded (109) that all presently known methods of crease proofing and stabilising cellulosic fabrics involve a heterogenous modification of the fibre. Another means to characterize the importance of cross-linking reactions in cellulose has been the competitive reaction principle, in which a second hydroxylated material is introduced in cellulose, whereby the resin can react with either one or both of them depending upon their local concentrations and their activities. These experiments have shown that cross-linking reactions could be the minimum requirements for obtaining major improvements in crease resistance and dimensional stability of cellulosic fabrics (109).

Alkaline and acid hydrolysis

It has been shown by Steele and Giddings (315) that 0.5N sodium hydroxide can hydrolyse the methylol group between the cellulose chain and the resin. Alkaline hydrolysis in the case of dimethylolurea separates the bound formaldehyde into two portions: formaldehyde bound in the form of methylol groups, which occurs during curing, and formaldehyde bound in the form of methylene groups, which occurs during drying with loss of formaldehyde.

It has been observed during acid hydrolysis that for 10% removal of the resin, 80% of the wrinkle recovery was lost, and for 36% of the resin removed, 95% of the wrinkle recovery was lost (10).

Recently a letter has been published by Mehta, et al. (208) regarding the kinetics of acid hydrolysis of urea-formaldehyde treated fabric, by which the activation energy of methylol and methylene linkages in a resin treated fabric has been calculated.

Finally a study of the susceptibility to acid hydrolysis of the products from the reaction of amido methylol compounds with cellulose carried out by Reeves, et al.(268), has shown a correlation between electron displacement and ease of hydrolysis. Substituent electron releasing groups attached to either the amido nitrogen or the carbonyl carbon, facilitate acid hydrolysis and thus depending upon the substituents, the susceptibility of resinous products to acid hydrolysis would be different.

Mechanical methods

Modifications due to the action of resin compounds on cellulose, and the nature of the changes in fabric properties other than changes in solubility, ease of hydrolysis and moisture absorption, have been reported in a host of papers (13,46,47,63,117,128,129,130,150,152,211, 214,239,250,251,252,260,261,278,287,309,321,378). The general effects may be summarised as follows: reduced extensibility, altered (reduced or increased) tenacity, reduced tear strength and abrasion resistance, increased modulus, increased elastic recovery and fabric crease recovery, and increased shrinkage resistance.

Tripp, et al.(346) have stated that the six fundamental properties of a fibre are strength, elongation, stiffness, toughness, elasticity and resilience, and that other physical properties can be related to one or more of these six, and thus a change in one property of the material may be expected to modify other properties. The relationship between changes of elastic recovery and the loss of strength when cellulosic fabrics are treated with resin finishes, has been the subject of much research and the results have been summarised by Steele and Giddings (313), where it has been shown that the changes in structure which lead to increased elastic recovery are also responsible for the reduction in strength, and that the same physical behaviour would be noted whatever the mode of interaction between resin and cellulose (105).

Gagliardi and Gruntfest (105), discussing the physical properties of resin treated fabric, attributed the loss in tensile strength to a physical modification; whereas Frick, et al.(100) showed that a part of the tensile loss resulted from hydrolysis of cellulose, and reported that with cyclic urea-formaldehyde as much as one half of the total loss has been due to factors other than cross-linking.

O'Brien and van Loo (235) on the other hand, indicated the importance of the hydrogen bond interaction, and stated that the effect of a cellulose reactant depended as much on the alteration of the hydrogen bond interaction between molecules as on the formation of covalent cross-links.

In the opinion of the present author, much of the conflicting evidence reported above may be due to failure to reconcile physical and chemical evidence in that those who claim a loss in mechanical properties as entirely due to physical modification have not evaluated chemical degradation, and no paper has been found where a thorough study has been made in measuring the possible chemical degradation of the resin treated material.

Two remaining points were the questions of identifying the type and amount of resin finish present in a material. The type of resin finish was known from information supplied with the fabric but an opportunity was taken to check the control samples so that an unknown could be verified if required. The amount of finish present on the original samples required to be checked, while it was necessary to be able to check the amount, after stripping, in order to be able to assess the efficiency of the stripping process and hence the inclusion of survey of test methods. A survey of literature suggested that the following tests might be useful.

Methods of identification

(a) Formaldehyde finish

One method (21) consists of stripping the resin in 5% sulphuric acid at boil, allowing to cool, and adding drops of the supernatant liquid to carbazole solution. If formaldehyde is present as a result of the hydrolysis of the resin, the solution will be coloured deep blue. It is stated that the presence of urea-formaldehyde resin in amounts as low as 0.1% may be detected. Another method, Schryver's test (333), consists of stripping the resin with 0.1N hydrochloric acid at boil, allowing to cool, and adding drops of freshly prepared 1% solution of phenylhydrazine hydrochloride to a few drops of the supernatant liquid. The solution is allowed to stand for 2-3 minutes and 1 ml of freshly prepared 5% solution of potassium ferricyanide and 5 ml concentrated hydrochloric acid is added, when the presence of formaldehyde produces a fuchsia red colour.

(b) Tests for urea, thiourea, melamine

According to the Furfural test (333), a red colour should develop within 5 minutes if any of these products are present, and to differentiate between them the test samples are dyed with 0.1% Solway Blue BN in 1% sulphuric acid when melamine formaldehyde treated samples are dyed to a heavy blue, compared with light blue of urea and thiourea samples.

Methods of resin removal

A survey of literature showed the following methods of stripping have been used by various workers.

(a) Treatment with 2% hydrochloric acid has been reported by Forziati, et al.(94) to remove urea-, melamine-, casein-formaldehyde resins, which were examined spectroscopically. No comment was made regarding the effect of the treatment on cellulose.

(b) Bernard (34) reported that treatment with 0.1N hydrochloric acid at 66°C for 25 minutes resulted in the complete hydrolysis of urea-formaldehyde resins.

(c) Treatment with 0.1N hydrochloric acid at 60°C for 1 hour was studied by Alvasaker and Turner (9) in 1955, by Tankard (330) in 1956, and has been recently recommended as a standard method for removing urea-formaldehyde resins. Tankard (330) compared this method with other methods, (g) and (h) reported below, and showed that the results of resin removal were nearly the same; whereas Best-Gordon (35) suggested that the strength of the acid was of particular importance since strong acid resulted in damage to the fibre and additional loss in weight.

(d) Treatment with 0.02N hydrochloric acid at boil for 30 minutes has been suggested by Morton and Beaumont (214) as a satisfactory method for removing urea-formaldehyde resins, but it has since been reported (45) that a greater loss in weight may be obtained due to removal of non-resinous matter.

(e) Treatment with 1.5% phosphoric acid in 5% urea solution at 85°C for 90 minutes was used by Cooke, et al.(67) on melamine- and urea-formaldehyde treated cellulose fabrics.

(f) Treatment with 1.5% phosphoric acid in 5% urea solution at 75°C on ethyleneurea-formaldehyde treated samples has been studied by Cooke and Roth (69), who found that over 95% of the resin was removed within 5 minutes.

(g) Treatment with 1% Tartaric acid at boil for x t 20 minutes on urea-formaldehyde samples has been found by Tankard (330) to effect complete removal of the resin.

(h) Best-Gordon (35) and Tankard (330) found that urea-formaldehyde resin was removed by treatment with buffered acetic acid solution, pH 4.6 at 95°C for 1 hour.

<u>Quantitative methods of estimation</u>

The resin content of a material may be estimated by checking the formaldehyde content, by measuring the loss in weight of a sample after acid hydrolysis, or by estimating the nitrogen content.

The formaldehyde content may be obtained by colourimetric methods using Schiff's Reagent (358), or by volumetric methods using Iodine reagent (9) or Sodium Sulphite reagent (358).

The loss in weight of a sample can be used where a resin treated sample of known weight is extracted with hot acids, the residue is then thoroughly washed, dried and weighed. The loss in weight is expressed as a percentage of the dry weight of the extracted specimen. Here the total loss in weight is assumed to represent the amount of resin finish (45).

The two standard methods of nitrogen estimation are the Dumas method and the Kjeldahl method (149a), the latter being the more popular method and the one used in the present work.

CHAPTER 3

EXPERIMENT, RESULTS AND DISCUSSION

Experiment

Test methods

Results and Discussion

Conclusions

Appendix

EXPERIMENT

Introduction

In this chapter changes in some properties of a viscose rayon material as a result of resin treatment have been studied using chemical and physical methods of investigation. Methods of stripping have been checked with respect to efficient resin removal and cellulose degradation, the latter also serving as an indication of the chemical state of the material as a result of resin treatment, and a study of the rate of acid hydrolysis of urea-formaldehyde treated viscose rayon has been attempted.

Material

A spun viscose rayon fabric (U1009) was obtained, lengths of which had been specially finished by Messrs. Courtaulds Ltd., whose courtesy and co-operation are acknowledged. These lengths were analysed, the structure being plain weave with a 30/1 tex warp and weft having 14.12 t.p.i. and 11.92 t.p.i. respectively. Other details of finishes have been given in Table 2 and ends/in and picks/in in Table 6, pp. 52

All samples were washed in 2 g/litre soap solution at boil for 30 minutes to remove any untreated resin and were then dried and conditioned at 20±1 C and 65±2% r.h.

Table 2

Resin Content and Absorption Properties of Viscose Rayon Fabrics

Fabric	Finish	Nitrogen Content %	Resin Content %	Moisture Regain %	Water Imbibition %
B	Untreated	Nil	Nil	14.1	95.3
i	Melamine-Formaldehyde	1.76	6.2	14.0	56.6
ii	Cyclic-Urea-Formaldehyde	1.34	7.0	13.7	58.1
iii	Methylatedurea-Formaldehyde	1.95	10.3	13.6	51.1
iv	Urea-Formaldehyde	1.67	7.3	13.7	55.0
v	Urea-Formaldehyde + Additive A	2.28	-	-	54.6
vi	Urea-Formaldehyde + Additive B	3.74	-	12.2	44.7

before any tests were made. The samples were washed in order to ensure that all processing strains were relaxed and that there was no interference by loosely held surface resin on the physical and chemical properties of the material.

Investigations into methods of stripping

Some methods of stripping have been reported but it was felt that further information was required about the action of these stripping agents on the material. This was obtained by carrying out stripping tests on the untreated samples, and using the fluidity values of the samples as an indication of the severity of the treatment. The various treatments and the fluidity values have been reported in Table 3. Only two readings were taken in each case as the results were always close and appeared to progress in logical sequence with regard to the time and temperature of treatment. It will be seen that except for 0.5N hydrochloric acid, the degradative effect of the stripping reagent on cellulose has been slight.

On the basis of these results, two methods, (a) 0.1N hydrochloric acid at 60°C and (b) 1.5% phosphoric acid in 5% urea solution were selected and were investigated in further detail to study the efficiency of these methods in stripping different resins from the fabric.

Table 3

Details of Acid Treatment on Viscose Rayon (Untreated)

Hydrolysing Bath				
Reagent	Concentration	Temperature C	Time, min.	Fluidity, reci. poise
Hydrochloric Acid	.1N	20	1220	9.1
Hydrochloric Acid	.1N	60	30	8.8
Hydrochloric Acid	0.2N	60	15	9.7
Hydrochloric Acid	0.2N	60	30	11.5
Hydrochloric Acid	(0.5N) 2.0%	60	15	15.0
Hydrochloric Acid	(0.5N) 2.0%	60	30	18.1
Phosphoric Acid in 5% Urea Soln.	1.5%	60	30	7.8
Formic Acid	1%	60	60	7.1
Nil (water)	-	60	60	7.1

Resin identification

Mention was made in the literature survey that there were a number of methods available for identification of the type of resin present in a material. In the present work the type of resin was known but the opportunity was taken to carry out check tests, a positive identification being obtained in all cases.

Stripping procedure

A stripping bath of the required concentration was prepared in a 5 litre pyrex beaker, the solution being raised to the required temperature (variation ±2° C) before the samples were introduced. Small squares (3" x 3") of a resin treated fabric were cut and about 14 of such samples were immersed in quick succession, the solution being stirred continuously. At intervals of 5 minutes two pieces selected at random were removed and washed first in cold water to stop the reaction and then in warm water till free from acid. The samples were labelled, dried at 105° C in an oven, conditioned at 20° C and 65% r.h. and then used for fluidity measurements and resin content tests. Since the stripping bath was large, the change in concentration due to evaporation at higher temperatures of experiment was not considered to be significant. A fresh stripping bath was prepared for each resin treated fabric.

Nitrogen determination

Since all the resins investigated were amido methylol compounds the Kjeldahl nitrogen estimation method was employed to calculate the amount of resin in the sample. This method has the advantage of being easy to adjust for different samples containing varying amounts of nitrogen, also the determination could be made and parallel analysis could be repeated without the necessity of preparing a fresh digestion. One disadvantage would appear to be in the variation of the reading from person to person (35). It was shown by Bradstreet (42a) that the outcome of the analysis would depend largely on the choice of the catalyst and the precision of the determination would be increased by using standard solutions of low strength, but following work by Frankfurt (98) on the selection of catalysts this disadvantage can be overcome.

A Macro-Kjeldahl distillation apparatus with Parnas-Wagner automatic discharge arrangement was employed (149a).

A sample of about 0.5g was put in a weighing bottle, and dried in an oven at 105°C, cooled in a desiccator and then weighed accurately. The sample was placed in a Kjeldahl flask and 5g of copper selenite catalyst (98) was added, the latter being prepared by mixing carefully 90g of potassium sulphate with 10g copper selenite. A grain of paraffin was added to prevent foaming during digestion process. To the contents of the flask were added 25 ml of concentrated sulphuric acid and the flask was shaken gently until the acid penetrated the sample, the solution turning black. The flask was then heated gently for 5 minutes and then more fiercely until the solution became clear green. The contents were allowed to cool and the volume made up to 500 ml with distilled water.

25 ml of the solution were pipetted out into the macro-distillation flask, and to ensure that the required amount of sodium hydroxide was added, a few drops of phenolphthalein indicator were put in the solution. Before sodium hydroxide was run through the funnel into the flask and steam introduced, 25 ml of 0.01N sulphuric acid was put in the receiver flask beneath the condenser and the tip of the condenser was placed under the level of the liquid. Steam was then let in and the distillation carried out until half of the liquid in the flask had distilled over into the receiver. The receiver was then lowered so that the tip of

the condenser was above the surface of the liquid and the distillation continued for a few minutes in order to wash down the condenser.

Methyl orange was used as an indicator with the acid in the receiver and it is important that the liquid remains red (acidic) until the end of the distillation. Before titration with standard alkali the solution in the receiver was boiled in order to eliminate any carbon dioxide which may have been in the solution. Blank determinations were also performed.

The nitrogen content was calculated

$$1 \text{ ml of } N/10\ H_2SO_4 \equiv 0.0014\text{g nitrogen}$$

from which the resin content of each sample was calculated by using the appropriate multiplying factor which is the ratio of the molecular weight of the monomer to that of nitrogen, multiplied by the number of molecules of nitrogen in a molecule of the monomer.

Fluidity measurements

Fluidity measurements were carried out using Shirley viscometers and standard cuprammonium hydroxide, the procedure followed being given in B.S. Handbook No.11 (45). The value of fluidity was calculated from the formula

$$F = C'/t$$

where C' is the viscometer constant and t the time in seconds for the flow between the two marks on the viscometer. If t was less than 200 seconds a kinetic energy correction k/t was applied, the value of k being also a constant for the viscometer. F then gives the value of fluidity in reciprocal poise of a 2% solution of viscose rayon in standard cuprammonium hydroxide.

Moisture regain

Viscose rayon fabric (ca 1g) was placed in a weighing bottle and heated at 105° C until a constant weight. It was then allowed to regain moisture in an atmosphere at 20° C and 65% r.h. for 48 hours and weighed again. The results are reported as grammes of moisture regained by 100g of oven dry material.

Percentage water imbibition

A piece of fabric (ca 1g) was steeped overnight in distilled water. It was then centrifuged in a partitioned centrifuging tube at 2000 r.p.m. for 5 minutes at room temperature, weighed accurately and the sample was then dried in an oven at 105° C. The results are reported as grammes of water imbibed by 100g of oven dried material.

Tensile properties

Tensile properties were measured on fabric and on yarn before and after resin treatment and also after resin stripping.

Breaking strength and extension

The breaking load and extension of fabrics was measured on a Denison testing machine TF 42 on 2" wide strips at 4.5" per minute constant rate of extension, specimen length being 8" (B.S. Specification). The value reported is a mean of 5 readings.

The tensile strength of yarns was obtained on a Baer single thread strength tester. The specimen length was 8" instead of 7" as specified in B.S. Specification (45) but otherwise the tests were conducted as per specification. 50 tests per sample were taken.

Yarn elastic recovery at 5% extension

Elastic recovery at 5% extension was measured on Instron tester. The procedure for determining tensile elastic recovery suggested by Meredith (210) was followed. Yarns were mounted in the jaws with a pretension of ½ tex of the yarn and extended to 5%, held for 1 minute and the jaws were then returned to their original position and after 1 minute another cycle was started. The tensile elastic recovery was taken as the amount of the extension recovered after final 1 minute expressed as a percentage of the total extension. The reported value is a mean of 5 readings.

Crease recovery

Opinions are divided on the most suitable method of measuring crease recovery. Reeves, et al.(267) and O'Brien and van Loo (235) used the Monsanto method, whereas Marsh (191) suggested the use of T.B.L. method, considering the Monsanto method to be more optimistic and the T.B.L. method to be more realistic. A comparative study of these two methods was made by Chipalgatti, et al.(57) who showed that the Shirley Test method (Monsanto) gave higher values for both dry and wet crease recovery. The difference is more pronounced in case of wet recovery and they suggested that these differences are largely due to the difference in handling procedures. In the present investigation the Shirley method (Monsanto) has been adopted as per specification (45). The value reported is a mean of 10 readings.

Tear strength

Tear strength measurements were carried out on Instron testing machine at constant rate of extension. The samples for tongue tests were prepared as per B.S. Specification (45). The value reported is a mean of 5 readings.

Abrasion resistance

Abrasion resistance was measured on an Accelerotor, the test being carried out at 3000 r.p.m. for 4 minutes and the abrasion resistance being measured as percentage loss in weight of sample. Details of the machine and the preparation of samples have been reported (182) and the subject has been considered in more detail in Part 2 of this thesis.

RESULTS and DISCUSSION

Methods of Stripping

Acid hydrolysis of resin treated samples in 0.1N hydrochloric acid at 60° C

Results of the study of acid hydrolysis of the resin treated samples in 0.1N hydrochloric acid at 60° C at different intervals of time have been reported in Table 4.

From the values of percentage nitrogen content in the fabric after different periods of hydrolysing treatment, it will be seen that over 95% of the resin has been removed within 10 minutes of the treatment for samples treated with ethyleneurea-methylatedurea-, and urea-formaldehyde, whereas the melamine-formaldehyde treated samples still retained approximately 20% and 10% of their original resin content after 10 minutes and 40 minutes treatment respectively. It will also be observed that the nitrogen contents of urea-formaldehyde resin treated samples containing additives (sample v and vi) were higher than that for urea-formaldehyde treated sample without additives (sample iv) which suggests that the additives were nitrogenous while the additive in sample vi was more easily hydrolysed than sample v. This point has been discussed at a later stage.

Table 4

Change in (a) Nitrogen Content and (b) Fluidity Value of Resin Treated Viscose Rayons Treated with 0.1N Hydrochloric Acid at 60°C for Different Intervals of Time

Time of Treatment, Min.		Sample						
		MF i	CUF ii	MUF iii	UF iv	UF_A v	UF_B vi	Untreated 'B'
0	(a)	1.76	1.34	1.95	1.67	2.28	3.74	0.00
	(b)	-	-	-	-	-	-	7.1
10	(a)	0.34	0.06	0.07	0.06	0.18	0.12	-
	(b)	8.0	8.3	8.5	8.2	8.3	8.0	8.3
15	(a)	0.23	0.05	0.05	0.03	0.14	0.10	-
	(b)	8.4	8.7	9.9	8.6	8.3	8.1	8.4
20	(a)	-	-	0.05	-	0.13	0.10	-
	(b)	8.4	8.8	9.2	8.7	8.4	8.7	8.6
25	(a)	-	0.04	-	-	-	-	-
	(b)	8.6	9.0	9.2	8.7	8.5	8.8	8.8
30	(a)	-	0.04	-	-	-	-	-
	(b)	8.6	9.1	9.5	8.9	8.6	8.8	8.8
40	(a)	0.19	0.04	0.04	0.02	0.12	0.09	-
	(b)	8.8	9.3	9.8	9.00	8.7	8.9	8.8

Table 4 also gives the values of cuprammonium fluidity of samples which suggest that there has been no degradation and little difference between different resin treated samples, and between resin treated and untreated samples, for the corresponding time of stripping.

Acid hydrolysis of resin treated samples in 1.5% phosphoric acid in 5% urea solution at 60° C

Results of the study of acid hydrolysis of resin treated and untreated samples in 1.5% phosphoric acid in 5% urea at different intervals of time has been reported in Table 5.

A study of the values of percentage nitrogen content in the fabric after different intervals of stripping show that with ethyleneurea-, methylatedurea-, and urea-formaldehyde samples, over 95% of the resin has been removed within 10 minutes but with melamine-formaldehyde a period of 25 minutes was required.

The fluidity of various stripped samples again show that there has been little or no difference between different resin treated samples themselves, and between resin treated and the untreated samples, for the corresponding time of stripping.

Change in (a) Nitrogen Content and (b) Fluidity Value of Resin Treated Viscose Rayons Treated with 1.5% Phosphoric Acid in 5% Urea Solution at 60°C for Different Intervals of Time

Time of Treatment, Min.		Sample						
		MF i	CUF ii	MUF iii	UF iv	UF_A v	UF_B vi	Untreated 'B'
0	(a)	1.75	1.34	1.95	1.67	2.28	3.74	0.00
	(b)	-	-	-	-	-	-	7.1
10	(a)	0.21	0.04	0.07	0.08	0.22	0.75	-
	(b)	7.2	7.4	7.3	7.2	7.2	7.1	7.1
15	(a)	0.12	0.04	0.05	0.07	0.17	0.68	-
	(b)	7.4	7.5	7.7	7.2	7.2	7.2	7.2
20	(a)	0.10	0.04	0.04	0.07	0.14	0.56	-
	(b)	7.3	7.7	7.6	7.2	7.3	7.4	7.2
25	(a)	0.08	0.04	0.04	0.06	0.11	0.56	-
	(b)	7.7	7.6	8.7	8.4	7.5	7.4	7.3
30	(a)	0.07	0.04	0.04	0.06	0.10	0.56	-
	(b)	8.2	9.1	9.1	8.8	8.2	8.5	7.8
40	(a)	-	-	-	-	-	-	-
	(b)	9.3	9.1	9.1	9.1	9.1	10.1	9.1

The effect of these two methods of stripping on resin removal is strikingly different, as 0.1N hydrochloric acid removes resins in samples iv and vi more effectively than 1.5% phosphoric acid in 5% urea, whereas with samples i and v, it is the other way round, phosphoric acid in urea being more effective than hydrochloric acid.

0.1N hydrochloric acid at 60° C which has a pH value of 1.00 is a stronger hydrolysing agent than 1.5% phosphoric acid in 5% urea solution at 60° C which has a pH value of 1.75 and this is easily observed from the fluidity values of untreated samples, the values being 7.8 recip. poise in case of phosphoric acid in urea solution as compared with 8.8 recip. poise in the case of hydrochloric acid, both after 30 minutes of the treatment. Comparing the two values at 40 minutes, the hydrolysing effect is nearly the same for both types of treatment. This might be explained on the grounds that phosphoric acid in urea is a buffer solution which maintains a constant concentration of hydrogen ions throughout the stripping period as opposed to 0.1N hydrochloric acid which is not a buffer solution and is bound to turn weak with the time of treatment. It is unfortunate that the pH values of the solutions were not measured again at the end of the experiment to justify the validity of the arguement. It may also be pointed out that urea is a known swelling agent for cellulose and hence cellulose is more accessible to the action of hydrolysis in phosphoric acid urea mixture than in hydrochloric acid. This also explains the anomaly that phosphoric acid urea mixture although being weaker than hydrochloric acid is a better stripping agent for bulky resin molecules like melamine-formaldehyde, (sample 1).

Moisture Regain and Water Imbibition

Results of moisture regain and water imbibition together with resin content have been shown in Table 2 (pp. 33) and Figure 5.

It would be seen from Figure 5 that the effect of resin content on moisture regain and water imbibition is interesting, in that the presence of resin has a much greater effect on water imbibition than on moisture regain, while with increasing resin content a smaller proportion of reduction in water imbibition is obtained but with a proportionately large change in the moisture regain characteristics of the material.

In the opinion of the author, water imbibition which is much more a volume characteristic as opposed to moisture regain which is predominantly a criteria of accessible reactive surface area, would therefore be easily

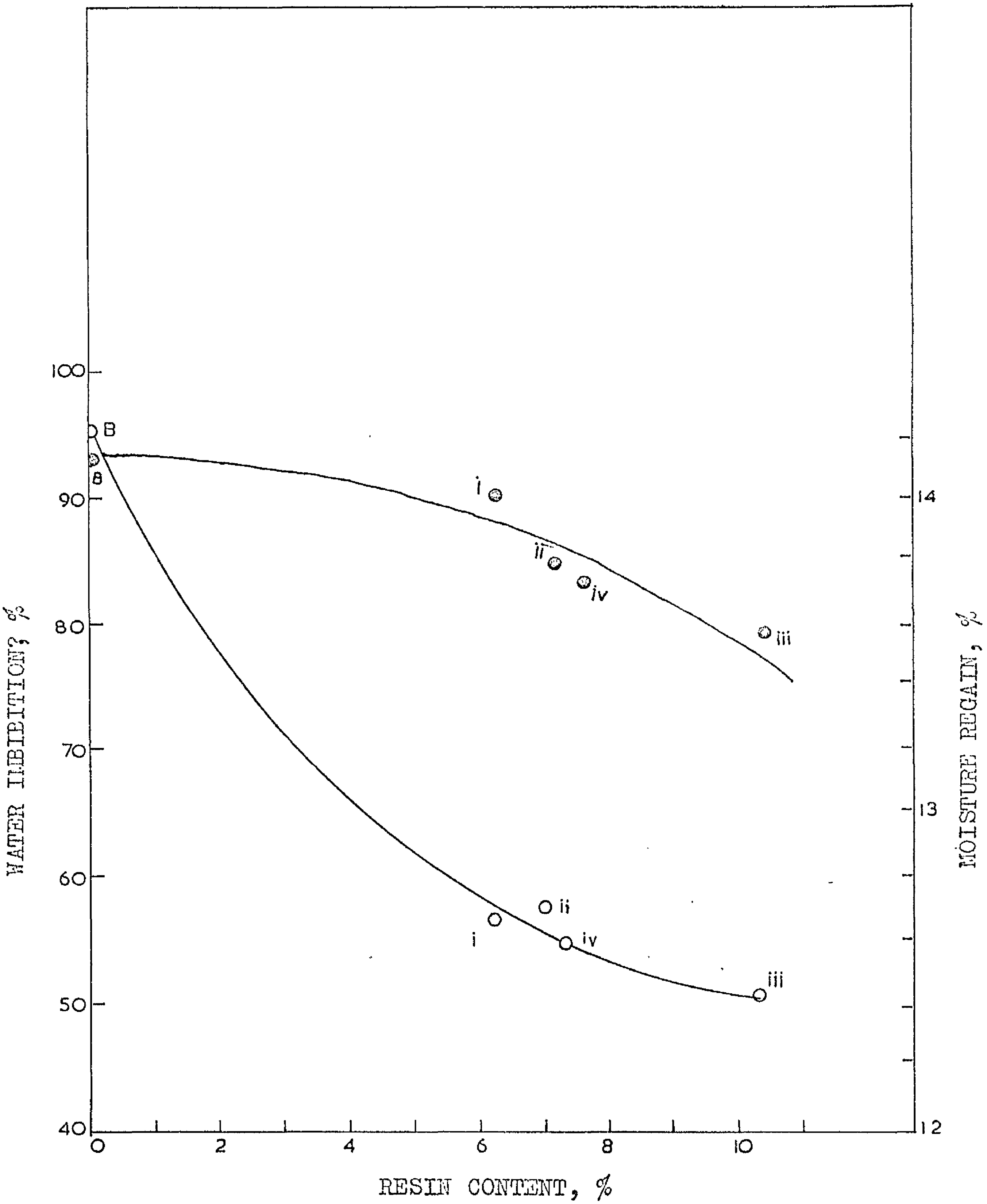

Figure 5 The Effect of Resin Content on (●) Moisture Regain and (o) Water Imbibition

altered by resin blocks which effectively alters the free volume or empty spaces in the fibre. As resin content is increased there would be less and less space available for the resin to go in and hence higher and higher proportion of the resin then gets deposited or reacted on the surface of the fibre and a corresponding lower proportion of reduction in water imbibition is obtained.

The effect of resin content on moisture regain is strikingly different, very little change in moisture regain is obtained in the initial stages up to about 7%. It appears therefore, that either the accessible area characteristics of the fibre are not much altered, or else the reactive sites in cellulose blocked by resin are compensated by the reactive sites on resin where moisture could be absorped. With increasing resin content and altered surface characteristics of the fibre, a rapid reduction in moisture content is obtained.

Tensile Properties

Breaking strength and extension

Results for the breaking strength and extension of both yarn and fabric samples have been reported in Table 6. The tensile strength of fabric in both warp and weft direction has been found to increase in all the resin treated samples investigated. A loss in strength on stripping was noted

Table 6

Tensile Properties of Viscose Rayon Fabrics and Yarns

Sample	i		ii		iii		iv		v		vi		'B'
	T	S	T	S	T	S	T	S	T	S	T	S	
Fabric Tensile Strength, kg													
per 100 ends	46.3	38.6	42.8	40.4	47.6	40.4	51.7	41.7	51.7	38.6	48.9	39.9	40.
per 100 picks	48.1	43.1	46.3	44.0	48.5	43.5	52.6	43.2	48.9	45.8	44.0	45.0	43.
Yarn Tensile Strength, kg													
warp	0.45	0.41	0.42	0.42	0.42	0.42	0.46	0.43	0.46	0.42	0.43	0.41	0.
weft	0.48	0.43	0.42	0.42	0.43	0.43	0.45	0.44	0.43	0.43	0.43	0.43	0.
Fabric Extension,%													
warp	18.0	19.6	16.4	21.0	17.2	21.0	19.5	21.0	18.0	20.0	14.1	20.2	21.
weft	14.8	17.2	15.3	18.8	15.6	19.9	19.0	20.0	17.3	18.8	11.7	18.8	20.
Yarn Extension,%													
warp	20.2		19.4		21.0		21.2		21.2		19.4		22.
weft	21.0		19.1		19.4		21.0		20.2		15.0		21.
Ends/inch	72	75	71	75	67	72	66	72	69	75	68	74	70
Picks/inch	57	67	58	65	58	66	58	66	56	65	57	64	61

T ⟶ Treated, S ⟶ Stripped

values approaching that of the untreated sample. It should be noted that the results have been reported on a basis of a constant number of threads rather than 2" width, for variations in the number of ends and picks between different resin treated samples was observed and values altered on stripping due to observed shrinkage. The tensile strength of yarn both warp and weft direction has also shown a tendency to increase but the increment has been relatively small as compared to the increment in fabric strength. This may be explained from the values of fabric assistance which are higher for resin treated samples than untreated sample.

Values of percentage extension at break for both fabric and yarn show that the extensibility is reduced on resin treatment and that the extensibility increases on resin removal, tending to the values of the untreated sample. The extensibility values for yarn have been higher than the corresponding values for fabric.

Stiffness

The use of this term taken as a ratio of breaking strength over extension has been discussed by Elder (78a) and while it was noted that there were objections to the use on theoretical grounds, it was shown that the term had a practical value particularly in denoting a change in property as a result of physical or chemical modification of the material. The results in Table 7 show that the value for fabric stiffness has been higher than the corresponding value for yarn stiffness and that the resin treated samples have higher stiffness value than the untreated sample.

Fabric assistance

The ratio of fabric strength to yarn strength times the total number of threads gives an indication of fabric assistance and is normally greater than one except for fabrics with excessively high ends and picks per inch resulting in thread jamming. It is confusing to find that the values of untreated and stripped samples to be less than one. In the opinion of the author, the present anomaly should not be attributed to the jamming of threads as the values of ends and picks per inch are too low to even conceive of such a possibility. One of the reason for the anomaly appears to lie in the fact that the fabric and yarn tensile tests were carried out on two different machines and prone to a constant error. Unfortunately, the error between the two instruments was not measured which makes the reported values of fabric assistance rather meaningless. However, assuming

Table 7

Stiffness and Fabric Assistance Properties of Viscose Rayon

Sample	i		ii		iii		iv		v		vi		'B'
	T	S	T	S	T	S	T	S	T	S	T	S	
Fabric Stiffness, kg/% extn.													
warp	2.57	1.97	2.60	1.92	2.76	1.92	2.65	1.98	2.87	1.92	3.47	1.98	1.92
weft	3.24	2.50	3.02	2.34	3.10	2.18	2.77	2.16	2.83	2.44	3.76	2.40	2.10
Yarn Stiffness, x10^{-2} kg/% extn.													
warp	2.23		2.16		1.77		2.17		2.17		2.22		1.91
weft	2.28		2.20		2.22		2.14		2.12		2.86		2.08
Fabric Assistance													
warp	1.03	0.94	1.02	0.95	1.13	0.96	1.12	0.97	1.12	0.92	1.13	0.97	0.94
weft	1.00	1.00	1.10	1.04	1.13	1.01	1.17	0.98	1.14	1.06	1.02	1.04	0.98

T → Treated, S → Stripped

a constant error between the two machines, the values could be justifiably accepted for comparison purposes and it would be seen that the resin treated samples have a higher value for fabric assistance than the untreated sample, which might be due to some modifications in surface properties.

Fabric crease recovery and yarn elastic recovery

The values of percentage crease recovery of fabrics show a small increase for all the resin treated samples over that of the untreated material (Table 8). Melamine and ethyleneurea-formaldehyde samples show little improvement in fabric crease recovery, compared to urea-, methylatedurea-formaldehyde treated samples, although the yarn elastic recovery values for melamine-, ethyleneurea-formaldehyde have been shown to be high. This can be better visualised from a study of Figure 6, a plot of warp fabric crease recovery against yarn elastic recovery at 5% extension. This signifies that the yarn elastic recovery on its own is not enough to predict fabric crease recovery and that the other tensile parameters, such as modulus, which are influenced by the type of resin, may be involved.

Recovery and Wear Properties of Viscose Rayon Fabrics and Yarns

Sample		i		ii		iii		iv		v		vi		'3'
		T	S	T	S	T	S	T	S	T	S	T	S	
Fabric Crease Recovery, degrees	warp	120	118	124	119	135	123	133	123	126	117	152	123	117
	weft	127	121	127	121	128	122	129	122	134	124	151	124	113
Increase in Crease Recovery, %	warp	2.6	0.8	6.0	1.2	15.1	5.1	14.0	5.1	7.7	0.0	30.0	5.1	-
	weft	12.0	6.8	12.0	6.8	12.8	7.7	13.7	10.7	17.0	9.4	32.5	9.4	-
Yarn Elastic Recovery, %	warp	55		62		51		54		52		64		50
	weft	65		65		66		64		61		70		55
Tear Strength, kg	warp	1.2	1.40	0.96	1.40	2.20	1.60	2.56	1.60	2.92	1.80	1.92	1.72	1.40
	weft	1.36	1.36	0.96	1.30	2.00	1.51	2.68	1.56	2.72	1.68	1.92	1.60	1.38
Abrasion Resistance, loss in weight, %		28		41		46		29		22		60		12

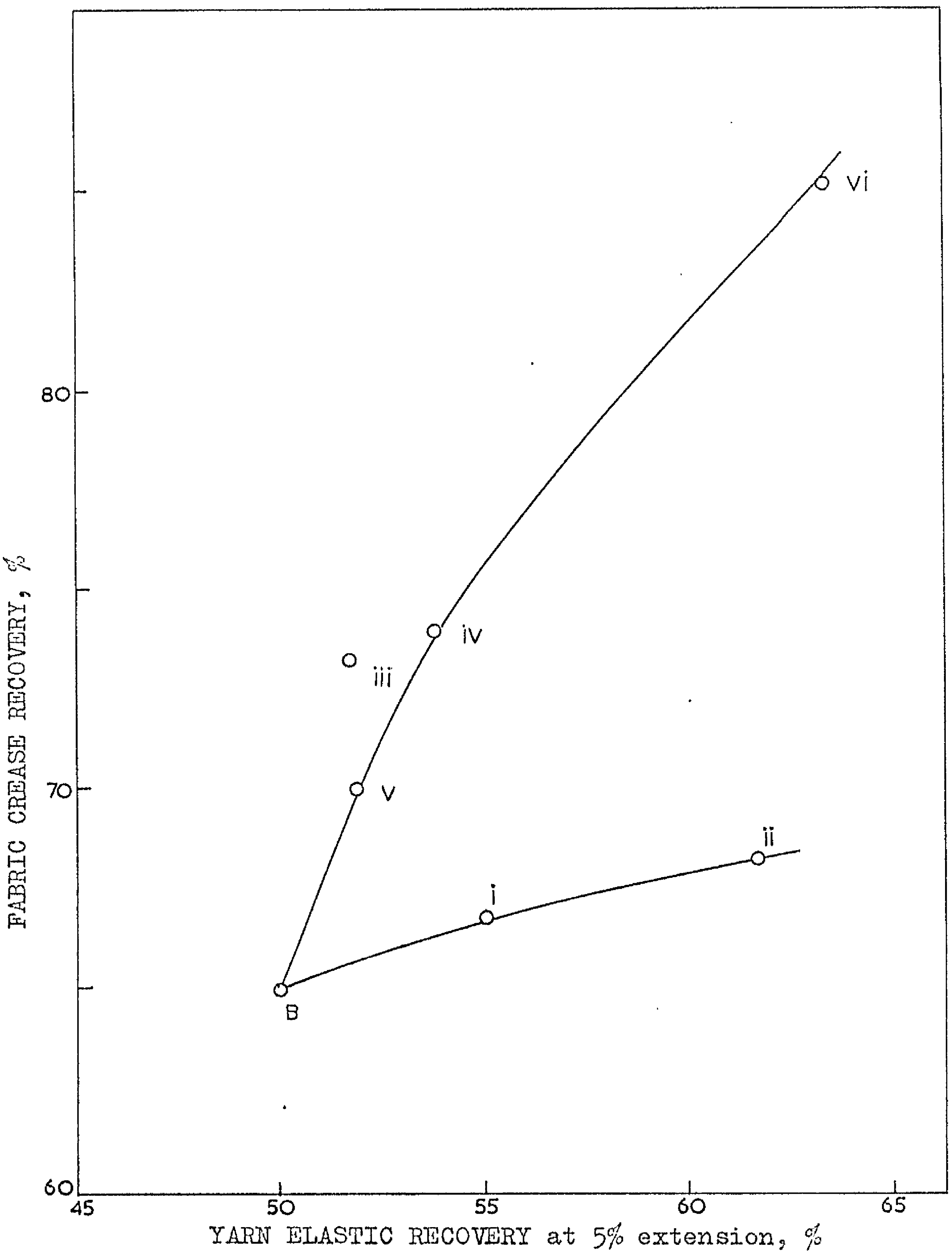

Figure 6 Effect of Yarn Elastic Recovery on Fabric Crease Recovery

Tear strength

Tear strength of melamine- and ethyleneurea-formaldehyde treated samples was found to decrease, whereas, methylatedurea- and urea-formaldehyde treated samples showed an increase in tear strength, but in all cases the tear strength of the samples after resin removal showed values nearly the same as that of the untreated sample and this is taken as confirmatory evidence that the samples have not suffered chemical degradation during resin treatment.

Abrasion resistance

The results of abrasion resistance have been reported in Table 8. The effect of additives on abrasion resistance appear interesting. Although the abrasion resistance of all samples have been poor as compared to the untreated sample, the sample v which had additive A had better abrasion resistance than the sample iv which had no additives and this in turn had better abrasion resistance than the sample vi which contained additive B. Thus it WILL be seen that the additives may or may not increase abrasion resistance.

CONCLUSIONS

Chemical Methods

From a study of the various methods of stripping reported in the literature and of the present work it can be concluded that:

(a) Using 2% hydrochloric acid at 60° C an appreciable amount of chemical degradation occurred .

(b) Treatment with 0.1N hydrochloric acid at 60° C removed most of the resin within 15 minutes, that no appreciable additional portion of the resin was stripped by further treatment and that little chemical damage occurred.

(c) Treatment with 1.5% phosphoric acid in 5% urea solution at 60° C removed most of the resin within 15 minutes and showed very little chemical damage up to 20 minutes of the treatment.

(d) 1% formic acid at 60° C removed ethyleneurea-formaldehyde resin but was not effective in the cases of the other resin treated samples.

It has been noticed that no single method of stripping can be suggested to remove all types of resin finishes, however, from the results of the nitrogen estimation and fluidity measurements, the most effective stripping methods for a particular finish would appear to be as follows:-

Stripping Agent	Resin
0.1N hydrochloric acid at 60° C for 20 minutes.	urea-formaldehyde, methylatedurea-formaldehyde.
1.5% phosphoric acid in 5% urea at 60° C for 20 minutes.	melamine-formaldehyde, ethyleneurea-formaldehyde.
1% formic acid at 60° C for 40 minutes.	ethyleneurea-formaldehyde.

These methods remove over 95% of the treated resin with little chemical degradation in cellulose.

The fluidity values of the stripped resin treated samples and the similarly treated control samples showed no significant difference. It has therefore been concluded that any change in property of a sample can not be ascribed to chemical degradation of the sample by resin finishing and further that no significant chemical degradation occurred if a suitable stripping technique was adopted.

It may be mentioned that very recently, in 1963, B.S. Institute has specified a method to estimate urea-formaldehyde resin content by loss in weight method using 0.1N hydrochloric acid at 60°C for 60 minutes. The present work supports this method and it may be further added that under this stripping condition, any amido-formaldehyde resin would be completely removed, and their alternative process of 0.02N hydrochloric acid at the boil for amido-formaldehyde resins, which in their opinion gives slightly higher loss in weight due to greater removal of non-nitrogenous matter, is really not necessary. It may be also added that with either of these conditions there would be a substantial chemical degradation.

It is now realised that perhaps further use might have been made of the test methods for the identification of resins, partly to check their sensitivity and partly to check the rate of stripping and the nature of the residue. It is considered that this should be done in any future scheme of work.

Physical Methods

The results of the fabric and the yarn physical tests carried out on the resin treated, stripped, and untreated samples also suggest that the loss in some tensile properties has been a result of physical modification.

It is noted that the main changes resulting from the formation of cross-linkages, either physical or chemical, between cellulose molecules have been the increase in the elastic recovery and increase in modulus, i.e. decrease in extensibility. This increase in modulus appears to aid in producing resistance to creasing. At the same time a higher modulus produces fabric with a lower capacity for energy absorption and consequently lower resistance to abrasion. However, the results of the tear strength appear interesting as in some cases the tear strength has actually increased, which might be due to the lubricating effect in those cases, which increases the ability of fibres and yarns to rearrange under load and share stresses.

It may be also noted that at comparable levels of elastic recovery the increase in yarn stiffness is not the same for all the resins used. It would be expected therefore, that different materials which can produce the same improvement in the yarn elastic recovery may not give the same value of fabric crease recovery as a result of the differences in yarn extensibility.

Effect of additives

It is regretted that the type and the amounts of additives used in samples v and vi were not known and hence, not much could be deduced . However, a comparison between samples iv, v, and vi, all urea-formaldehyde treated samples, could be made and has been reported below in the order of rating.

	Sample iv	Sample v	Sample vi
Tensile strength	1	2	3
Extension at break	1	2	3
Moisture regain	1	2	3
Water imbibition	1	2	3
Tear strength	2	1	3
Abrasion resistance	2	1	3
Fabric crease recovery	2	3	1
Elastic recovery at 5%	2	3	1

1 indicates value higher than 2 which is higher than 3

It will be noticed that the strength and the extension properties of both samples with additives are lower than that without additive and yet sample v, with additive A possesses improved tear and abrasion performance and sample vi, with additive B possesses improved crease resistance and elastic recovery properties compared with the sample without additive (iv).

APPENDIX

Rate of Acid Hydrolysis of Urea-Formaldehyde Polymerized in Viscose Rayon

Very little work on the acid hydrolysis of resin treated cellulose has been reported, although acid hydrolysis of the resin polymer itself has been studied. deJung and deJunge (158) and Landquist (175) calculated the activation energy for the hydrolysis of urea-formaldehyde resins in solution at different pH, while Mapen, et al. (78) calculated the activation energy for the hydrolysis of urea-formaldehyde resins in cellulose.

Nuessle, et al. (231) listed nine possible reactions when a difunctional resin precondensate is polymerized with cellulosic fibres. Of these, three reactions involve only resin polymerization with no bonding with cellulose, while the remaining six involve respectively, (a) simple cross-link, (b) linear polymer cross-linked to cellulose, (c) polymer network cross-linked to cellulose, (d) monomer attached to only one cellulose chain, (e) linear polymer linked to one cellulose chain, or (f) polymer network linked to only one cellulosic chain.

The removal of a resin from the fabric depends not only on the hydrolysis of the terminal N-CH$_2$O-Cell bonds but also of the N-CH$_2$-N bonds in the resin polymer. It has been shown that the former bond is hydrolysed faster than the latter, during acid hydrolysis of dimethylol ethyleneurea (271) and during alkaline hydrolysis and acid hydrolysis of dimethylol urea (315) applied to cotton under usual conditions. It is therefore expected that during the initial stages of acid hydrolysis, resin linked as (a), (b), (d), or (e) would be hydrolysed at a rapid rate, whereas polymer networks(c), (e), or (f) cannot be removed by hydrolysing only the end methylol groups and must be further broken down by the hydrolysis of methylene groups before they could be removed from the material.

In the present experiments urea-formaldehyde treated samples were hydrolysed with 0.1N hydrochloric acid at 75° C, 50° C, and 25° C, and with 0.01N hydrochloric acid at 50° C, and 25° C, for various lengths of time and the percentage nitrogen was estimated on these hydrolysed samples.

The data of residual nitrogen have been plotted against time of hydrolysis as a first order reaction in Figure 7, 8, 9. From Figure 7 it will be seen that the curve with 0.1N hydrochloric acid at 75° C and 50° C and to a certain extent the curve with 0.01N hydrochloric acid at 50° C exhibit a sudden change of slope, whereas the curves with 0.1N and

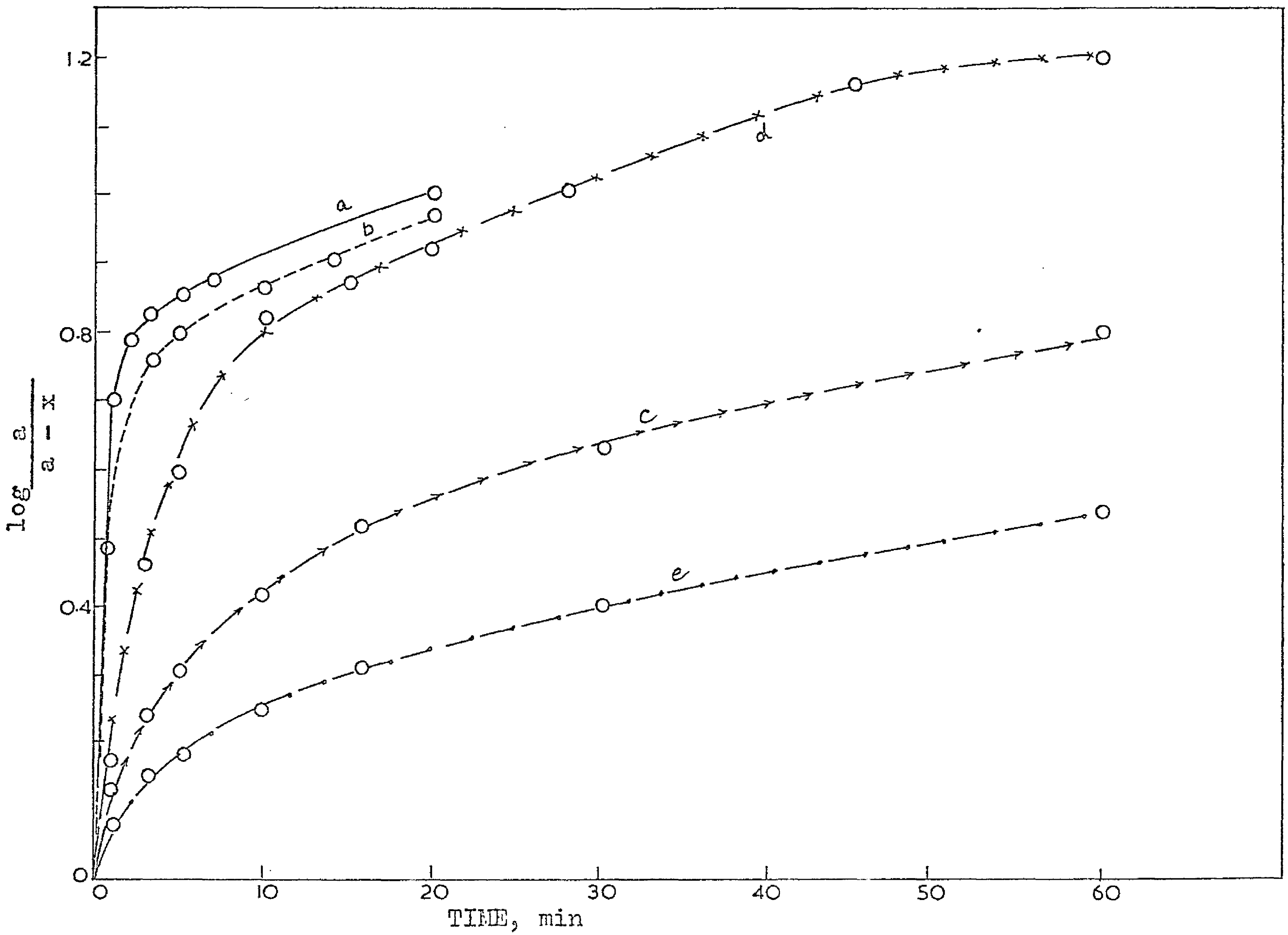

Figure 7 Rate of Nitrogen Loss with Time of Hydrolysis in Hydrochloric acid
(a) 0.1N, 75°C; (b) 0.1N, 50°C; (c) 0.1N, 25°C; (d) 0.01N, 50°C; (e) 0.01N, 25°C

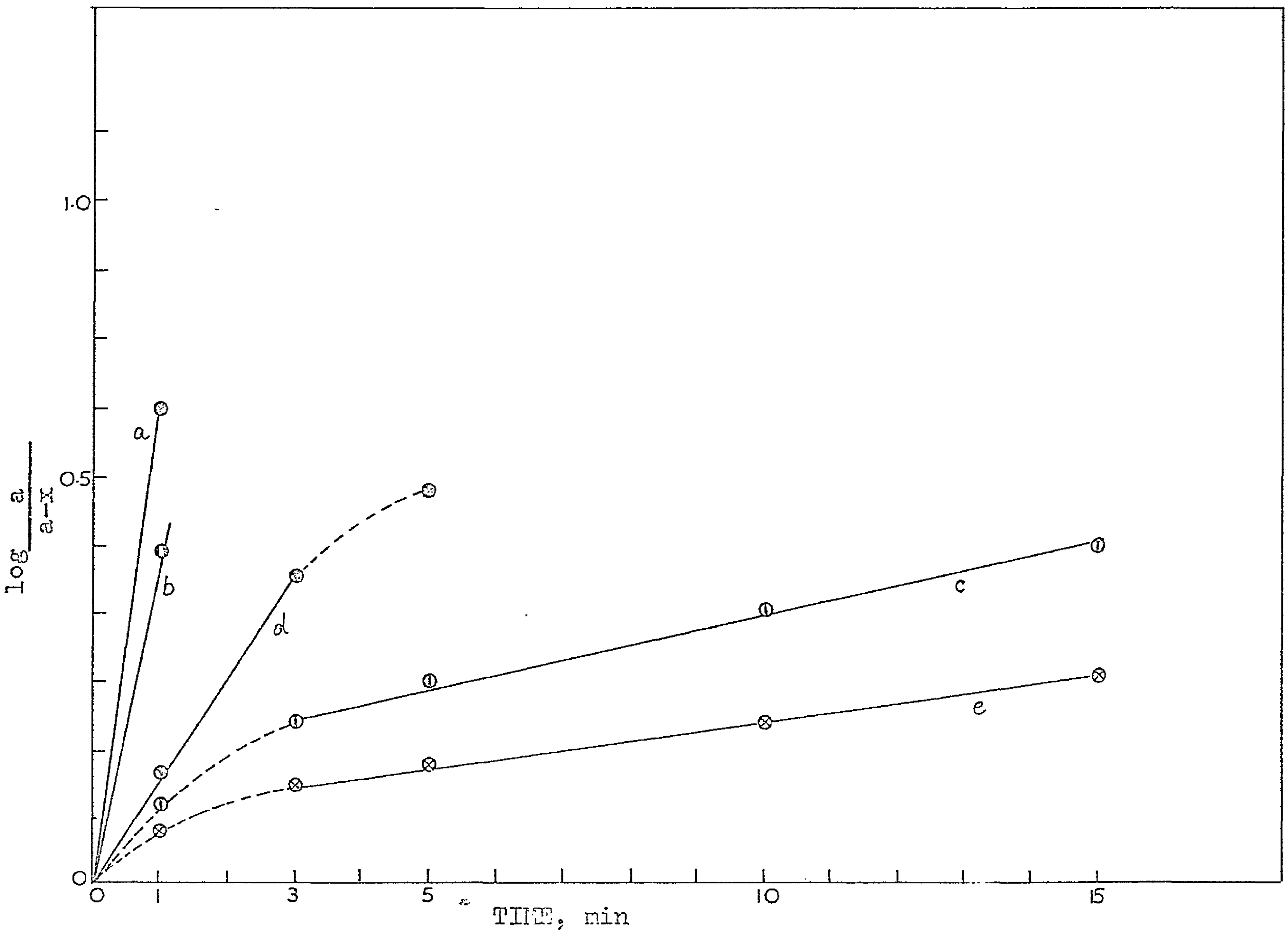

Figure 8 Rate of Nitrogen Loss with Time of Hydrolysis in Hydrochloric Acid
(a) 0.1N, 75°C; (b) 0.1N, 50°C; (c) 0.1N, 25°C; (d) 0.01N, 50°C; (e) 0.01N, 25°C

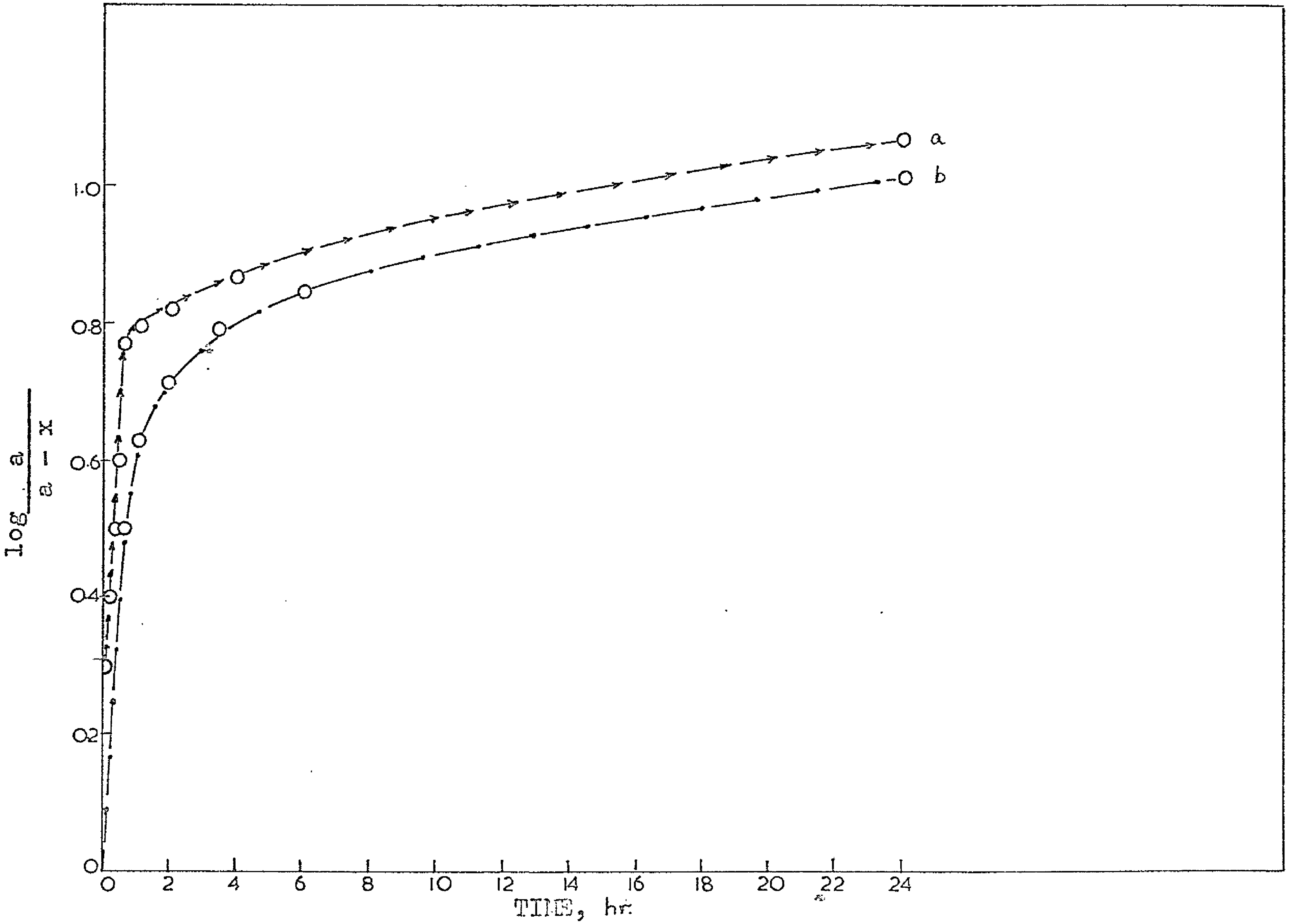

Figure 9 Rate of Nitrogen Loss with Time of Hydrolysis in Hydrochloric Acid (a) 0.1N, 25°C; and (b) 0.01N, 25°C

0.01N hydrochloric acid at 25°C show a typical pattern of a fast and slow reaction occurring simultaneously. The initial portion of Figure 7 has been replotted in Figure 8 and shows a possibility of the separation of two reactions with 0.1N and 0.01N hydrochloric acid at 25°C, whereas no separation is observed with the other curves. Figure 9 shows the complete hydrolysis curves with 0.1N and 0.01N hydrochloric acid at 25°C and a sudden change in slope will be noted which appears very similar to the other three curves in Figure 7. It can be suggested that the sudden change in slope may be the result of a near completion of hydrolysis and in all cases the sudden change appears at about 85% resin removal. Results have been reported in Table 9.

One of the major objections to the conditions employed in the present investigations is the use of unbuffered solutions, although the material to liquor ratio was very large.

It could be concluded that although the work failed to separate the fast and the slow rate of hydrolysis of resin polymerized in the fibres, at all temperatures and concentrations of acid investigated, it has given sufficient guidance as to the range of concentrations to be employed in future experiments where it may be probable to separate the two rates of reaction of hydrolysis, if at all possible.

Table 9 Acid Hydrolysis of Urea-Formaldehyde Treated Viscose Rayon

Temperature, °C	Concentration of HCl N	Time Reqd. for 85% Resin Removal Min.	Resin Removed Near Completion of Hydrolysis %
75	0.1	2	84.5
50	0.1	5	84.5
50	0.01	10	86.5
25	0.1	45-60	85.5
25	0.01	180	86

PART 2

PHYSICAL PROPERTIES OF RESIN TREATED VISCOSE RAYON

CHAPTER 4

SURVEY OF LITERATURE

Introduction

The handle and crease recovery properties of many viscose rayon fabrics originally tended to be poor, and resin finishing has been widely used to improve these characteristics. However, resin treatment affected other properties such as strength and durability, and reports over the years have tended to be contradictory so that it cannot be categorically stated that the addition of a resin improves, or impairs, the quality of a viscose rayon fabric.

It was felt that a useful contribution could be made if the influence of various types of resin finish on physical properties of viscose rayon was compared with the abrasion results obtained on two commercial wear testers, the American Accelerotor and the British Booking Abrader (B.F.T. Mark 1Va). Such is the work reported in the following chapters.

The terms 'abrasion' and 'wear' have been used interchangeably over the years to refer to the mechanical distruction of textiles both in the laboratory and in actual service use. The terms are not synonymous but a distinction is not always made between them. 'Abrasion' should mean a rubbing action involving relative motion between one material and another, whereas 'wear' should be a more comprehensive term and refer to the effects of all types of action, mechanical or chemical in nature, which have a deleterious effect on the properties of the material. Abrasion has been defined (205) as the physical destruction of fibres, yarns, and fabrics resulting from the contact with a relative motion of a textile surface over that of another surface which may be grit, wood, metal or frequently another textile. Wear may result from the relative motion and bending of the fibres and yarns over each other in a fabric structure; damage to many textile articles in actual service probably resulting from a combination of direct rubbing, commonly referred to as 'flat' or surface abrasion, and flexing or bending, generally termed 'flex' abrasion. Loss of mechanical properties, or weakening of a fabric, may result from the removal of, or damage to, individual fibres and three possible mechanisms have been suggested as contributing to the mechanical breakdown during abrasion, namely, frictional wear, cutting and plucking or snagging of fibres (23,215,247).

One form of frictional wear may occur if the surface of the abradant is relatively smooth and the fibres are firmly held in the yarn structure. It is likely that closely woven fabrics containing yarns of high twist are more susceptible to frictional wear than loosely woven fabrics containing low twist yarns.

Among the several theories of friction, the two most widely considered have been the 'abrasive' and the 'adhesion' theories (23,37,56,241,248,286,324). Most present-day authorities agree that molecular adhesion plays the principal role in frictional phenomena, but other investigators have attributed friction to the ploughing of soft surfaces by harder ones and to electrical forces (241). On one hand, friction and constriction may lead to wear as a result of bending and flexural fatigue. On the other hand, when fibre cohesion is relatively poor the frictional force can displace, or remove, fibres from their normal position in the yarn. Thus breakdown of structure occurs without appreciable fibre damage.

Fibres will be cut if abradant surface areas are very small and sharp compared to that of the fibre. Fine abrasives, such as emery paper and sand paper used in laboratories, cause a cutting action when rubbed over a fabric surface (292). The cutting process is known to be associated with the development of complex stress patterns which can lead to fibre tensioning, bending or slippage in addition to the direct damage caused by cutting (23).

In addition to cutting and frictional effects, plucking or snagging of fibres and yarns can take place as the abradant traverses the fabric surface. Plucking will be more pronounced when the normal forces between the abradant and fabric are large, since deeper yarn penetration will occur. Depending upon the force exerted by the abradant and the extent to which the fibre is bound in the yarn, rupture on first contact, slippage, or repeated stressing can result. Loosely woven fabrics containing low twist yarns would be more subject to abrasion damage due to plucking than tightly woven fabrics containing yarn of high twist. In the latter, fabrics would be more severely bound in the yarn and therefore less accessible to the abradant.

Sufficient evidence exists to prove that innumerable small fibre particles of various sizes are removed during abrasion. Abrasion testing with blade type abradants removed particles from the cotton fibre as small as 100-200 Å (292). Other observations have shown that particles 2-3μ wide and 40-50μ long are torn away from cotton fabrics during actual wear. In the study of the fragmentation of cotton fibres during dry abrasion (75), chiplike particles 0.15-0.5μ in diameter and 1-3μ long were obtained by rubbing together two heavy pieces of canvas. Wet abrasion, on the other hand, produced very long fine fibrils 100-200 Å in diameter. Because of the inherent flexibility and ease of deformation of fibres, it is not likely that abrasive wear will occur predominantly through removal of fibre particles. Observations of fibres from worn textiles shows that abrasion causes gross fibre damage rather than gradual wear through the removal of fibre material, fibrillation (354), cuticle damage (60) and traverse cracking having been reported.

Factors Determining Durability

The durability of fabric might be expected to be dependent on the mechanical properties of the fibre, and on yarn and fabric construction and finish.

Mechanical properties

Tensile, shear and flexural properties of fibre are important variables determining durability.

Tensile properties

Numerous studies have shown that abrasion resistance of fabrics is higher for fibres which have greater capacity to absorb work under conditions of repeated stretching (5,106,126,327), one suggestion being the measurement of the area under the stress-strain curve after mechanical conditioning (326).

The capacity for work absorption during repeated stretching depends upon the strength, extensibility, and elasticity of the fibre, and fibres which are deficient in these, particularly the latter, normally would be expected to have poor wearing properties.

It has been suggested that the reduction in laboratory abrasion resistance accompanying resin treatment of cellulosic fabrics resulted from changes in the stress-strain properties of the fibres (105,106). It has also been suggested that chemical cross-linking and resin deposition within fibrils, between the fibrils, and between growth layers, of the cotton fibre reduces the relative movement between these structural elements (231) and extensibility is therefore reduced. The elastic recovery is increased since there is less tendency to form new forces of attraction resulting from movement of structural elements from their old positions, but the strength is lowered because the fibrils are less free to move into more orientated positions along the fibre axis.

The net result is that the work absorption capacity of the resin treated fibre is less than that of the original fibre.

The increased elastic recovery of resin treated fibres would be expected to compensate somewhat for their lowered extensibility because although their resistance to higher strains is less, their ability to recover from lower strains is increased. Studies with viscose rayon have shown that the difference in laboratory abrasion resistance between resin-treated and untreated fabrics depends greatly upon the test conditions (107). At the high loads normally used in accelerated laboratory tests the abrasion resistance of resin treated fabrics was considerably less than that of the untreated fabrics. As the severity of the test conditions decreased, the difference in abrasion resistance between the two became smaller, until, under very mild test conditions, abrasion resistance of resin treated fabrics actually exceeded that of the untreated. Thus, there is evidence that while high work absorption is necessary for more severe abrasion conditions, elasticity is more important under the mild conditions more likely to be encountered in service. If there is any connection between the tensile properties of a fibre and durability and low strains are involved, then consideration should be given to the initial modulus, while the relative effects of conditions, other than time, might also be important. Thus a major contributing factor to the poor wet abrasion performance of viscose rayon has been stated to be its low wet strength (217), while on the other hand, fibre swelling could stiffen fabrics and reduce the flexibility needed to prevent development of high abrasive stresses. (23).

Shear properties

Shear stress is the result of forces acting perpendicularly to the main axis of the fibre. The inherent flexibility and freedom of motion of fibres in a textile structure are such that stresses other than tensile should seldom develop to any appreciable magnitude (250). However, when sharp abrasive surfaces are present, or fibre movement is restricted, the resistance of the fibre to shear becomes important (26). Field service tests indicated that an optimum balance between shear and tensile properties is desirable, depending upon the abrasive conditions (205).

It has been stated that resistance to shear provides further explanation of cottons' comparatively high abrasion resistance, in spite of its relatively low work absorption during repeated stretching (291). It is suggested that cottons resistance to shear (32) is a major factor accounting for its low abrasion damage. While longitudinal orientation provides improved tensile strength, orientation of structural elements transverse to the fibre axis contributes to improved shear strength (205). Abrasion studies have indicated that too much lengthwise orientation resulting from 'over-stretching' of fibres lowers abrasion resistance (327).

It has been suggested that an approximate order of abrasion resistance of textile fibres can be obtained by calculating the ratio of the shear tenacity to initial modulus. Such ratios computed for nylon, cotton, viscose, and acetate have shown a marked resemblance to the order of abrasion resistance of these fibres (23).

<u>Flexural properties</u>

The bending resistance of fibres and the tensile stress developed from interfibre friction are important factors determining internal abrasion damage resulting from fabric flexing (25). Tests on the flexing performance of nylon and wool flags indicate the importance of interfibre friction (23). Improvement in fibre flex abrasion resistance from the use of lubricants also indicates the contribution of interfibre friction (14,93,349).

Fibre bending creates tensile strain on the outside curvature of the bend and compression on the inside (105). Since buckling occurs easily the net result is that tensile strain is high, while compression is believed to be relatively small (205). Thus fibres with high elastic extensibility show good bending resistance so that the order of inherent abrasion resistance might be somewhat similar to that for flexing endurance. On the basis of flexing endurance, abrasion resistance of wool should be significantly greater than that of cotton and on a par with that of nylon. Again, the discrepancy can be explained by considering the importance of other properties, such as shear strength or ultimate tensile strength.

Yarn and fabric construction

Yarn and fabric construction and geometry are some of the major parameters in determining the abrasion resistance of different fabrics (37,127,349,383).

Yarn diameter

Increased abrasion resistance with large diameter yarns has been noted. Thicker yarns may not necessarily improve flex abrasion to the same extent as flat abrasion. The larger mass to be abraded may be offset to some extent by the higher strains on fibres in the outside curvature of large diameter yarns (119).

Yarn twist

Abrasion resistance increases with twist to an optimum value beyond which a further increase in twist causes a decrease in abrasion performance (24,146,119). Increasing twist to the optimum value improves abrasion resistance by improvement in fibre cohesion. Twist beyond the optimum value impose large stresses on fibres with no further improvement in cohesion.

Yarn crimp

High crimp in a given direction projects yarn in that direction to the rubbing surface and the complementary yarns containing lower crimp are protected (24). Thus highly crimped yarns might be expected to suffer greater abrasion damage than the protected yarn, other things being equal.

Threads per inch

Trials have demonstrated (24,292) that abrasion resistance increases with threads per inch. The larger surface area exposed to rubbing permits better distribution of abrasive stresses, and fibre binding is also improved since more yarn intersections are available. Although very tightly woven structures have improved resistance to flat abrasion, damage from flex abrasion is increased considerably (24).

Weave

Plain weaves provide better fibre binding than twills and sateens because they contain more yarn cross-overs. However, when the advantages of higher yarn counts are desired, twills, sateens and similar constructions give adequate binding with less loss in fibre and yarn movement than that occurs in plain weave. Selection of weave is also largely dependant on end use (24).

Effect of finishes

Additive finishes and/or chemical finishes have been applied to modify the properties of material. Additive finishes are deposited on fibre surfaces and can alter abrasion characteristics through the mechanism of fibre binding, protection and lubrication. In contrast, the more recent chemical finishes impart chemical modifications which are usually accompanied by changes in wear performance.

Additive finishes

Additive finishes are binding agents such as polymeric materials like starches, gums, proteins, and thermosetting and thermoplastic resins having a particle size too large to penetrate the fibre. They are deposited on fibre or yarn surfaces either as discrete particles or as films, cementing the fibres together and physically protecting them from the abradant (119,230,345,363,369). Binding and coating agents generally improve resistance to flat abrasion but may be less beneficial in flex abrasion depending upon the degree to which fibre mobility is restricted (36,300,301). Lubricants, usually of the fatty hydrocarbon type, increase mobility, improvements in flex abrasion being attributed to a reduction in surface friction, but too much lubrication can be harmful because of excessive fibre slippage (92).

Chemical finishes

Chemical finishes modify cellulose by reacting either inside or on the surface of the fibre and can have different effects on the abrasion resistance. Some agents alter abrasion performance because they affect fibre mechanical properties, while others produce fibre swelling and affect the surface characteristics of the fibre (84,119,318).

Some finishes for wrinkle resistance markedly lower the abrasion resistance of cellulosic material as measured by accelerated laboratory tests, the loss in abrasion performance resulting mainly from changes in fibre mechanical properties (119), while on the other hand, acetylation and cyanoethylation increase flat abrasion resistance but have an adverse effect on flex abrasion resistance (50,116). Carboxymethylated cellulose is the only chemically modified cellulose which appears to have both improved flat and flex abrasion resistance (64).

Wear testers

Inspection of literature has shown that there have been a considerable number of instruments designed to test the durability of textile materials (22,43,68,72,290,291,322,323, 325). The bulk of these may be classed as abrasion machines, the fibre, yarn, or fabric being rubbed either to breaking point or for a predetermined period of time. Other instruments may be classified as wear testers, the material being subjected to varied actions such as rubbing, flexing or folding, and the Accelerotor (68) is an example of this type of instrument. The Bocking Abrader (43), (B.F.T. Mk.1Va) is also a wear tester but measures three properties of fabric breakdown separately, namely, flexibility, toughness and resistance to flat abrasion.

As the main purpose of this work was the consideration of the effects of resin finishes on viscose rayon, it was felt that a comparison of the results of tests on two instruments would be useful. Breens and Morton (43) suggested that some correlation should exist between B.F.T. results and fibre, yarn, or fabric properties but gave no actual results, neither have any examples been found relating to the Accelerotor.

CHAPTER 6

EXPERIMENT

Wear tests

Introduction

Tensile properties of yarn and changes in wear performance of a viscose rayon fabric, as a result of resin treatment, have been measured.

The methods of measurements of tensile properties and calculations; the working of wear testers - Accelerotor and Bocking Abrader (B.F.T. Mark 1Va) and the results of preliminary trials; such is the work reported in this chapter.

Material

A second batch of spun viscose rayon fabric U1009, (some details have been given in Ch.1, p.4), lengths of which were specially finished by Messrs. Courtaulds Ltd., was examined. These lengths were analysed and details have been given in Table 10.

Inspection will show that there has been some differences between these fabrics suggesting that there might be some changes in the geometry of the fabrics, which could also influence physical test results, as well as the effects of the resin finishes themselves.

The chemical state of the fabrics was checked by the methods discussed in Part 1 of this thesis and no signs of chemical tendering was noted.

Table 10

Fabric Details

Sample No.	Ends/Inch	Picks/Inch	Yarn Crimp, %		Fabric Weight g/m^2
			Warp	Weft	
B	70	66	22	13	204
1	66	61	16	8	189
2	66	63	16	8	200
3	66	62	12	8	191
4	66	60	14	10	198
5	66	62	15	10	198
6	68	62	12	10	194
7	66	62	16	9	195
8	66	62	17	10	194

For details of resin contents see Table 1, p. 4

Tensile Tests

All yarn tensile tests were carried out on an Instron Tester Model TM, using a 2 inch test length and a constant rate of extension of 1 per cent per second. A minimum of ten tests per sample were carried out.

As the yarns were crimped, the point of zero extension and the test length could not be ascertained easily therefore a load corresponding to a pretension of $\frac{1}{2}$ tex has been applied to the yarn before clamping and this was taken as a point of zero load.

A typical load-extension trace of the yarn is shown in Figure 10. The initial portion of the curve OB is due to crimp in the yarn. As the yarn is stretched, more and more of the crimp is removed until all the fibres in the yarn are stretched leading to the elastic region BC. C is the yield point and D the point of rupture. The dotted line ANM corresponds to the load of $\frac{1}{2}$ tex. 'A' is taken as a point of zero load and N, which is the intercept of the extrapolated linear portion BC and the zero load line AM, is taken as a point of zero extension and thus knowing the calibration of the instrument in terms of load and chart speed, values of various parameters may be obtained.

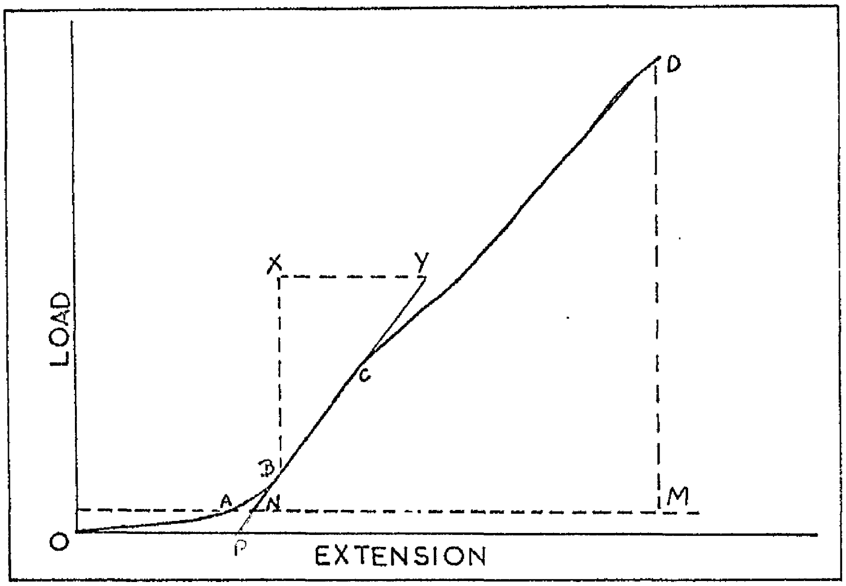

Figure 10 Typical Load-Extension Curve for Viscose Rayon.

MD is the measure of breaking load and has been expressed as grammes per tex and MN represents breaking extension and expressed as a percentage. The initial modulus has been expressed in dynes per square centimeter and was calculated from the slope BC.

$$E = \frac{g}{l} \times L \times 981 \times \frac{\rho}{T} \times 10^5 \qquad \ldots \quad \ldots \quad (1)$$

where E - modulus in dynes/cm^2
$\frac{g}{l}$ - slope BC
g - load in grammes
l - extension in cm
L - specimen length in cm
ρ - density in grammes/cubic cm.
T - tex (yarn)

The ratio of the breaking load to breaking extension has been used as a measure of stiffness of the material. Elder (78a) has examined a number of these samples and found reasonable agreement between the ranking of fabric stiffness using this term and the flexural rigidity obtained from bending tests. This could be a chance correlation or be due to the fact that bending stiffness approaches a final value which is equivalent to the final tensile stress-strain behaviour of the material. The stiffness is expressed in dynes per square centimeter and calculated from equation 1 where 'g' is the breaking load and 'l' the breaking extension.

The area under the curve ABN is considered to be a measure of the energy required to remove the crimp and has been expressed as energy per unit mass in joules per gramme, while the area under the curve NDM is a measure of the energy to rupture and has also been expressed as energy per unit mass in joules per gramme. It can be calculated from the equation

$$\text{Energy per unit mass, joule/g} = (\text{work factor}) \times \text{stress, g/tex} \times \text{strain,\%} \times 1 \times 10^{3} \times 981/10^{7}$$

$$\text{where} \qquad \text{work factor} = \frac{\text{area under stress-strain curve}}{\text{stress, g/tex} \times \text{strain, \%}}$$

Elastic recovery was measured as per the method suggested by Meredith (210). Samples were extended to give 5 per cent extension and held at that length for 1 minute. The crosshead was then returned to the original gauge length and the samples allowed to recover for 1 minute. Finally, the sample was re-extended and the amount of recovery noted and expressed as percentage elastic recovery.

Wear Tests

Accelerotor

The Accelerotor was developed in the laboratories of the American Association of Textile Chemists and Colourists at Lowell, Massachusetts, to give rapid methods for determining fastness to washing and resistance to abrasion (68,182). It consists essentially of a water tight chamber fitted with a collar, liner and rotor. Several different collars and rotors may be used and the speed of the rotor varied, depending on the effects desired.

A fabric specimen is driven by an impeller (rotor) in a random path so that it repeatedly impinges on the walls and abradent liner within the chamber. The specimen follows a zigzag course in a generally circular orbit and is subjected to abrasion, flexing, impact, compression and stretching. The reproducibility of results has been reported to be excellent (182).

In the present work samples of fabrics 4½ inch square were unravelled for ⅛ inch on all sides and the edges coated with a free flowing adhesive (Type Ubabond Adhesive M-7817). The samples were allowed to condition at 20° C and 65% r.h. for 24 hours and were then weighed. An M7769A liner and a 4½ inch pitched rotor were used and the samples were run dry at 1500 r.p.m. for periods of time rangeing from 1 minute to 20 minutes, a constant speed being maintained by manual control of the rheostat. Samples were shaken to remove excess detritus, conditioned for 12 hours and then weighed. The liner was brushed before each test and replaced after 12 tests, each liner being abraded with a control sample before testing was resumed.

The percentage loss in weight after a certain time may be taken as a measure of wear resistance but trials were continued and the effects of using different rotors and speeds were investigated.

Of the four different rotors available the pitched rotors were found to be better than the S shaped rotor where the material got repeatedly entangled, and the 4½ inch pitched rotor was used for all tests.

Two different speeds of 3000 and 1500 r.p.m. were tried over periods of time rangeing from ½ minute to 20 minutes. The percentage loss in fabric weight has been plotted against time of abrasion and the results shown in Figure 11. It will be seen that the curves are nearly linear up to about 40% loss in weight; at 3000 r.p.m. about 45% of the loss in weight was obtained in 4 minutes, whereas at 1500 r.p.m. the loss was of the order of 40% after 20 minutes.

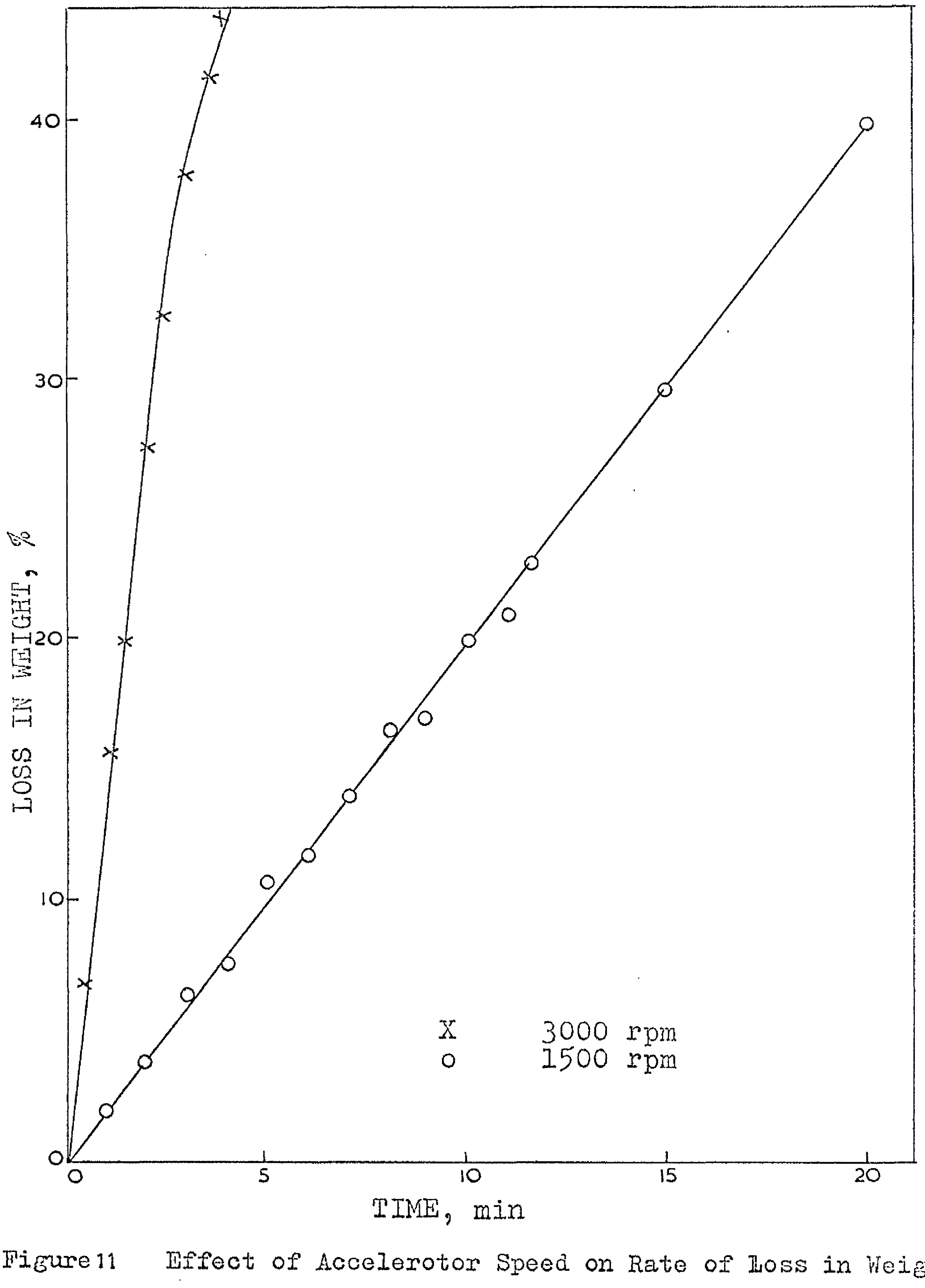

Figure 11 Effect of Accelerotor Speed on Rate of Loss in Weight

A study of the loss in yarn strength was carried out on the abraded samples and the results have been reported in Figure 12 and show that the warp yarn has been more severely damaged than the weft yarn, a fact which can be attributed to the effect of crimp, the warp yarn possessing more crimp. A relationship between percentage loss in fabric weight and percentage loss in yarn strength has been shown in Figure 13 and it will be seen that a very rapid initial loss in strength occurred which may be due to loosening of the yarn structure. There also appears to be no difference between the curves at 3000 r.p.m. and 1500 r.p.m. suggesting that both properties are similarly affected by a change in time scale and that an increase in speed need not imply an increase in actual severity of abrasion.

An interesting point is that a comparatively small loss in weight is accompanied by major deterioration in the serviceability of the material. Another interesting aspect is that the durability of a material depends on the recovery from deformation as well as resistance to deformation. This is partly covered by the results shown in Figure 14 where the recovery of the weft yarn has been maintained.

From this preliminary investigation, 1500 r.p.m. was selected as the standard speed as more samples could be

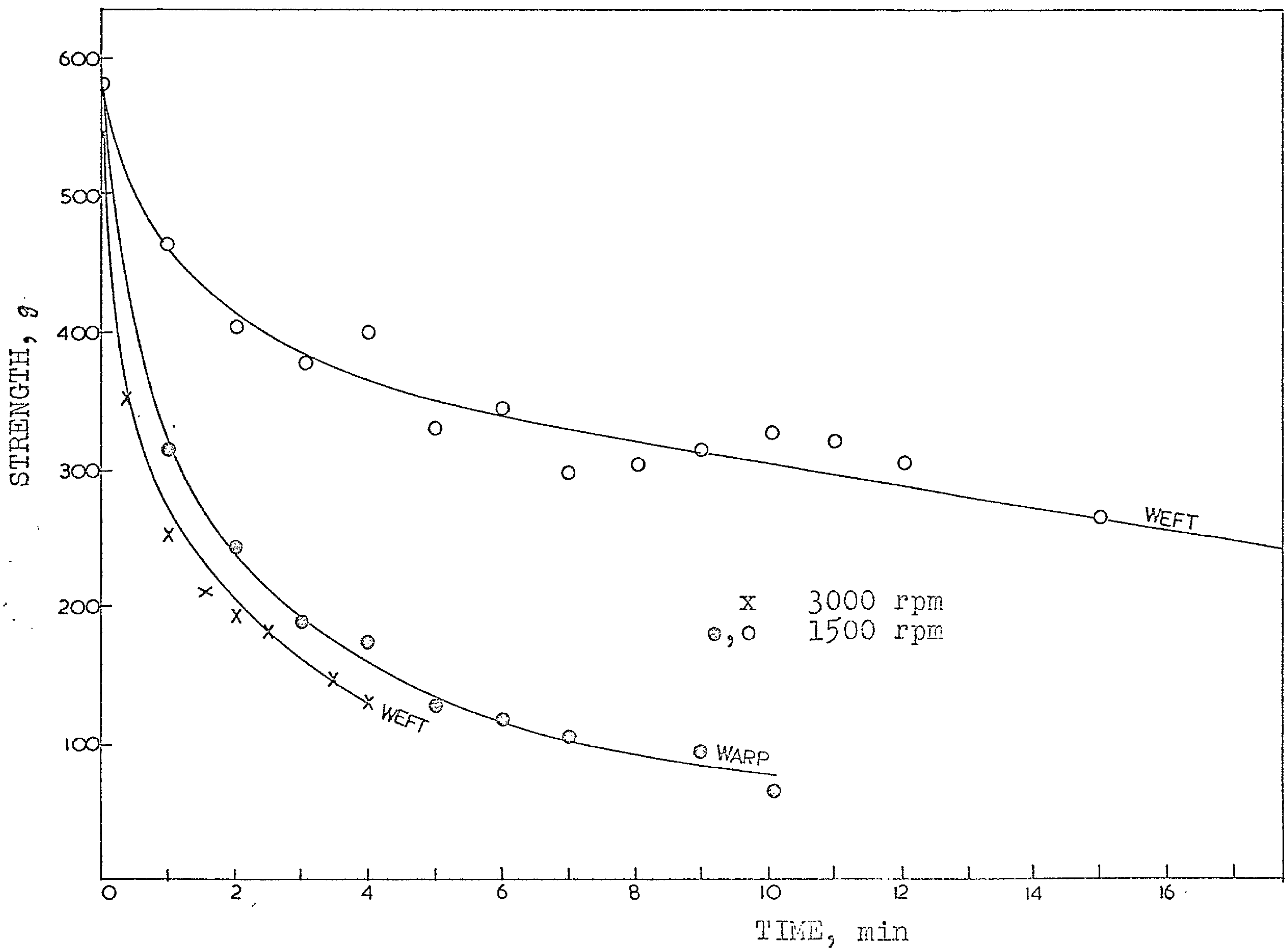

Figure 12 Effect of Accelerotor Speed on Rate of Loss in Yarn Strength

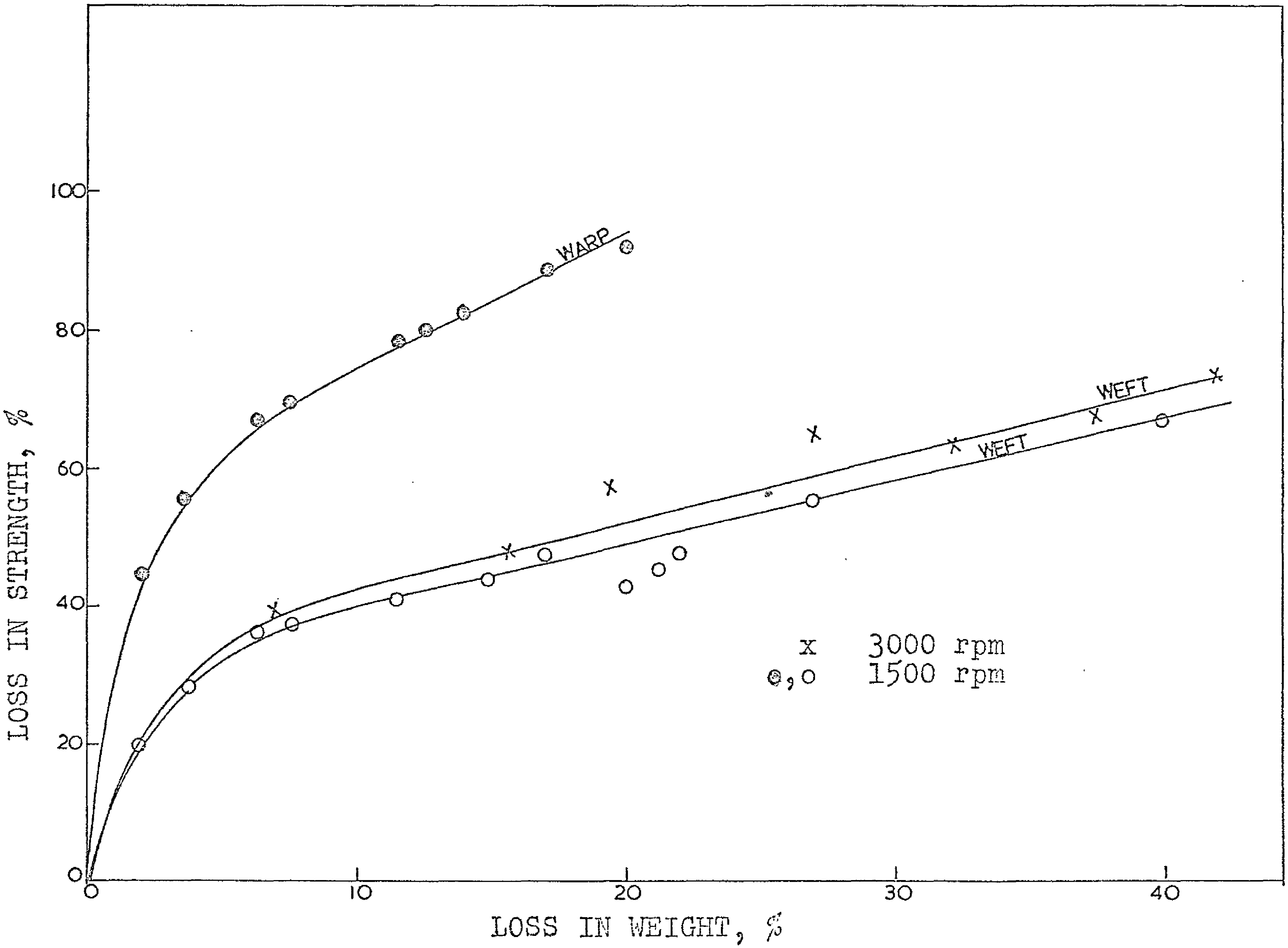

Figure 13 Loss in Strength and Weight of a Sample During Abrasion

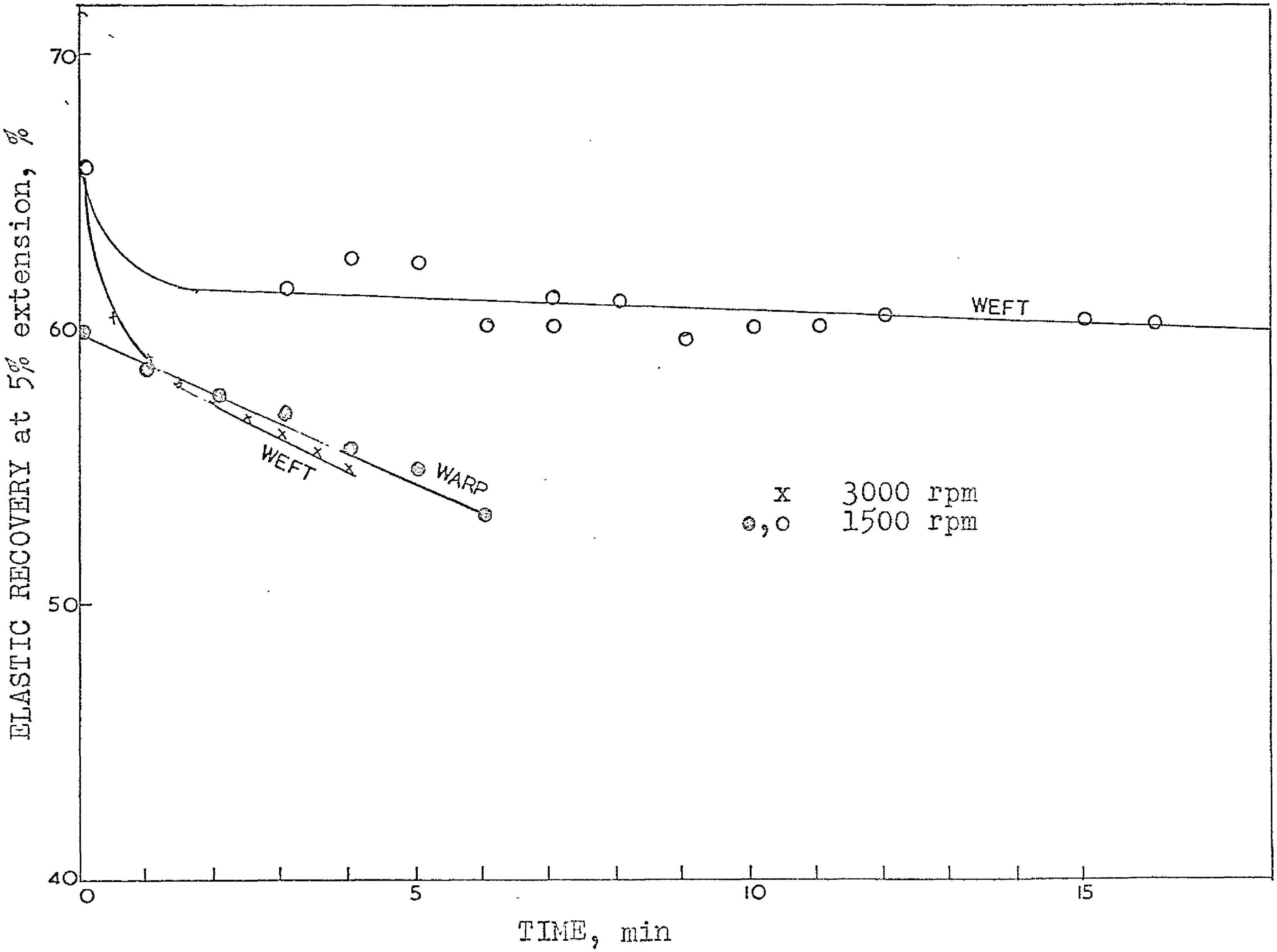

Figure 14 Effect of Abrasion on Elastic Recovery of Yarn

studied at different intervals of time with less risk of error in the measurement of abrasion resistance due to an error in measuring time.

Subsequently, tests were carried out on different resin treated samples using 4½ inch rotor at 1500 r.p.m. for different intervals of time ranging from 1 minute to 20 minutes. The percentage loss in weight of the fabric samples was calculated and plotted against time of abrasion, Figure 15. The slope of the curve which is the rate of percentage loss in weight per minute has been taken as the measure of abrasion resistance, the higher the value the lower the abrasion resistance of the material. There was a linear relationship between loss in weight and the time of test but the rate of loss in weight will be seen to differ for each fabric.

One important point that was checked was that the percentage resin content did not change with abrasion. The resin content being measured by the method discussed in Part 1 of this thesis. Figure 16 shows that any change was small and varied uniformly with the time of abrasion. It is considered unlikely that any change in a physical property of a material can be attributed to a change in resin content.

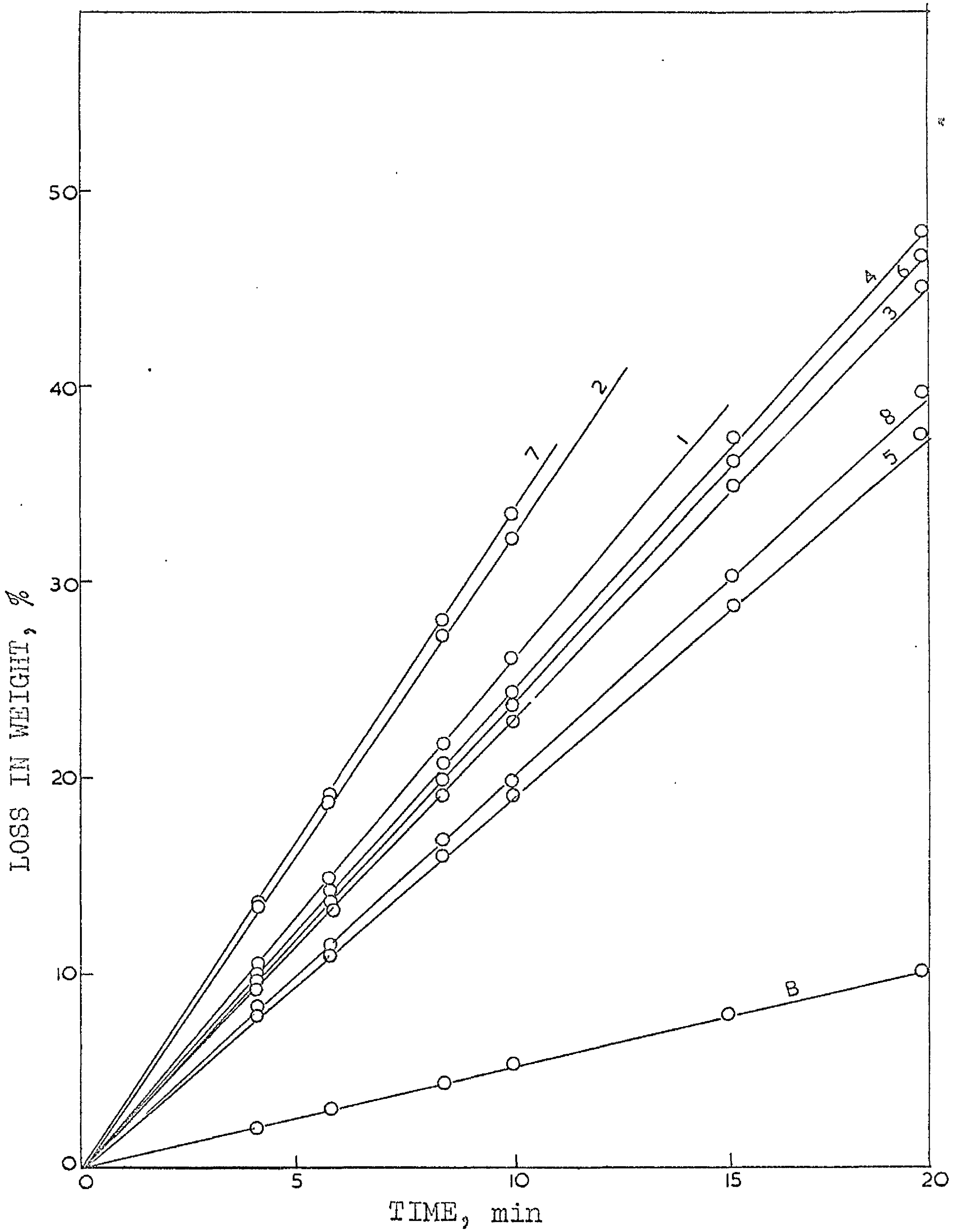

Figure 15 Effect of Time of Accelerotor Abrasion on Loss in Weight of Resin Treated Samples

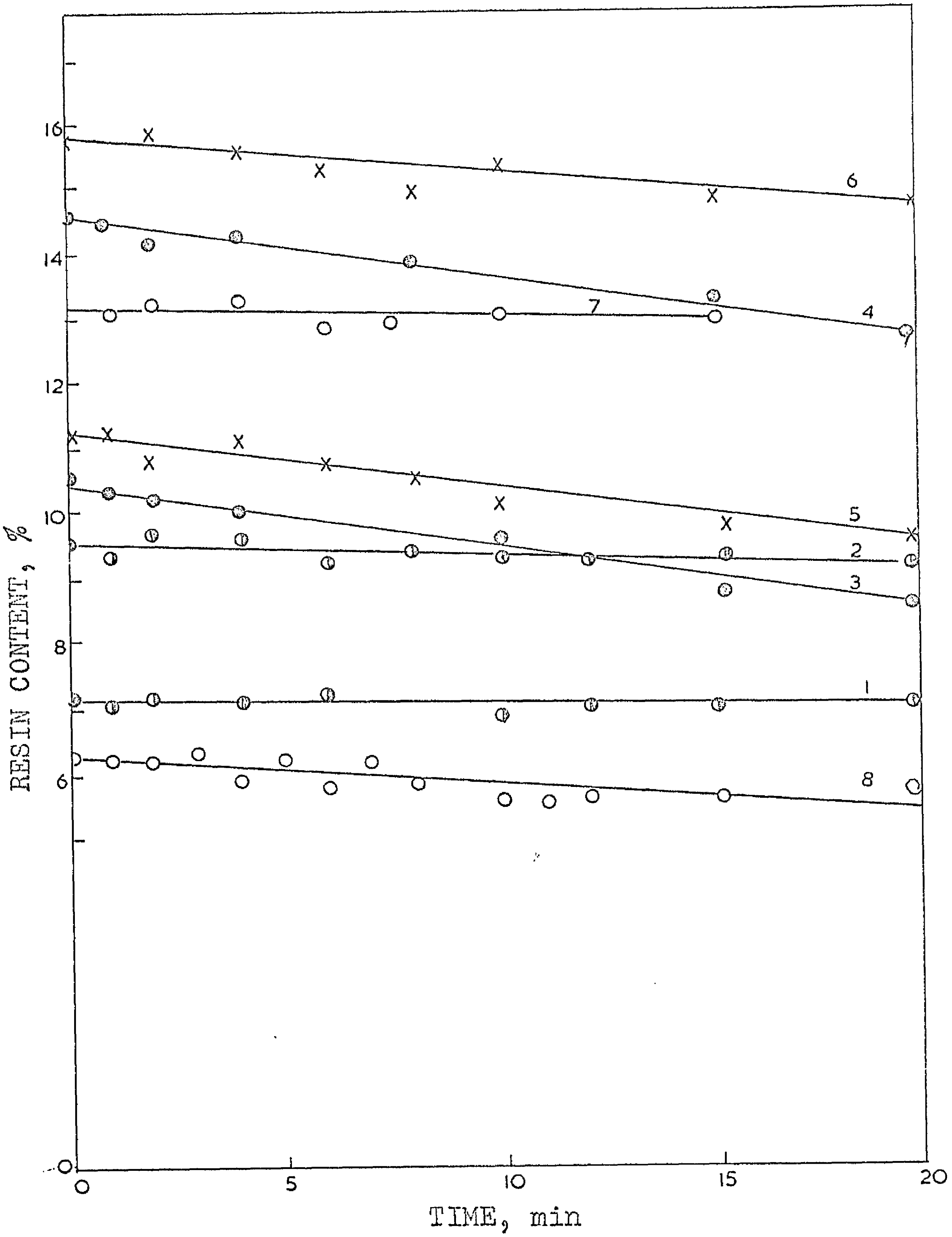

Figure 16 Effect of Time of Abrasion on Resin Content

B.F.T. (Mark 1Va)

This instrument has been developed from an earlier prototype whose use has been discussed by Breens and Norton (43). The Mark 1V tester with a flat abrading mechanism added to the ball penetration and flexing mechanisms of the earlier prototype can be adapted to the testing of the abrasion resistance of fabrics of various materials structures and finishes. A perspective view of the B.F.T. (Mark 1Va) has been given in Figure 17.

It consists essentially of a heavy platform to the right of which is a steel runway on which a solid aluminum carriage (G) mounted on ball races reciprocates in a ⅜" stroke at 700 r.p.m. This motion is produced by a connecting rod (J) running to a crank arm at the left of the platform; the crank spindle is geared to a six decade counter (A). The carriage and the head (F) are furnished with rows of stenter pins on which the fabric is mounted. Above the carriage is the head which is capable of moving vertically in a heavy parallel link motion (B) counterpoised so that with no weights on the head spigot, the whole of the head motion is in equilibrium. By placing weights (D) on the spigot vertical head loadings may be given. The design of the carriage and head with a high thermal capacity and

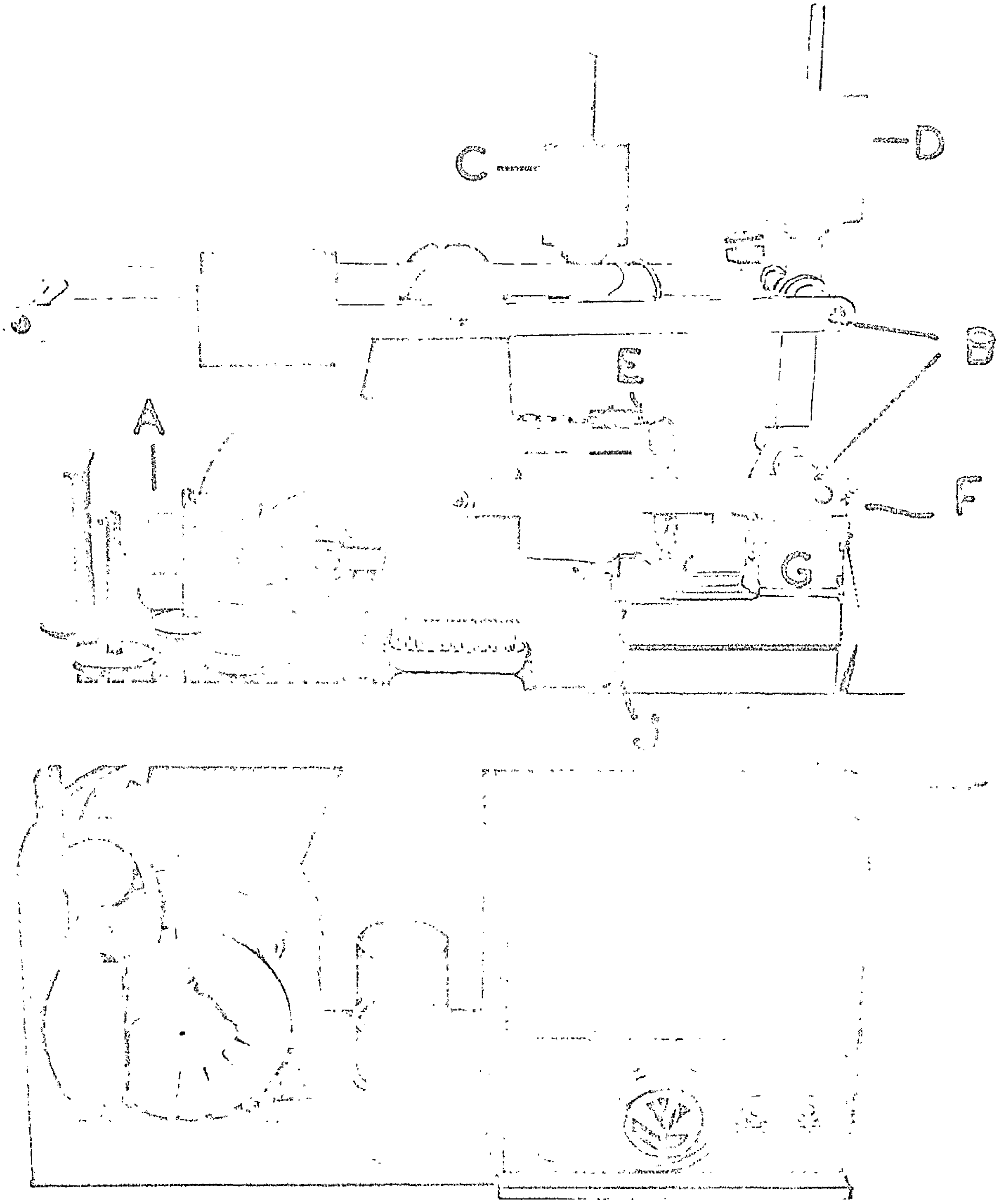

FIGURE 17 B.F.T. MARK IVA

conductivity is such that temperature rise during flex, flat or ball abrasion is negligibly small (37a).

Flex Abrasion

The flexing of the fabric occurs round the specially constructed plate which is pulled to the left by a stirrup and link motion (E), the tension is applied to a stirrup by a weight (C) working through a counterpoised bell-crank and chain. An essential feature of the design is that the chain is attached to a dead point in the link motion so that the machine may run at a high rate with the flex plate weight (C) stationary thus avoiding large inertia effects. The end point is taken when the test strip breaks. As the tension in the chain is lost the bell crank moves under weight (C) and makes a contact which stops the motor.

Ball Penetration Test

In the ball penetration test a 3/16 inch steel ball in an appropriately insulated collet is inserted into the centre of the head. The fabric is secured across the top surface of a specially sprung plate secured in turn to the reciprocating carriage. The end point is given by contact of the ball with the top of the carriage, the motor being stopped by means of a thyratron relay.

Flat Abrasion Test

In the flat abrasion test the flat attachment is placed at the centre of the head; the essential part of the attachment is the abrading surface consisting of a specially prepared woven stainless steel gauze set with its weft at 5° to the direction of reciprocation of the carriage below. The fabric to be tested is attached across a block of electrically conducting plasticised polyvinyl chloride which is fixed in a holder to the top of the reciprocating carriage. The end point is given when gauze makes electrical contact with the block which then stops the motor.

Calibration of the instrument

The machine was calibrated using (standard) calibration fabrics and the calibration checked from day to day at the beginning of the tests.

Ball penetration and flat and flex abrasion tests were carried out under different loads to study the effect of pressure and the results have been reported in Figures 18 19, 20, ~~21~~, a linear relationship being shown between the pressure and the logarithm of the cycles for penetration.

Dry flex abrasion tests were not carried out at different pressures, because the readings at the maximum available pressure of 8 pounds were large enough and

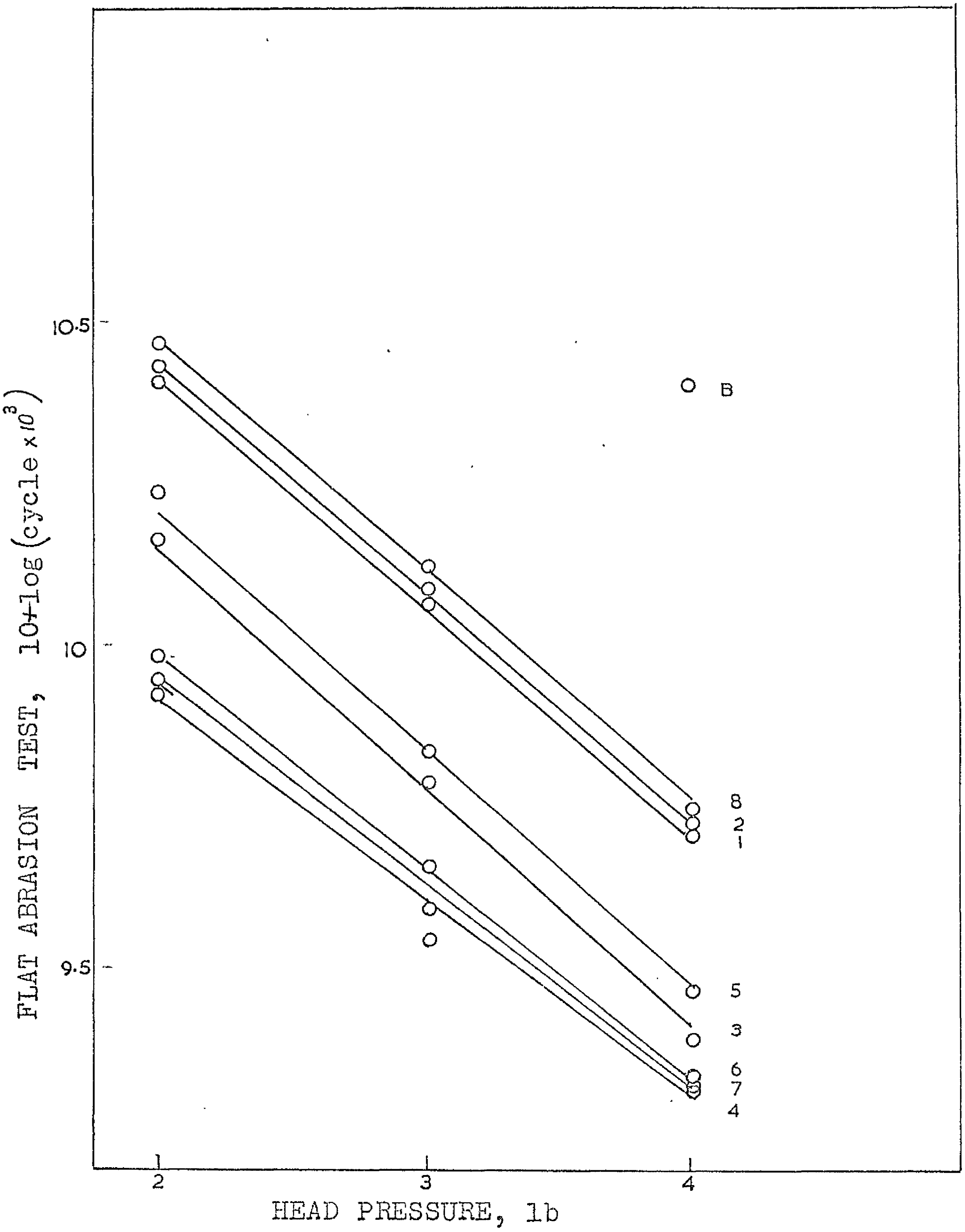

Figure 18 Effect of Pressure on Flat Abrasion Results

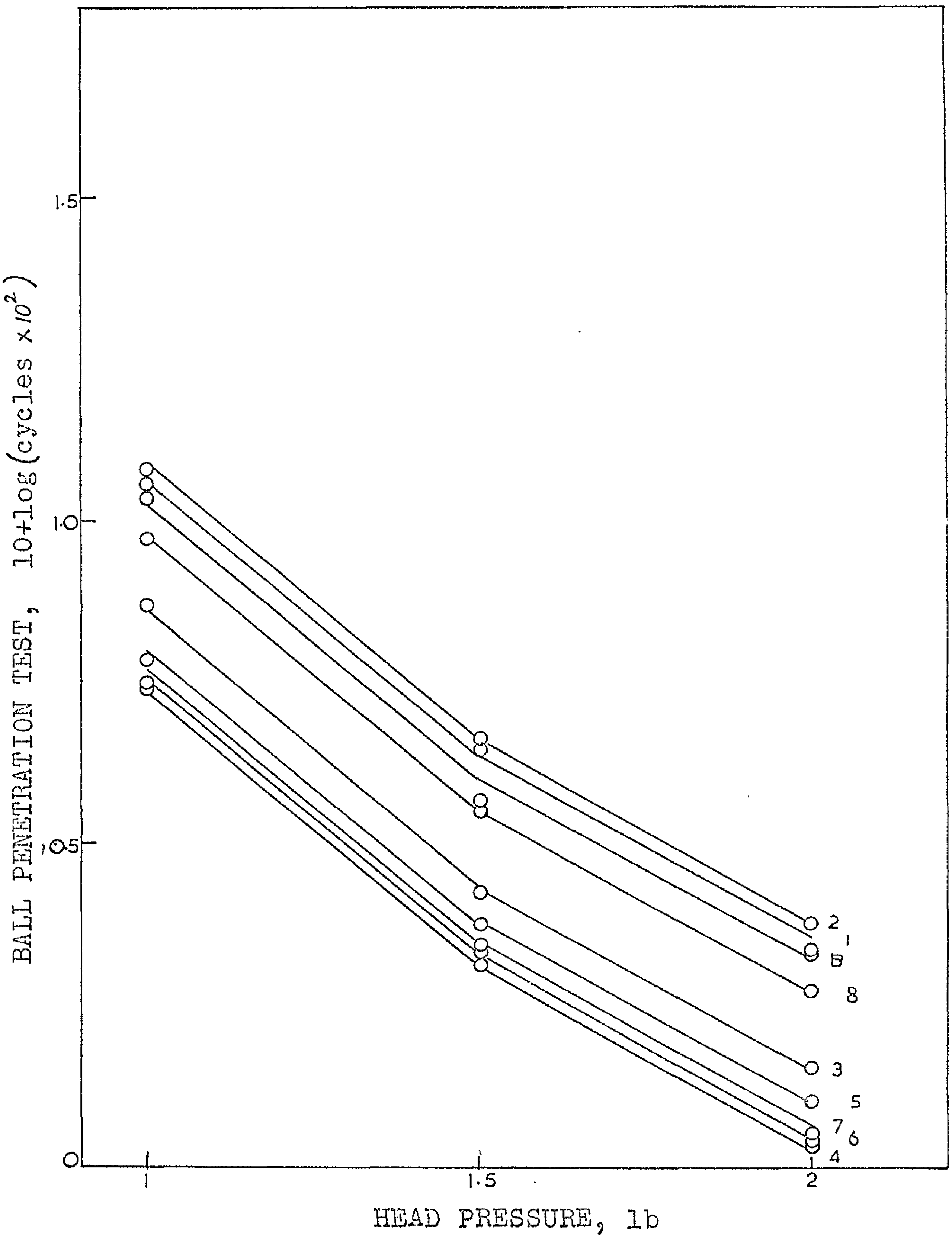

Figure 19 Effect of Pressure on Ball Penetration Results

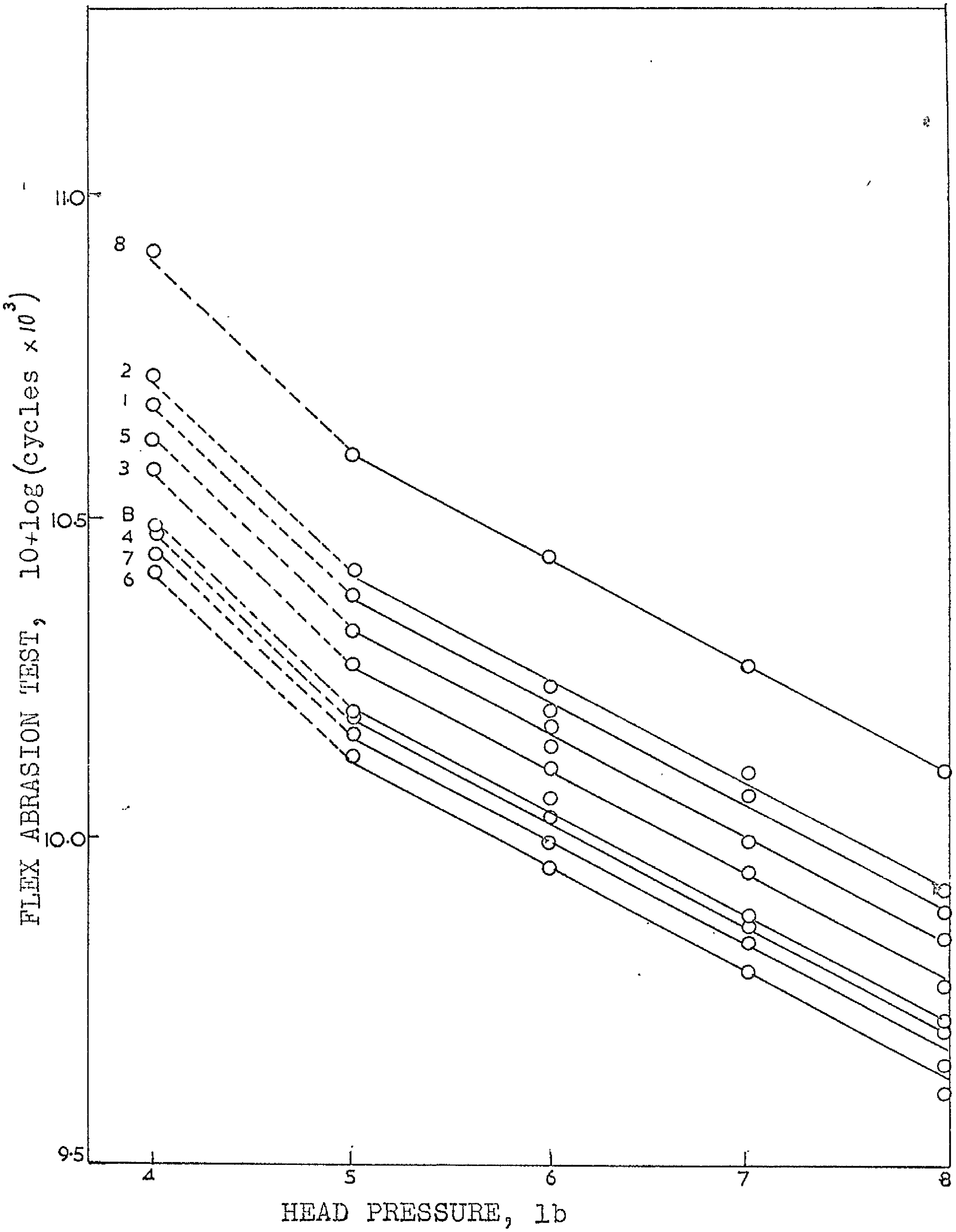

Figure 20 Effect of Pressure on Wet Flex Abrasion Results

comparable to that of ball penetration at 2 pound pressure and flat abrasion at 2 pound pressure. A decrease in the number of rubs to effect penetration due to the increase in pressure will be noted and also all the samples have maintained a relative ranking to each other, so that any difference in the results between various samples does not appear to be due to local variations in pressure.

It was considered advisable to have the values of the respective tests within a reasonable range to avoid a test bias when expressing Duty Factor or Figure of Merit. Thus tests have been carried out and the Duty Factor and the Figure of Merit calculated using the following values:

Ball penetration test at 2 lb pressure
Flex abrasion test at 8 lb pressure and
8 lb tension
Flat abrasion test at 2 lb pressure

Expression of Results

The three values of abrasion namely, the Ball penetration, Flex abrasion and Flat abrasion, may be considered separately or another expression, the Duty Factor, reported to be a guide to erosive wear, is the Harmonic mean of B and F calculated from the expression:

$$\text{Duty Factor} = \frac{2}{\frac{1}{B} + \frac{1}{F}}$$

A useful method of fabric classification according to wearability is reported to be the use of the Figure of Merit (the harmonic mean of the normalised, B, F, and F factors):

$$\text{Figure of Merit} = \frac{3}{\frac{1}{B} + \frac{1}{F} + \frac{1}{F}}$$

where B = Ball penetration test cycles $\times 10^{-2}$

F = Flex abrasion test cycles $\times 10^{-3}$

F = Flat abrasion test cycles $\times 10^{-3}$

Accuracy

Five tests per sample were made and the coefficient of variation for the tests were 20%, 10%, and 15% for Ball penetration, Flex abrasion and Flat abrasion respectively.

CHAPTER 6

RESULTS AND DISCUSSION

Discussion of Results

RESULTS

Tensile Properties

The results of tensile tests on yarn taken from resin treated viscose rayon fabrics (second batch) have been given in Tables 11 and 12. Although the main aim with these was to seek correlation with wear test results some observations may be made at this stage. There has been no major change in the strength of the yarns as a result of resin treatment but the breaking extension has been reduced and there is a considerable drop in the toughness as evidenced by the results for the energy required to rupture the material. Both the initial stiffness and final stiffness as represented by the initial and final tensile moduli increased with resin treatment and the resin treatment has also increased the elastic recovery of the yarns. The other parameter that was measured was the energy to remove crimp and reflect marked changes in the particular yarn characteristic as a result of resin treatment.

On the hypothesis that a fabric property is influenced by yarn property which in turn is influenced by fibre property, fibre and yarn strength and extension were compared and the results have been shown in Figures 21 and 22. There appears to be a correlation but also a scatter of results which may

Tensile Properties of Resin Treated Viscose Rayon Yarns

Sample No.	Tensile Strength, g/tex		Extension at Break, %		Energy for Rupture, joule/g		Crimp Energy, x 10^{-2} joule/g		Stiffness, x 10^{9} dyn/cm^2	
	warp	weft	warp	weft	warp	weft	warp	weft	warp	weft
B	12.7	12.4	20.5	20.0	15.1	14.9	6.2	7.4	8.8	8.8
1	13.6	13.4	18.0	17.4	12.4	12.0	9.0	9.6	11.2	11.5
2	14.0	13.3	16.6	15.5	12.1	10.7	8.5	10.2	12.6	12.8
3	13.0	12.5	15.7	14.0	11.0	8.6	8.3	9.1	13.2	13.3
4	13.4	12.7	12.6	12.3	10.6	7.9	9.3	11.2	15.8	15.8
5	12.3	11.9	14.6	14.3	8.6	8.3	7.7	8.4	12.5	12.4
6	12.5	11.2	13.4	13.3	8.2	7.6	8.5	9.4	13.8	13.6
7	13.9	13.9	13.1	13.1	9.1	9.0	8.2	9.1	15.8	15.9
8	14.5	14.4	17.1	17.0	12.3	12.0	7.7	7.9	12.7	12.3

Table 12

Modulus and Elastic Recovery of Resin Treated Viscose Rayon Yarns

Sample No.	Initial Modulus, x 10^9 dyn/cm^2		Elastic Recovery at 5% extn., %		Yield Stress, g/tex	
	warp	weft	warp	weft	warp	weft
B	13.8	12.9	46.5	49.1	4.2	3.6
1	16.9	18.1	51.2	56.0	5.1	5.1
2	18.4	19.0	58.3	61.7	6.2	5.7
3	16.6	16.7	58.2	60.2	5.4	4.7
4	19.4	17.2	62.9	65.9	5.8	4.9
5	15.2	15.9	56.6	56.8	5.0	4.6
6	20.2	16.9	59.1	61.3	6.0	5.1
7	20.3	20.8	60.9	63.5	6.6	5.4
8	16.6	17.4	59.8	63.0	4.9	5.2

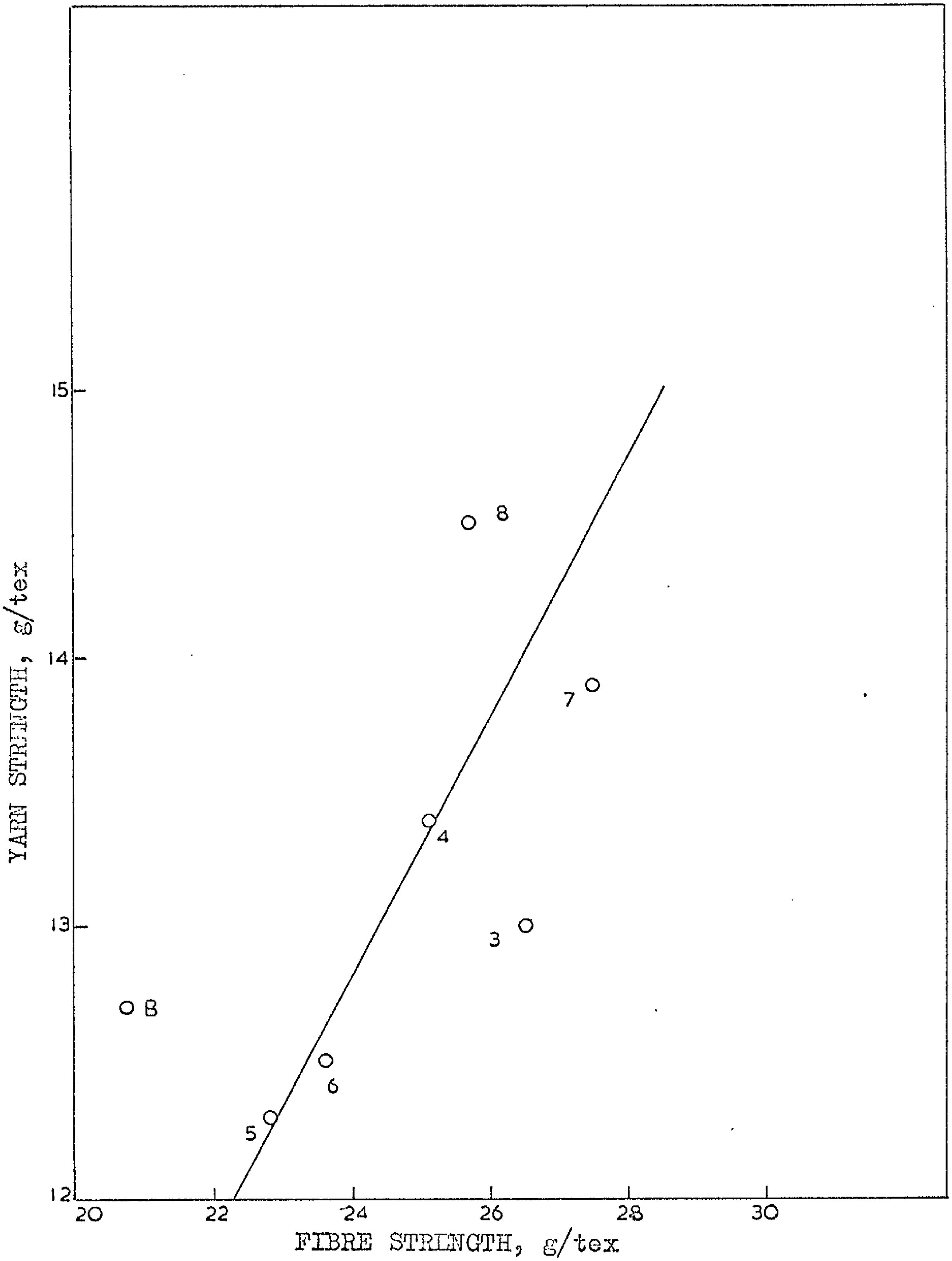

Figure 21 Comparison of Yarn and Fibre Strength

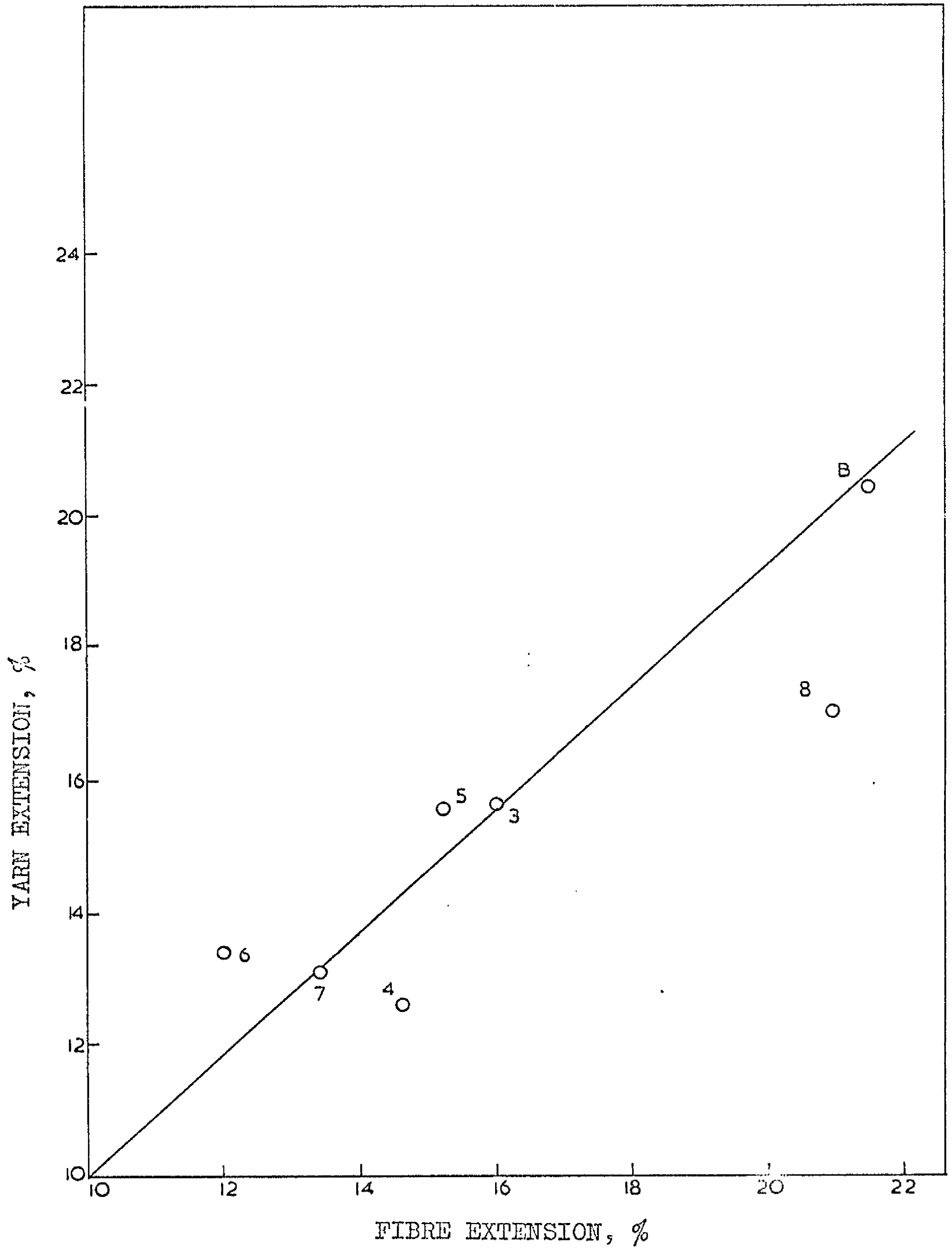

Figure 22 Comparison of Yarn and Fibre Extension

be an effect of variability in fibre modification and/or insufficient number of tests.

Wear Tests

Results of the wear tests on the Accelerotor and Bocking Abrader (B.F.T.Mark 1Va) have been given in Table 13. The rate of loss in weight of the resin treated samples during the Accelerotor test has been markedly increased, being dependant on the amount and the type of resin. On the other hand, the results on the Bocking Abrader also show that the wear performance has been reduced as a result of resin treatment but is dependant on resin content not on the type of resin. The results for the ball penetration tests on samples 1 and 2 which show an improvement over the untreated sample remains unexplained.

The values for Duty Factor and Figure of Merit have been included because they allow consideration of combined tests using a single value but the results are not directly comparable with other published values for these factors because of the different loads employed and because the flex tests were also carried out in the dry (conditioned) state. Although the harmonic mean has been used on this occasion, there is perhaps not such a great need because of the parity of results of Ball, Flex and Flat abrasion tests.

Table 13

Accelerator and B.F.T. Abrasion Tests

Sample No.	Accelerator % loss in wt/min.	B. F. T. Ball Penetration, x 10^2 cycles	Flex Abrasion, x 10^3 cycles	Flat Abrasion x 10^3 cycles	Duty Factor 'D'	Figure of Merit 'M'
B	0.52	2.1	4.9	8.5	2.9	3.8
1	2.73	2.3	2.4	2.6	2.4	2.4
2	3.22	2.4	1.5	2.7	1.9	2.1
3	2.30	1.4	1.4	1.4	1.4	1.4
4	2.46	1.1	1.0	0.8	1.0	1.0
5	1.89	1.3	1.3	1.6	1.3	1.4
6	2.42	1.1	1.1	1.0	1.1	1.1
7	3.32	1.2	0.9	0.9	1.0	1.0
8	2.00	1.9	2.3	3.0	2.1	2.3

Yarn Extension

The relationships between the extension of a yarn at break and the results of Accelerotor and B.P.T. tests have been shown in Figures 23, 24, 25, 26, 27 and 28.

A linear relationship appears to exist with the Accelerotor results and it is dependant on the resin content. An increase in resin content with a decrease in yarn extension results in an increased loss of weight, the rate of such a loss is dependant on the particular type of resin.

The Ball penetration results suggest a difference in response between melamine-formaldehyde treated samples which offer increased resistance to penetration are linearly related to weight of resin, whereas the other finishes reduce the resistance and again are linearly related to resin content.

The Flex and Flat Abrasion results both lie in a curve such that a decrease in yarn extension results in a decrease in resistance to abrasion. The effect of increasing the resin content of any specific resin is to reduce the resistance to abrasion. Both suggest that there are limiting values beyond which an increase or decrease in yarn extension would exert little effect.

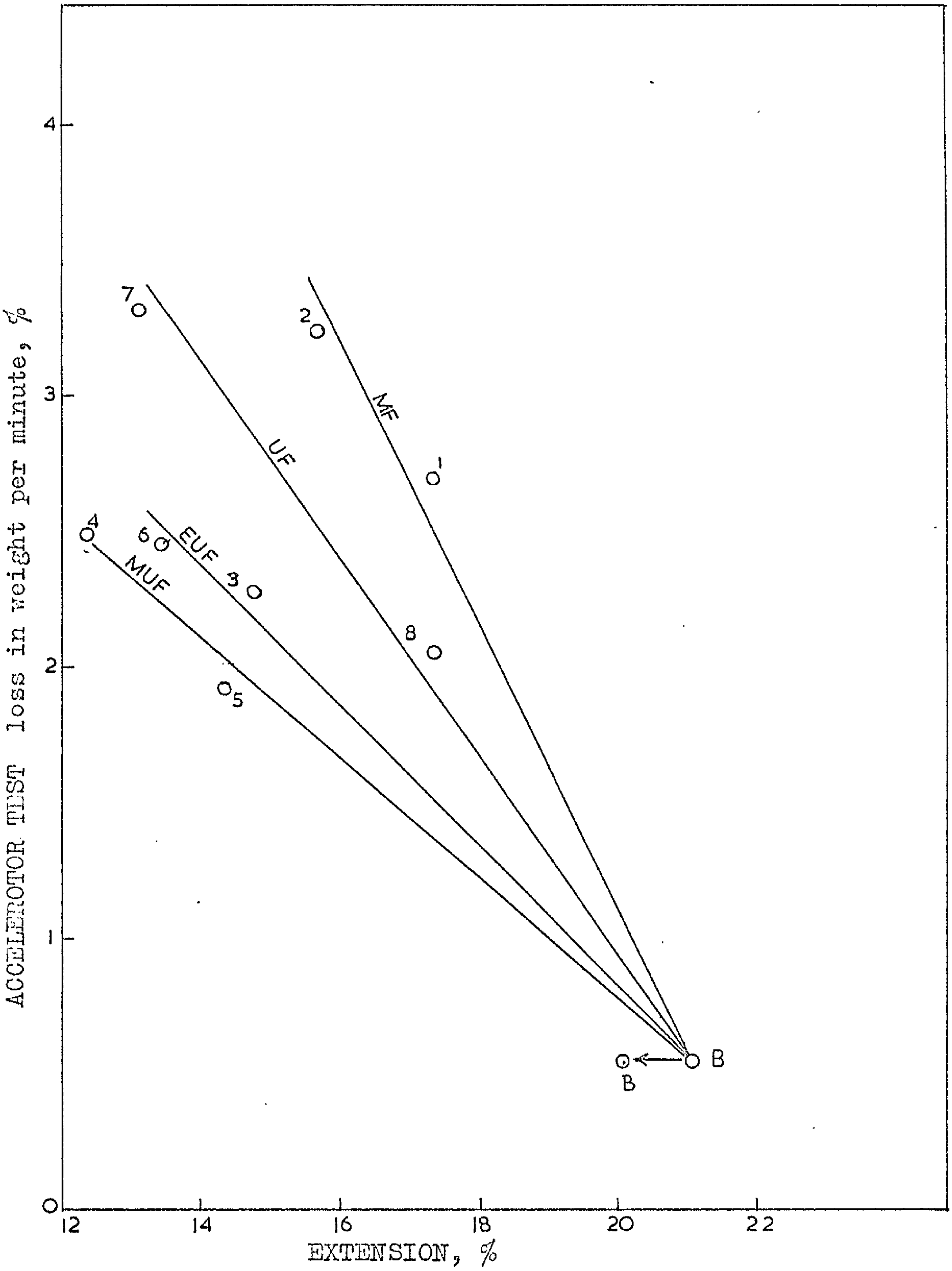

Figure 23 Relationship Between Yarn Extension and Accelerotor Results

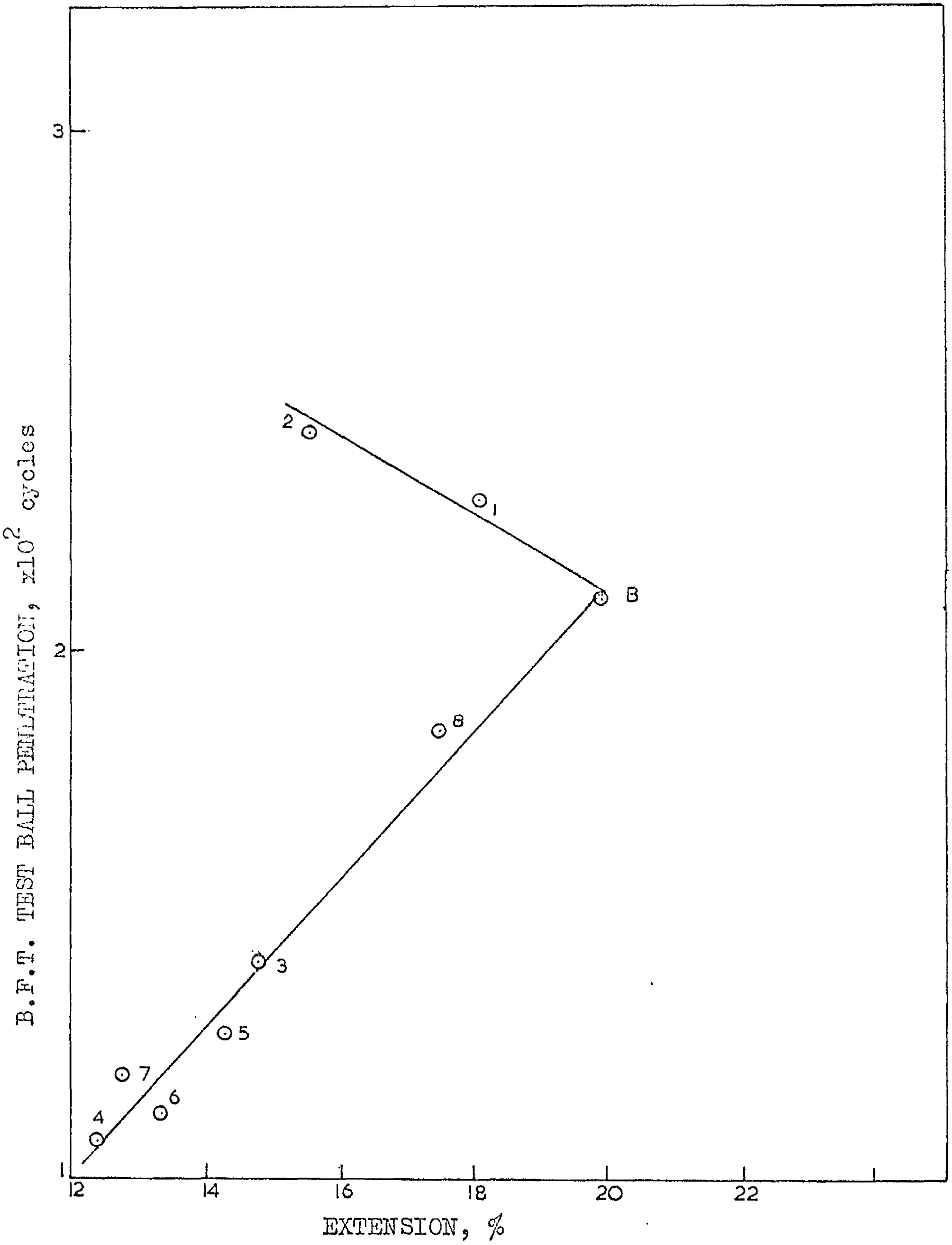

Figure 24 Relationship Between Yarn Extension and Ball Penetration Results

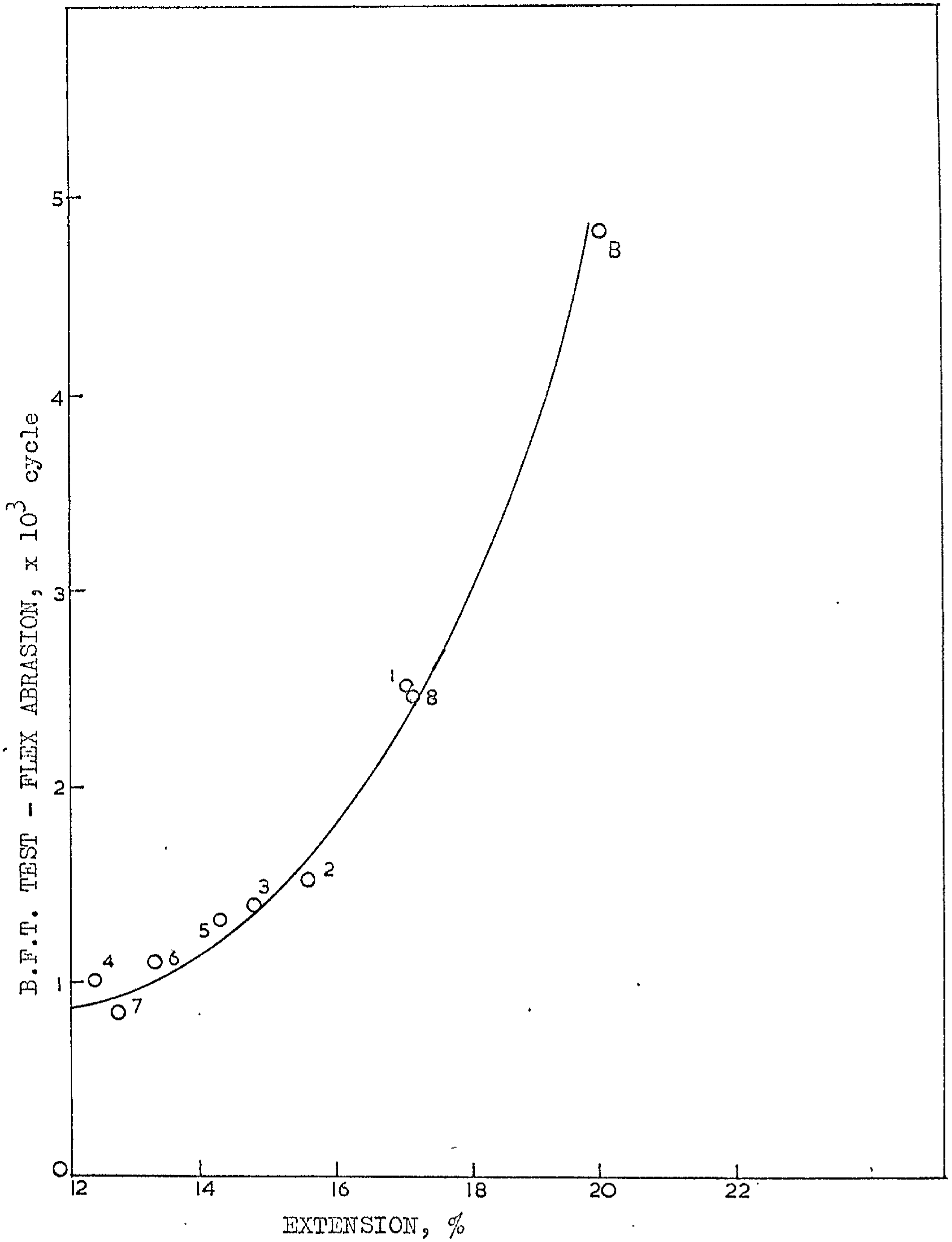

Figure 25 Relationship Between Yarn Extension and Flex Abrasion Results

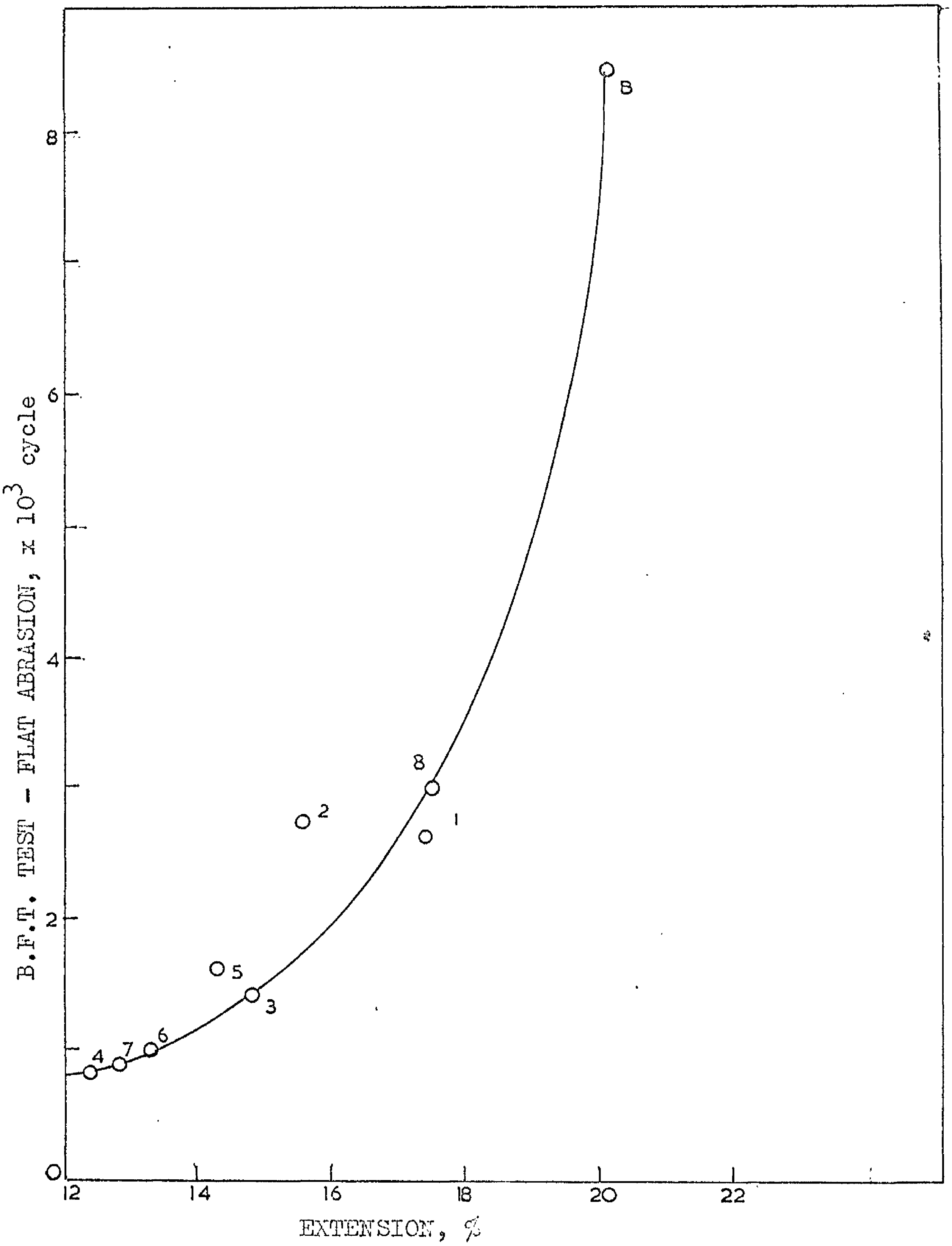

Figure 26 Relationship Between Yarn Extension and Flat Abrasion Results

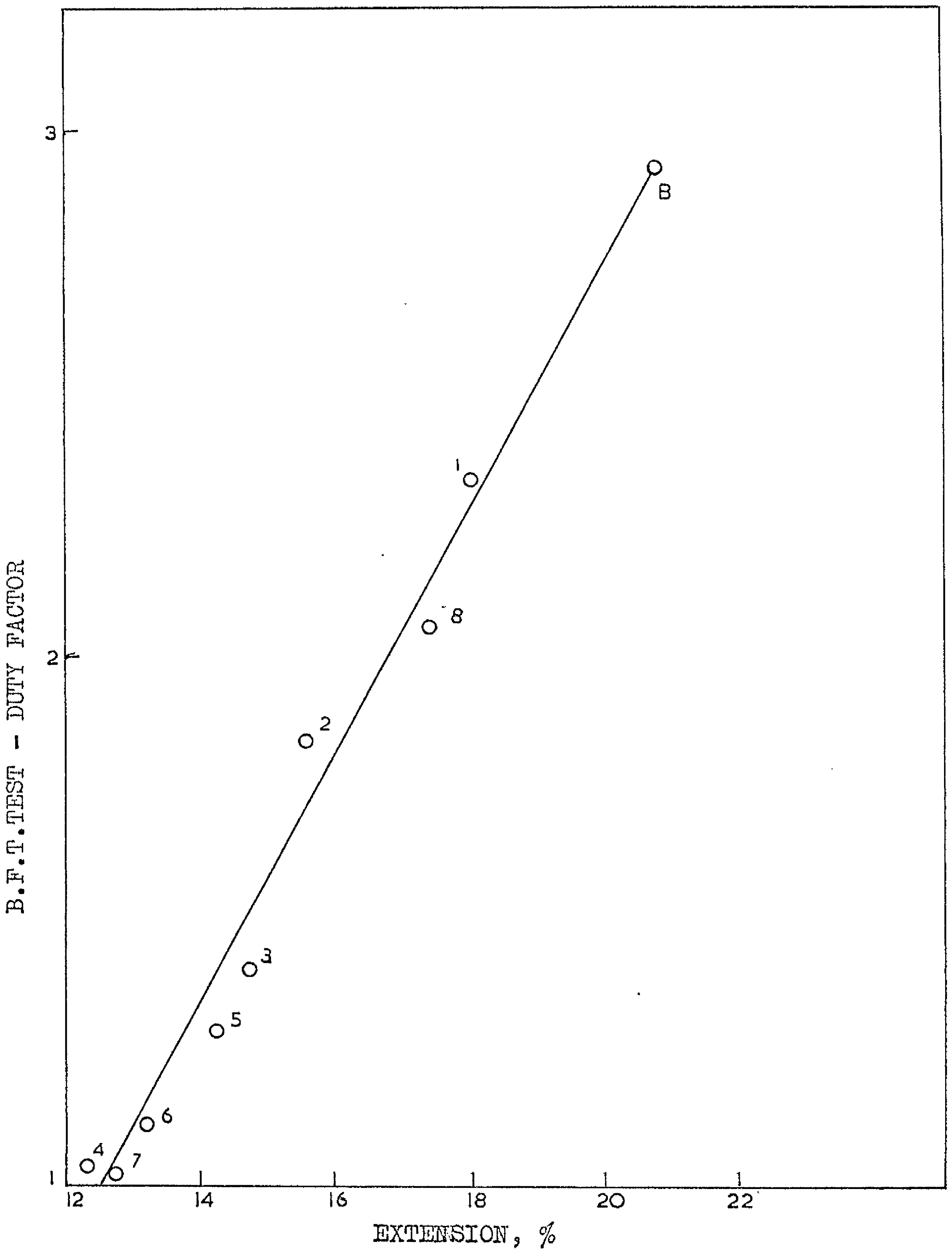

Figure 27 Relationship Between Yarn Extension and Duty Factor

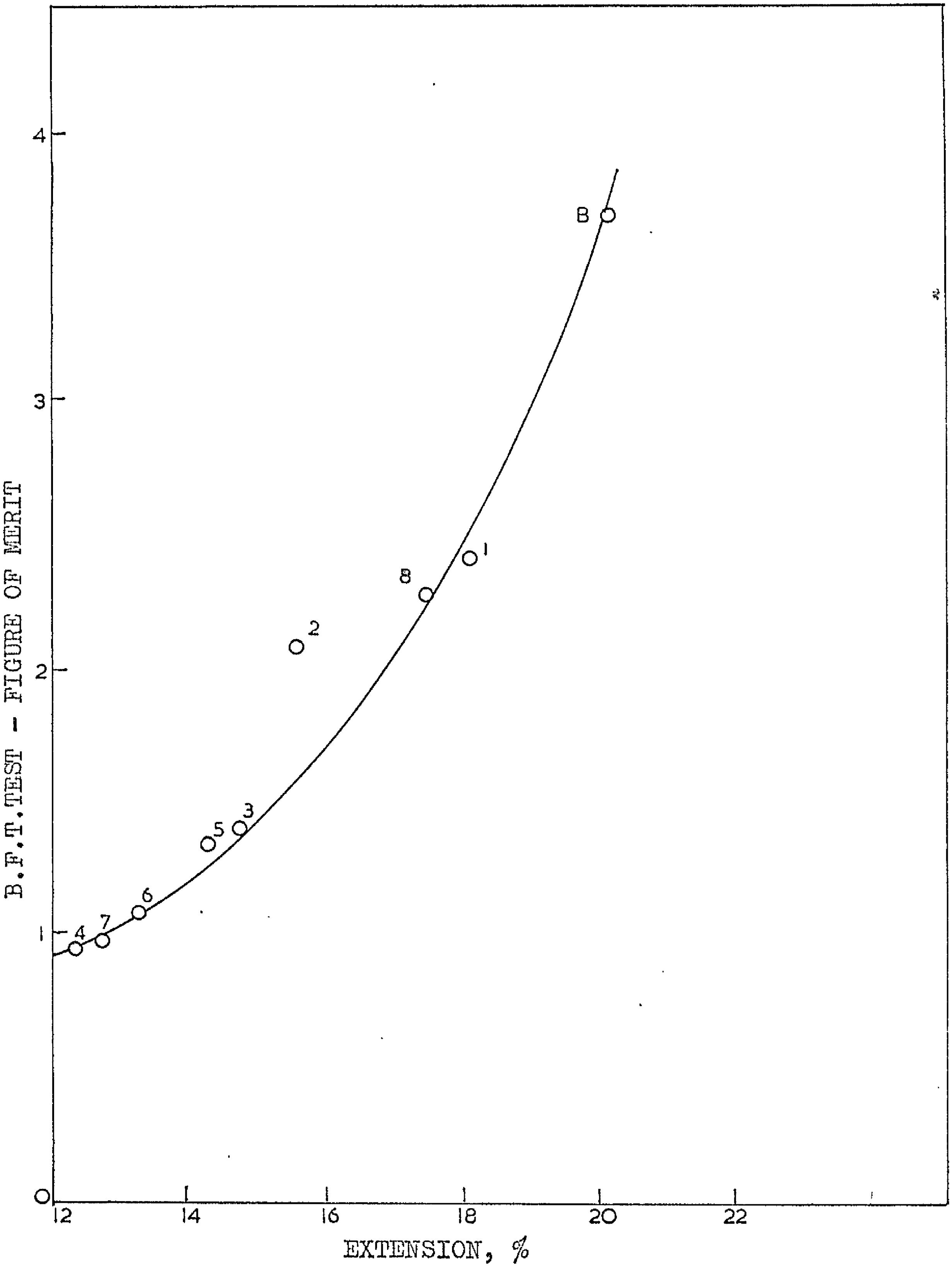

Figure 28 Relationship Between Yarn Extension and Figure of Merit

A linear decrease is shown in the Duty Factor with decreasing yarn extension and increasing resin content, while the Figure of Merit is also reduced although not in a linear fashion, the curve being similar to that for the Flex and Flat abrasion results.

Thus the Accelerotor results are influenced by the type of resin present and the degree of yarn extension, any reduction in extension resulting in an increased rate of wear. The B.F.T. results also reflect the degree of yarn extension but are largely independant of the type of resin. The results in Figure 29 show that yarn extension in fact varies linearly with the resin content and is independant of the type of resin.

Energy for Rupture and Stiffness

The relationships between the energy required to break a yarn and the results of Accelerotor and B.F.T. tests have been shown in Figures 30 and 31.

The relationships appear to follow the same pattern as those for yarn extension and Figure 32 also shows a linear relationship between resin content and energy for rupture.

Thus the higher the energy required for rupture the better the wear property registered by both the

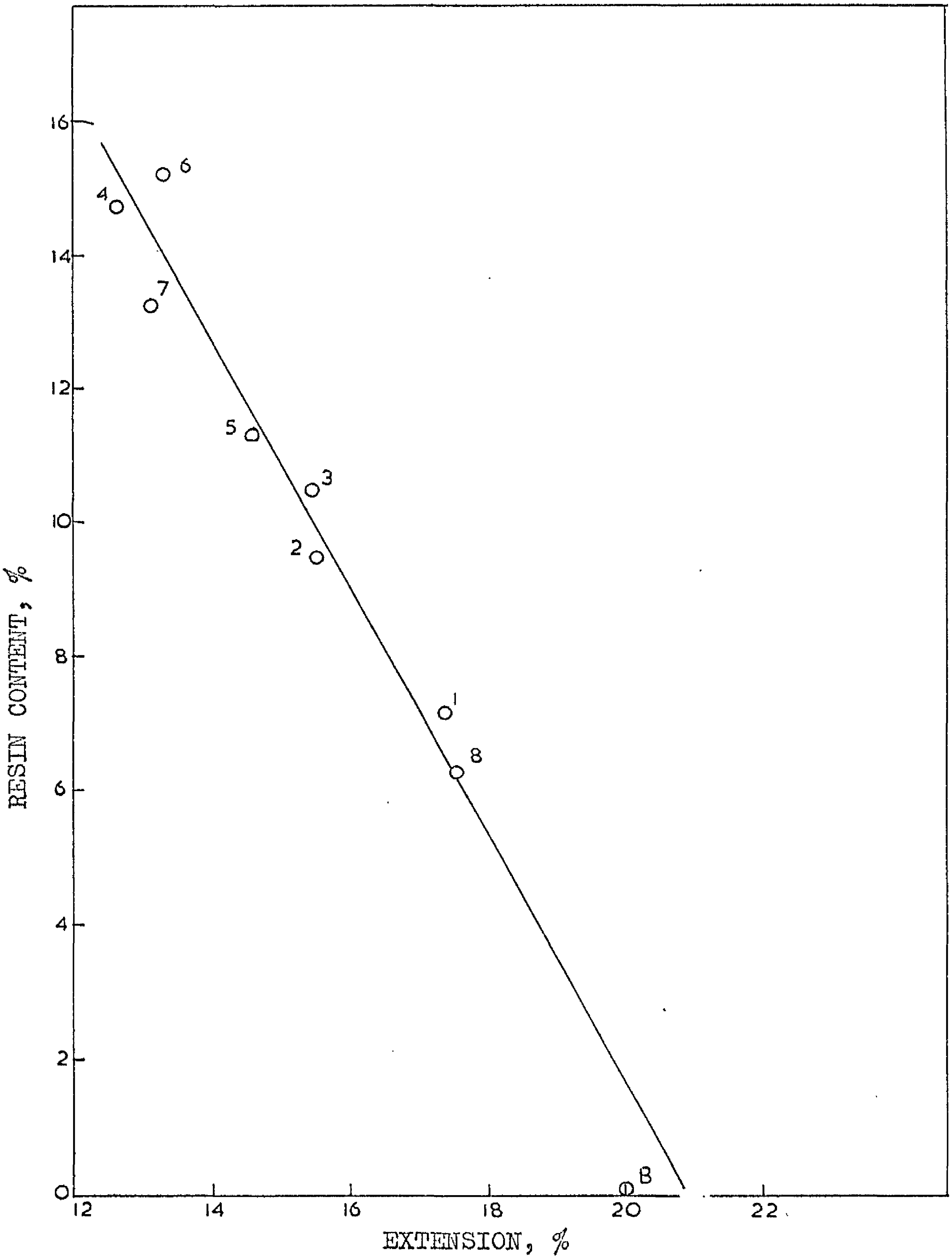

Figure 29 Relationship Between Yarn Extension and Resin Content

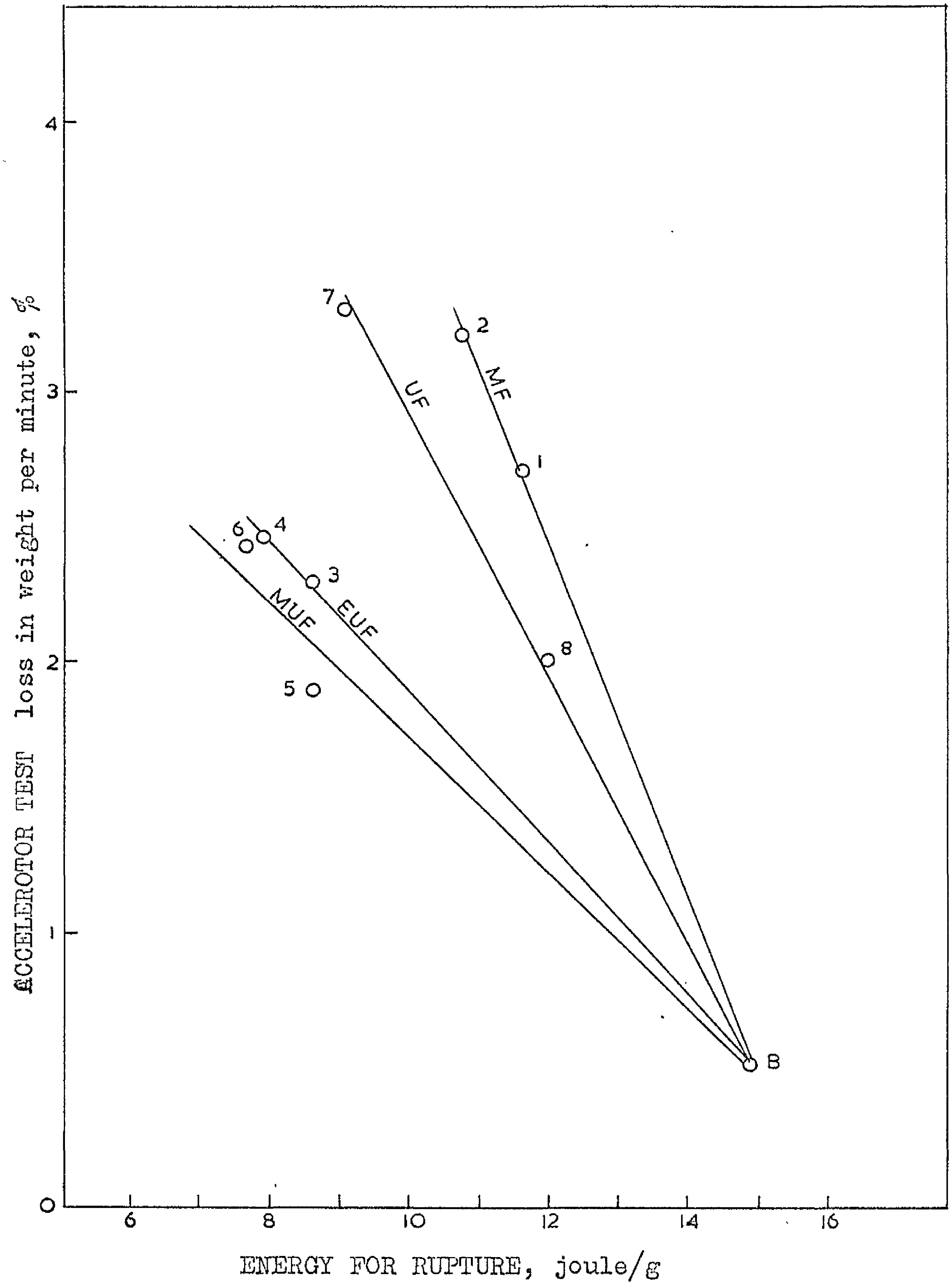

Figure 30 Relationship Between Yarn Energy for Rupture and Accelerotor Results

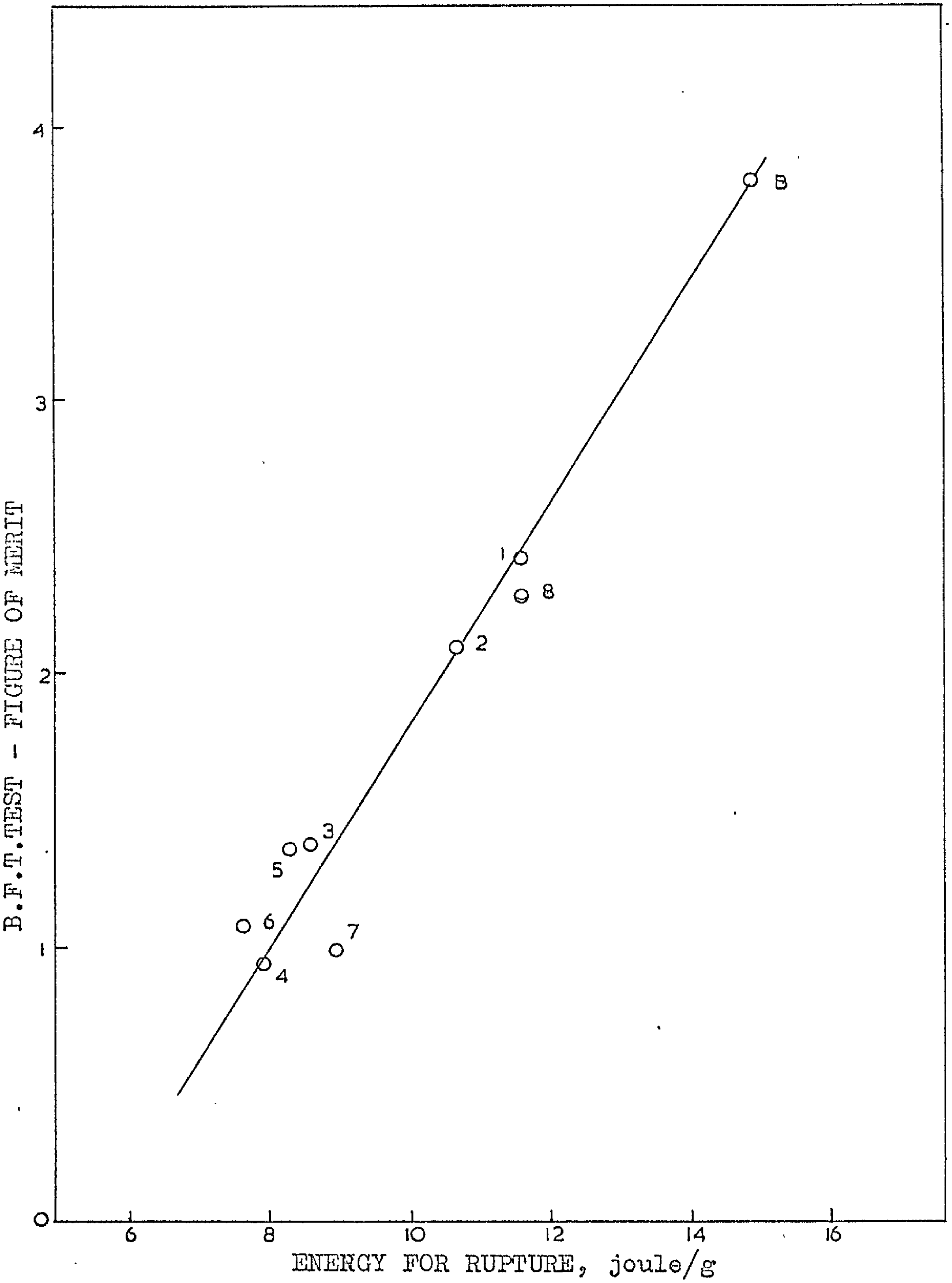

Figure 31 Relationship Between Yarn Endrgy for Rupture and Figure of Merit

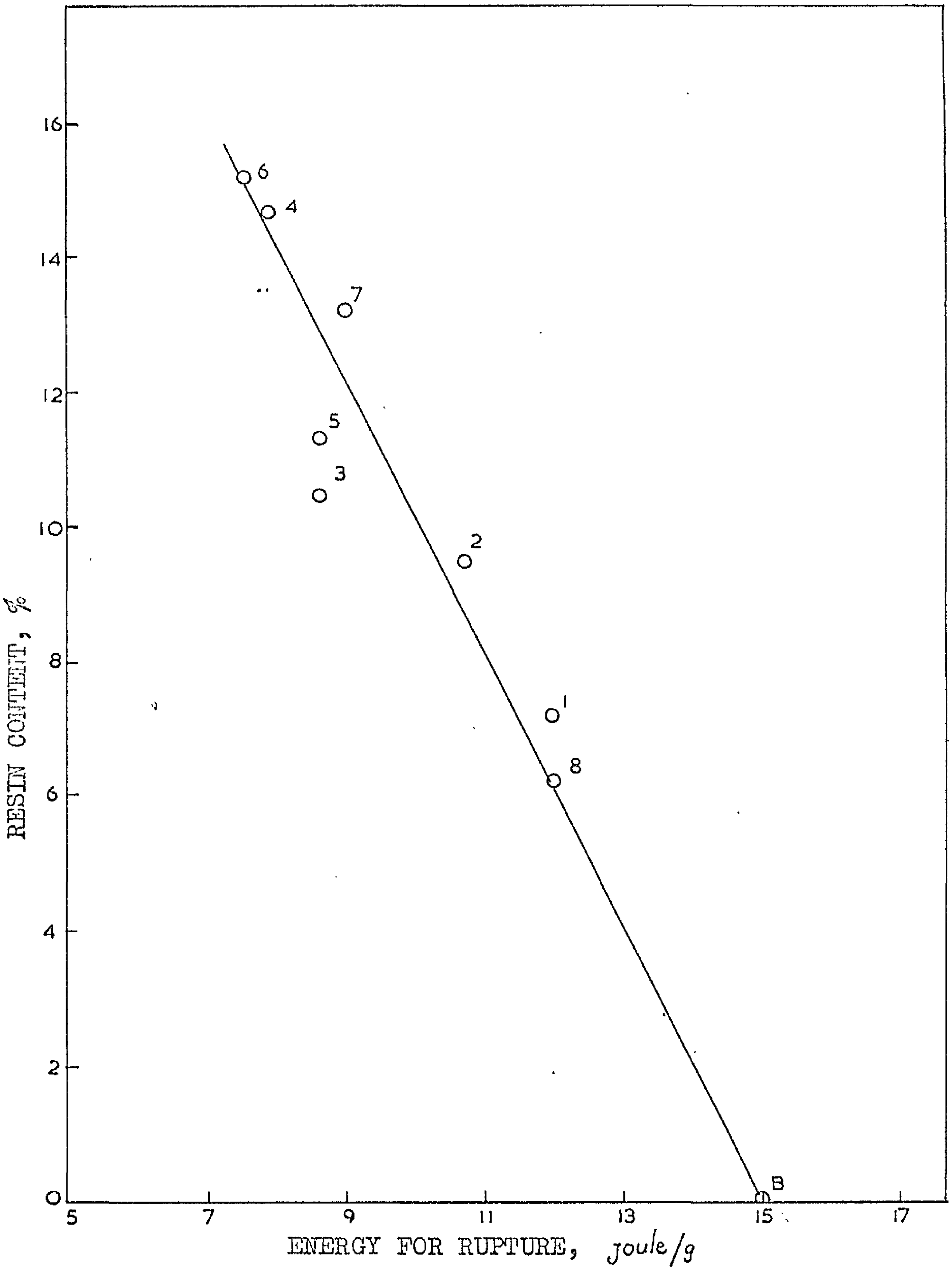

Figure 32 Relationship Between Yarn Energy for Rupture and Resin Content

Accelerotor and the B.F.T. (Figure of Merit) and again the B.F.T. values were independent of, and the Accelerotor values dependent on, the type of resin.

The relationships between the (tensile) stiffness of a yarn and the results of Accelerotor and B.F.T. tests have been shown in Figures 33, 34 and 35.

The pattern is similar to those above and it may be concluded that the stiffer the yarn the lower the abrasion resistance of the yarn, but the property of stiffness is dependant on the type of resin as well as the amount.

Initial Modulus and Yield Stress

The relationships between the initial modulus of a yarn and the results of Accelerotor and B.F.T. tests have been shown in Figures 36 and 37.

The results suggest a reversal of the previous pattern in that it is the Accelerotor results which show an absolute linear relationship, whereas, the B.F.T. results, while linear in respect to specific resin content, discriminate between the types of resin present in the material. In both cases an increase in initial modulus corresponds with a decrease in durability. The increase in modulus would appear to result from an increase in resin content but the rate of increase varies with different resins, Figure 38.

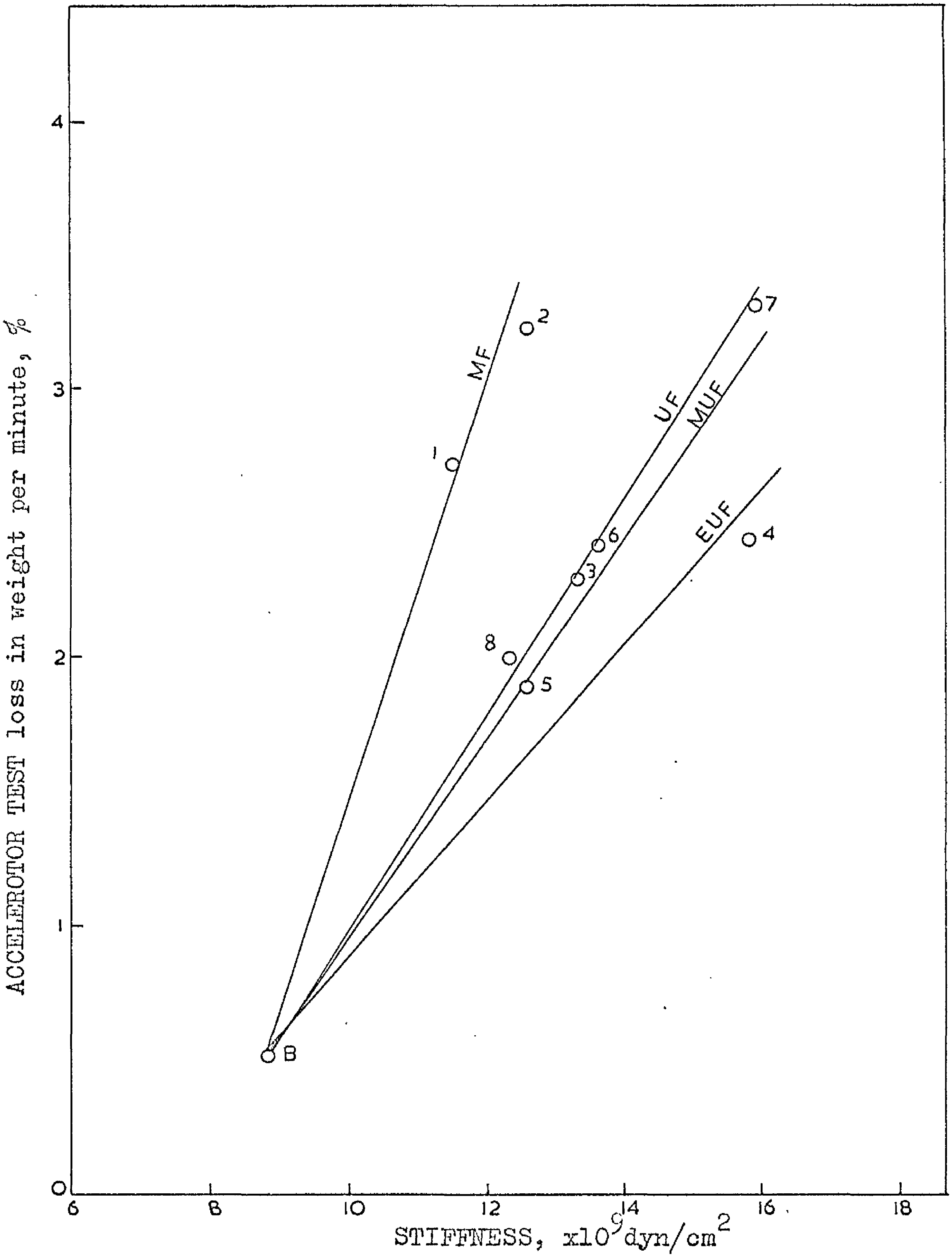

Figure 33 Relationship Between Yarn Stiffness and Accelerotor Results

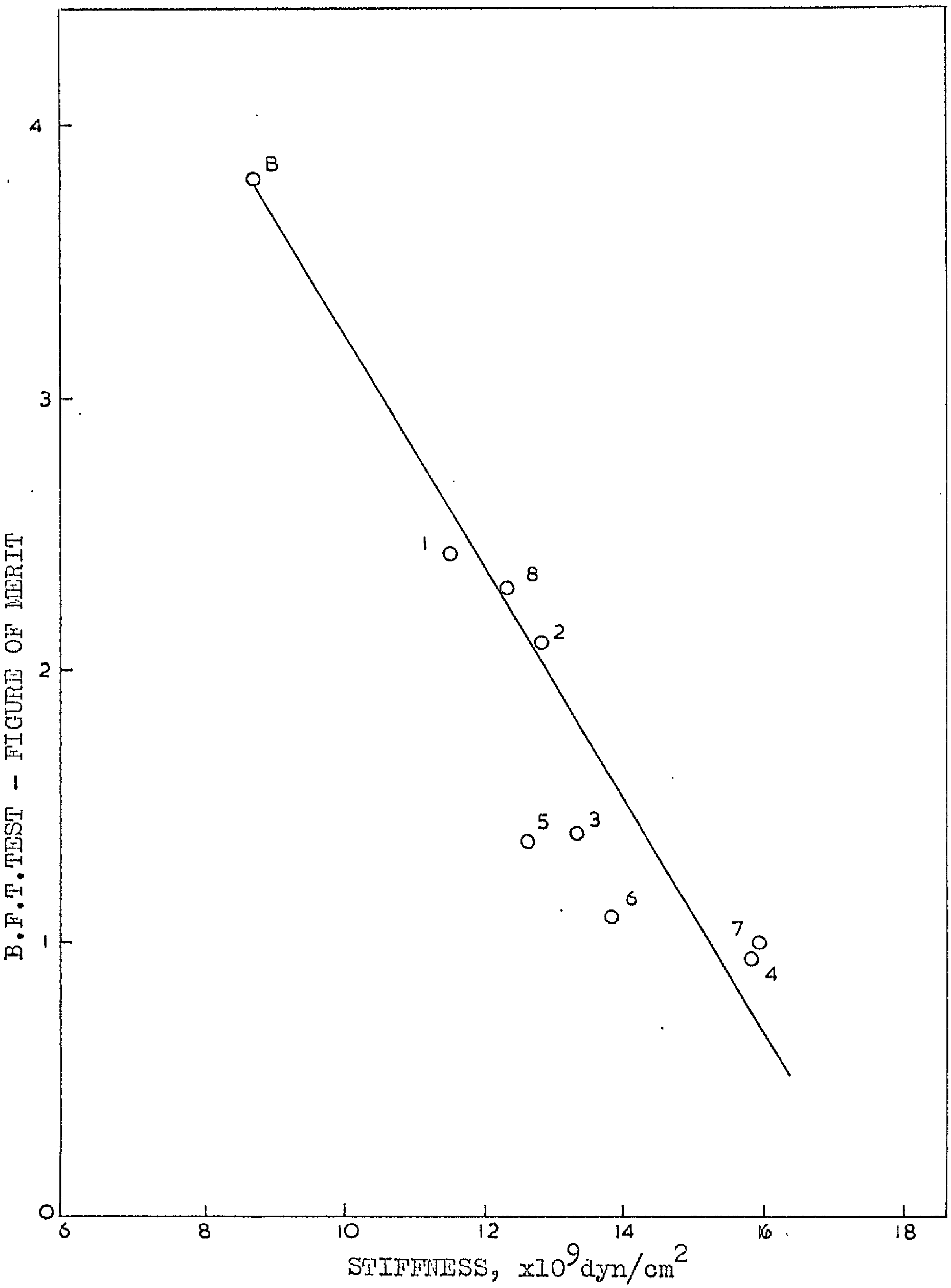

Figure34 Relationship Between Yarn Stiffness and Figure of Merit

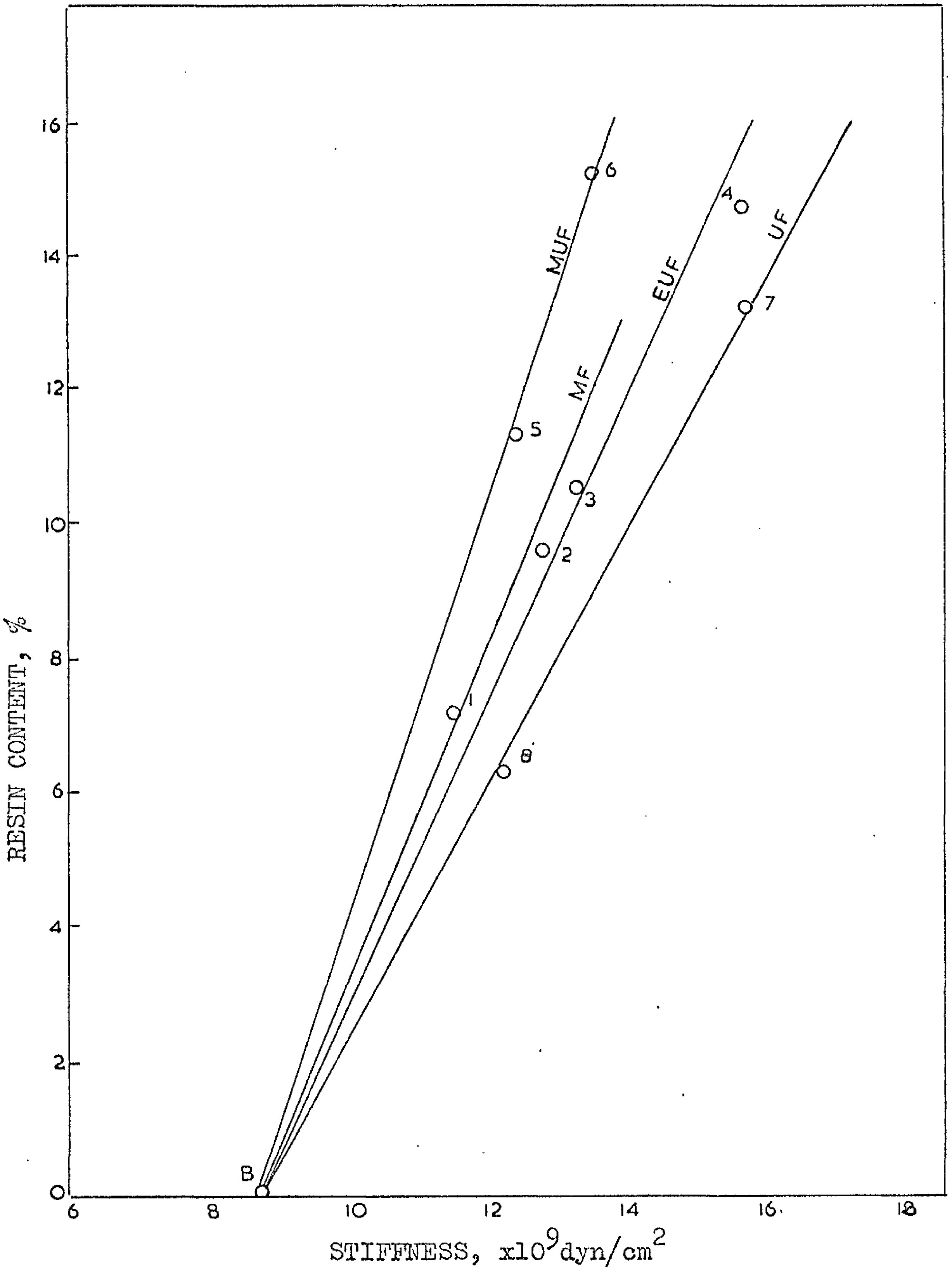

Figure 35 Relationship Between Yarn Stiffness and Resin Content

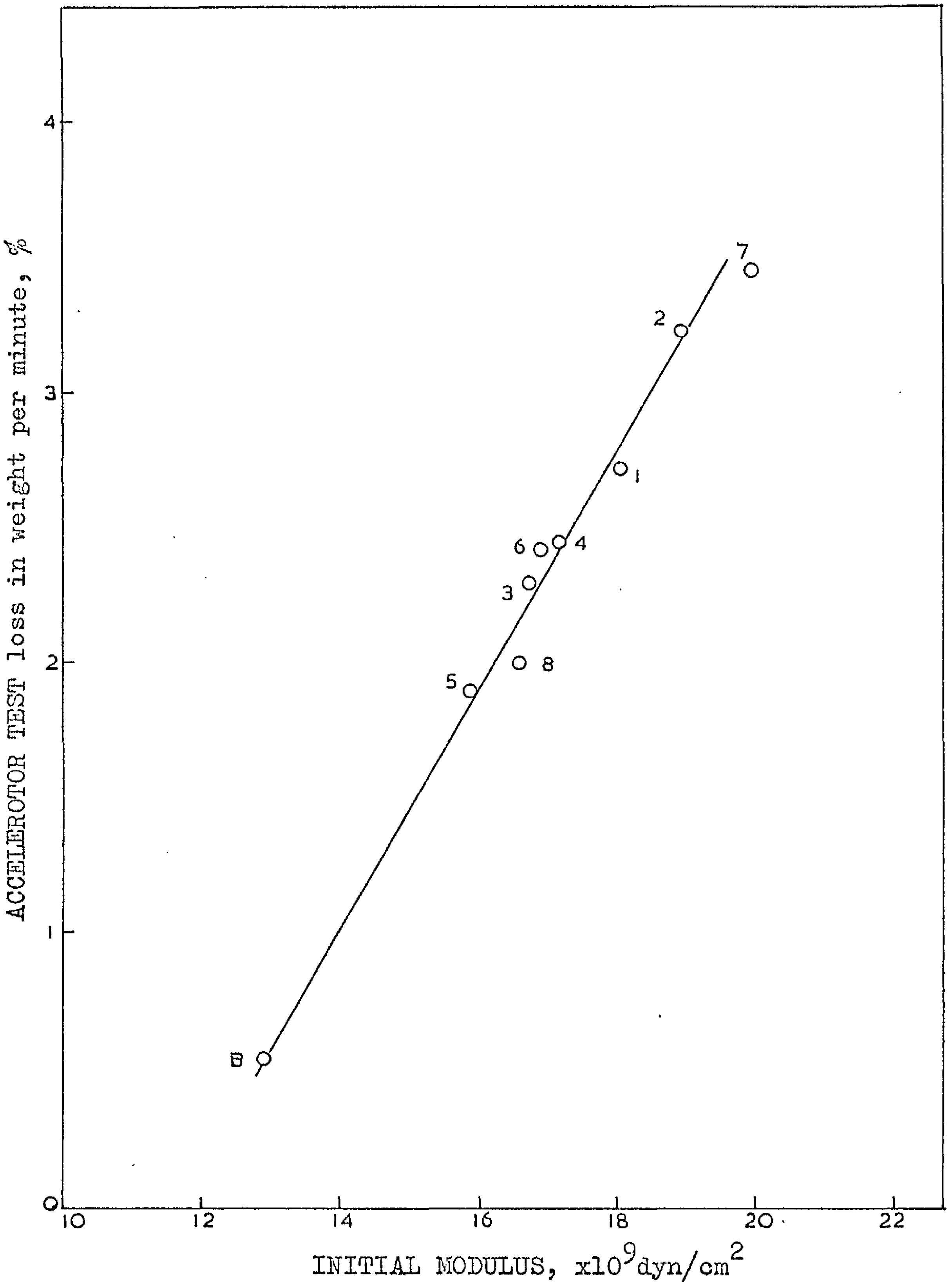

Figure 36 Relationship Between Yarn Initial Modulus and Accelerotor Results

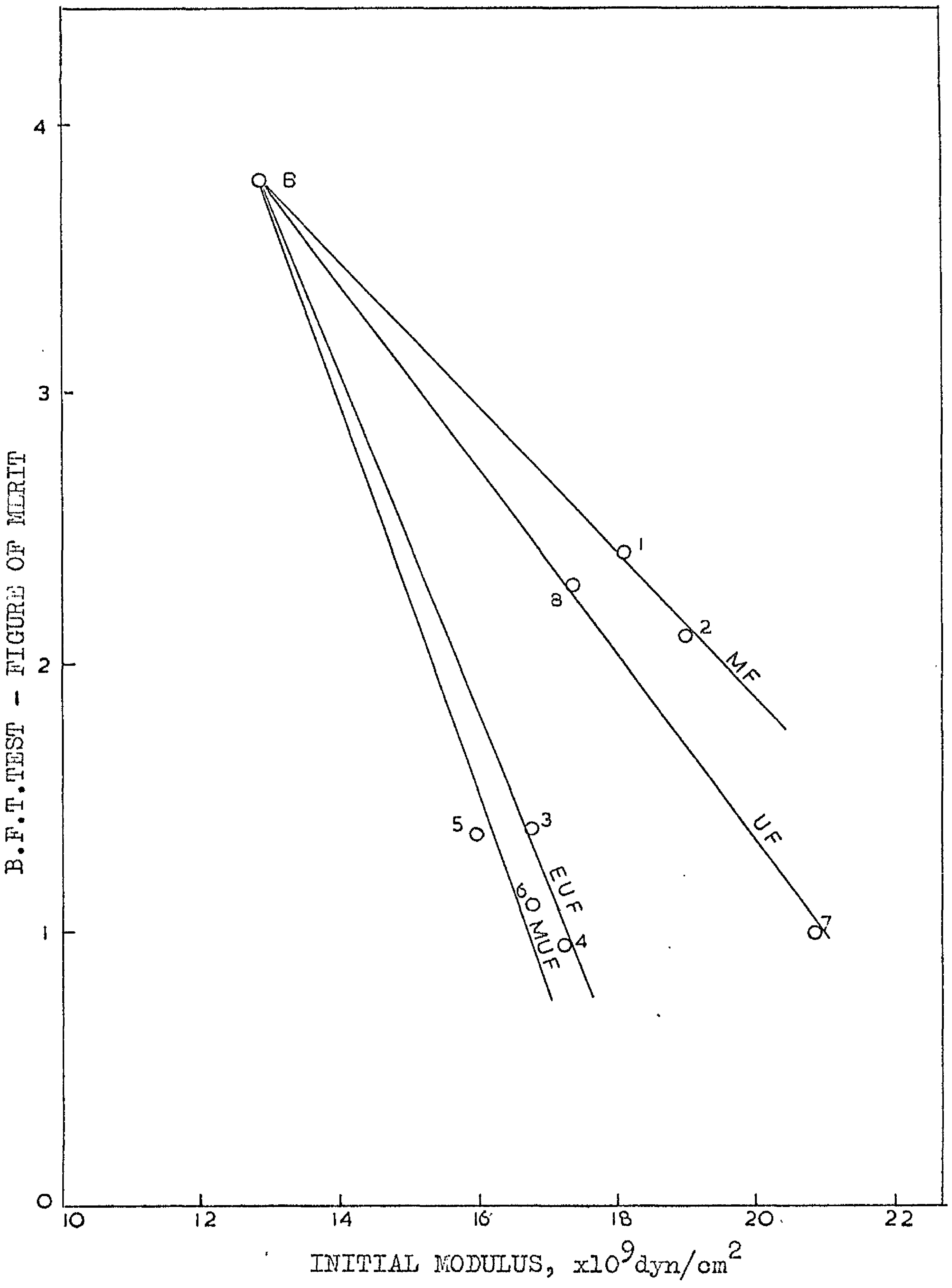

Figure 37 Relationship Between Yarn Initial Modulus and Figure of Merit

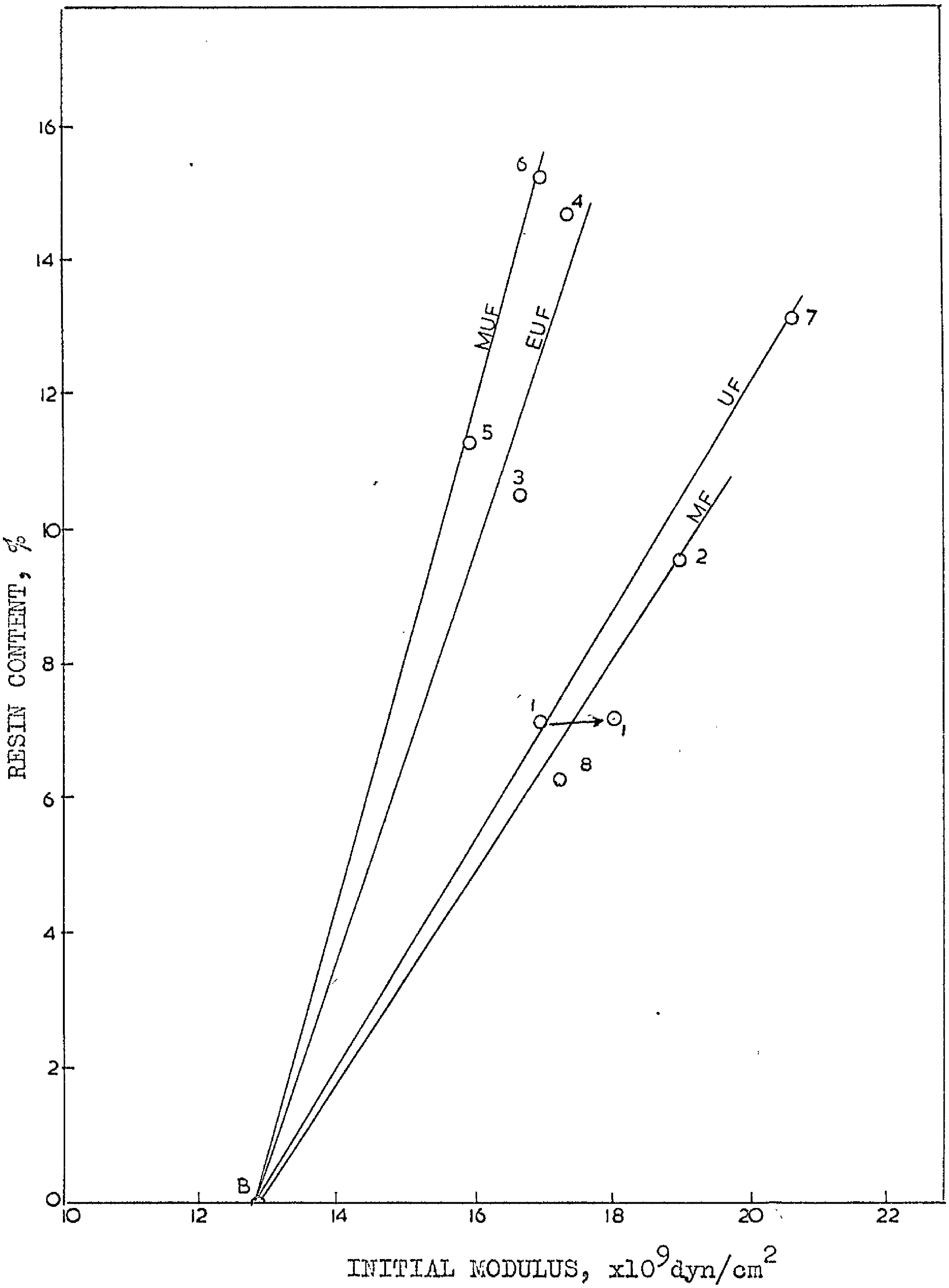

Figure 38 Relationship Between Yarn Initial Modulus and Resin Content

The relationships between the yield stress of a yarn and the results of Accelerotor and B.F.T. tests have been shown in Figures 39, 40 and 41.

The pattern is similar to that for initial modulus.

Elastic Recovery

The relationships between the elastic recovery of a yarn from 5% extension and the results of Accelerotor and B.F.T. tests have been shown in Figures 42 and 43.

In both cases an increase in the power of recovery from deformation would appear to be accompanied by a reduction in the durability of the material. The Accelerotor results distinguish to some extent between the finishes, whereas, the B.F.T. results appear to be independent of the type of finish.

Inspection of Figure 44 will show that the elastic recovery appears to increase with an increase in resin content but the rate of increase varies with different resins.

Accelerotor and B.F.T. Abrader

Up to this point a number of properties have been compared with both the instruments in use. A reference to Figures 45 and 46 will show a comparison between the instruments and the effect of resin content. It would appear that if the type of resin and the content is known

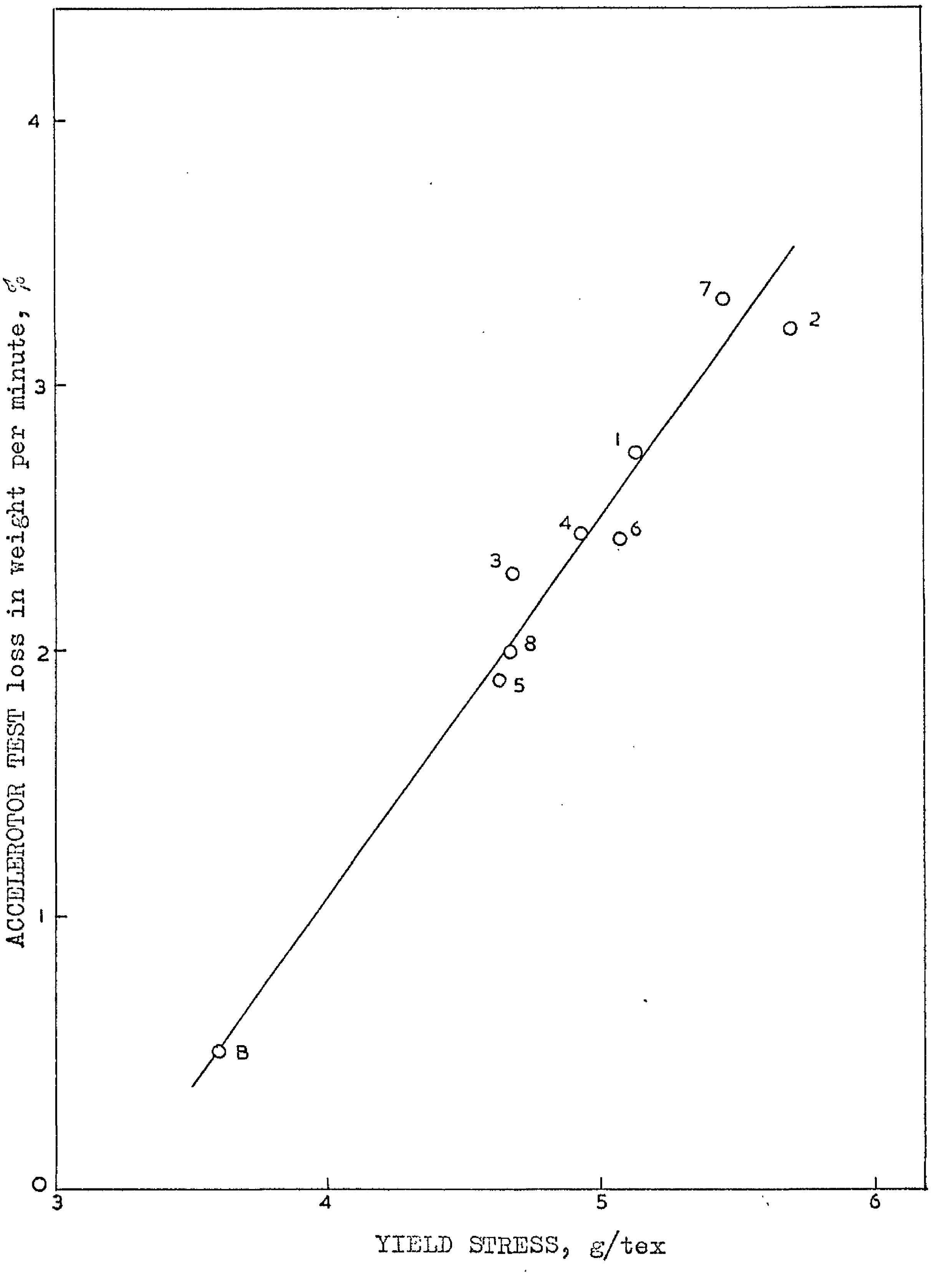

Figure 39 Relationship Between Yarn Yield Stress and Accelerotor Results

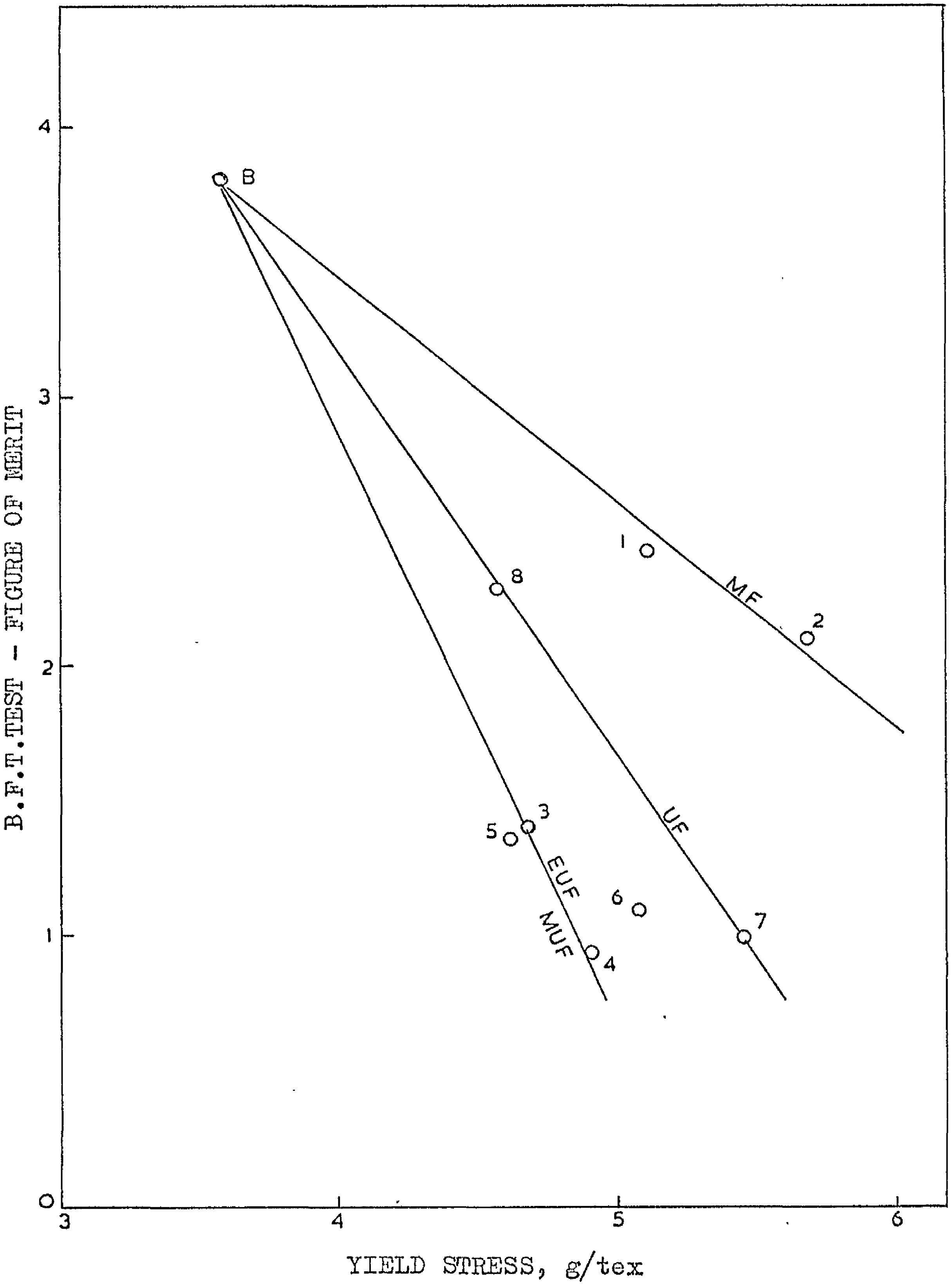

Figure 40 Relationship Between Yarn Yield Stress and Figure of Merit

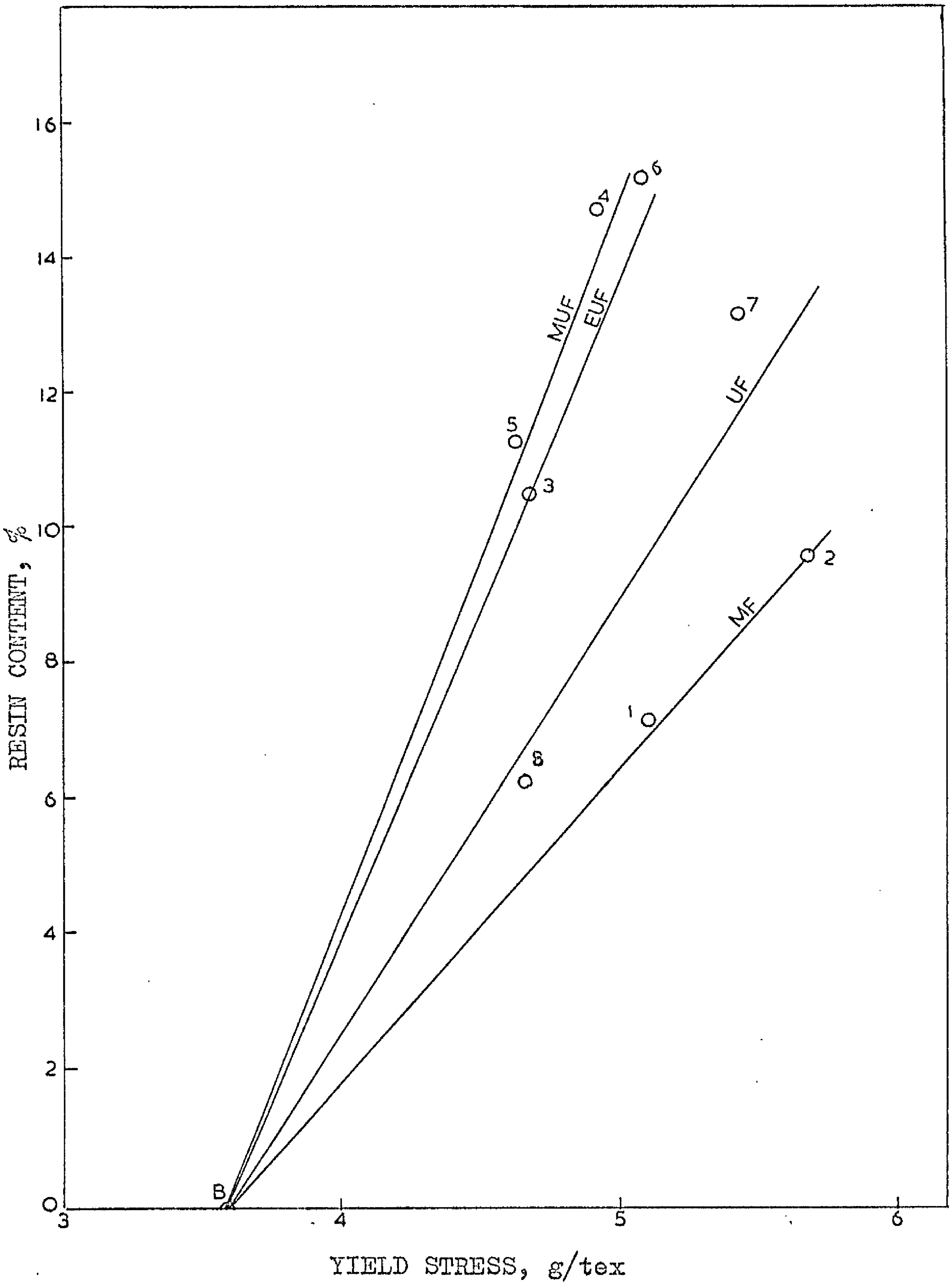

Figure 41 Relationship Between Yarn Yield Stress and Resin Content

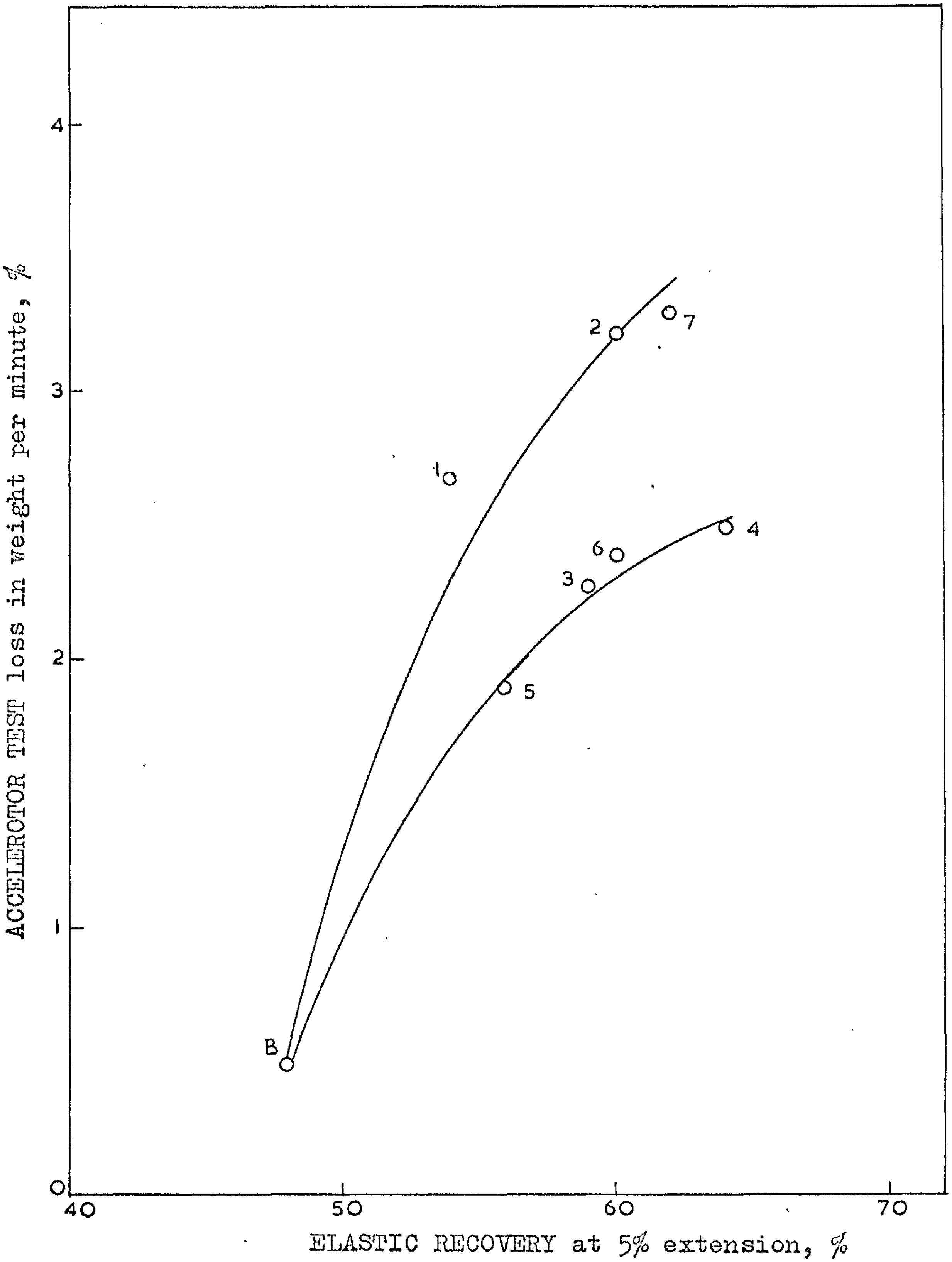

Figure 42 Relationship Between Yarn Elastic Recovery and Accelerotor Test

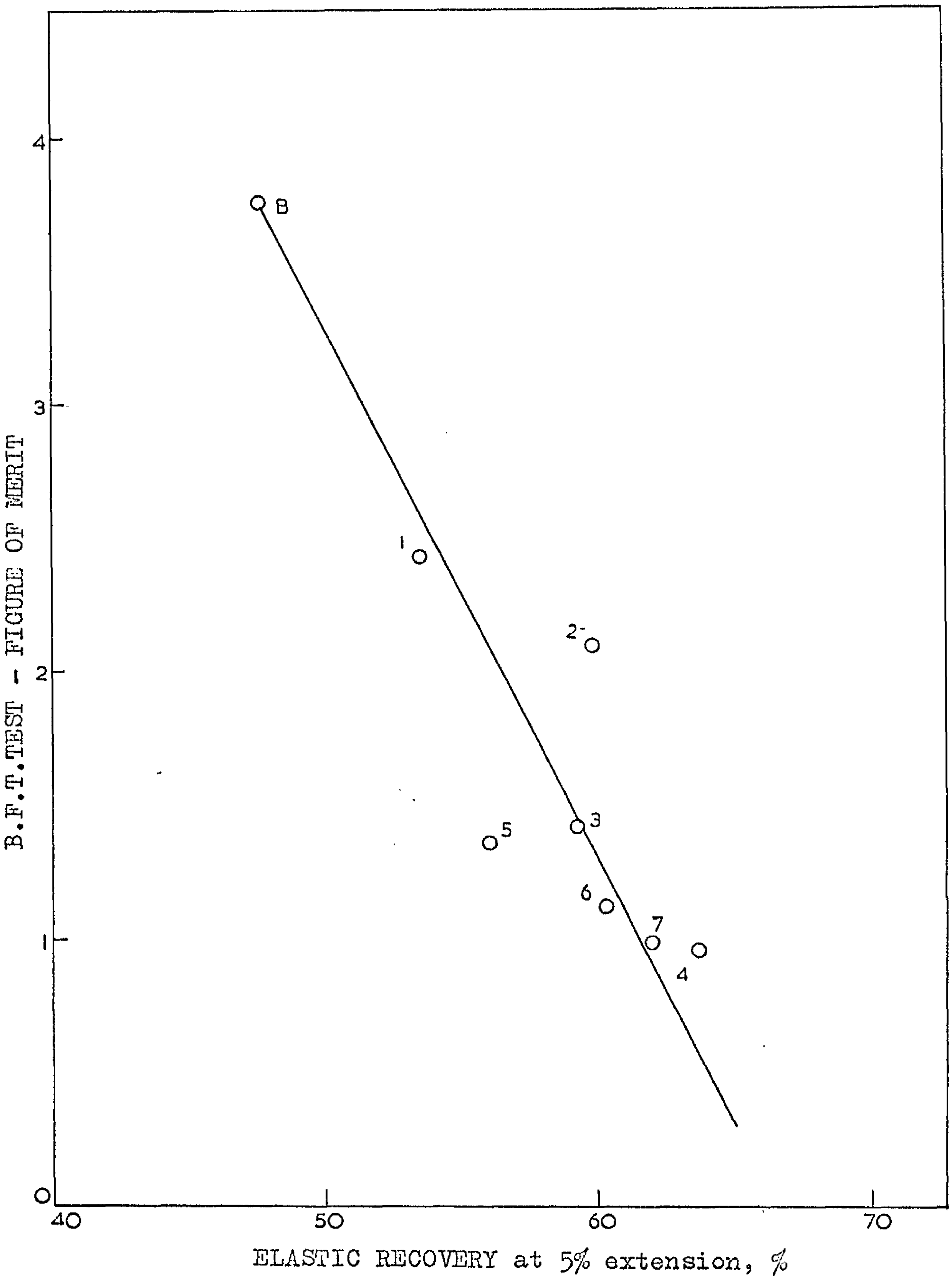

Figure 43 Relationship Between Yarn Elastic Recovery and Figure of Merit

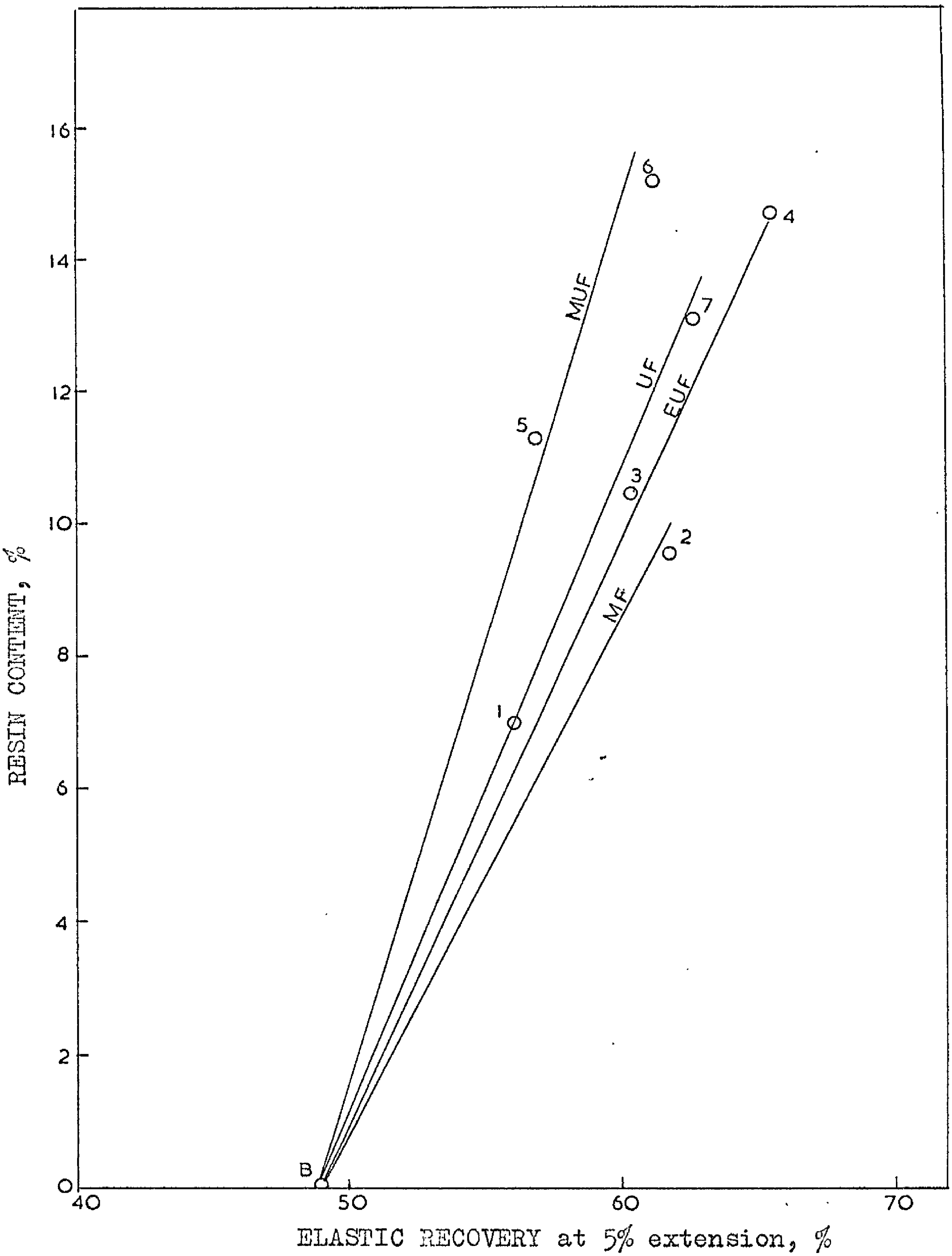

Figure 44 Relationship Between Yarn Elastic Recovery and Resin Content

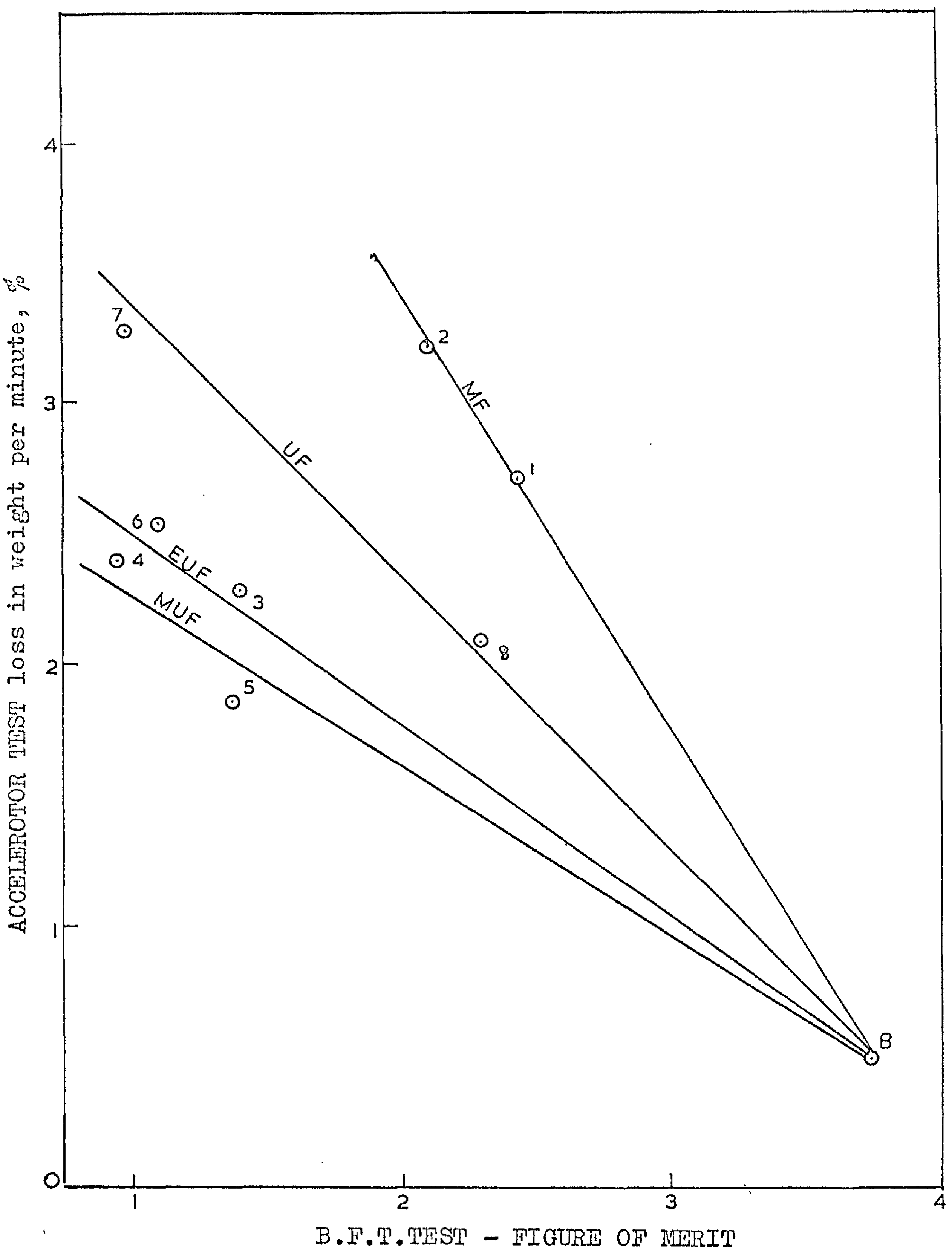

Figure45 Correlation Between Accelerotor Results and Figure of Merit

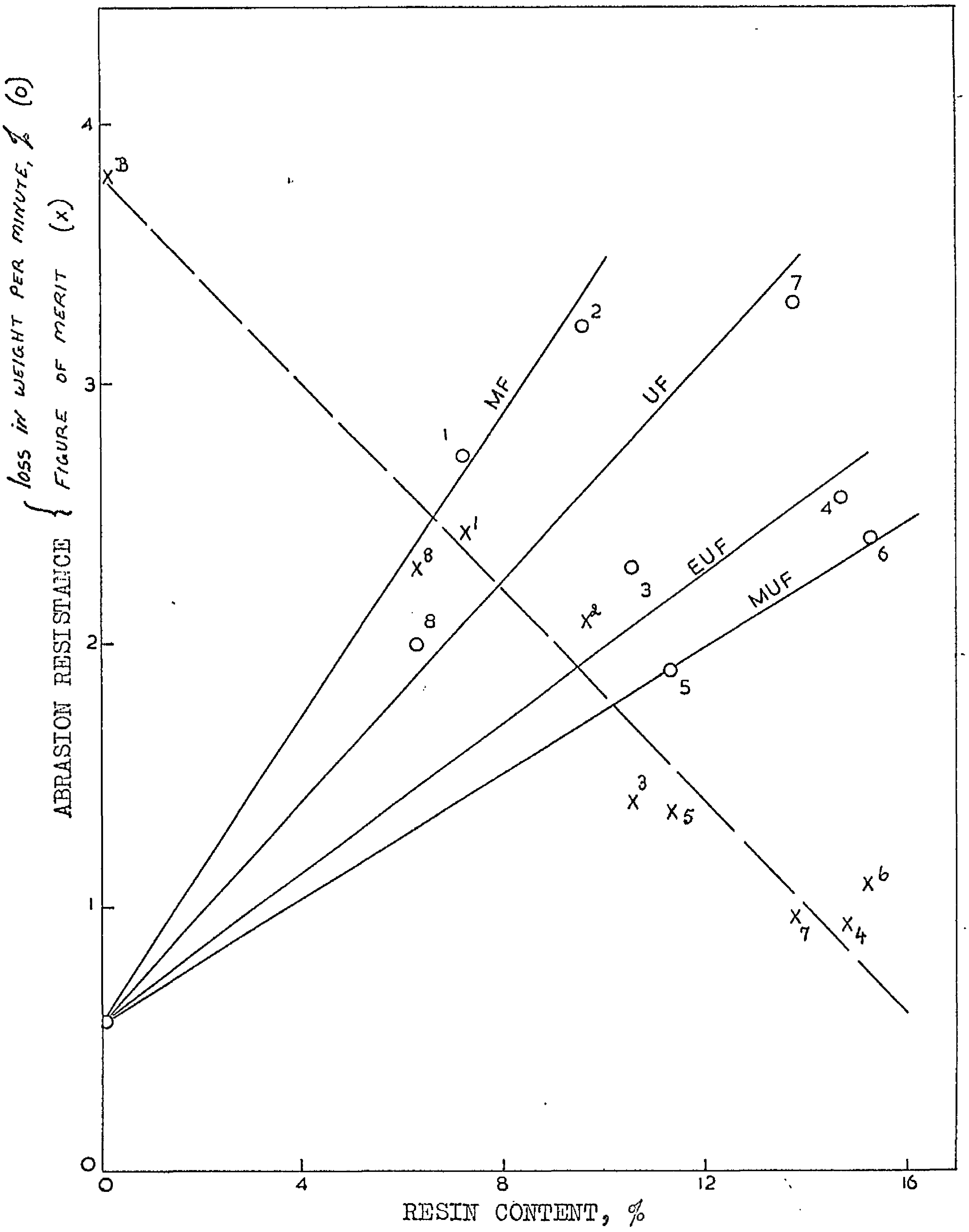

Figure 4b Effect of Resin Content on Abrasion Resistance as Measured by (o) Accelerotor, and (x) B.F.T.

a forecast can be made of the probable rate of loss of weight on an Accelerotor test, whereas only the content must be known for a forecast of the probable Figure of Merit and that the likely end result of either test can be forecast provided one is known together with the type of resin. With both instruments an increase in the resin content of the present fabrics has resulted in a linear decrease in durability but the Accelerotor results have also been influenced by the type of resin present.

Discussion of Results

The present work was undertaken to evaluate the physical properties and the resistance to abrasion of the same fabric treated with various resins. The yarn and fabric geometry was reasonably constant throughout the study but with some variation in yarn and fabric construction, principally set and crimp.

Abrasion resistance is known to increase with increase in threads per inch (24,292), but the variations in the present samples (ends/inch 66-70 and picks/inch 60-66) would not be expected to cause any appreciable change in abrasion resistance.

Crimp distribution determines the relative vertical displacement of each set of yarn above and below the plane of the fabric, and high crimp in a given direction projects yarn in that direction so that the complimentary yarns containing low crimp are protected (24). The curves, Figure 12, of yarn strength against time of abrasion showed a steep curve for warp yarns, indicative of a higher rate of damage than the weft yarn as expected from the data on crimp values. However, no correlation could be found between crimp and either Accelerotor or B.F.T. Abrader results and it is considered therefore that the changes produced in abrasion resistance are due to changes in the mechanical properties of the fibre, yarn and fabric.

Comparison of Instruments

Accelerotor

As far as is known, the Accelerotor was designed as a general purpose instrument with which the influence of liquids on materials could be measured in fastness and shrinkage tests as well as the use of the instrument as an abrader.

A recommended procedure (68) was the measurement of loss in sample weight after 4 minutes at 3000 r.p.m. This condition was found to be too drastic for resin treated viscose rayons with a loss in weight of the order of 50-60%, while beyond 40% loss in weight the curve of loss in weight against time of abrasion, Figure 11, was no longer linear, largely due to excess of debris in the chamber effectively reducing fabric liner contact. A similar effect was also observed after 20 minutes at 1500 r.p.m. In the opinion of the present author, the slope of the linear portion of the curve, which is the rate of loss in weight, is a better measure of abrasion resistance and this has been used throughout.

In the present tests the instrument has only been used on materials in the dry state and with one type of abradant liner. The reproducibility on repeated tests has been found to be excellent and no appreciable error seems to be caused by slight variations in the application of the binder used to prevent undue fraying of the edges of the test samples.

The effect of the speed of the impellor has been shown to leave no effect other than to alter the time scale of the rate of loss in weight of the material. Increasing speed by two fold, from 1500 to 3000, reduced the time scale by a factor of about 5. This can be visualised from the fact that as the number of revolutions per interval of time is increased, the centrifugal force on the fabric is increased and consequently the normal force between the fabric and the liner, resulting in much higher rate of loss in weight.

The rate of loss in weight was altered by a change in both the amount and the type of resin finish present on the material and possible reasons for this will be discussed under the appropriate sub-section.

Booking Abrader

In the Booking Abrader tests the material is generally used in the dry state but wet flex tests are recommended in those cases where dry test cycles are excessive (37a). The results of the present study with wet and dry flex tests do not support such an alternative as the ratings by the two tests are different, (p.109, 118) possibly due to the difference in water imbibition values. Therefore, all tests involving Figure of Merit results were carried out on dry samples.

The reproducibility of B.F.T. results was found to be generally poor, probably due to the fact that a very small area of the fabric is abraded. The Ball Penetration test, where a ½ inch reciprocating motion of the ball is involved, gave a variation in result of ±10%; Flat Abrasion, where the abrading area is ½ sq. inch., gave a variation of ±8%; and in Flex Abrasion, where the bending action occurs over an area of 1 inch by ½ inch, gave variation of ±5%.

The investigation into the effect of normal pressure between the fabric and the abradant showed the fabrics to be ranked in the same order, and a linear relationship between the pressure and the log of cycles was obtained. The shift from the linearity under low pressure has been attributed to machine vibrations resulting in reduced area of contact.

This investigation was helpful in the selection of the appropriate pressures to give nearly the same corrected values for ball, flat and flex tests, thus avoiding test bias.

The value of Figure of Merit was altered by a change in the amount of resin finish, irrespective of the type of finish present on the material and possible reasons for this will be discussed in the subsequent sub-section.

The ranking by the two testers, both used to assess wear properties, has been contradictory as shown by the following table where the samples have been arranged in increasing order of abrasion resistance.

Accelerotor test	7	2	1	6	4	3	8	5	B
B.F.T. test (Figure of Merit)	4	7	6	5	3	2	8	1	B

Although there is apparent contradiction in ranking the samples, a linear correlation for a specific resin finish has been shown, Figure 46.

The reasons why there is no general correlation between the two wear testers for the resin treated samples may be two fold, (a) different forms of abrasion with a predominance of a particular type of wear, e.g. frictional wear, cutting or plucking, and (b) difference in the magnitude of strains involved, possibly linked with the different end points of the test and some guidance may be found from correlations with different mechanical properties of fibre, yarn and fabric.

No conclusive answer regarding the contribution from cutting or plucking of fibres could be given at this stage of the study unless the microscopical investigations of the debris after various tests is critically made which would throw light on the type of fracture, longitudinal or transverse, and the amount of cutting and plucking of the fibres.

From the knowledge of the relevant reports on optical investigations reported in Chapter 4, it may be said that if the surface of the abradant is small and sharp, like the one used in Accelerotor where the abradant is a very fine carborundum cloth, the fibres are more susceptible to the action of cutting and this is suggested to be associated with the development of complex stress patterns leading to tensioning, bending or slippage, whereas the increase in the normal force between the abradant and the fabric would cause greater plucking of the fibre as larger areas of true contact between the two bodies would occur; however, the ranking of results of both Abrasion tests has not altered under range of pressures investigated.

A major form of abrasion is the contribution of frictional wear and two forms of this have been suggested. An adhesive form of frictional wear, where molecular welds between the fabric and the abradant are sheared by the relative motion producing wear particles, has been reported in B.F.T. tests (370); whereas an abrasive form of frictional wear, where actual penetration of the surface of the material by the abradant and ploughing out of the abraded substance by relative motion, is more predominant with the Accelerotor.

Recently Weiner and Pope (371) reported work on correlation of different abrasion testers (B.F.T. but not Accelerotor) using fibres of different generic groups, various blends and different fabric construction, and mentioned that a correlation coefficient of 0.9 (good) was obtained between abrasion testers which had the same mode of frictional wear, either adhesive or abrasive, and a correlation coefficient of less than 0.4 (poor) between abrasion testers which had different modes of frictional wear. Their mathematical formuli were computed from the results of wear and no consideration was given to any other property which might influence abrasion.

Considering the magnitude of strains involved and the different end points of the test, the end point in the B.F.T. test is the complete breakdown or disintegration of the yarn as compared with the rate of removal of fibrous material from the fabric in case of Accelerotor. Weiner and Pope (370) showed a good correlation between the B.F.T. and the Stoll tester (322) and between Taber (22) and Sand tester (22) but poor correlation between the two sets of machines and attributed this to the form of frictional wear, the former set having a predominant adhesive form of frictional wear and the latter having a predominant abrasive form, and completely ignored the fact that the former set has a breaking point as the end point, whereas the latter is judged by visual inspection after a fixed number of revolutions.

However, from a study of actual wear trials on fabrics (370), it was suggested that the abrasive form of frictional wear generally appears to predominate in the serviceability testing of combat, utility and work clothing, which suggests that the Accelerotor may provide more useful information than the B.F.T. It should be remembered, however, that the B.F.T. was designed principally for the evaluation of resin treated viscose rayon.

The effect of mechanical properties of the yarn on abrasion resistance, as measured using the two testers, is discussed in the next section.

Yarn Properties and Fabric Wear Tests

Physical properties of fabric and yarns were reported in Part 1 of the thesis and yarn and fibre properties in Part 2 where for experimental convenience measurements were made on yarn rather than fibre, the results of yarn properties being much more consistent than those on single fibres, especially after resin treatment.

Among the effects of treating viscose rayon yarn with resin, the following seem to be of importance with regard to abrasion properties:-

(1) A reduction in yarn extensibility, resulting in reduced energy for rupture and reduced stiffness.

(2) An increase in tensile elastic recovery.

(3) An increase in initial modulus and yield point stress and a reduction in yield point strain.

It is interesting to note that yarn extensibility, and hence energy for rupture and stiffness, is not related to the initial modulus, yield stress or yield strain, whereas elastic recovery is influenced by both the extensibility and the initial modulus.

Figures 29, 38 and 44 make an interesting study, where extensibility, initial modulus and elastic recovery are plotted respectively against resin content. Different types of resins gave different slopes vs elastic recovery, as compared to extensibility where a single slope for all types of resins was obtained. However, the difference in different slopes was much smaller compared with the differences obtained in the modulus plot.

A comment that reduced extensibility was accompanied by increased elastic recovery has been cited in literature (17, 105, 106, 107, 214), but comments were usually restricted to amounts of a specific resin.

Gagliardi and Nuessle (107) have shown that in rapid abrasion tests, reduced fibre extensibility leads to poor abrasion performance, simply because of less favourable stress distribution. In less rapid abrasion tests, where the magnitude of stress is low, the low fibre extensibility is no longer a major contributing factor and increased elastic recovery is predominant and at very low magnitude of stresses the resin treated samples, because of their higher elastic recovery, are actually better than untreated samples.

The present study shows that as elastic recovery increases, abrasion resistance decreases, suggesting that with either B.F.T. or Accelerotor any tendency to improved abrasion resistance due to increased elastic recovery is overwhelmed by other factors and a correlation is not justified as the magnitude of stress involved is perhaps not low enough.

The correlations between yarn mechanical properties and abrasion resistance, using B.F.T. and Accelerotor, is unique. Extension at break, energy for rupture, and final stiffness give a positive correlation with B.F.T. wear results whereas initial modulus and yield stress give a positive correlation with Accelerotor. Arranging the 4 different types of resin finishes in decreasing order of extensibility gives: untreated, melamine-formaldehyde, urea-formaldehyde, ethyleneurea-formaldehyde and methylatedurea-formaldehyde and that is exactly the order of rateing with the B.F.T. tester. Arranging according to the increasing order of modulus gives: untreated, methylatedurea-formaldehyde, ethyleneurea-formaldehyde, urea-formaldehyde and melamine-formaldehyde and that is the order of rateing with Accelerotor. In other words, melamine-formaldehyde samples were the best of the four types of resin finishes according to B.F.T. tester and the worst of the four types according to Accelerotor test.

Why is it that the two abrasi~~ve~~or testers have such a diversive correlation? It may be suggested that the B.F.T. tester correlates with tensile properties beyond the yield region whereas Accelerotor correlates within the yield region of the tensile characteristics. This may be the effect of magnitude of stress involved during abrasion or the effect of the end point of the test. If so, then this could suggest that a lower magnitude of stress is involved during abrasion using Accelerotor and that this instrument should be more realistic in assessing actual wear performance than B .F.T. On the other hand, the contribution of shear properties in Accelerotor abrasion might be important, as has been suggested (26) when sharp abrasive surfaces are present, so that shear and flexural properties of the yarn should be measured in future investigations. If shear properties did have a substantial contribution, then the Accelerotor results might be unrealistic, for the inherent flexibility and freedom of motion of fibres in a structure are such that stresses other than tensile should seldom develop to any appreciable magnitude (250).

PART 3

STRESS-RELAXATION

CHAPTER 7

SURVEY OF LITERATURE

Introduction

When a sample exhibiting both elasticity and flow is deformed and then constrained to retain the deformation, the internal flow which takes place gradually relaxes the stress so that smaller and smaller forces are required to keep the sample deformed (7). This decay in stress with time is called stress-relaxation at constant strain. In the experimental study of time effects on fibres, creep tests are more frequent than relaxation tests because it is easier to maintain constant load and measure the extension (creep) than to maintain constant extension and measure the load (stress-relaxation). However, relaxation tests are of greater theoretical importance because the external form of the sample remains constant throughout the test, and there is no continuous change in cross-section as in a simple creep test (210).

In the reaction-rate-theory of visco-elastic behaviour three types of motion were postulated by Tobolsky and Eyring (337): motion due to decay of the primary structural elements of fibre network; motion due to relaxation of secondary cross-bonds permitting units of network structure to slip on the application of stress;

and motion of the mobile segments of the long molecules or groups of molecules. In the experimental determination of stress-relaxation, the sample is rapidly stretched to a given length which is then held while the stress decay with time is measured. In this type of experiment, relaxation due to mobile segments of the long molecules or groups of molecules has been stated to be rapid and hence not observable; conversely, motion due to decay of the primary structural elements of the fibre network was stated to be very slow (51). The observed stress decay has thus been attributed to the relaxation of the secondary network bonds.

Various other aspects regarding the definition, history and discussion of visco-elastic behaviour and stress-relaxation have been presented by Leaderman (177), Alfrey (7), Mark and Tobolsky (185), Wakeham (356) and Bueche (49). Of the work reported on cellulosic fibres, the final retractive force supported by the fibres has been studied by Hermans (138) while the mechanical properties of cotton and viscose fibres have been investigated by Andersen (11) and Meredith (209). Andersen (12) also suggested that the magnitude of the tension had a direct influence on the degree of orientation of wet viscose rayon, but would not generally increase the degree of orientation of dry cellulosic fibres. At a high degree of stretch the relaxation proceeded more slowly and this was assumed to be the result of greater binding energy.

Some workers have suggested the use of stress-relaxation as a method of measuring the accessibility and structural behaviour of textile fibres by studying the effects of various reagents on the stress-relaxation behaviour of a fibre, and noting the divergence from the normal relaxation behaviour. Stress-relaxation behaviour of wool in various reagents which attack cystine and other salt linkages has been included in the present review in case some relevant information regarding cross-linkages might be applicable to resin treated viscose rayons.

Katz and Tobolsky (165) studied the stress-relaxation of wool in water, and by replacing water with sodium bisulphite, showed that the decay of stress was due to the reduction of cystine linkages.

Mooney, et. al.(213) and Tobolsky, et al.(338) studied the effect of oxygen on stress-relaxation and creep measurements of cellulose, while Mark and Tobolsky (185) suggested that the knowledge of the accessibility of cellulose to various reagents could help in determining the percentage crystalline content.

Reese and Eyring (263) studied the effect of acids, bases, oxidising agents and reducing agents on the stress-relaxation behaviour of hair under constant elongation to determine the amount of mechanical strength contributed by various bonds, while Kubu (170) studied stress-relaxation behaviour of wool, silk and nylon in water and wool in different reducing agents.

A later study on wool by Kubu, et al.(171) showed that the respective salt solutions of sodium chloride, potassium chloride, ammonium chloride, potassium bromide, potassium fluoride, potassium iodide, lithium chloride, sodium sulphate, ferric chloride, and magnesium chloride produced varying rates of relaxation behaviour of wool in water and that there was a further reduction of the order of 20% when the salt solutions were replaced by 0.1N hydrochloric acid, indicating that the salt sensitive linkages were distinct from acid sensitive linkages. They concluded that the water sensitive linkages were hydrogen bonds and that acid sensitive linkages were salt bridges.

Lasater, et al.(176) studied the mechanical properties of cotton fibres using stress-relaxation in air, water, acids, and alkalis and found that the principal portion of the free energy of activation relaxation was in the entropy term.

They suggested that relaxation occurred through segmental motion of the chains or groups of molecules rather than through movement of a complete chain at one time; the acid solutions causing an instantaneous relaxation whenever the acid concentration was above a critical minimum. The nature of the reagents, and the rapidity of the reaction, suggested that the bonds that were attacked by the acid were hydrogen bonds, and that the limiting value of the force reduction was a function of the accessibility of the fibre and therefore the accessibility would change with temperature.

On the other hand, Lemiszka and Whitwell (178) found no apparent change in the stress-relaxation rate of viscose rayon in water after 24 hours when water was replaced by hydrogen bond breaking reagents like lithium fluoride salt solutions. They concluded that after 24 hours the relaxation rate was not controlled by secondary bonds or hydrogen bonds, and the increased rate of stress-relaxation of viscose rayon in acid solution was due to breakdown of primary bonds, which can be interpreted in terms of accessibility. Nylon with larger draw ratios showed smaller rates of relaxation in water, the absolute stress supported by the fibre being greater. Normally oriented specimens of various materials including wool, silk, rayons and synthetic fibres showed a similar stress-relaxation behaviour in distilled water at 30° C, and it was concluded that the stress-relaxation in water was caused by scission of the weaker secondary linkages peculiar and common to all the materials investigated.

Subsequently, Valentine (352) questioned the stress-relaxation method of determining accessibility of fibres to hydrochloric acid because the influence of the preliminary extension and relaxation on the accessibility was unknown. It was suggested that there were at least three factors involved: the degree and ease of penetration of fibres by acid; the degree of hydrolysis of the polymer; and the degree of relaxation and redistribution of strain depending on the number of bonds bearing the stress. Any one of these might affect the rate of relaxation and the judgement of accessibility.

Very little work on stress-relaxation of resin treated viscose rayon has been reported. The only paper that could be traced was by Steele and Giddings (314) who reported work on the stress-relaxation behaviour of cotton and rayon fibres treated with mono-methylolurea and dimethylolurea. Stress-relaxation was carried out on fabric at 65% r.h. and 75° C. The results correlated with the molecular structure of the particular fibre.

Finally, an investigation of the stress-relaxation of several common plastics was made by Watson, et al.(364) and this reference has been included because they found that an increase in the content of the plasticiser generally increased the rate of relaxation.

The present work was undertaken to investigate the stress-relaxation behaviour of resin treated viscose rayon fibres in water and in acid solution. The latter should hydrolyse the resin polymer in the fibre and break the cross-linkages and allow interpretation of the resin-fibre interaction. Consideration has been given to the hypothesis that the relative accessibility of viscose rayon could be measured from the reaction rate of acid hydrolysis as indicated by Lessator, et al.(176) and Lemiszka and Whitwell (178).

The work is linked with that of Part 1 and Part 2 in the need for knowledge of the stress-strain-time relationships of a material and the separation of physical and chemical effects.

A study of the stress-relaxation in water, of viscose rayon, cuprammonium rayon, cellulose acetate, silk, nylon, polypropylene and polyvinyl alcohol fibres has been made, and finally similar work has also been carried out on different viscose rayon fibres, bright Fibro, strong Fibro 48, Vincel and Durafil.

Since the present work was carried out on single fibres and loads of the order of 1 gramme were envisaged, resistance wire strain gauges were constructed.

CHAPTER 8

EXPERIMENT

Gauge characteristics

Apparatus

The necessary requirements of an apparatus for stress-relaxation experiments are: a device which will allow accurate measurement of the small forces involved, and means whereby an accurate extension (strain) may be produced and maintained on the sample throughout the stress-relaxation investigations.

Force can be measured in various ways (32, 148, 203, 310, 335) but resistance wire strain gauges have been employed frequently because of their accuracy in measurement combined with simplicity in construction, while the fibre may be stretched by the dropping of a dead weight, hand pulling, use of a screw assembly, or by spring expansion methods.

In the present investigations four resistance wire strain gauges were used, and the fibres were stretched by means of a screw type assembly fitted with a hand driven mechanism. A gauge consisted of four unbonded elements of (0.001 in.) S.W.G. No.50 KARMA resistance wire. Karma (44) is essentially an 80/20 nickel-chromium alloy with additions of aluminium and iron. It has been designed to give high specific resistance combined with a very low temperature coefficient, low thermal e.m.f. against copper and stable over long periods of time under high stresses and average gauge density. The wires were mounted on a Tufnol base as shown in Figure 47a and connected into a DC Wheatstone bridge circuit as shown in Figure 47b, where D is the strain sensitive element. The force to be measured was applied at the mid-point, E, through a thin glass rod, F, the wires being approximately 10 cm. long. One element, D, was mounted with a 24° sag giving a mechanical advantage of more than 2. When a force is applied to the glass rod, D elongates slightly thus increasing its resistance and a small voltage output is produced. The four elements of the gauge A, B, C, and D were silver soldered to brass tabs, made from ¼" lengths of 1/16" diameter brass tubing, following a special technique. Since it was difficult to solder the elements to equal lengths, a short length of No.36 (B. & S.) Karma resistance wire was added to the appropriate arm to bring the bridge to near balance. Single pole resistor switches M and N were used for coarse and fine balance respectively, resistors O and P were for exact zero voltage output adjustment and R' was a 0-50 ohm. rheostat used to vary the gauge sensitivity, Figure 47c.

<u>Temperature Control</u>

Although the temperature coefficient of resistance of the KARMA wire used was relatively low, Coefficient of Electrical Resistivity 0.00002 per °C (20-100°C) and Coefficient of

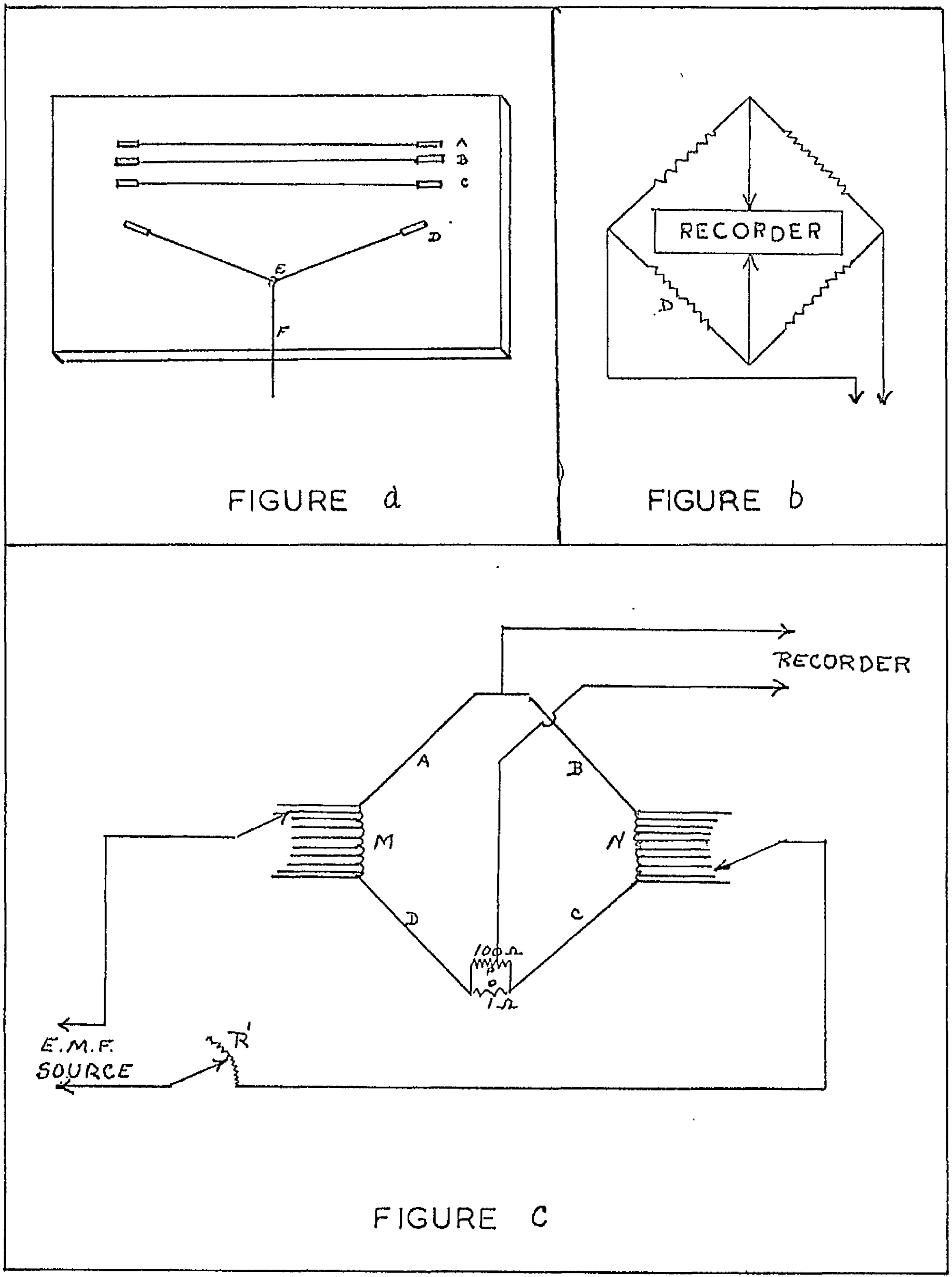

FIGURE a

FIGURE b

FIGURE c

Figure 47 (a) (b) (c) Wire and Circuit Diagram of the Resistance Wire Strain Gauge.

Linear Expansion 0.0000133/°C (20-100° C), it was found to be necessary to thermostat the gauges in order to obtain stability over a long period of time. This was accomplished by mounting the gauges within a thermostatically controlled chamber (±0.2°C), the temperature being controlled by a mercury-toluene regulator and a valve relay unit connected to a hot bulb heating unit. An electric fan was used to circulate the air to give an even distribution of temperature.

Input Voltage Regulation

A FARNELL stabilised power unit Model SSU 12/1 which gave a constant DC voltage output was used in preference to dry cell batteries as no alteration or replacement was needed provided that special regulated rectifiers were also used. On connecting the stabilised power unit to the gauge circuit, a considerable time lag in recording was noted. This difficulty was overcome by by-passing one of the fixed resistor limbs of the strain gauge bridge by a large electrolytic capacitor ($5000 \mu F$) thereby effectively coupling together the low potential side of the input of the recorder and the positive side of the output from the stabilised power unit as shown in Figure 48.

Recorders

Two recording units were used in these investigations to cover 5 log (time) cycles.

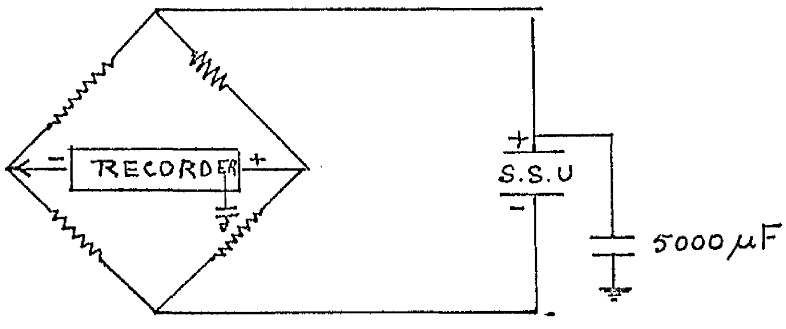

FIGURE 48

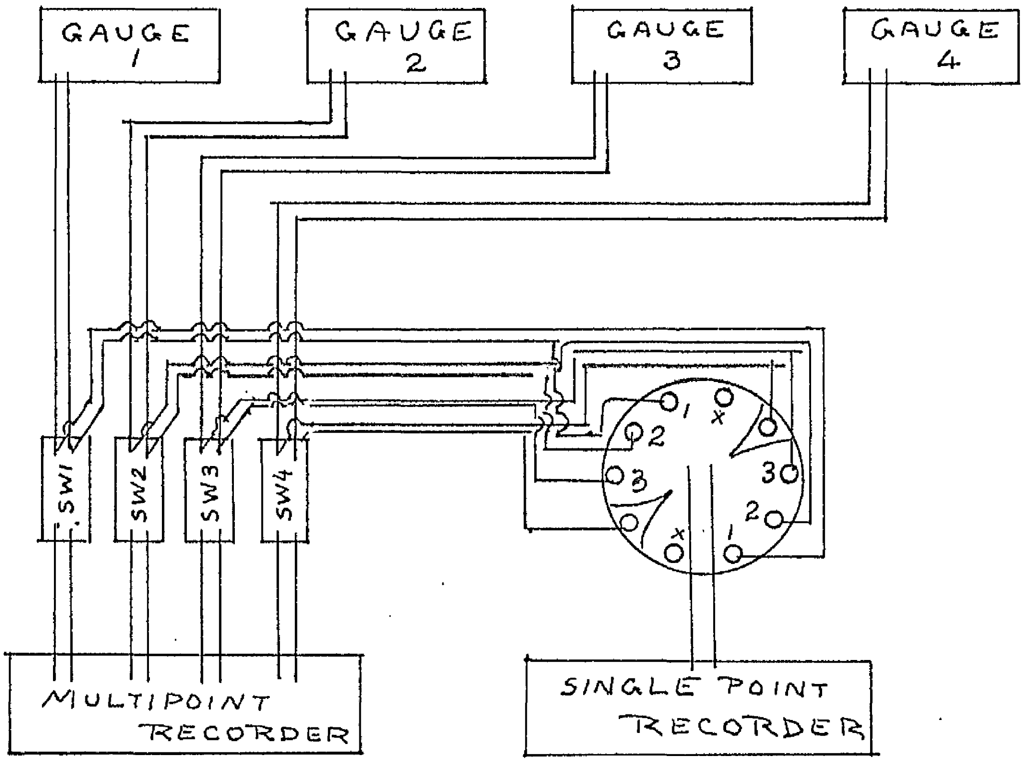

FIGURE 49

Figure 48 Modified Circuit Diagram of the Resistance Wire Strain Gauge.

Figure 49 Switch Circuit Diagram

A single point Bristol Dynamaster Potentiometer, MC1 series was used to record the initial or early part of stress-relaxation, the unit being run at high speed (0.5"/min) for the first twenty minutes of the experiment to obtain a magnified record of the decay of stress within this period. Further recording was carried out on a multipoint Cambridge recorder which ran at low speed (0.5"/hr) for the period of observation which was usually twentyfour hours. The switch connection between the two recorders and the four resistance wire strain gauges consisted of four two pole two way 2 amp switches and a two pole five way break before make 2 amp switch, Figure 49.

Gauge Characteristics

Gauge sensitivity

Gauge sensitivity has been defined as the voltage output (Δ E) per volt input (E) per gram of force (F). Experimentally, with a force of one gramme on the gauge, $\Delta E = 0.0045$ volts, at $E = 7.5$ volts, giving a gauge sensitivity of 0.60 millivolts per gram load per volt input.

Gauge load limits

It has been reported (335) that a 20g load on the gauge produced a stress in the wire of 69000 p.s.i. while the yield stress for KARMA wire was stated to be approximately 95000 p.s.i. A 20g load was therefore taken as the limiting load that could be applied to a 0.001 inch diameter at 24° sag.

Linearity

It is obviously desirable that the gauge voltage output be a linear function of the load applied on the gauge and it was found that complete linearity was observed up to the limiting load of 20g.

Gauge Calibration

Each gauge was calibrated by placing a series of known weights on the loading arm of the gauge and recording the corresponding reading of the voltage output in millivolts. The sensitivity of the gauges could be changed by changing the voltage input. Each gauge was calibrated and standardised to give 0.9 millivolt output corresponding to a tension of 2g for an input voltage of 7.5 volts.

Strain Applying Device

The general arrangement of the apparatus has been shown in Figure 50a,b. A 9in. long and ¼in. diameter glass rod (A) was bent near one end to a U shape, the smaller arm of which was narrowed down to form a hook to engage the lower end of the specimen (B) and formed a moveable arm of the straining system. The fixed arm (C) was attached to the loading wire (D) of the gauge. The strain was applied to

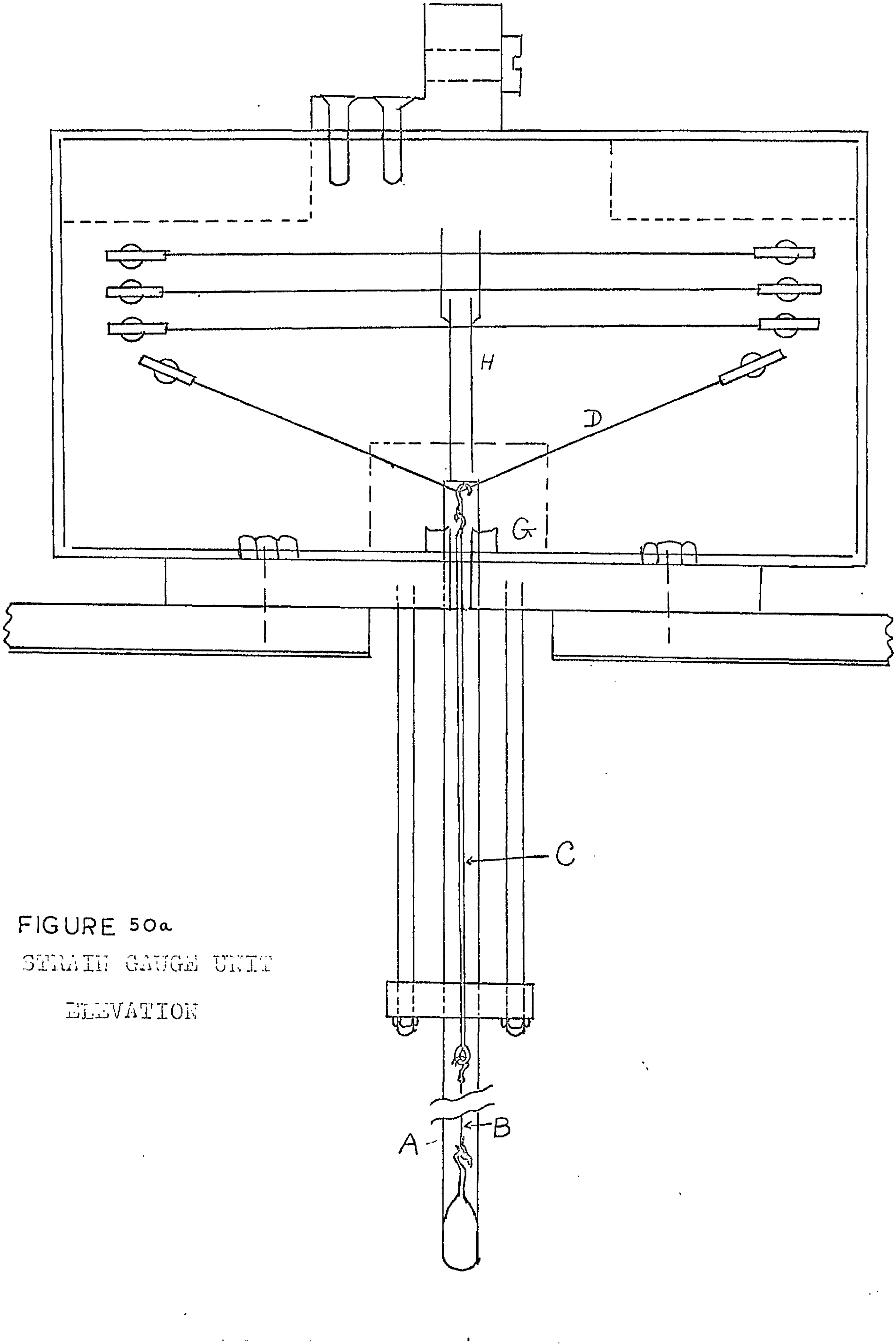

FIGURE 50a

STRAIN GAUGE UNIT

ELEVATION

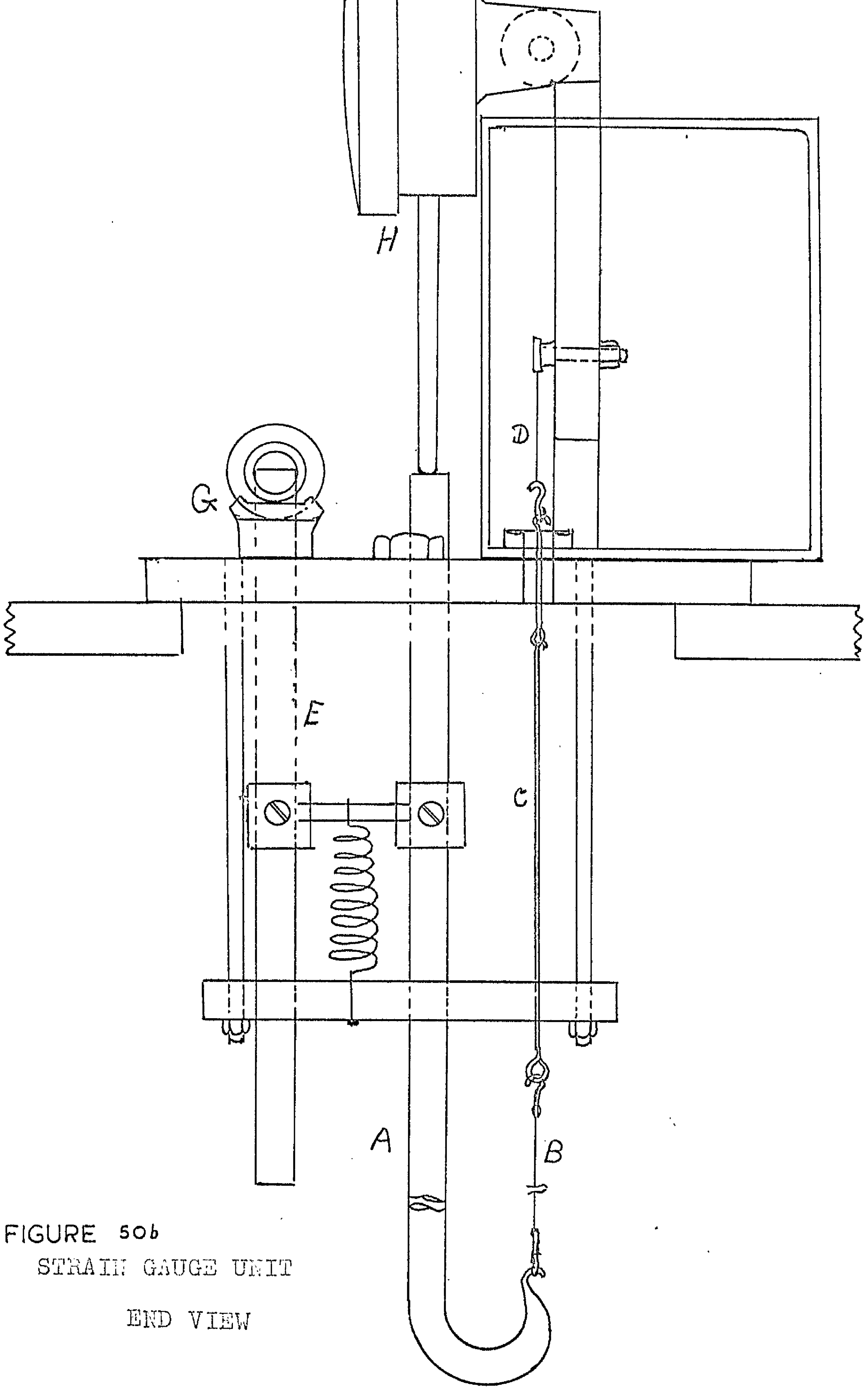

FIGURE 50b

STRAIN GAUGE UNIT

END VIEW

the specimen by the vertical movement of the movable arm (A) by coupling it to a threaded rod (E) which could be raised or lowered by bevel gears (G). The displacement of the movable arm was measured by the dial gauge (H) to an accuracy of 0.001 cm.

Materials

(a) Fibres used for the study of stress-relaxation in water and in hydrochloric acid were taken from fabric U1009, (for fabric details refer Table 10) a staple viscose rayon fabric, lengths of which had been treated with different resins to enable comparison to be made between resin treated and untreated samples and also between the various resin treated samples themselves. Details of the various concentrations of resins in the padding bath, the amount and type of catalyst used, and the percentage of resin content have been shown in Table 14, while the tensile properties have been shown in Table 15. The stress-strain curves of the resin treated viscose rayon samples (fibres) at 65% R.H. and 20 ±1° C and in water at 20° C have been given in Figure 51 and 52 respectively.

(b) Fibres used to study the relative rates of relaxation of different materials in water were obtained from the following yarns:-

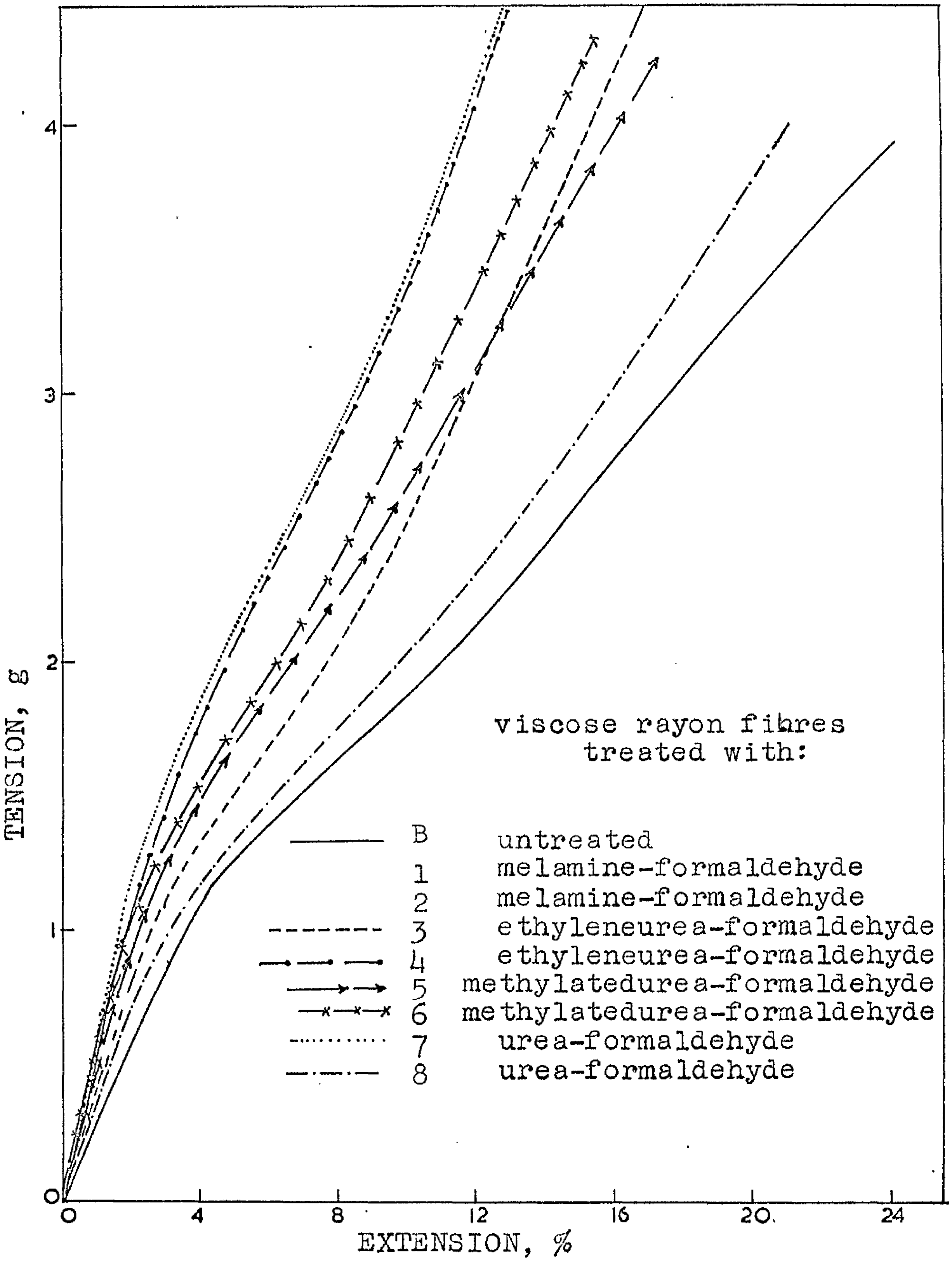

Figure 51 Load Extension Curves at 65% r.h. of Viscose Rayon Fibres Treated with Different Resins

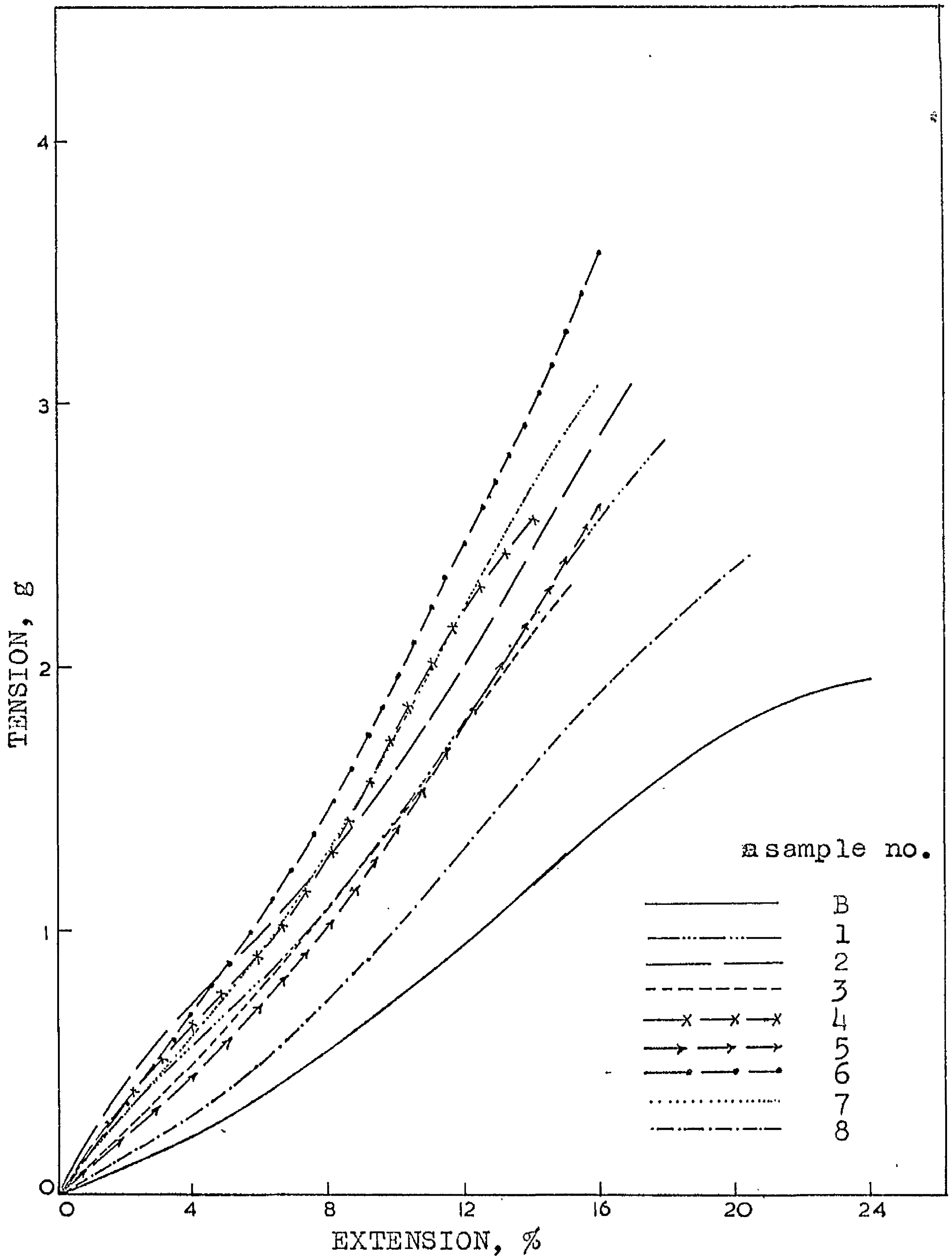

Figure 52 Load Extension Curves in Water of Viscose Rayon Fibres Treated with Different Resins

Table 14

Details of Resin Treatment on U1009 Viscose Rayon Fabric

Sample Number	Commercial Code Number	Resin			Catalyst	
		Type	Concentration % in Padding Bath	Concentration % on Fabric	Type	Concentration % on weight basis
1	BT 309	Melamine-formaldehyde	14.7	7.2	Magnesium Chloride	2.5
2	BT 309	Melamine-formaldehyde	22.0	9.5	Magnesium Chloride	2.5
3	BT 324	Ethyleneurea-formaldehyde	25.0	10.5	Magnesium Chloride	2.5
4	BT 324	Ethyleneurea-formaldehyde	37.5	14.7	Magnesium Chloride	2.5
5	BT 322	Methylatedurea-formaldehyde	25.0	11.0	Ammonium Thiocyanate	0.5
6	BT 322	Methylatedurea-formaldehyde	37.5	15.5	Ammonium Thiocyanate	0.5
7	-	Urea-formaldehyde	32	13.5	Not known	1.75
8	-	Urea-formaldehyde	22	6.5	Not known	1.75

Some Tensile Properties of Viscose Rayon Fibres Treated with Different Resins

Sample No.	Tenacity, g/tex			Breaking Extension, %			Modulus(Stress at 5% Extension), g/tex		
		Wetting Period			Wetting Period			Wetting Period	
	65% r.h.	1 hr.	24 hr.	65% r.h.	1 hr.	24 hr.	65% r.h.	1 hr.	24 hr.
1	-	17.1	16.0	-	18	18	-	4.1	3.8
2	-	18.5	15.2	-	17	17	-	5.0	4.3
3	27.0	13.8	13.9	17	18	18	9.1	3.7	3.4
4	27.5	15.2	—	13.5	14	14	12.3	4.6	5.2
5	21.3	15.6	15.5	16	16	16	10.1	3.4	3.9
6	25.4	21.5	20.6	15	15	15	10.4	5.1	5.7
7	28.4	18.0	18.4	14	16	16	12.4	4.6	3.8
8	24.0	14.4	14.8	21	20	20	7.9	2.3	2.8
'B' Untreated	23.6	11.7	11.7	24	24	22	7.7	1.8	2.3

1. viscose rayon filament yarn
2. cuprammonium rayon filament yarn
3. cellulose acetate filament yarn
4. silk (degummed) yarn
5. nylon 66 filament yarn
6. polypropylene filament yarn
7. polyvinyl alcohol filament yarn

These yarns were ordinary normal drawn yarns, details of which have been reported in Table 16. Their stress-strain curves in water at 20° C are given in Figure 53.

Fibres used to study the relative rates of relaxation of different viscose rayons in water were obtained from the following yarns:-

1.	bright Fibro	3.	Vincel [1]
2.	strong Fibro 48	4.	Durafil [2]

---

[1] Vincel polynosic fibre belongs to the regenerated cellulose group of fibres derived from a modified manufacturing process. Fibre structure is chiefly characterised by high crystallinity and high orientation.

[2] Durafil is a tough high tenacity viscose fibre produced by a process having many features in common with that by which the highest strength continuous filament type yarns are made. The fibre has high dry and wet tensile strength, high work of rupture, and good abrasion resistance properties.

Some Physical Properties of Filaments used in Set 4 Experiments

Material	Yarn Specification Denier/Filament	Filament Tex	Wet Tenacity g/tex	Breaking Extension, %
Viscose Rayon	300/50	.67	7.9	32
Cuprammonium Rayon	165/110	0.17	5.6	17
Cellulose Acetate	300/50	0.67	6.4	38
Silk	170/28	0.67	4.95	20
Nylon 66	100/33	0.33	36.8	32
Polypropylene	200/40	0.56	49.7	31
Polyvinyl Alcohol	240/36	0.74	37.0	9

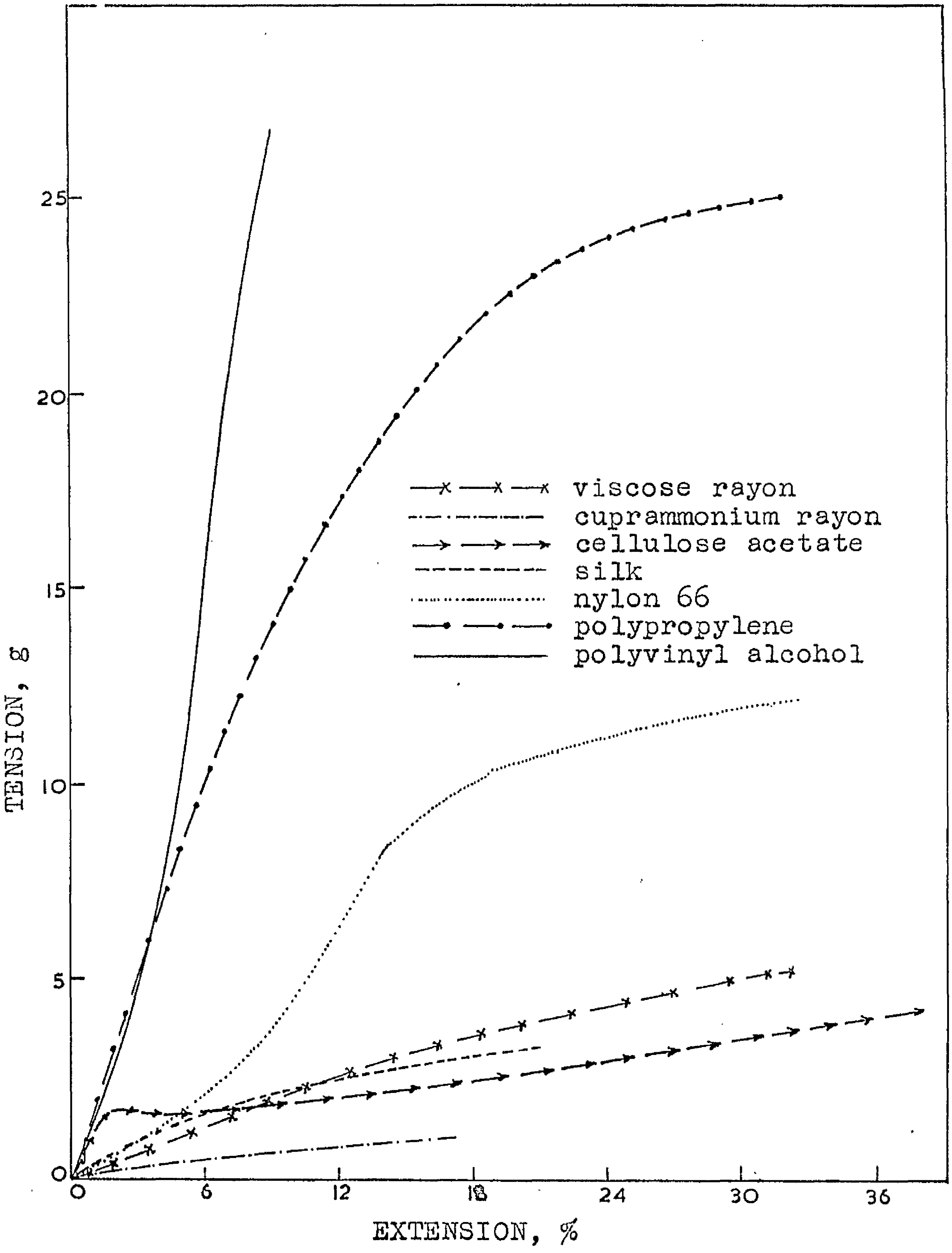

Figure 53 Load Extension Curves in Water of Filaments in Set 4 Experiments

Details of these fibres have been reported in Table 17 and their stress-strain curves in water at 20° C are given in Figure 54.

All the stress-strain curves were measured using an Instron tester, and they are means of three determinations. The cross head speed and the chart speed were selected as 1.2"/min and 12"/min respectively, to obtain satisfactory curves at about one per cent per second constant rate of extension, the specimen length being 2 inches.

Details of fibres

In all cases the tex of the fibre was checked using a Shirley Cantilever microbalance, as described by Lord (181). About 20 test readings were taken and as the mean values were not found to be different from the reputed tex (within 2%) the latter values have been accepted.

Preparation of the test specimen

Since the experiments were carried out on single fibres, most of them of fine denier and restricted length, special arrangements to grip the fibres were necessary; it was desirable to standardise the procedure and the following technique was used:

Single fibres were attached to the steel needle hooks by low temperature curing Araldite. Hooks were made

Table 17

Tensile Properties of Fibres used in Set 5 Experiments

Material	Tenacity, g/tex		Breaking Extension %		Wet Modulus, g/tex (Stress at 5% Extension)	Elastic Recovery, % (at 5% Extension)	Water Imbibition, %
	Conditioned	Wet	Conditioned	Wet			
Bright 'Fibro'	22.5	11.7	18	22	2.16	45	95
Strong 'Fibro' 48	-	20.3	17	22	2.52	-	-
Vincel	31.2	20.7	7	8	10.8	62	68
Durafil	34.2	24.6	30	35	2.16	-	68

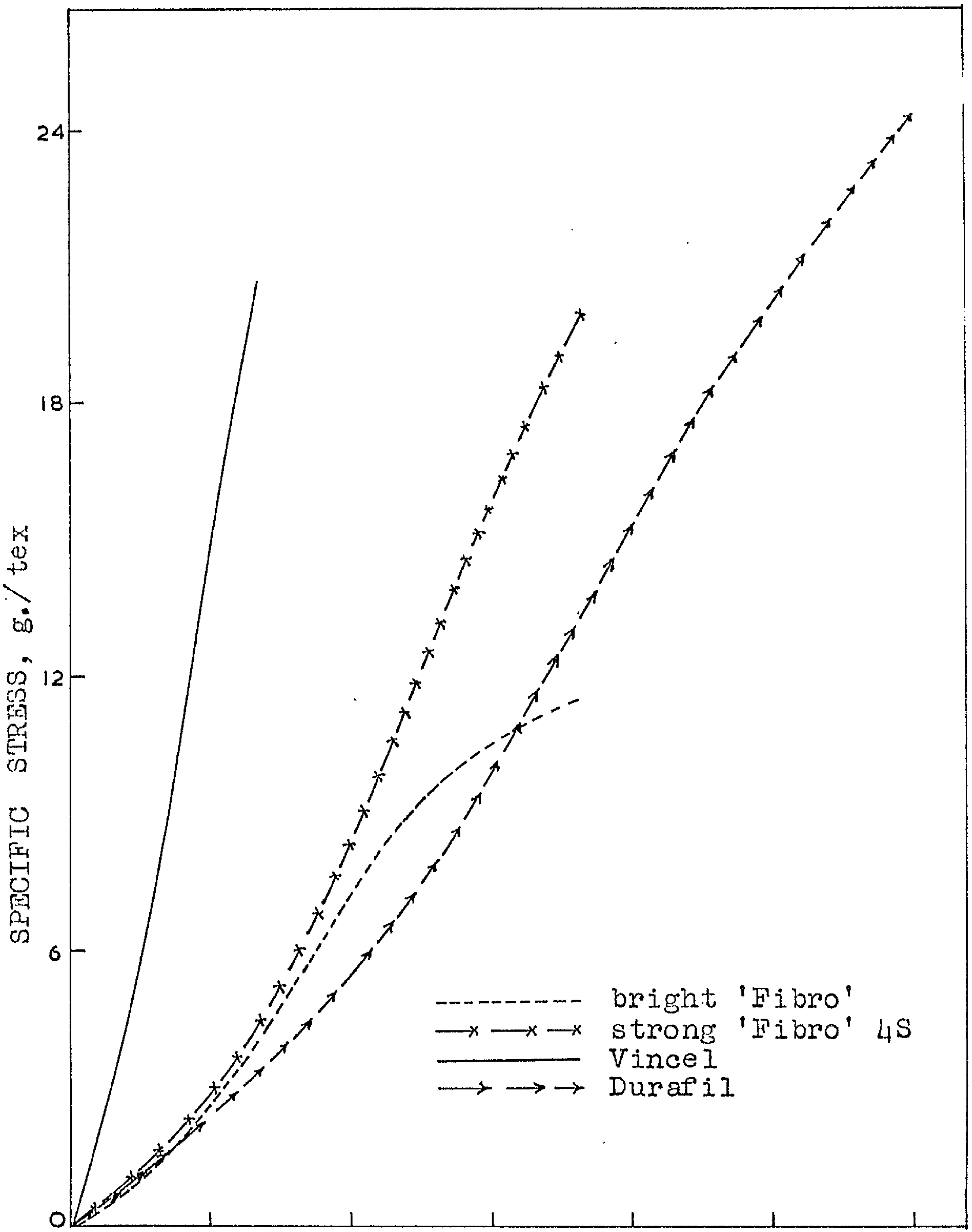

Figure 54 Specific Stress-Extension Curves in Water of Fibres in Set 5 Experiments

from commercial needles by cutting them to 1.5 cm lengths, retaining the eyelet, and bending the cut end to form hooks of about 1 cm length.

A single fibre was threaded through the eye of the hook and fixed temporarily on the stem of the hook by Durofix. The other end of the specimen was then threaded on the second hook, the first hook being allowed to hang at a preset distance to give about the required specimen length (1") and the specimen was then attached to the second hook by Durofix. The hooks were clamped in a small screw clamp in the upright position and the fibres sealed in the eyes of the hooks with Araldite. The unit was then cured at 50° C for 12 hours and the specimen conditioned at 65% r.h. and 20° C for 24 hours before test.

Test conditions

Although in the present investigation experiments were carried out in water at one temperature only (25° C), the apparatus was designed so that work could be carried out at different humidities and temperatures. To allow control due to ambient temperatures it was felt necessary to partition the condition chamber into an upper (or gauge) chamber and a lower (or specimen) chamber. The wire body of the strain gauge would then be in the upper chamber and the specimen holder of the gauge unit in the lower chamber. The chambers were well insulated from each other so that experiments at different temperatures could be performed by merely changing the temperature of the lower chamber, maintaining the upper chamber at 25°C throughout the course of the investigation.

For work in the dry state and/or at different humidity the specimen holder of each gauge was enclosed in an air-tight metallic rectangular cabinet (4" x 4" x 12") with perspex windows. Humidity could be controlled by blowing air over the appropriate salt solution into the air-tight chambers through a closed circuit. The humidity in the chamber was measured by a thermocouple hygrometer.

For wet condition testing, one-litre PYREX glass beakers, tall form, were used as reagent vessels in which preconditioned distilled water or preconditioned standard acid solutions were placed. The vessels were inserted in the cabinet, raised and supported, so that the test samples were immersed in the liquid completely. For the stress-relaxation study in acid solutions, the specimen was conditioned for 24 hours in distilled water, the reagent vessel containing distilled water removed and replaced by one containing preconditioned acid solution and the specimen stretched immediately to obtain the required tension and the change in tension recorded for 24 hours.

The acid used in the present investigation was chemically pure hydrochloric acid and the stress-relaxation study was carried out at six different concentrations ranging from 10^{0}N to 10^{-5}N by steps of 10^{-1}N.

The various sets of experiments carried out during the present investigations have been summarised in Table 18. For the effective comparison of various materials in any one set of the experiments, identical conditions were maintained throughout the set.

Specimen length, Tension and Extension

A specimen mounted and conditioned as described above was brought to experimental condition in a freely hung state in distilled water for an appropriate length of time, care being taken to avoid strain in handling of the specimen. The movable arm of the gauge was lowered by hand turning of the knob attached to bevel gears until the specimen was just taut, any tension applied being easily observed on the recorder. The exact initial length of the specimen was measured by a cathetometer to an accuracy of 0.01 cm while the reading on the dial gauge was taken as the initial reading for calculating extension.

Table 18

Details of Stress-Relaxation Experiments

SET No.	Stress-Relaxation Study at 25°C			Tension at Start of Experiment g	Materials Tested	Figure No.	Table No.
	Medium	Time of Conditioning hr.	Duration of Experiment hr.				
1	Water	1	150	0.7–1.2	Viscose Rayon Fibres (from U1009 fibro fabric)	55-57	19
2	Water	1	24	0.7	Resin Treated Viscose Rayon Fibres	58	20
3	Water, Acid Solutions	24	24	0.95	Resin Treated Viscose Rayon Fibres	59-67	21
4	Water	1	24	1.2 0.75 Cu Am	Viscose, Cuprammonium, Cellulose Acetate, Silk, Nylon, Polypropylene, Polyvinyl Alcohol	68	22
5	Water	1	24	0.8 0.5 - (b)	(a) Bright 'Fibro' (b) Strong 'Fibro' (c) Vincel (d) Durafil	69	23

The specimen was then quickly stretched until the tension observed on the recorder reached the predetermined value (Table 18). The reason for a particular choice of tension has been reported in the results of set 1 experiments.

The reading on the dial gauge was taken and extension calculated by subtracting the initial reading (if any).

Continuous readings were made during the experiment using the two recorders so that knowing the chart calibration the tension on the sample at any time could be obtained. Zero time for measuring relaxation was taken as the time when maximum tension had been reached (76).

Experimental Accuracy

1. Error due to temperature variation of the gauge chamber

The temperature of the gauge chamber was maintained at 25 ±.2° C and there was no variation in the reading or voltage output due to temperature variation of the gauge chamber.

2. Error due to temperature variation of the specimen chamber

The temperature of the specimen chamber was maintained at 25 ±.5° C and it was considered that any error in the experimental results due to temperature variation could be neglected.

3. Error due to rate of straining

Since the specimen was stretched by a hand mechanism, the time taken to reach a predetermined tension could vary slightly from experiment to experiment which could lead to a significant error between test results in the very early stages (up to 10 sec.) of stress-relaxation. The error was neglected because the tension was normalised after relaxation for 1 minute and measurements were carried out over a large period of time - 20 hrs.

4. Sensitivity of the load measurements

As the voltage input was maintained at 7.5 volts, which gave a pen deflection of 9 in. for a 2g load, the deflection could be measured accurately up to 0.05 in. and load up to 0.01g, so that the accuracy of measuring tension was of the order of 1% per gram load.

Thus it was considered that the overall accuracy of the apparatus was satisfactory for the purposes of the present experiments and that reasonable accuracy of results was obtained by taking an average of at least two independant experiments.

CHAPTER 9

RESULTS AND DISCUSSION

Discussion of Results

Results

Various physical properties of fibres have been reported in Table 15, 16, 17. Table 15 gives some physical properties of viscose rayon fibres treated with different resins used in set 1, 2, 3 experiments. Table 16 gives physical properties of fibres in set 4 experiments; whereas physical properties of fibres in set 5 experiments have been reported in Table 17.

The load extension curves for all fibres have been shown in Figures 51, 52, 53, 54. The curves (with one exception Figure 54) have been plotted as load in grammes against percentage extension, in preference to the presentation of stress or specific stress against strain, to enable direct comparison of the tensile behaviour to be made when the effect of extension on the rate of stress decay is considered. Figure 51 shows the load extension curves of viscose rayon fibres at 65% r.h. and 20° C of untreated and resin treated samples. It will be seen that the general effect of the resin treatment is to increase the initial modulus, strength and stiffness and to reduce the extensibility and that the sharp yield point so characteristic of normal viscose rayon tends to disappear with resin treatment. Figure 52 shows the load extension curves of these fibres in water at 20°C, after conditioning in water for 1 hour. It will be seen that the general effect of the resin treatment on viscose fibres in wet state is similar to that in the conditioned state. The load extension behaviour of these fibres in the wet state, but after conditioning in water for 24 hours, has not been shown as a curve as no appreciable change in the curve characteristics was observed from that in the wet state after conditioning for 1 hour but some values have been reported in Table 15. The typical load extension curves of fibres in set 4 experiments, namely, viscose rayon, cuprammonium rayon, cellulose acetate, silk, nylon, polypropylene and polyvinyl alcohol in wet state after conditioning in water for 1 hour, have been shown in Figure 53 and the results agree favourably with those published by Farrow (41). A plot of specific stress against percentage extension of different viscose rayons, bright Fibro, strong Fibro, Vincel, and Durafil have been reported in Figure 54, tests again being made on the fibre in the wet state after conditioning for 1 hour. The results of tenacity, extensibility, and modulus agree favourably with those reported in trade publications of Courtaulds Ltd.

Stress-relaxation curves

The stress-relaxation curves plotted as normalised force against logarithm of time in seconds were obtained from the readings taken from the recorders and have been shown in Figures 58 to 69. These experiments being carried out to cover 5 decades on log time scale and it will be noted that the general shape of the curves is nearly linear.

Normalised force f_t/f_{t_0} at any time 't' is the tension at time 't' divided by the tension at any arbitrarily chosen time 't_o'. The start or the zero time of relaxation is taken at the point of maximum tension (76). In the present experiments tension at 1 minute has been chosen for normalised force calculation. When such a force is plotted against log time, the curve gives the relative rate of relaxation, which is of assistance in comparing different fibres at given set of conditions.

Representation of results

The results of the stress-relaxation experiments could be completely represented from the relative rate plot, if the tension at the time of normalising (which was 1 minute), denier or tex of the fibre, density, and percentage extension were known.

(i) Plot of tension in grammes against log time

Tension in grammes at any time 't' would be normalised force at time 't' multiplied by tension at the time of normalising

$$f_t = f_t/f_{t_0} \times f_{t_0}$$

(ii) Plot of specific stress against log time

Specific stress in g/denier or g/tex at any time 't' would be tension in grammes at time 't' divided by denier or tex.

(iii) Plot of stress in dynes/sq.cm against log time

Stress in dynes/sq.cm at any time 't' would be

$$= \frac{f_t \times 9 \times 981 \times 10^5 \times \text{density}}{\text{denier}}$$

(iv) Plot of modulus, E, against log time

Modulus in dynes/sq.cm at any time 't' would be

$$= \frac{f_t \times 9 \times 981 \times 10^7 \times \text{density}}{\text{denier} \times \text{percentage extension}}$$

Set 1: Stress-relaxation of untreated viscose rayon fibres in water at 25°C

This was a preliminary investigation and formed the basis for subsequent work in the present study. Of the possible variables in the study of stress-relaxation - temperature, humidity, tension or extension and time - only the latter two needed investigation as the work was carried out in water at 25°C. In order to determine the amount of tension to be applied to the fibre and the number of decades of time over which observations be made, a study was carried out on the untreated viscose rayon fibres at four different extensions and over six decades of time (150 hrs) and results have been shown in Figures 55, 56 and 57.

Figure 55 shows the relative rates of relaxation, the force being normalised after 1 minute. It was found that the relative rate of relaxation at 5% extension was higher than that at 8% which in turn was higher than that at 10% extension and 12% extension had the lowest relative rate. The plot of stress against log time has been shown in Figure 56. It was noted that very little change in tension occurred after 20 hours of relaxation (at 5% extension from 20 hrs to 150 hrs tension decay was 0.005g, at 8% extension tension decay was 0.015g). Thus it would appear that the

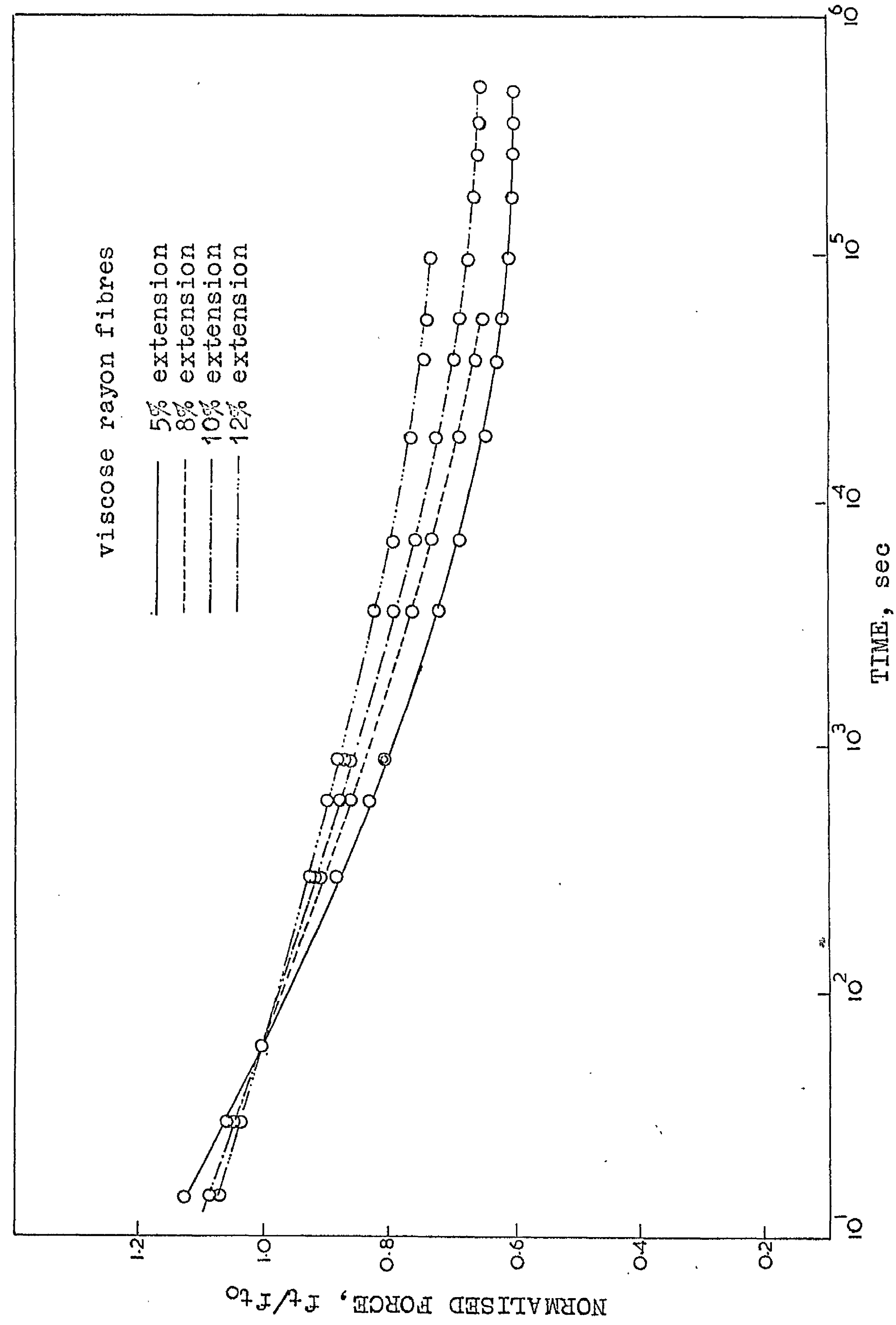

Figure 55 Relative Rates of Relaxation of Viscose Rayon Fibres at Different Extensions

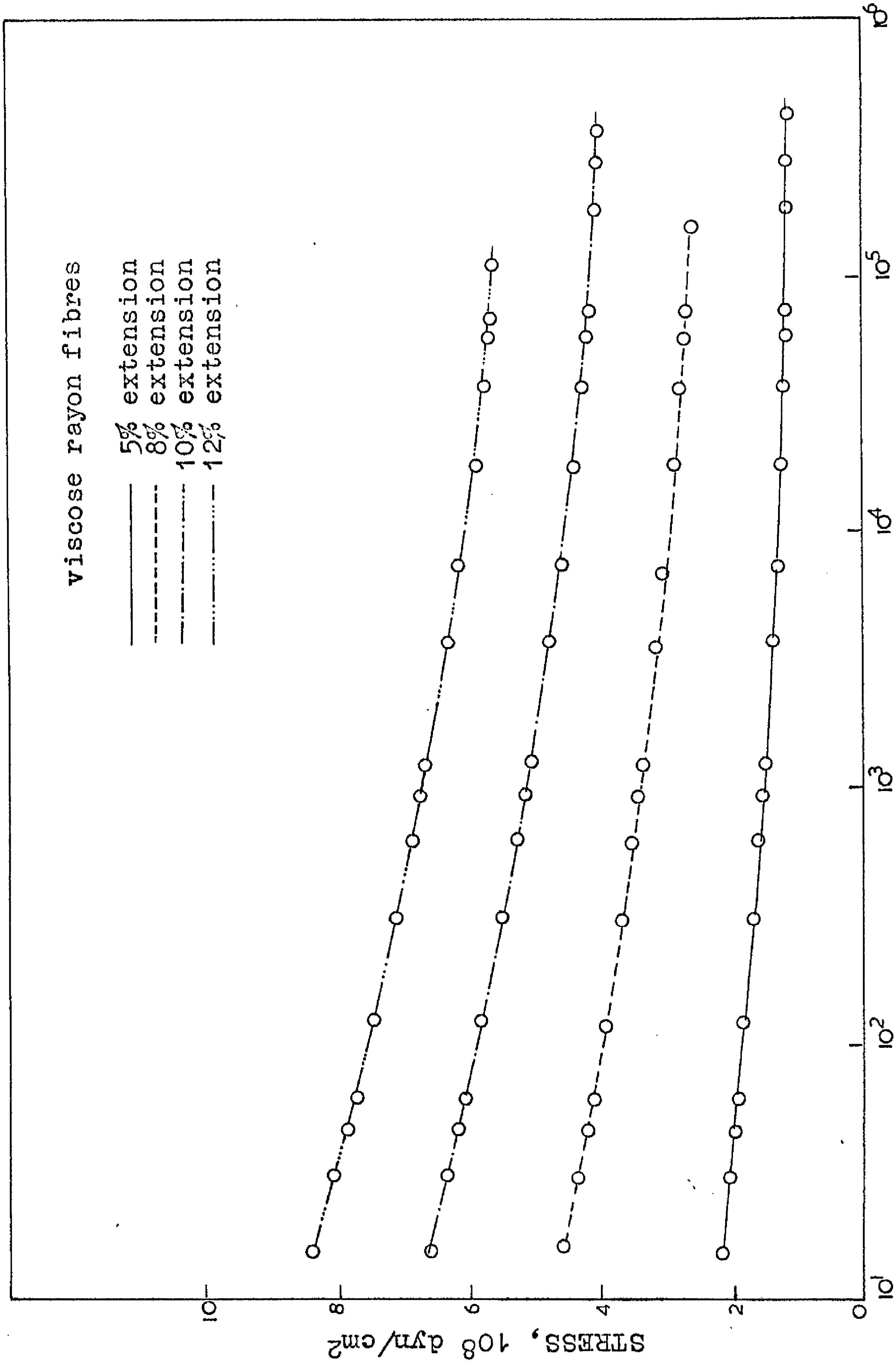

Figure 56 Rate of Stress-Relaxation of Viscose Rayon Fibres at Different Extensions

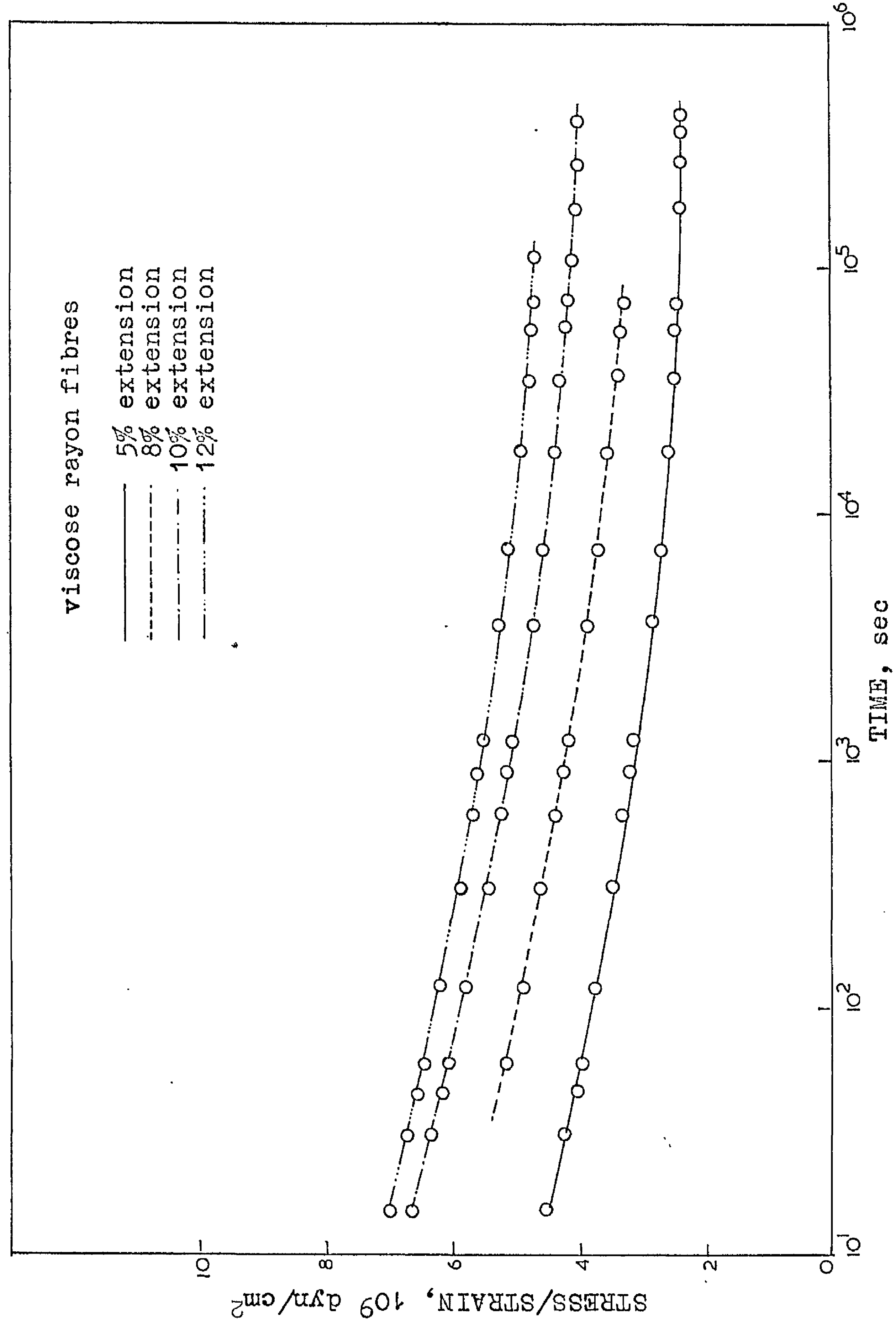

Figure 57 Rate of Change of Modulus of Viscose Rayon Fibres at Different Extensions

relaxation was nearly complete after 20 hrs and that the force after 20 hrs could be taken as the final retractive force. Modulus plotted against log time has been shown in Figure 57, but for reasons already mentioned no attempt could be made to compute a composite curve by shifting the modulus plot along log time axis.

Further details regarding tension after 1 minute relaxation and average percentage change in tension per decade of time have been reported in Table 19.

In the subsequent work the study of stress-relaxation was carried out over 5 decades of time and the samples were extended to record the initial tension in the range of 0.7 - 1.2g. A tension of 4g had been reported in previous work (178) but in present work this would approach or exceed the breaking strength of the fibres. A range of 0.7g - 1.2g was suggested for the present investigation, the higher value of 1.2g was taken for filaments in set 4 experiments, where filaments had denier values between 4 and 6, and lower value of 0.7g for fibres in set 2 where fibres were 1.5 denier. However, for stress-relaxation in acid solutions, set 3 experiments, a slightly higher value of ≈1g was taken.

Table 19

Details of Stress-Relaxation Study in Set 1 Experiments on Untreated Viscose Rayon Fibres

Tension, g at 1 min. Relaxation f_{t_0}	Extension, %	Rate of Decay in Tension, % per Decade in Time	Density of Fibre at 0% r.h.	Tex	Figures
0.22	5	11.7	1.521	0.167	55,56,57
0.51	8	11.0			
0.70	10	10.2			
0.88	12	8.4			

Results of the subsequent sets of experiments have been reported in the form of rate plots supplemented by other relevant information in tables, thus eliminating the necessity of a large number of figures.

Set 2: Stress-relaxation of untreated and resin treated viscose rayon fibres in water at 25°C

The relative rates of stress-relaxation of these fibres have been shown in Figure 58 and Table 20. It will be seen that the rate plots were nearly linear for all samples except samples 3 and 4 which showed a considerable divergence from linearity, the rate of tension decay being a maximum between 10^3 and 10^4 seconds. Also the relative rates of resin treated samples were higher than the untreated viscose rayon sample, with the exception of sample 3 which showed a lower relative rate in the early stages of the experiment (1-10 min). It could be said therefore, that the general tendency of resin treatment has been to increase the rate of relaxation and the final retractive force after 20 hours was high in case of untreated sample followed by sample 8, 5, 6, 1, 7, 2, 3 and 4 in that order.

One reason for the anomalous behaviour of samples 3 and 4 (both ethyleneurea-formaldehyde treated viscose) could be that the time of conditioning in water (1 hour)

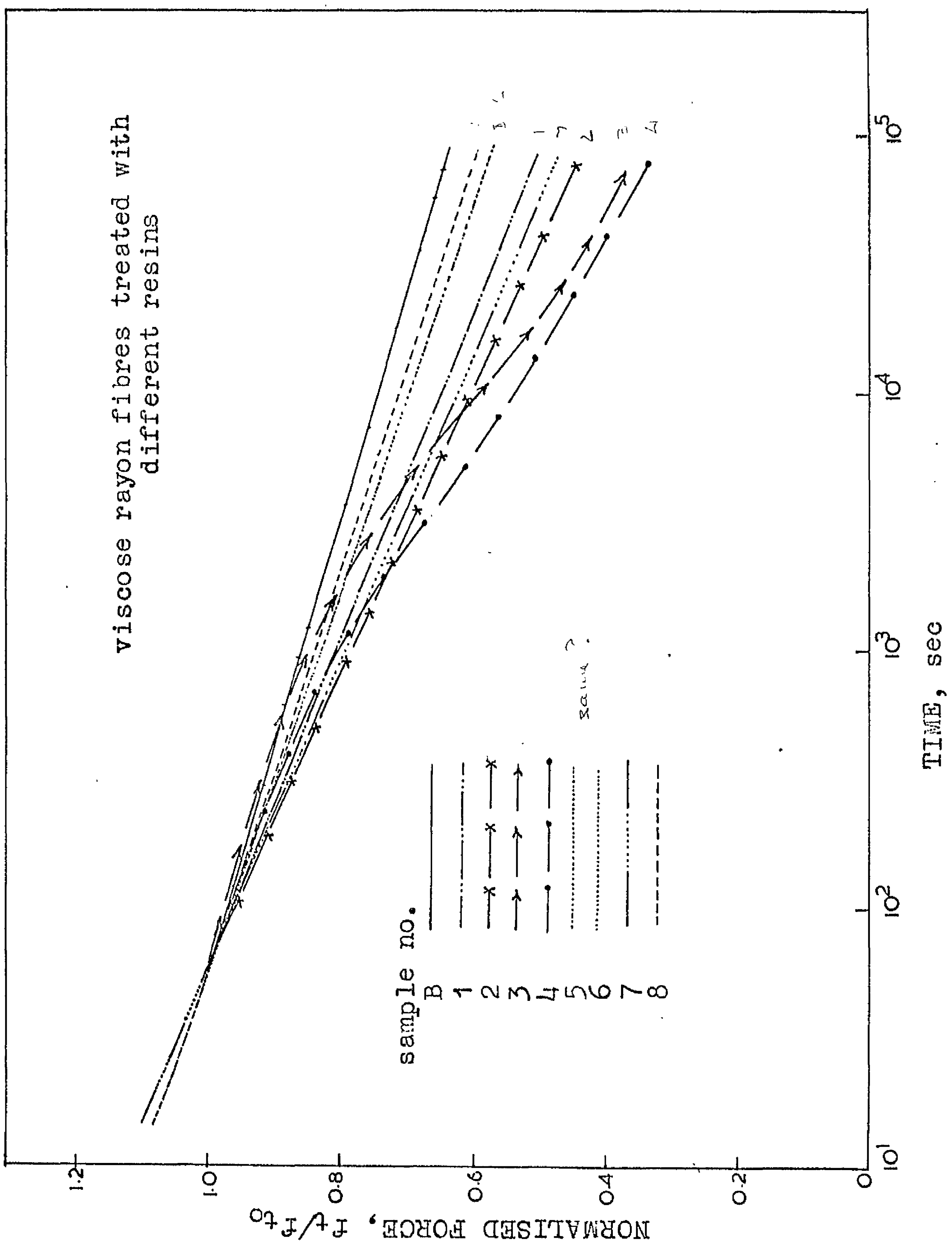

Figure 58 Relative Rates of Relaxation of Fibres in Water at 0·7g Tension

Details of Stress-Relaxation Study in Set 2 Experiments

Sample No.	Fibres Treated With	Tension, g at 1 min. Relaxation f_{to}	Extension %	Rate of Decay in Tension % Per Decade of Time	Tex	Density 0% r.h.	Figure
1	Melamine-Formaldehyde	0.476	5.8	16	0.179	1.514	58
2	Melamine-Formaldehyde	0.400	4.8	18	0.183	1.511	58
3	Ethyleneurea-Formaldehyde	0.558	6.5	21	0.184	1.509	58
4	Ethyleneurea-Formaldehyde	0.578	5.0	22	0.191	1.506	58
5	Methylatedurea-Formaldehyde	0.50	6.0	13	0.185	1.517	58
6	Methylatedurea-Formaldehyde	0.49	4.5	13	0.193	1.514	58
7	Urea-Formaldehyde	0.50	4.7	17	0.190	1.514	58
8	Urea-Formaldehyde	0.50	7.5	13	0.178	1.519	58
B	Untreated	0.51	8	11.0	0.167	1.521	58

might not be sufficient to wet these samples completely and/or that the distilled water might be acidic enough (pH 5) to cause hydrolysis of ethyleneurea-formaldehyde resins in the sample. These points led to the following set of experiments being carried out.

Set 3: Stress-relaxation of untreated and resin treated viscose rayon fibres in water and in acid solutions

The study in this set differed from the preceding sets as far as the time of conditioning in water was concerned, it being considered necessary to investigate the behaviour after a prolonged time of wetting. A stress-relaxation study was therefore carried out for all samples after 24 hours conditioning in water.

The relative rates of stress-relaxation of these fibres have been shown in Figures 59 to 67 and Table 21. It was observed that for experiments in water the rate plots were nearly linear for all samples, the least relative rate of decay being observed in the case of sample B (untreated) followed by 3, 4, 8, 5, 6, 7, 1 and 2 in increasing order. The final retractive force after 20 hours was highest in the case of sample B and least for sample 2, with the other samples lying in the same order reported above which is very

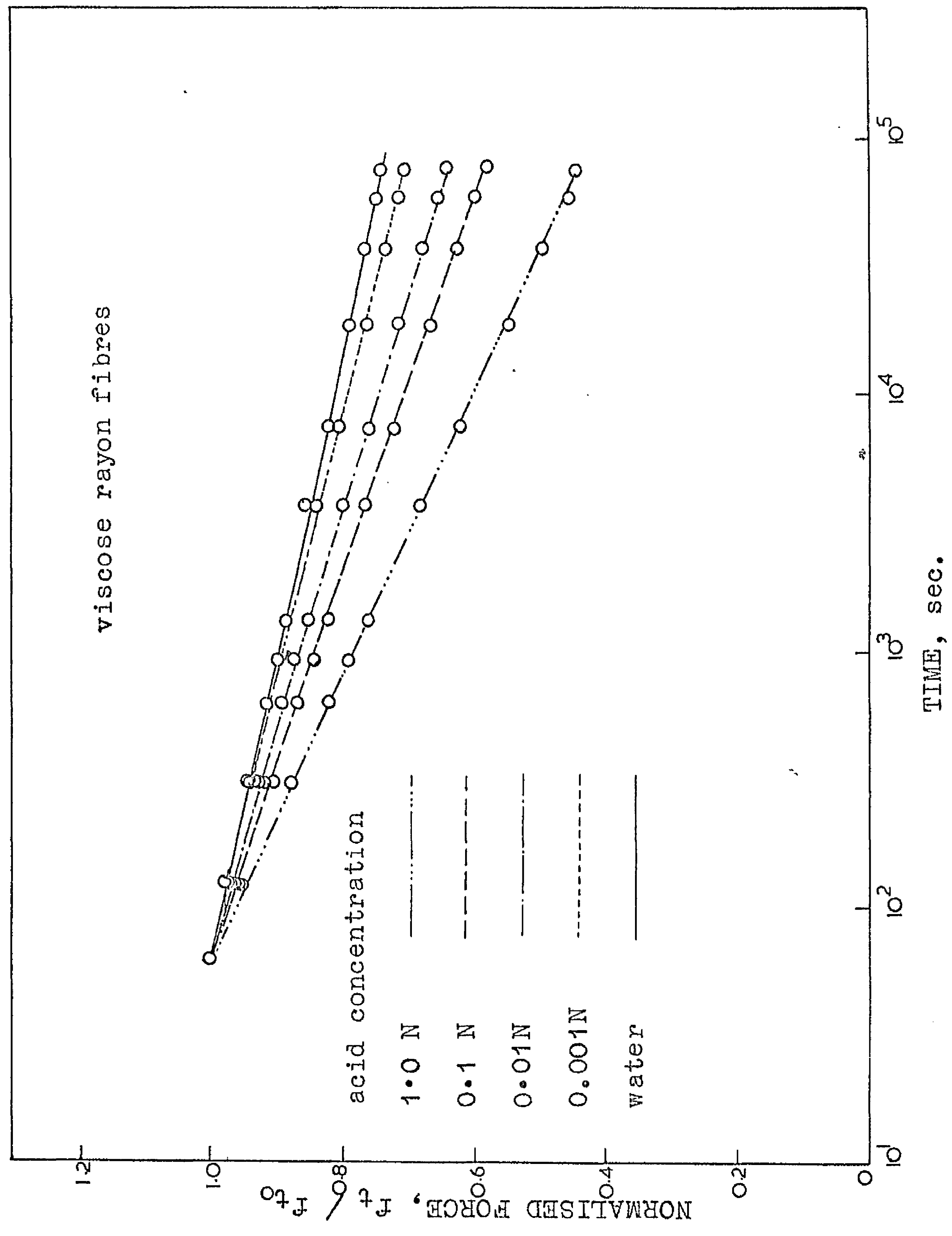

Figure 59 Relative Rates of Relaxation of Fibres in Water and in Acid Solutions at 0·95g Tension

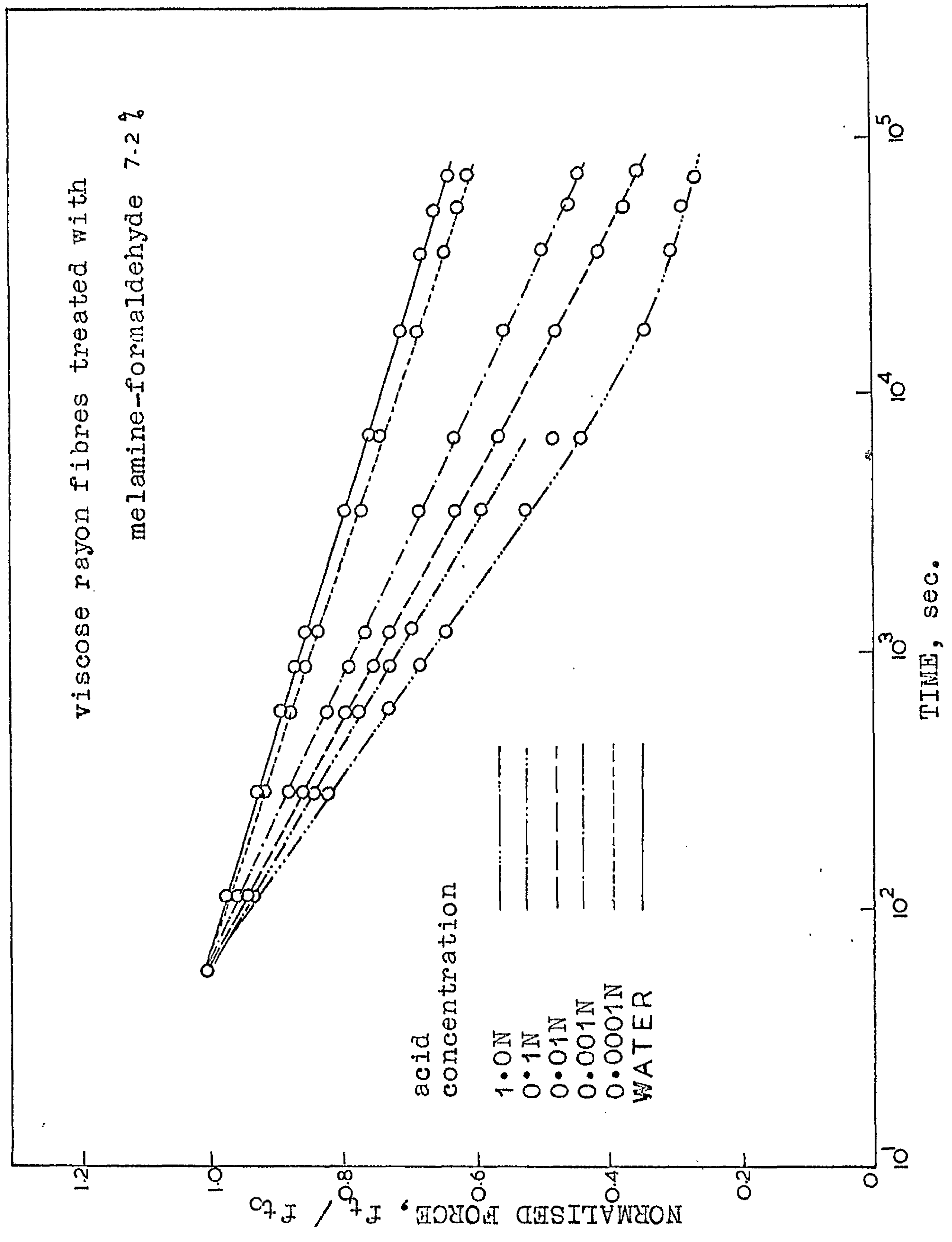

Figure 60 Relative Rates of Relaxation of Fibres in Water and in Acid Solutions at 0•95g Tension

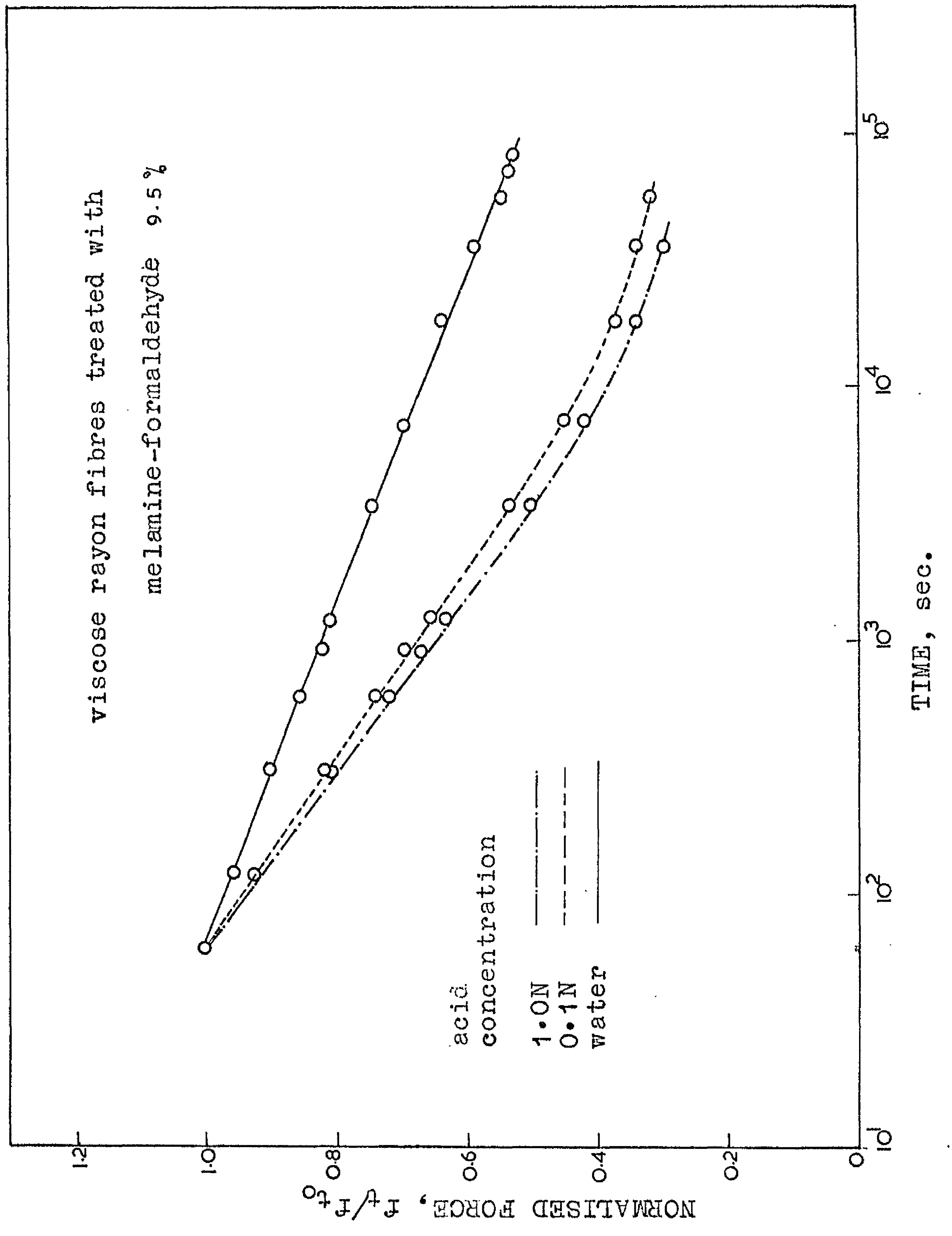

Figure 61 Relative Rates of Relaxation of Fibres in Water and in Acid Solutions at 0·95g Tension

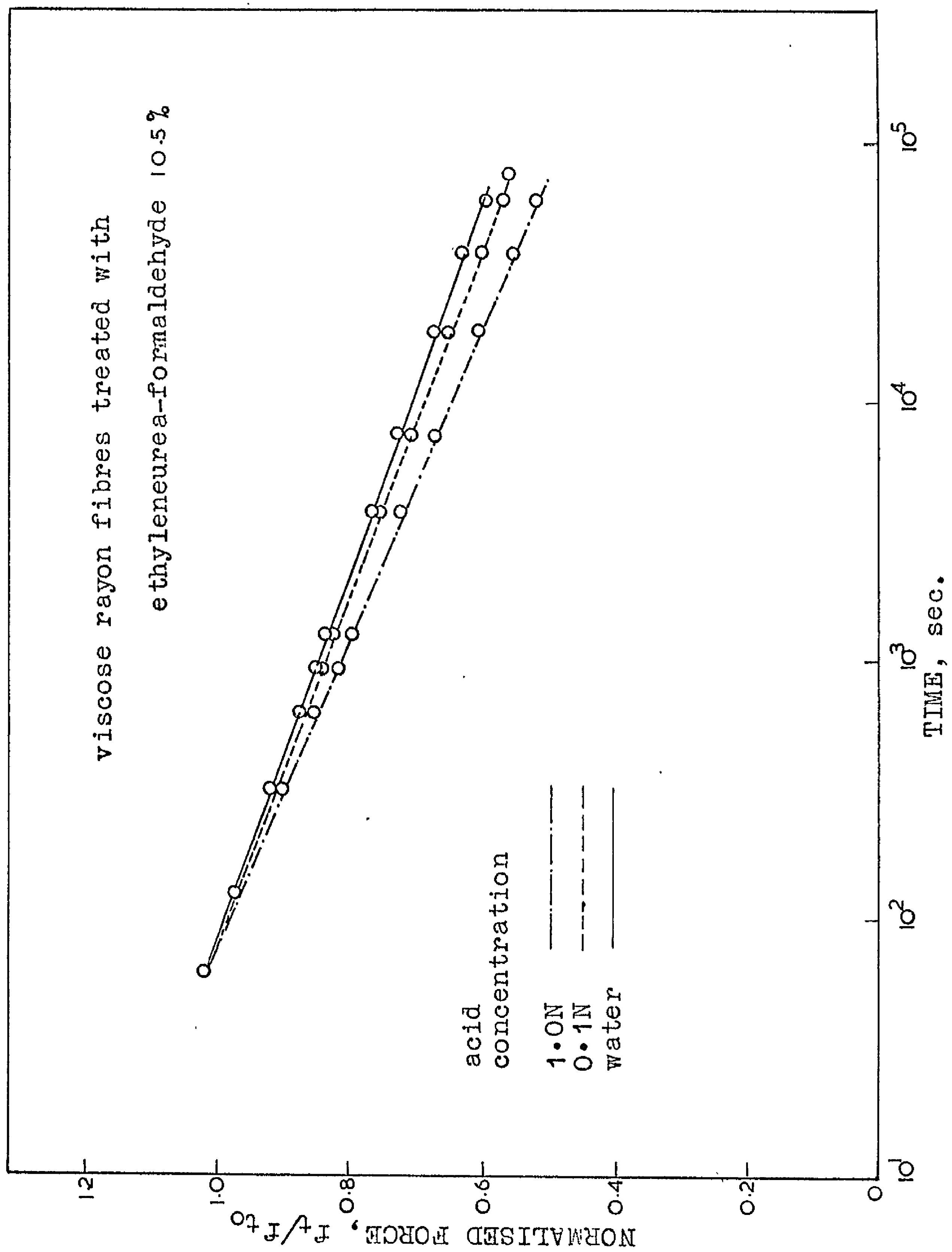

Figure 62 Relative Rates of Relaxation of Fibres in Water and in Acid Solutions at 0·95g Tension

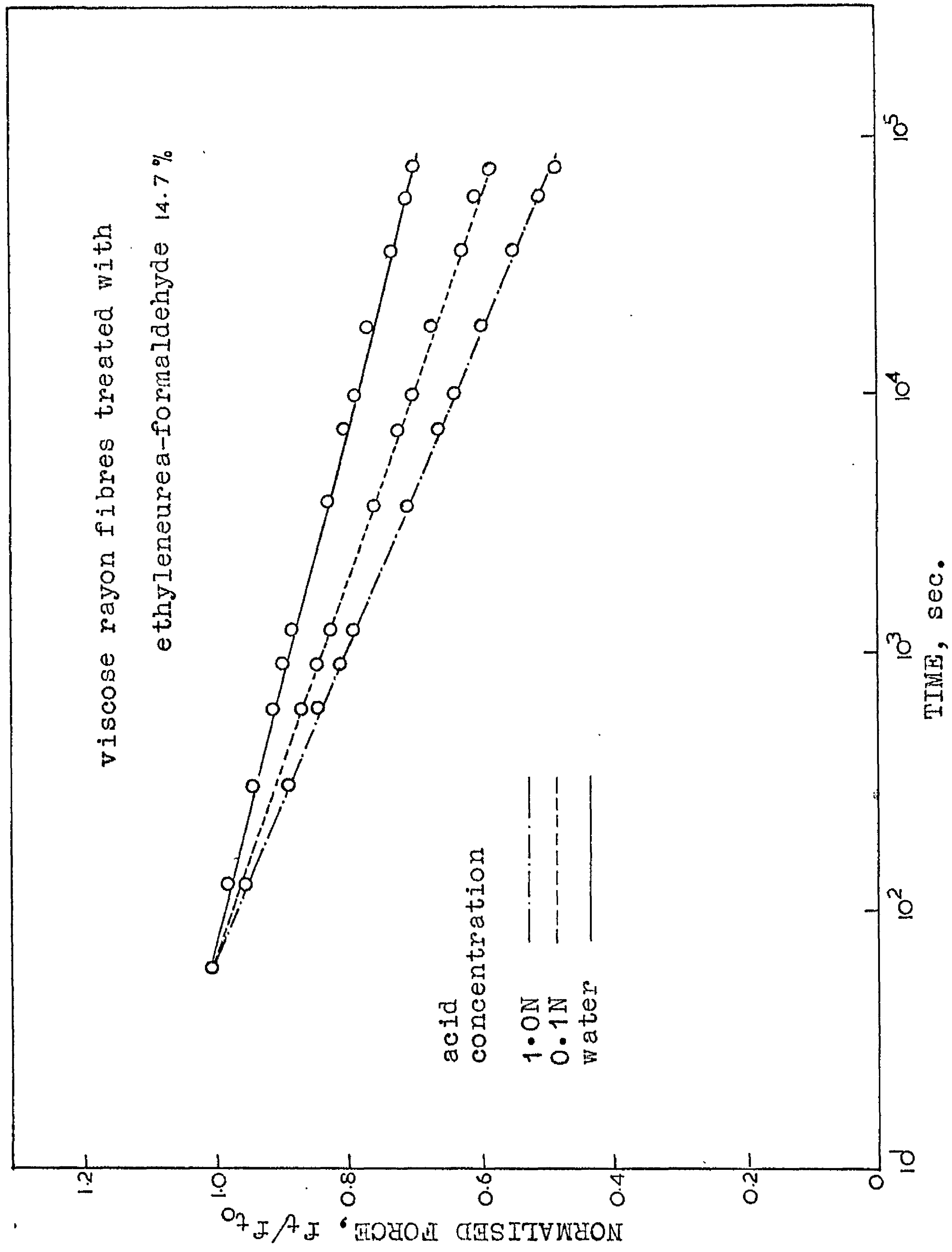

Figure 63 Relative Rates of Relaxation of Fibres in Water and in Acid Solutions at 0·95g Tension

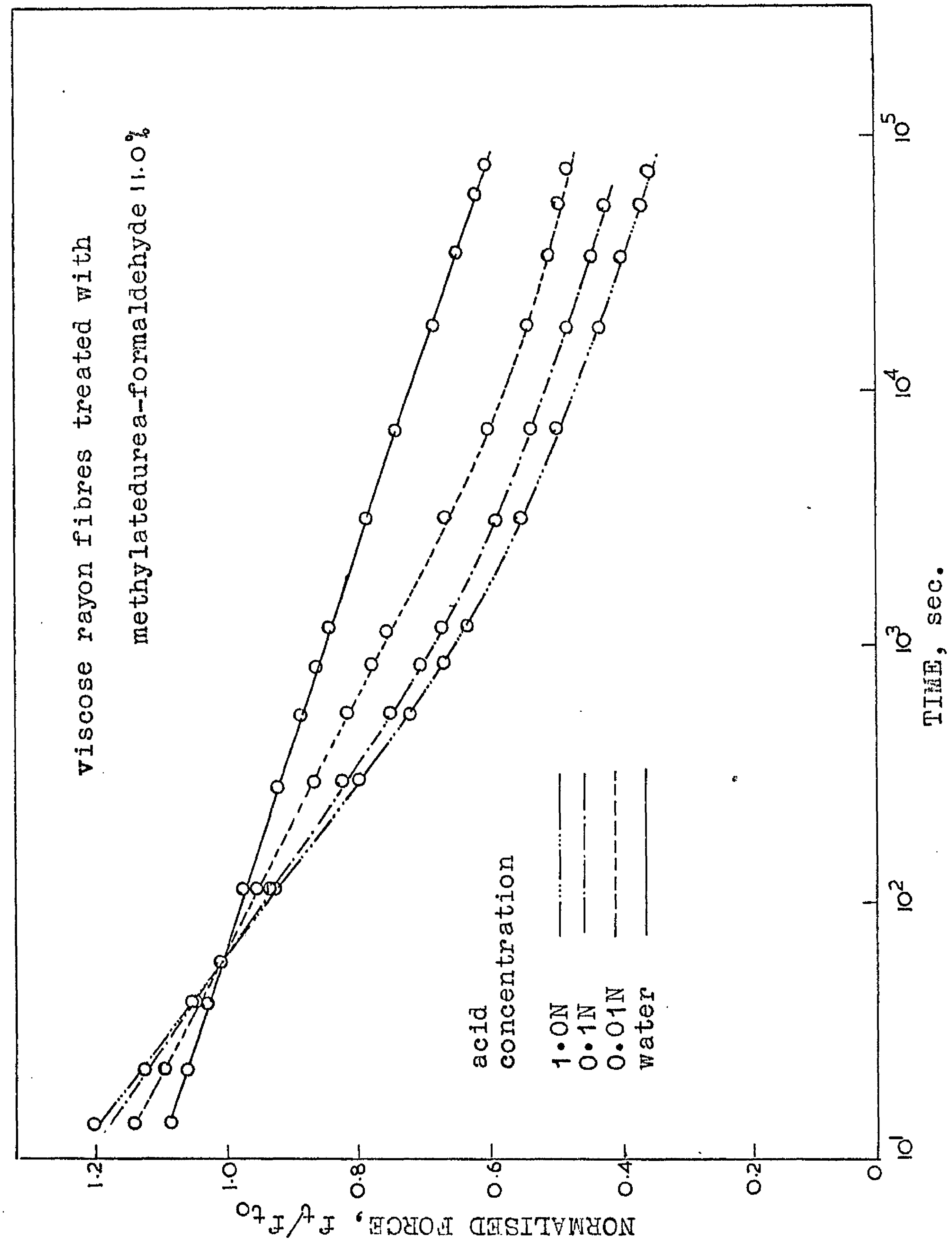

Figure 64 Relative Rates of Relaxation of Fibres in Water and in Acid Solutions at 0·95g Tension

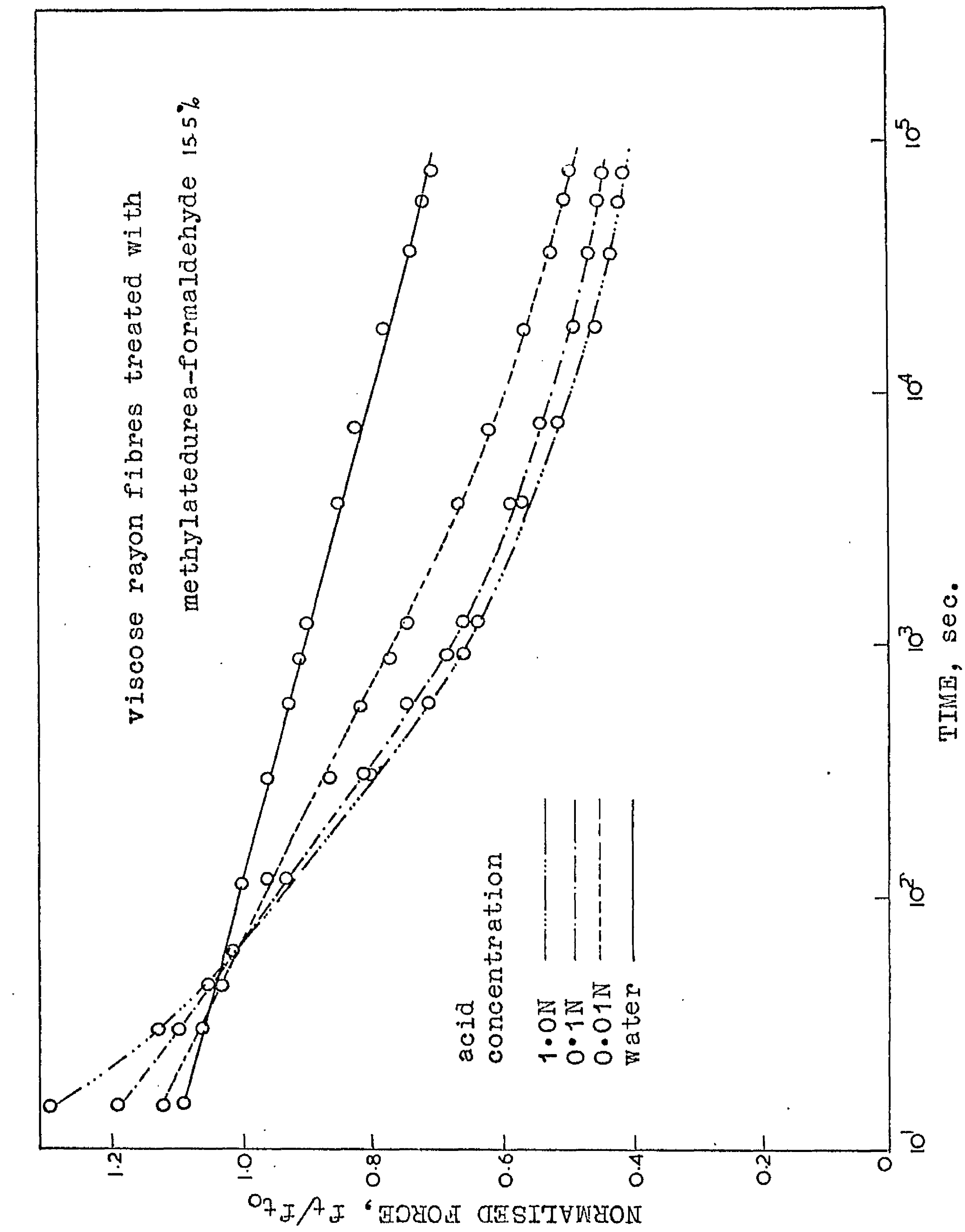

Figure 65 Relative Rates of Relaxation of Fibres in Water and Acid Solutions at 0·95g Tension

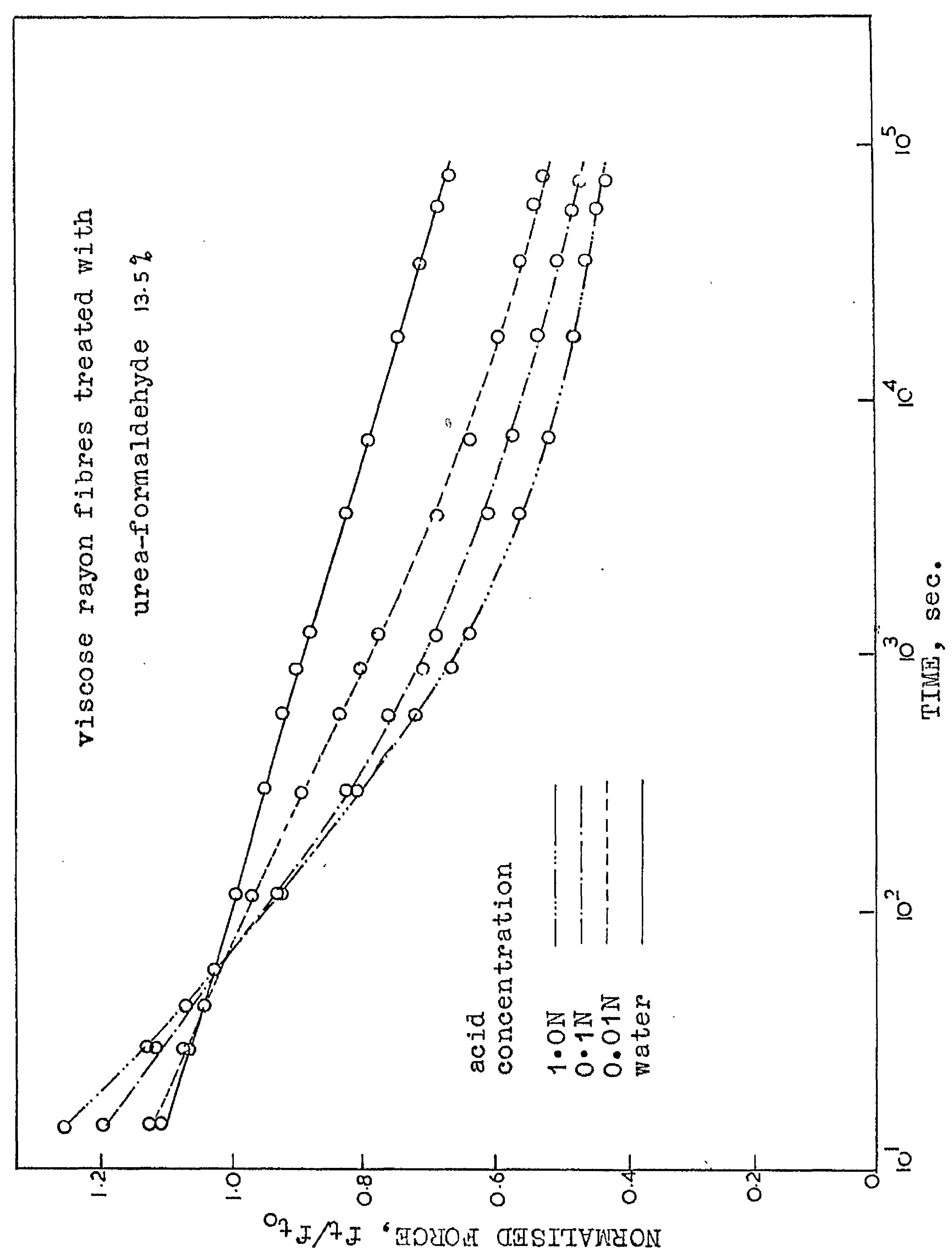

Figure 66 Relative Rates of Relaxation of Fibres in Water and in Acid Solutions at 0·95g Tension

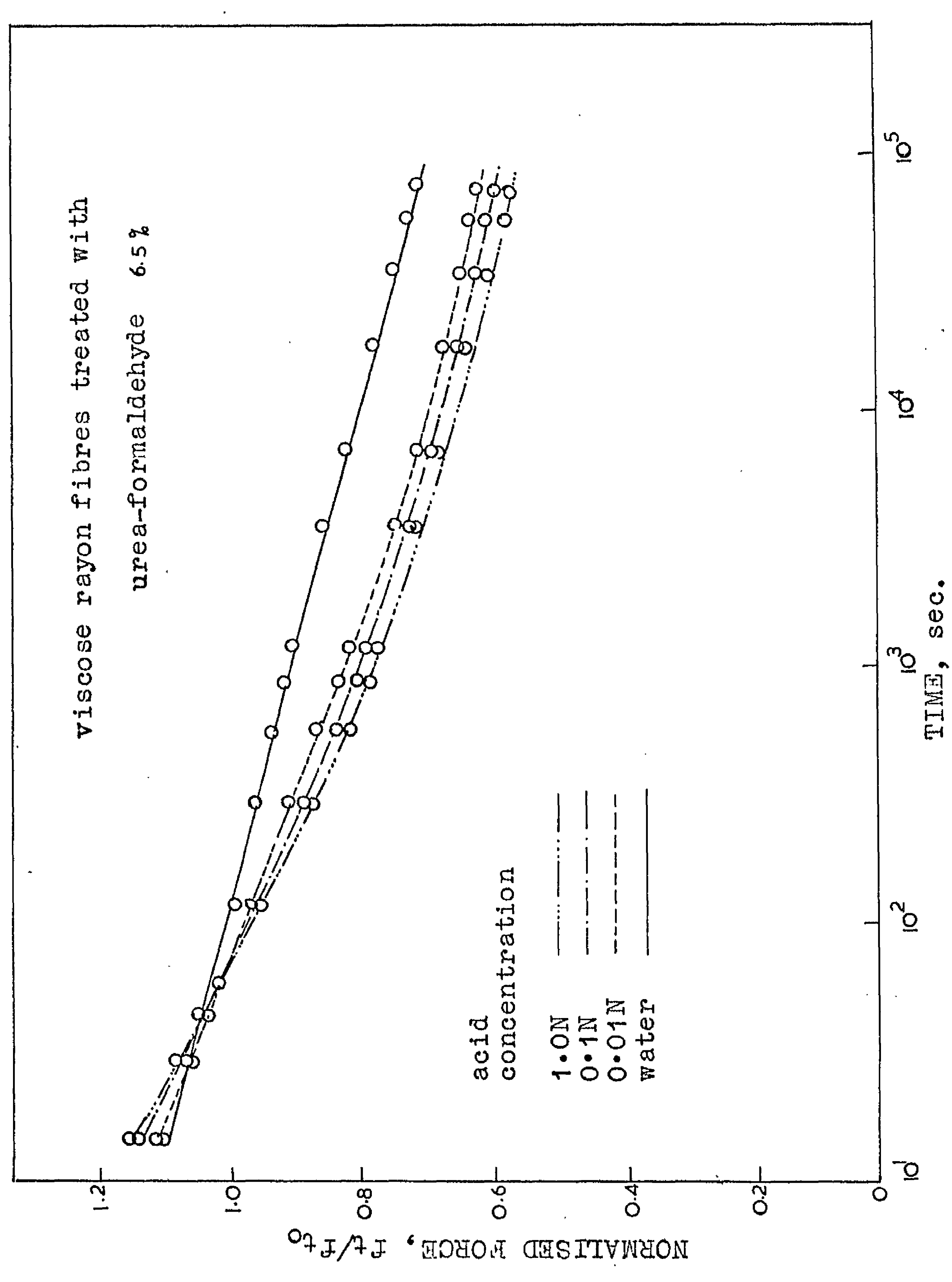

Figure 67 Relative Rates of Relaxation of Fibres in Water and in Acid Solutions at 0·95g Tension

Table 21

Effect of Acid Concentration on Stress-Relaxation of Fibres in Set 3 Experiment

ample No.	Tension at 1 Min.	Extension %	Rate of Decay in Tension % Per Decade of Time				Fig. No.
			1.0N HCl	0.1N HCl	0.01N HCl	Water	
B	0.665 1N 0.69 .1N 0.725 .01N 0.78 Water	11	18	13	11.7	8	59
1	0.56 0.575 0.58 0.625	7.5	27	23	22	11.2	60
2	0.55 0.565 - 0.61	6.8	28	25	-	15.5	61
3	0.655 0.700 0.725 0.73	8.5	17	14	14	10.4	62
4	0.655 0.67 0.75 0.755	7.0	18	14.5	14	10.6	63
5	0.55 0.56 0.585 0.72	7.8	29	26	20	10.8	64
6	0.56 0.57 0.64 0.75	6.0	32	30	20	10.8	65
7	0.56 0.57 0.64 0.69	7.0	35	29	17	11.7	66
8	0.625 0.665 0.685 0.71	10.0	20	18.5	14.5	10.7	67

nearly the same as that in set 2 experiments, except that the relative rates of relaxation of samples 3 and 4 were now nearly the same as that of the untreated sample B.

Further tests were carried out by replacing water after 24 hours conditioning with acid solutions, and the relative rates of relaxation of untreated viscose rayon sample B in different concentrations of hydrochloric acid have been shown in Figure 59. It will be seen that the relative rates of relaxation were greater the higher the concentration of the acid solution, and that the rate plots were linear at all concentrations.

When similar (acid) investigations were carried out on sample 1, it was observed that the curves in 1N and 10^{-1}N hydrochloric acid solution were not linear, Figure 60. They showed rapid relative rates up to almost 10^4 seconds and thereafter the rate suddenly dropped, whereas in weaker acid solutions, and in water, the curves showed linear relative rates and the rate decreased with lower concentrations of acid. In all cases the relative rates were higher than those of the untreated sample B.

Similar effects were observed on samples 2, 5, 6, 7 and 8. Sample 2, Figure 61, gave rapid linear plot up to 10^4 seconds and thereafter the rate dropped in 1.0N and 10^{-1}N HCl. Also the rates with sample 2 were higher than the corresponding rates with sample 1.

Samples 5, 6, 7 and 8 as shown in Figures 64, 65, 66 and 67 gave rapid linear curves in 1.0N and 10^{-1}N up to 10^3 seconds, whereas with 10^{-2}N acid linear curves up to 10^4 seconds were found and thereafter the rate dropped. Greater resin concentration produced a higher rate of relaxation.

Linear curves for all concentrations of acid investigated were found for Samples 3 and 4, Figures 62, 63 and furthermore, the relative rates of relaxation were nearly the same as those of the untreated sample B for all corresponding concentrations of acid.

Set 4: Stress-relaxation of viscose rayon, cuprammonium rayon, cellulose acetate, silk, nylon, polypropylene, and polyvinyl alcohol in water at 25°C.

The relative rates of stress-relaxation of these fibres have been shown in Figure 68 with further details in Table 22. It was found that the relative rates of viscose rayon, cuprammonium rayon, silk, nylon and polyvinyl alcohol could be shown by a single curve, shown as 'B' in the Figure 68 and that it is nearly linear. The same curve has been redrawn by normalising after 1 hour instead of 1 minute and has been reported as 'A', Figure 68. The dark circles on the curve 'A' are the points taken from the work published by Lemiszka and Whitwell (178) on stress-relaxation of

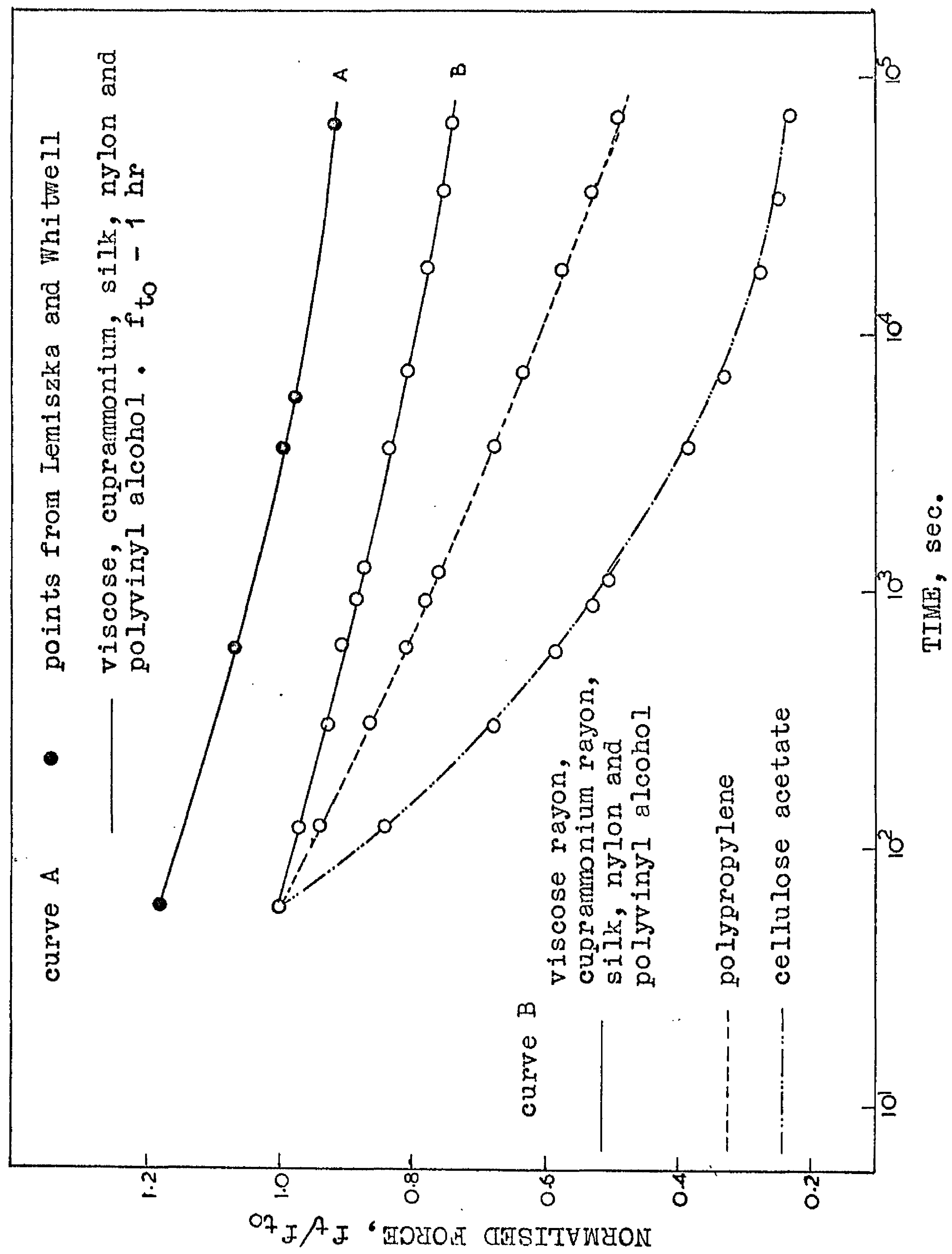

Figure 68 Relative Rates of Relaxation of Fibres in Water at 1·2g Tension

Table 22

Details of Stress-Relaxation Study on Fibres in Set 4 Experiments

Material Tested	Tension at 1 Min.	Extension %	Rate of Decay in Tension Per Decade in Time	Figure
Viscose Rayon	0.9	5	8.3	68
Cuprammonium Rayon	0.59	9.5	8.3	68
Cellulose Acetate	0.5	5	21.6	68
Silk	0.88	4.8	8.3	68
Nylon 66	0.91	4.0	8.3	68
Polypropylene	0.8	1.2	15.9	68
Polyvinyl Alcohol	0.87	1.5	8.3	68

different materials in water at 30° C. Polypropylene, however, has a higher relative rate but a linear plot, whereas cellulose acetate gave an extremely high relative rate and a nonlinear plot.

Set 5: Stress-relaxation of bright Fibro, strong Fibro 48, Vincel and Durafil in water at 25°C.

The relative rate of stress-relaxation of these fibres have been shown in Figure 69 with further information in Table 23. It will be seen that the relative rates of these fibres have been represented by a single curve which is nearly linear.

Discussion of Results

Stress-relaxation of different fibres

Stress-relaxation studies of the following standard or normally oriented textile fibres have shown that viscose rayon, cuprammonium rayon, silk, nylon 66, and polyvinyl alcohol exhibit the same relative rate of relaxation, in spite of the fact that these materials contain different types or amounts of primary and secondary bonds. It has been suggested by Lemiszka and Whitwell (178) that since the secondary linkages are known to have bond strengths of

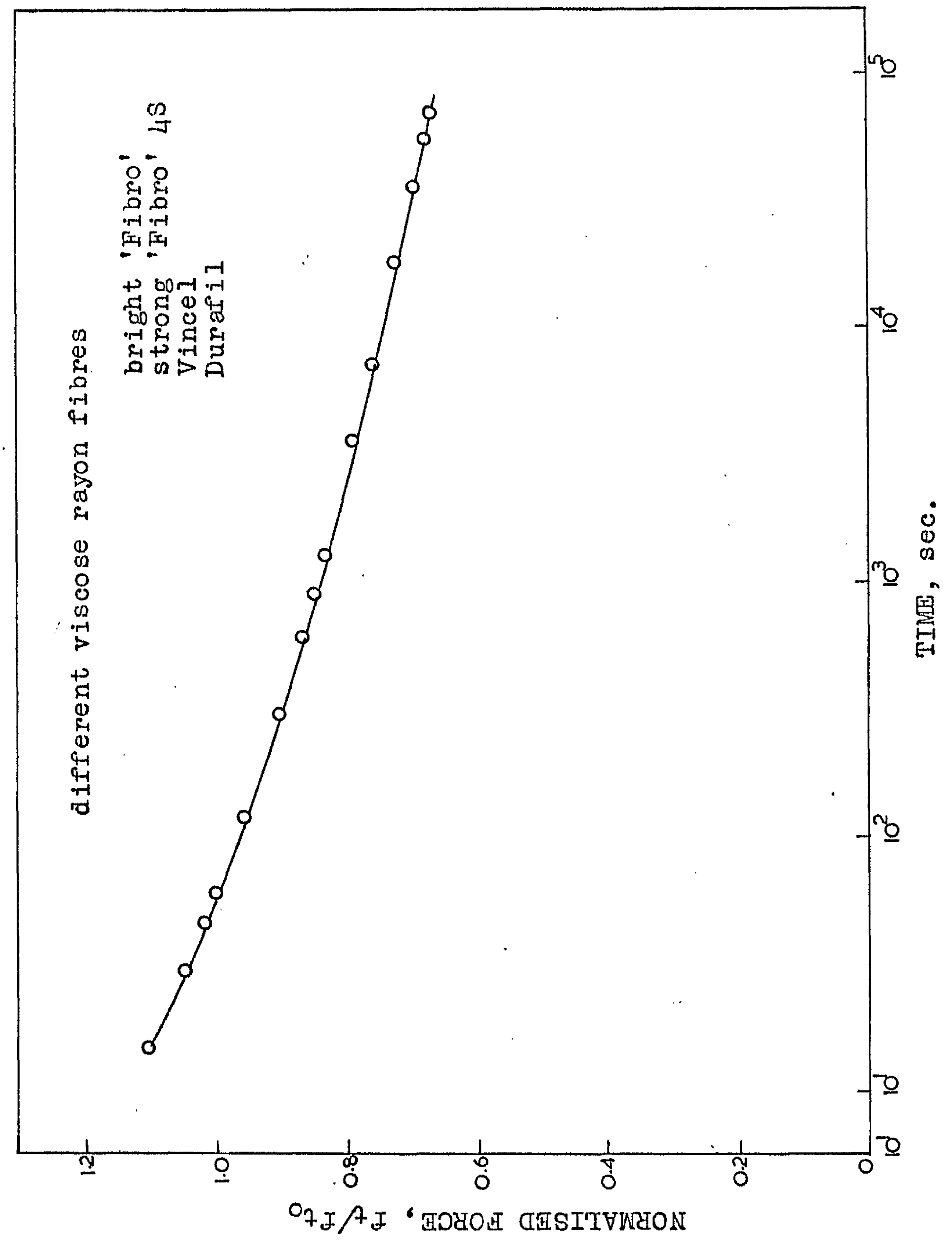

Figure 69 Relative Rates of Relaxation of Fibres in Water at ~~0.8g~~ Tension 4.8g/tex

Table 23

Details of Stress-Relaxation Study of Fibres in Set 5 Experiments

Material Tested	Tension at 1 Min. g	Extension %	Percentage Decay in Tension Per Decade in Time	Density 65% r.h.	Tex	Figure
Bright 'Fibro'	0.56	9	10.3	1.507	0.167	69
Strong 'Fibro' 48	0.387	8.5	10.3	1.498	0.11	69
Vincel	0.6	3	10.3	1.511	0.167	69
Durafil	0.54	11	10.3	1.496	0.167	69

approximately 4.5 Kcal/mol or less compared to values of 150 Kcal/mol or more for primary linkages, it seems probable that the stress-relaxation in distilled water has been brought about by the breakdown or scission of the weaker secondary bonds common to all materials for the rate of relaxation to be in agreement. However, it could be argued that these materials might have varied rates of relaxation, but since the stress-relaxation curves in water would occupy the far or the near completion end of a composite relaxation curve, calculated from stress-relaxation data at different humidities using superimposition principles, the difference in the relative rates of different fibres could then tend to be insignificant.

Cellulose acetate and polypropylene seemed to behave differently. Results concerning peculiarities in stress-relaxation behaviour for cellulose acetate have been given by Meredith (210) and confirmed by Wegener (365). Meredith (210) also showed that the anomalous behaviour, in which the stress after 10^3 seconds was greater at 2% extension than it was at 5% and 10% extensions for the first relaxation, disappeared on mechanical conditioning. Higher extensions produce higher stresses at all times and the convergence of the relaxation curves for all extensions from 1% to 10%

in to a single curve beyond 10^5 second has been demonstrated. The reason for the disappearance of the anomaly was stated that with mechanical conditioning, plastic flow was eliminated so that the temperature of the fibre was not raised on stretching, i.e. relaxation takes place at constant temperature. Since the present investigation was carried out in water, any rise in temperature due to plastic flow should be quickly dissipated and the anomaly should disappear; nevertheless a very high rate of relaxation was observed. It has been reported by Farrow (85) that the time of wetting plays an important part on stress-strain behaviour of cellulose acetate. After a short period of soaking the initial high modulus part of the stress-extension curve is practically eliminated but with continued soaking the feature of the curve is progressively re-established. In water at 20° C a period of some days is required to reach equilibrium. Since in the present investigation the time of wetting was 1 hour an interim situation could occur.

Polypropylene was the other fibre which gave a higher rate of relaxation and while as it might be suggested that the form of polypropylene could be an important factor, the unpublished work on different polypropylene samples carried out in this department by Fyfe (104a) is of special interest as it has been shown that the rate of relaxation of the polypropylene sample used in the present investigation was higher than the other polypropylene samples used in his study and the difference in the rate of relaxation can be explained on the basis of different molecular weights observed. Explaining these anomalies, it might be suggested that different fibres relax at the same relative rate in water when stretched to a predetermined tension. The above results are further supported from the reported work by Lemiszka and Whitwell (178) who also obtained the same relative rates of relaxation for all the fibres and these included cellulose acetate and polypropylene. Unfortunately, their work gave no indication of the stress-strain behaviour nor the tex of the filaments used, the region of the stress-relaxation study is not known from their tension values. Nevertheless, it is interesting to note that their values of normalised force for all fibres fitted the relative rate plots of viscose rayon, cuprammonium rayon, silk, nylon and polyvinyl alcohol presently investigated.

Stress relaxation of viscose rayon treated with different resins

Having observed that different textile fibres, including viscose rayon, relaxed at the same relative rate, the different relative rates of relaxation of resin treated viscose rayons were surprising.

Two aspects of resin finished fibres which might have an important bearing may be recalled:-

(a) Alteration in physical structure

Some alteration in physical structure of a resin treated fibre might be expected with the bulky polymer of resin deposited and/or chemically reacted in the amorphous or less ordered regions of the fibre which would prevent the chains in the vicinity of the resin polymer coming closer and hence leave a more open structure. Also a small fraction of the resin is reported (235) to be involved in the formation of covalent cross-linkages, with the balance being taken up in the formation of intramolecular or intrachain bridges of some sort, which would reduce the possibility of hydrogen bond cross-linking between cellulose molecules. The result would be the formation of covalent cross-links at the expense of hydrogen bonds. Thus bulkier the resin polymer, the more open the structure, the more the physical blocking of secondary forces, the easier the segmental motion, and the greater would be the rate of relaxation.

(b) Chemical effects

It has been shown in Part 1 that resins could be removed by acid hydrolysis under mild acidic conditions, it would be logical to surmise that some of the acid sensitive bonds between the resin and the cellulose could be ruptured in distilled water, which tends to be acidic due to the absorption of carbon dioxide from the atmosphere and in this case had a pH value of 5.2 so that the differential reactivity of acid sensitive bonds of different resins would give different relative rates. This argument is strengthened by the paper of Reeves et al. (268) who showed the susceptibility to acid hydrolysis of amino methylol compounds with cellulose and that the partial removal of many finishes under less acid conditions of pH 4 - 5 could occur.

Considering the above aspects and the results reported in Part 1 (chemical) and in Part 11 (physical), it might be suggested that melamine-formaldehyde being the bulkier of the resins investigated should ~~have~~ lead to a higher relative rate of relaxation, followed by urea-formaldehyde, ethyleneurea-formaldehyde and methylatedurea-formaldehyde in the decreasing order, and also the relative rate should increase the higher the concentration of the resin polymer in the fibre. Whereas, ranking according to their susceptibility to hydrolysis, would be ethyleneurea-formaldehyde, methylatedurea- and urea-formaldehyde followed by melamine-formaldehyde in the decreasing order. The present results of stress-relaxation in water compare favourably with the order postulated on the size of the resin except in the case of ethyleneurea-formaldehyde. This anomaly has been discussed later from the chemical aspect and the results of stress-relaxation in acid solutions.

From the study of the kinetics of acid hydrolysis of viscose rayon treated with urea-formaldehyde, reported in Part 1, it has been shown that over 80% of the resin was removed within 3 hours (about 10^4 seconds) using 0.01N hydrochloric acid at 25°C, whereas similar amount of resin was removed in 1.8×10^3 seconds in 0.1N hydrochloric acid. These values correspond very well to the time in the stress-relaxation experiments on urea-formaldehyde treated viscose rayon, where the relative rates of relaxation in 0.01N and 0.1N hydrochloric acid change their slope. Thus it may be argued that a change in slope of the relative rate plot is an indication of near completion of acid hydrolysis of the resin polymer in the fibre. On comparing the relative rates and the time at which change of slope occurs, it could be concluded that melamine-formaldehyde is more resistant to acid hydrolysis than methylatedurea- and urea-formaldehydes. Ethyleneurea-formaldehyde, however, gave no change in slope and whose relative rate was nearly the same as that of the untreated viscose rayon, which would suggest that the resin was hydrolysed prior to acid addition and during its conditioning period of 24 hours in distilled water. This arguement is further substantiated from the result of stress-relaxation study in distilled water after 1 hour of conditioning, where a sudden rapid change in slope was noted after relaxation had proceeded for some time. Thus it is concluded that the anomaly in case of viscose rayon treated with ethyleneurea-formaldehyde has been largely due to its susceptibility to hydrolysis in very mild acidic conditions of ethyleneurea-formaldehyde resin in the fibre. This is well supported by the study of rate of reaction of resins on cellulose reported by O'Brien and vanLoo (235), where it has been shown that the rate of reaction in the case of ethyleneurea-formaldehyde is about three times faster than that in case of melamine-formaldehyde under identical conditions.

Discussion on Measurement of Accessibility from Stress-relaxation Data

Accessibility is normally calculated as a ratio of available reactive sites to the total reactive sites of a material. In cellulose, for example, the availability of the 'OH' groups can be measured from moisture regain (with some reservations), heat of wetting etc. or the rate at which they undergo certain chemical reactions. Nickerson (219, 220, 221), Conrad, et al. (62), Assaf, et al. (20), have observed that hydrolysis, oxidation, and other chemical processes in which the reactive groups of cellulose were involved, started at a higher rate but slowed down after a certain conversion to a slow "Zero Order Reaction". The initial steep slope was attributed to a rapid reaction in the easily accessible or loosely packed fraction of the sample but as soon as these highly reactive domains were saturated, the reaction slowed down because it took place in the densely packed and less accessible regions of the fibre. It seemed therefore, that at least a qualitative estimate of the ratio of crystalline and amorphous state was possible. However, all differential rate reactions need not be a criteria of physical structure as they might involve chemical reactivity of different reactive groups of cellulose, as pointed out by Hauser (131).

Lemiszka and Whitwell (178) have suggested that elative accessibility could be obtained from stress-elaxation study in acid solution. On the assumption that he rate of scission of bonds should vary continuously from ery rapid in the amorphous regions to very slow in the rystalline regions and if the logarithm of stress supported y the fibre was plotted against time, a curve should result hich would approach linearity when all the stress supporting onds in the amorphous region have been ruptured and if that ortion of the curve was extrapolated to the ordinate, a alue would be obtained which would be a function of bonds n the non-accessible region at zero time and on this ssumption the accessibility of viscose rayon in hydrochloric cid was calculated, attributing the initial rapid relaxation n acid to the breakdown of primary bonds in the accessible egions, and the latter, slow relaxation as the result of he breakdown of primary bonds in the non-accessible regions n cellulose. The present author refutes such a possibility n the grounds that by the time the breakdown of the main hains of cellulose ceased in the accessible regions and roceeds predominantly in the non-accessible regions, there ould be no such thing as fibre left. The present study of cid hydrolysis of viscose rayon in 1N hydrochloric acid the highest concentration of acid used by Lemiszka and hitwell) at 25°C showed that the fluidity of a 2% solution of viscose rayon, in cuprammonium hydroxide, changed from reciprocal poise to 10 reciprocal poise after 25 hours indicating little chemical degradation and in no way comparable to the suggestions made by the above authors. Also the work reported by Nickerson (219, 220, 221) on the kinetics of acid hydrolysis under severe conditions of 2.4 molar solution of hydrochloric acid in 0.6 molar solution of ferric chloride at vigourous boil favoured the present author's argument, the rate of hydrolysis changing after hours to a slow linear rate.

It would be reasonable to believe that the rapid initial rate of relaxation in hydrochloric acid was predominantly due to further scission of hydrogen bonds as also suggested by Lasater et al. (176). Lemiszka and Whitwell (178), however, ruled out such a possibility on the grounds that when water was replaced by the hydrogen bond breaking reagents like lithium chloride, a rapid change in rate of relaxation was not observed. It could be argued that the 10% solution of lithium chloride used by the above authors where the lithium ions in the solution were completely solvated, would cease to be an effective hydrogen bond breaking reagent. To quote, "A 100% solution of lithium chloride would disintegrate nylon but a 10% solution had little effect".

It is felt that there is no theoretical justification on the grounds of the above arguments for such a definition where "Relative accessibility" has been defined as one minus the ratio of the final tension (after 20 hours) or extrapolated value of tension at zero time to the initial (maximum) tension. Nevertheless, using this technique the calculated 'relative accessibility' of cellulosic fibres - ramie, Fibre G, Fortisan, tyre cord, textile rayon and experimental rayon - agree favourably with the values of moisture regain (178).

Assuming that a correlation exists between $fo - f20/_{fo}$ in acid solution and density or moisture regain, then from the above arguments $fo - f20/_{fo}$ calculated from stress-relaxation experiments in water should also correlate with density and moisture regain.

The $fo - f20/_{fo}$ values from stress-relaxation experiments in water and in hydrochloric acid of various resin treated viscose rayons, together with density and moisture regain values, have been reported in Table 24, whereas a correlation between $fo - f20/_{fo}$ and density has been shown in Figure 70. It must be pointed out that the values of density need not be a measure of accessibility of resin treated viscose rayons as the density of different resins themselves would be different and might not be comparable to the density of the fibre. The main significance

Table 24

Figures of $fo - f20/_{fo}$, Density and Moisture Regain of Resin Treated Viscose Rayon Fibres

Sample Number	$fo - f20/_{fo}$ in					Density, g/cc		Moisture Regain, %
	Water 0.7g	Water 0.95g	1.0N HCl 0.95g	0.1N HCl 0.95g	0.01N HCl 0.95g	0% r.h.	65% r.h.	
B	44.4	32.0	57.4	47.6	47.6	1.531	1.523	14.03
1	59.4	50.2	75.6	74.1	74.1	1.526	1.520	12.69
2	65.7	55.2	76.3	73.8	73.8	1.523	1.521	12.15
3	-	-	-	-	-	1.522	1.520	12.37
4	-	-	-	-	-	1.520	1.519	11.52
5	56.5	51.8	70.0	69.0	69.0	1.528	1.523	12.90
6	54.2	42.0	69.0	69.0	69.0	1.524	1.522	12.13
7	58.6	42.0	64.9	66.3	66.3	1.526	1.525	11.52
8	49	39.7	57.3	53.6	53.6	1.529	1.523	13.32

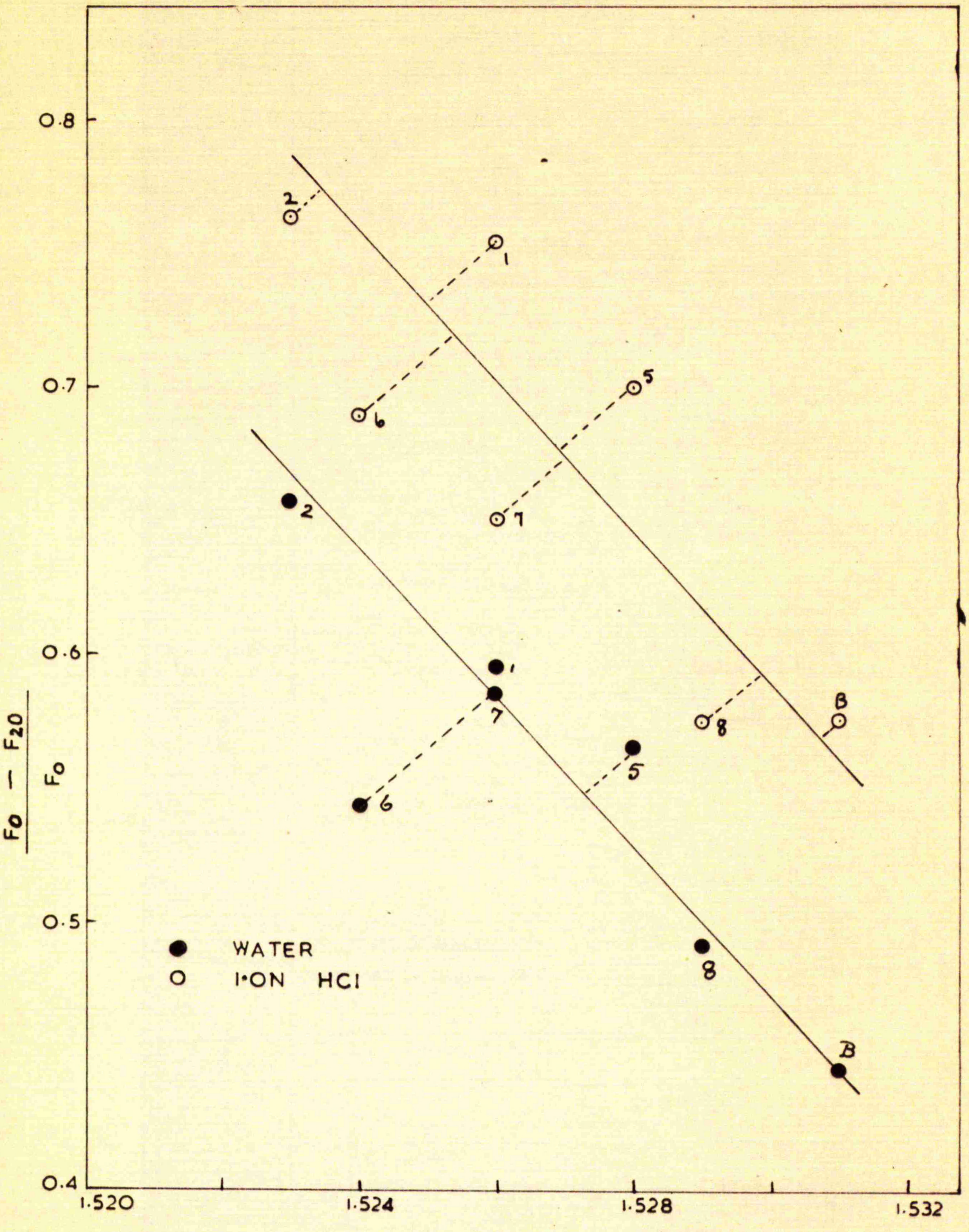

FIGURE 70 CORRELATION BETWEEN STRESS RELAXATION AND DENSITY OF RESIN TREATED VISCOSE RAYON

f the figure was merely to illustrate that $fo - f20/_{fo}$ alues in water and in acid have been nearly similar since he slope remains the same with a constant shift to higher alue in acid solution.

To justify the density values, a correlation etween density and moisture regain has been shown in igure 71. It has been observed that resin treatment educed the density of the fibre, and that when the resin ontent is increased this density is decreased. The fact hat the density of the resin treated samples was lower than he density of the untreated sample would suggest fibre welling. The molecular chains of cellulose were pushed urther apart and held there by crosslinks and/or by the ery presence of the resin polymer in the accessible regions f cellulose, and yet the moisture regain of resin treated amples had been reduced. This could be due to the blocking f the reactive sites in cellulose by resin polymer. Thus, lthough the main chains of cellulose have been pushed urther apart, the accessibility of the reactive sites in ellulose had been reduced. However, a plot of $fo - f20/_{fo}$ n water and in acid solution against moisture regain Figure 72) gave a completely reverse correlation indicating igher moisture regain and lower accessibility. This clearly hows that $fo - f20/_{fo}$ does not measure accessibility.

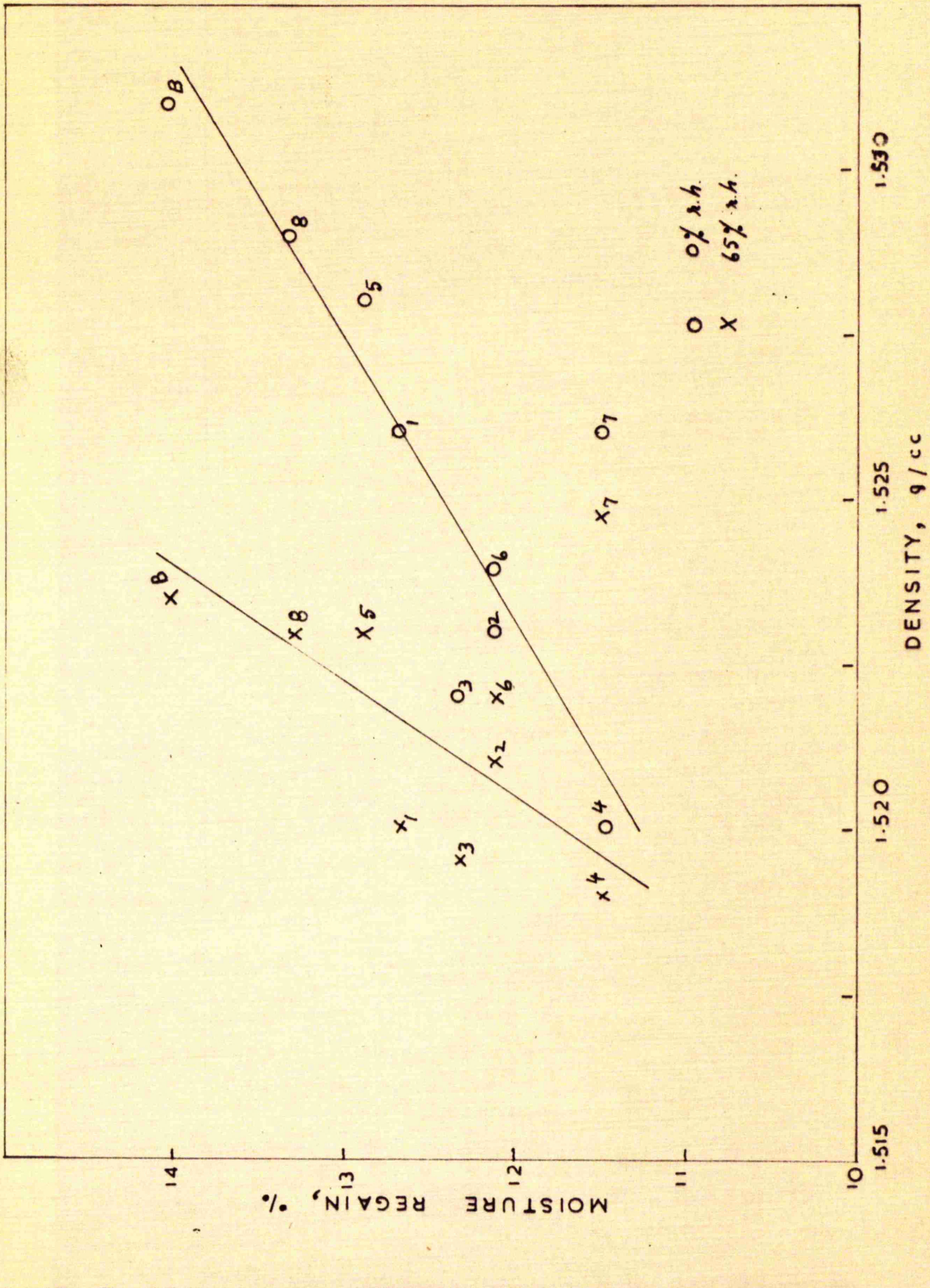

FIGURE 71 CORRELATION BETWEEN DENSITY AND MOISTURE REGAIN OF RESIN TREATED VISCOSE RAYON

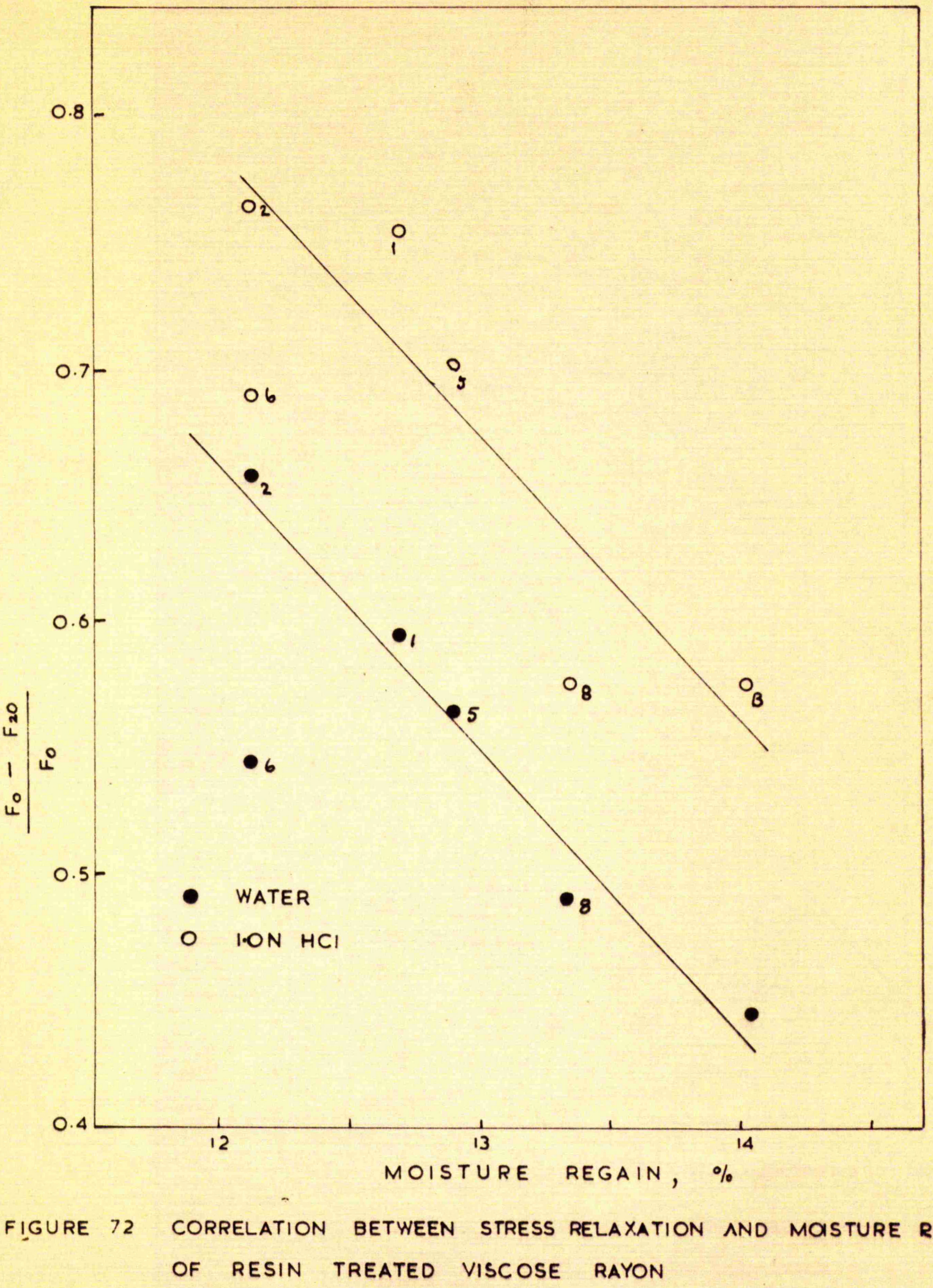

FIGURE 72 CORRELATION BETWEEN STRESS RELAXATION AND MOISTURE REGAIN OF RESIN TREATED VISCOSE RAYON

f not, the question is whether the observed correlation (178) etween fo - f20/$_{fo}$ and moisture regain of cellulosic fibres s a chance correlation or what is the attributing factor?

Recollecting all the experimental evidence in brief, t is observed that

(a) All standard or normally oriented textile fibres xhibit the same relative rate of relaxation in water (178) nd (Figure 68).

(b) Nylon, decron etc. of different draw ratios xhibit different relative rates of relaxation in water (178), he higher the draw ratio the lower the rate of relaxation ecomes.

(c) Viscose rayon treated with different resins xhibit different relative rates of relaxation in water Figure 58).

(d) Different viscose rayons with largely different rystallinity exhibit a similar relative rate of relaxation n water (Figure 69).

The argement that the stress-relaxation in water has een brought about by the breakdown or scission of the weaker econdary bonds common to all materials and therefore the ate of relaxation would be the same (178) or the fact that he stress-relaxation curves in water would occupy the near ompletion end of a composite relaxation curve and therefore ot be sensitive to measure differences in different fibres.

Neither of these arguments could justify the observed effects (b) and (c).

Also if it was possible to compute accessibility from stress-relaxation experiments then viscose rayons of different crystalline/amorphous ratios should give different relative rates of relaxation. But this was not conclusively observed from Figure 69, although $fo - f20/_{fo}$ calculated for these fibres did show a difference of about·08 units and did correlate with density. Since the difference was not large enough to support the above argument the values have not been reported in the present thesis.

The observed experimental evidence could be explained in terms of orientation or order in the amorphous regions of the fibre.

All normally oriented fibres and standard viscose rayons of different crystallinity would be expected to give the near same relative rate of relaxation in water, whereas fibres of nearly the same crystallinity but of different orientation would be expected to give different relative rates of relaxation in water. In resin treated viscose rayon fibres where the resin, known to be cross-linked and/or deposited in the amorphous regions, would effectively hold the main chains of cellulose apart causing increased disorientation and therefore should give higher relative rates of relaxation.

Since orientation to some extent could be correlated density and moisture regain, it was not surprising that - $f20/_{fo}$ correlated to a certain extent with density and ith moisture regain and need not necessarily mean that - $f20/_{fo}$ measured accessibility.

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