THE EFFECT OF CHEMICAL TREATMENTS ON THE ABRASION RESISTANCE OF WOOL FABRICS

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by

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Preface

The low abrasion resistance of wool fabrics compared with many man-made fibre fabrics is known to be a frequent cause of consumer dissatisfaction particularly in pure wool suiting fabrics. Accordingly this project was undertaken to attempt to improve the abrasion resistance in order to maintain the quality image associated with wool fabrics and improve their market competitiveness vis-à-vis other fabrics.

Although several workers have discussed the effects of particular finishes on specific fabrics, very little systematic investigation of the effects of chemical treatments on the abrasion resistance of wool fabrics has been carried out.

In the current study the difference in abrasion rates of woven wool fabrics composed of different structures have been studied in relation to the abrasion resistance and other relevant physical properties.

The work carried out in this thesis is divided into two parts. A review of the literature is followed by a description of the experimental work carried out.

The review of the literature summarises current views on the general mechanisms and factors involved in abrasion processes for textile fabrics and the effects of selective finishing treatments on the abrasion resistance of wool fabrics. In addition details of the abrasion testing conditions used in this work for determining fabric abrasion resistance have been described.

The experimental work is concerned with the changes in wool fabric abrasion resistance produced by the following treatments:

(i) Application of polymer shrink-resist finishes by padding and by exhaustion treatments,

(ii) Treatment with organic solvents,

(iii) Treatment with ethylene glycol at 150°C,

(iv) Deamination and esterification,

(v) High temperature steaming (130°C),

(vi) Dyeing,

(vii) Wet abrasion.

Because of the great commercial importance of polymer shrink-resist finishes for wool fabrics, the main objects of the experimental work were to establish the effects of a range of polymer shrink-resist finishes applied by conventional padding and exhaustion techniques on the abrasion resistance of wool fabrics and the mechanisms by which the abrasion resistance is improved.

CONTENTS

Page

CHAPTER 1

CHAPTER 2

CHAPTER 3

Page

CHAPTER 4

CHAPTER 5

CHAPTER 1

THE ABRASION RESISTANCE OF TEXTILE FABRICS

Textile materials are used for many purposes, both decorative and functional, and the appearance and handle plays an important role in the aesthetic appeal. Another consideration which is becoming increasingly important is the serviceability of the fabric with regard to wear.

A high abrasion resistance for textile materials is a very desirable property for almost all types of textile fabrics, and considerable attention has been given by fibre scientists and textile technologists to the study of this property.

The terms "wear" and "abrasion" have often been used interchangeably to refer to the mechanical destruction of textiles both in actual use and in the laboratory but, according to Peirce (1), in consulting the Oxford dictionary: "wear is the condition of being gradually impaired in quality by friction" and Elder and Ferguson (2) as well as A.S.T.M. (3) describe abrasion as: "The progressive loss of substances from a material brought about by mechanical action". Ball (4) comments as follows: "Abrasion", derived from the verb "to abrade", very distinctly suggests a "rubbing off". The word "abrasion" as an objective might properly be applied therefore to those machines or tests in which rubbing is the only or at least the major, characteristic.

The term "wear" is believed to be more closely associated with the thought of the conditions surrounding every-day use and service and implies the combined effect of several factors of which abrasion or rubbing is only one. It is suggested therefore that "wear" be considered to have a broader scope than "abrasion", and be used to apply wherever other important destructive actions with or without abrasion exist. According to Backer (5), "abrasion resistance should be restricted in meaning to the ability of a fabric to withstand direct rubbing under conditions of intended use".

Hamburger and Lee (6) have also made a distinction between "abrasion" and "wear". They define abrasion as the type of destruction resulting from frictional forces on fabrics, and they refer to the "rubbing away of fabric by attrition" which may occur as a result of the friction of fabric on fabric, or fabric on an external object, as well as the friction between fibres and dust or grit within the fabric. Skinkle (7) has also made a distinction between "serviceability", "wear" and abrasion. "Serviceability" is the length of life of a fabric up to its end of usefulness, which is when one necessary property becomes deficient. "Wear" is the amount of deterioration due to breaking, cutting, or removal of fibres.

Factors causing these actions are:

1. Direct force on the fabric - never in normal wear, only under abnormal stress.
2. Impact effects - important only in floor coverings.
3. Flexing; or friction of fibre on fibre and yarn on yarn due to bending of the fabric; this is ordinarily minor because wear is slow except in sized or weighted fabrics.
4. Abrasion:
    (a) Friction of cloth on cloth occurs only locally e.g. as in the rubbing of the sleeve on a coat.
    (b) Friction on external objects - probably the most important factor.

(c) Friction of fibres on the dust or grit in the fabric, which results in cutting of the fibres.

It must be pointed out that the results obtained on any abrasion tester are comparative only. In many cases, the order of resistance of fabrics to abrasion is also the order of wear, but in many other cases the order is different. The abrasion test must not be considered purely as a measurement of serviceability, the abrasion test is simply a test of the quality of the fabric as to its resistance to a combination of flexing and cutting of the fibres and its results should be considered in connection with other tests and not as a single criterion of the suitability of a fabric for a given use. Those involved with textile testing should continually keep in mind that abrasion is not the only factor in wear, and that wear is not the only factor in serviceability.

Nevertheless, abrasion, according to Mann (8) and Tait (9) is the most important single factor in wear and, for this reason, many textile technologists have simplified the "wear problem" by studying the resistance of fabrics to abrasion, rather than wear in general. Abrasion resistance is difficult to define precisely and cannot be expressed in fundamental units, because it is determined by a complex combination of several factors, such as:

(i) The inherent mechanical properties of the fibres,

(ii) The structure of the yarns,

(iii) The construction of the fabrics ,and

(iv) The type of finishing treatment, and the amount of any applied finishing materials. In addition the ambient conditions during testing are also of importance.

An account of the wear that occurs in service was given by Clegg (10) who examined the worn structures of cotton fabric by using the Congo Red staining method. This investigation showed that although textiles in service undergo a varying amount of chemical deterioration through laundering, exposure to light, and atmospheric conditions, failure is mainly due to weakening of the structure caused by mechanical break-down of the individual fibres. The break-down is caused either by fibre abrasion, transverse cracking or by some gentle fibre abrasion and transverse cracking occurring concomitantly.

Stoll (11) after an examination of worn cotton articles indicated that in normal wear the mechanical factors of actual destruction and gradual disintegration can be divided approximately into:

30% Plane abrasion,
20% Flexing and folding,
20% Edge and projection abrasion,
20% Tear and
10% Other mechanical actions.

It has also been found that the relative importance of the wear factors can be of a very different order due to the specific intrinsic properties of the fibre material, e.g. in viscose, and viscose/cotton blended fabrics, the resistance to plane abrasion in a wet condition and to flex abrasion in a dry state are the critical wear factors in many applications. In the case of resin-treated cotton fabrics, edge abrasion in connection with flexing and folding is of the highest relative importance for many uses. In the formation of a hole apparently caused by plane abrasion, for example, other factors may also have been partially responsible, such as tearing or the uneveness of the fabric.

These analyses and deductions indicate consistently that as far as mechanical disintegration of the fabric, yarn structure and gradual breaking up of the individual fibres are concerned, the following must be considered as major mechanisms of fabric wear:

(a) Plane or flat abrasion;

(b) Abrasion on edges, folds and projections,

(c) Abrasion by flexing and bending.

The mechanical reactions of fabrics to all three cohesive forces (12), namely:

(a) Cohesion between the abrasive and the fibres,

(b) Cohesion between contiguous fibres,

(c) Cohesion between the structural parts of the fibres themselves.

It should be possible therefore, theoretically at least, to predict the resistance of textiles to the various types of abrasion on the basis of the inherent and geometrical properties of the fibre material, the form factors of the yarn and fabric structures, and the frictional forces between the fibres or fabrics and the various abrasives. However in practice abrasion and wear are very complex phenomena and so far only generalised approaches to the problem of abrasion resistance have been made.

The detailed results of many studies in relation to fibre, yarn and fabric variables as well as the effects of wet processing are discussed in detail in section 1.4. et seq.

1.1 Fabric Abrasion Mechanisms

The resistance of a textile specimen to abrasion is not well understood and the mechanisms are extremely complicated. Microscopical examination of fibres and yarns indicates that fabric breakdown results from: (i) direct fibre damage, (ii) displacement and removal of fibres from the yarn, and sometimes (iii) by untwisting of the yarn (10). According to Hamburger (13), abrasion is definitely a repeated stress application which is caused by forces of low magnitude. He suggested that there is a correlation between the abrasion resistance of textile materials and the energy-absorption, because to resist destruction, a fibre must be able to absorb energy during the application of the stress and release it afterwards. Generally on removal of the stress, most of the energy is released immediately and some slowly with delay, the latter being called "creep", which may be divided into two classes:

(a) "Primary creep", which is the recoverable portion of the delayed deformation and,

(b) "Secondary creep", which is the non-recoverable portion.

The fundamental physical properties of materials govern their ability to absorb and retain energy. Ideal properties might include "perfect elasticity" or "complete elasticity". The material with these properties may withstand many cycles of stress, thereby resulting in a high resistance to abrasion.

Hamburger (13) considered the basic cause of fabric failure from an interpretation of the load-elongation curves of mechanically conditioned specimens. He listed the desirable properties of materials subjected to repeated stress applications as being:

(i) Low modulus of elasticity,

(ii) Large immediate elastic deflection,

(iii) High ratio of primary to secondary creep,

(iv) Large amount of primary creep,

(v) High rate of primary creep.

Backer (5) later proposed a general mechanism of fabric abrasion which differs from the process of surface attrition of rigid solids because of the complex geometry of fabric surfaces, and the visco-elastic properties of textile fibres. He believed that Hamburger's analysis is valid only for forces acting along the fibre axis. He concluded that the overall mechanism has three elements, the relative magnitude of which depend upon the nature of the abradant, the fibre behaviour in the fabric structure and the general condition of rubbing. He recognised elements of (i) direct frictional wear (ii) surface cutting and (iii) fibre plucking or slippage

(i) Direct frictional wear:

If the fibres in the yarn structure are firmly held and the surface of the abradant is relatively smooth, then the surface of the fibres is subjected mainly to frictional wear.

(ii) Surface Cutting:

Fibres will be cut if the abradant surface carries sharp asperities. Such a cutting process develops a complex stress pattern within the individual fibre which can lead to fibre tensioning, bending or slippage in addition to the damage caused directly.

(iii) Fibre plucking or slippage

Plucking or snagging of fibres and yarns can take place as the abradant traverses the fabric surface. If the abradant is composed of particles which are large in comparison with the fibre diameter, fibres will be pulled out of the yarn or broken. Plucking will be more pronounced when the normal forces between the abradant and the fabric are large, because deeper yarn penetration will occur.

Depending upon the forces exerted by the abradant and the extent to which the fibres bound in the yarn, rupture on first contact, slippage or repeated stressing can result. Loosely woven fabrics containing low twist yarns, are more susceptible to abrasion damage due to plucking than tightly woven fabrics containing yarns of high twist. In the latter, the fibres are more securely bound in the yarn and, therefore, less accessible to the abradant.

1.2 Morphological Changes in Wool Fibres during Fabric Wear and Abrasion testing.

It has been pointed out that the relationship between the laboratory results obtained from various abrasion testers and the actual wear performance of the fabric is often poor (14). Some changes in fibre morphology during actual wear trials have been observed (10,15), but there are few detailed results on the effects of abrasion machines. Thus an understanding of the changes in the fibre morphology that occur during abrasion would greatly assist in the interpretation of the results of abrasion testing.

Anderson and Robinson (16) examined the morphological changes in wool fibres during actual fabric wear and during abrasion testing. Their investigations showed that fibre breakdown caused by actual wear begins with removal of the cuticle, followed by fibrillation of the cortex, often by longitudinal fracture at cortical cell-boundaries. The fibre thus breaks by transverse fracture of some cells in the fibrillated regions. Fibre fibrillation has also been observed in other studies (10, 15). With continued rubbing, the fractured fibrils are worn away and round-ended fibres are produced. It was also pointed out that fabric thinning in actual wear was caused primarily by the production and removal of short fibre lengths from the fabric and not by thinning of individual fibres (16). Scanning electron micrographs of wool fibres damaged during normal wear are shown in Fig. 1-5 (16).

In the same study (16) it was demonstrated that laboratory abrasion tests caused morphological changes in the fibres somewhat different from those obtained in actual wear. In the Stoll flex-abrasion test (11) where the fabric passes over a sharp metal

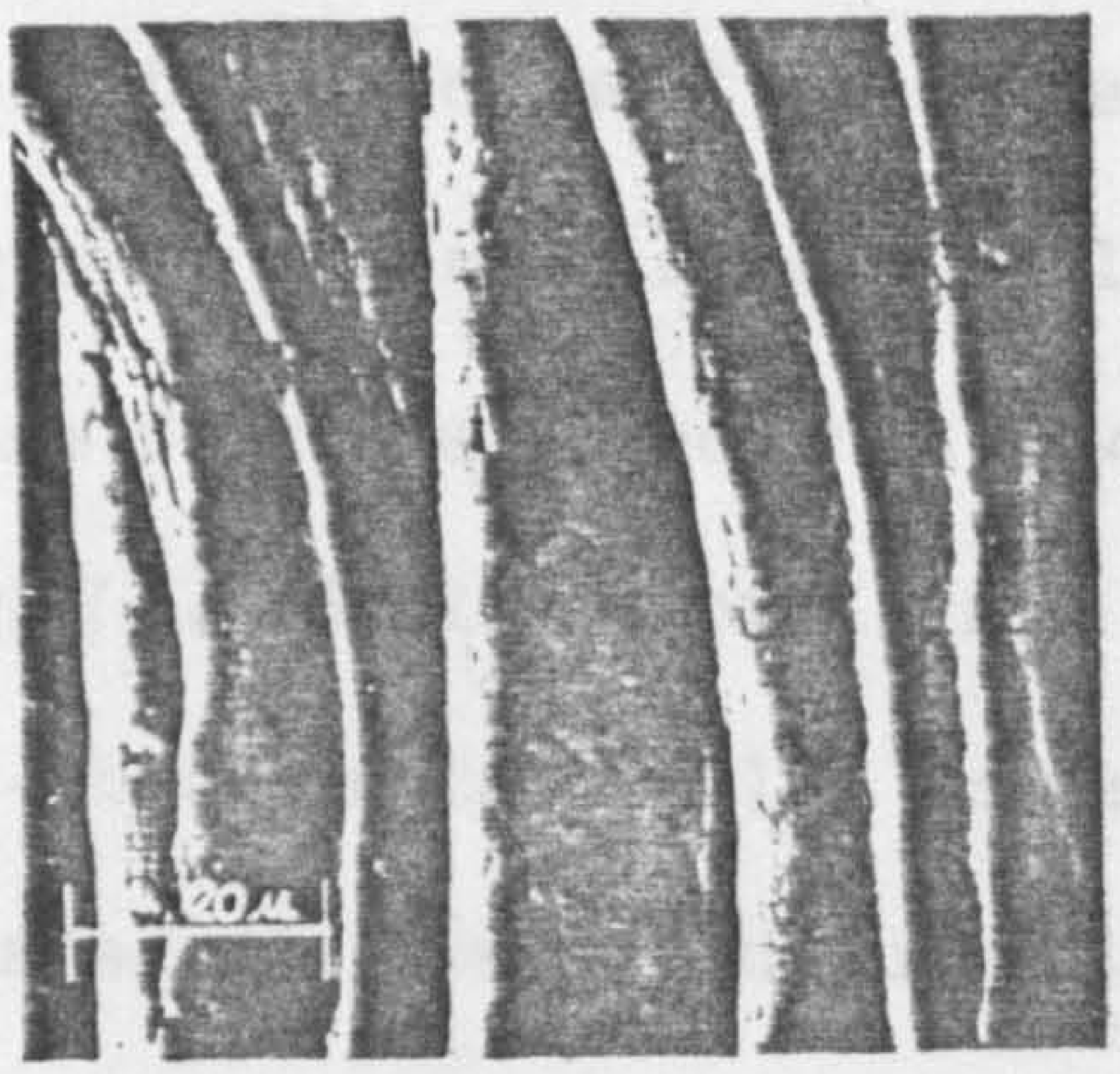


Fig. 1
Removal of cuticle

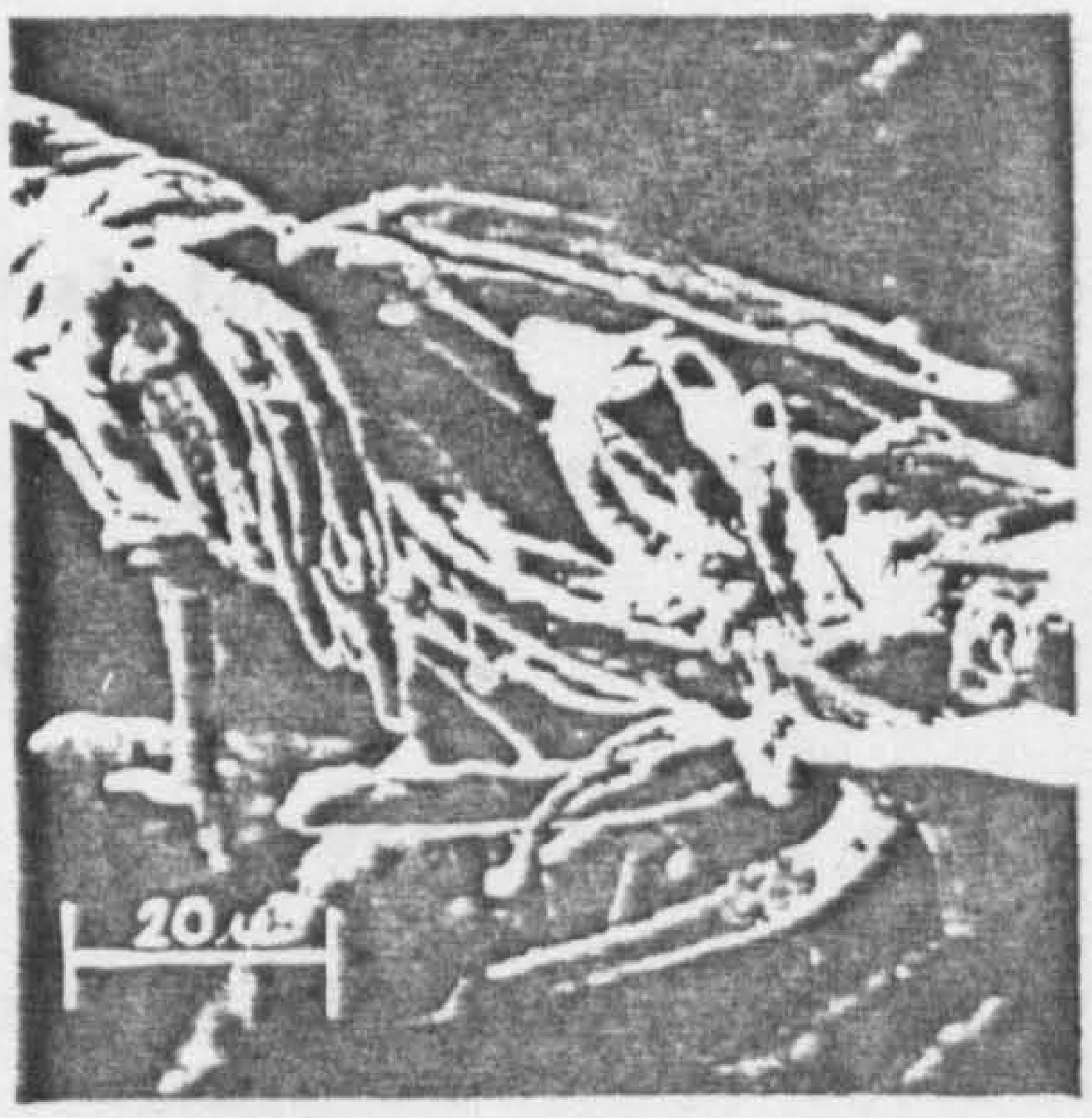


Fig. 2
Fibrillated fibre

Fig. 3
Fibrillated fibre end

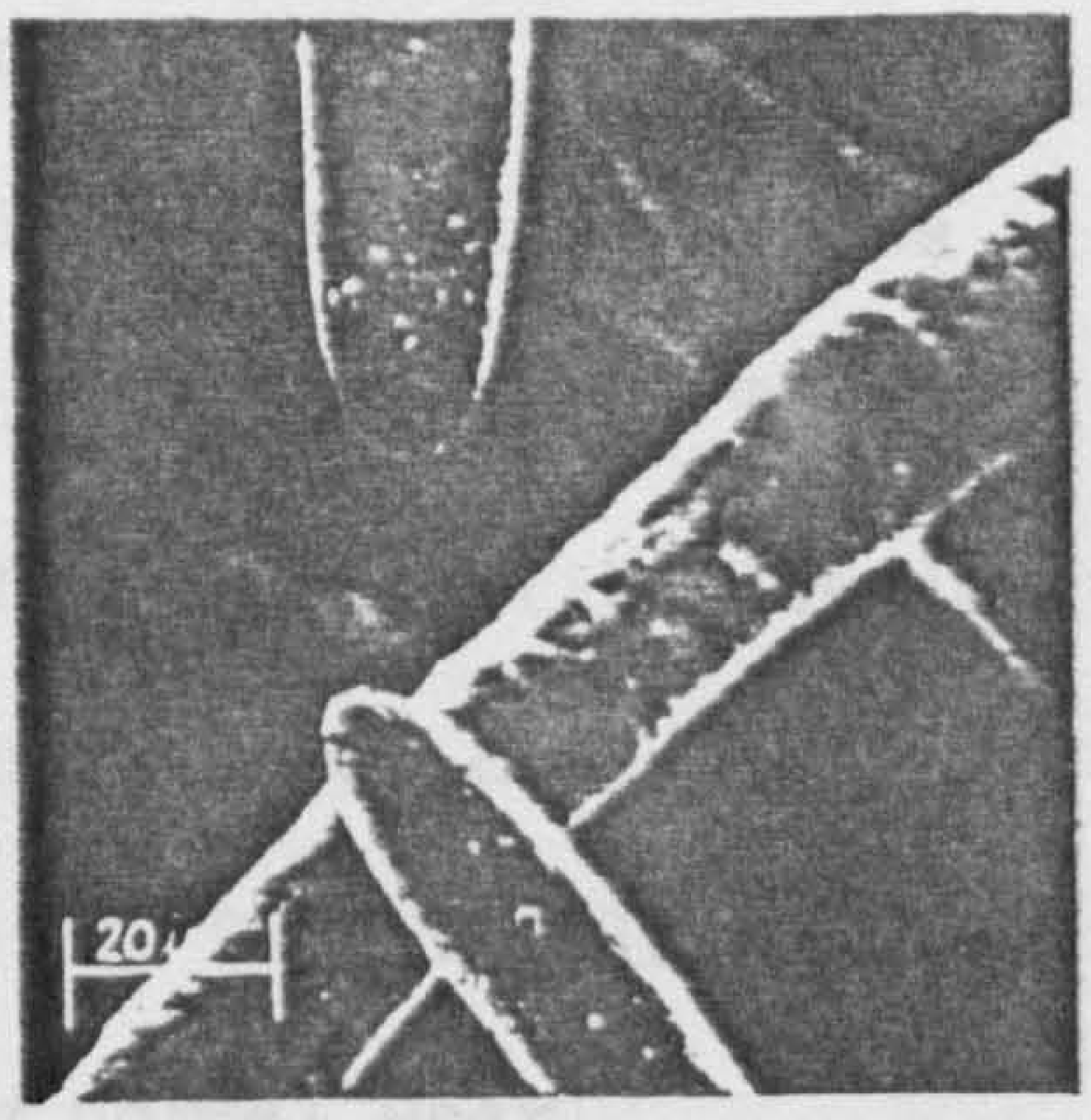


Fig. 4
Rounded fibre ends

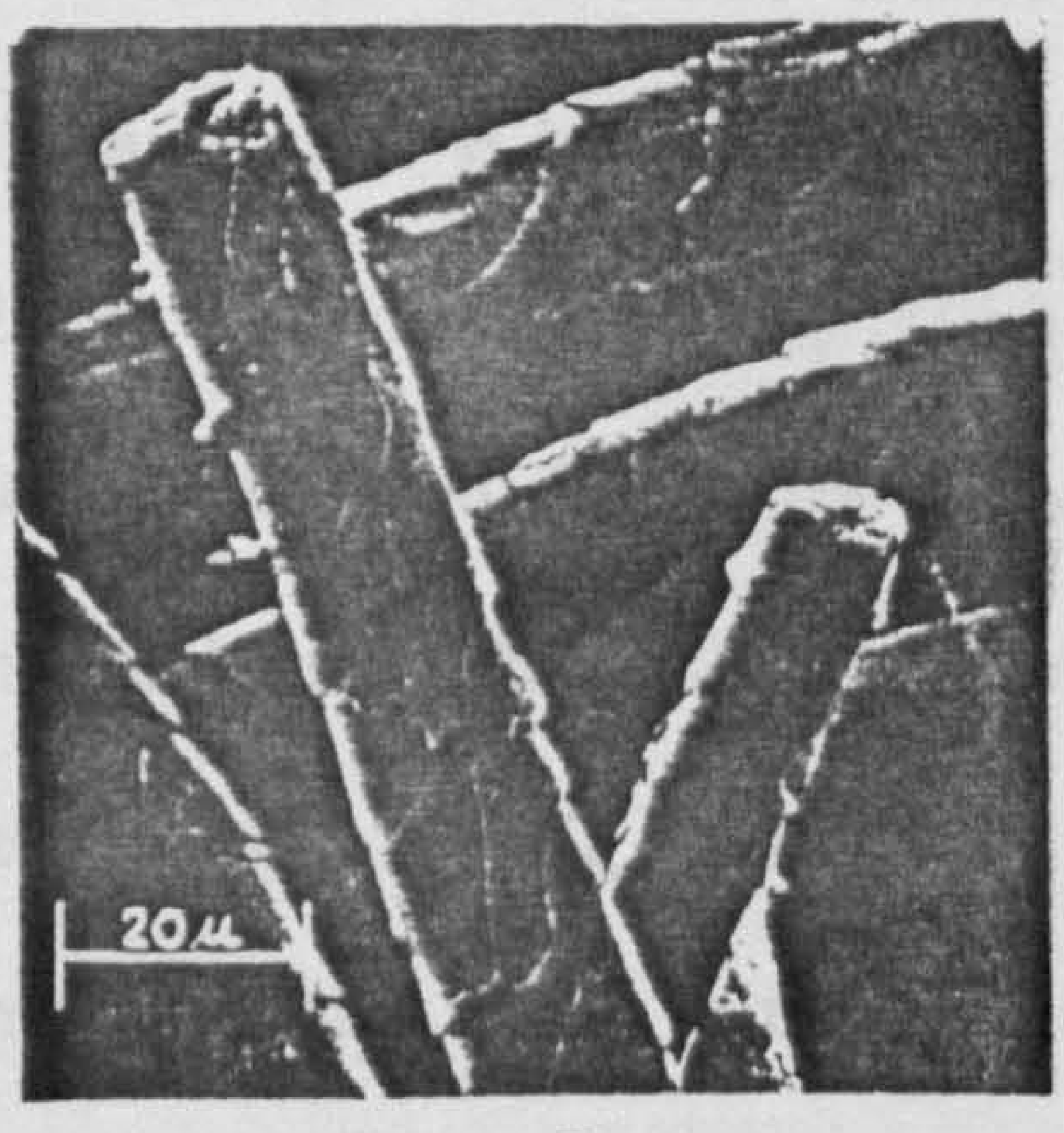


Fig. 5
Transversely fractured fibre end

Scanning electron micrographs of wool fibres damaged during normal wear

bar, a fairly clean transverse fracture of the intact fibre occurred (Fig. 6). There was no fibrillation or gradual thinning of the fabric before fracture although a few fibres had been split longitudinally (Fig. 7). Scale removal from the fibres also occurred. The Stoll flat-abrasion test (11), in which the fabric is stretched over an inflated diaphragm and rubbed against a stainless-steel wire mesh, resulted in the removal of the cuticle, and extensive fibrillation occurred before fibre fracture (Fig. 8). The fibrils were slightly longer than those produced during normal wear.

In the Accelerotor test (17), the fabric repeatedly impinges upon a corrugated metal liner and the walls of the chamber. The characteristic features of the abraded wool fibres were fibrillation, a small amount of transverse fracture, and the removal of cuticle immediately adjacent to the fracture (Fig. 9). The fibrils were generally thicker than those occurring during normal wear.

The Martindale abrasion tester (18, 19) has also been used with several abradants (18). When the standard abrasion fabric and a weight of 600g were used at 20°C and 65% r.h., the cuticle was damaged in a manner similar to, but less extensive than, that occurring in actual wear. Fibrillation occurred before fracture (Fig,10), but the fibrils were slightly shorter and thinner than those occurring in actual wear (Fig. 2). When a lighter weight (185g) was used, the fibrillation pattern was again as shown in Fig. 10, but the cuticular damage was more representative of that occurring during actual wear and the ends of some broken fibres were rounded. Compared with the pattern obtained at 20°C and 65% r.h., abrasion at 30°C and 85% r.h. produced more extensive removal of cuticle and longer less flattened, and less splayed fibrils (Fig. 11). These are somewhat similar to those observed in actual wear (Fig. 3).

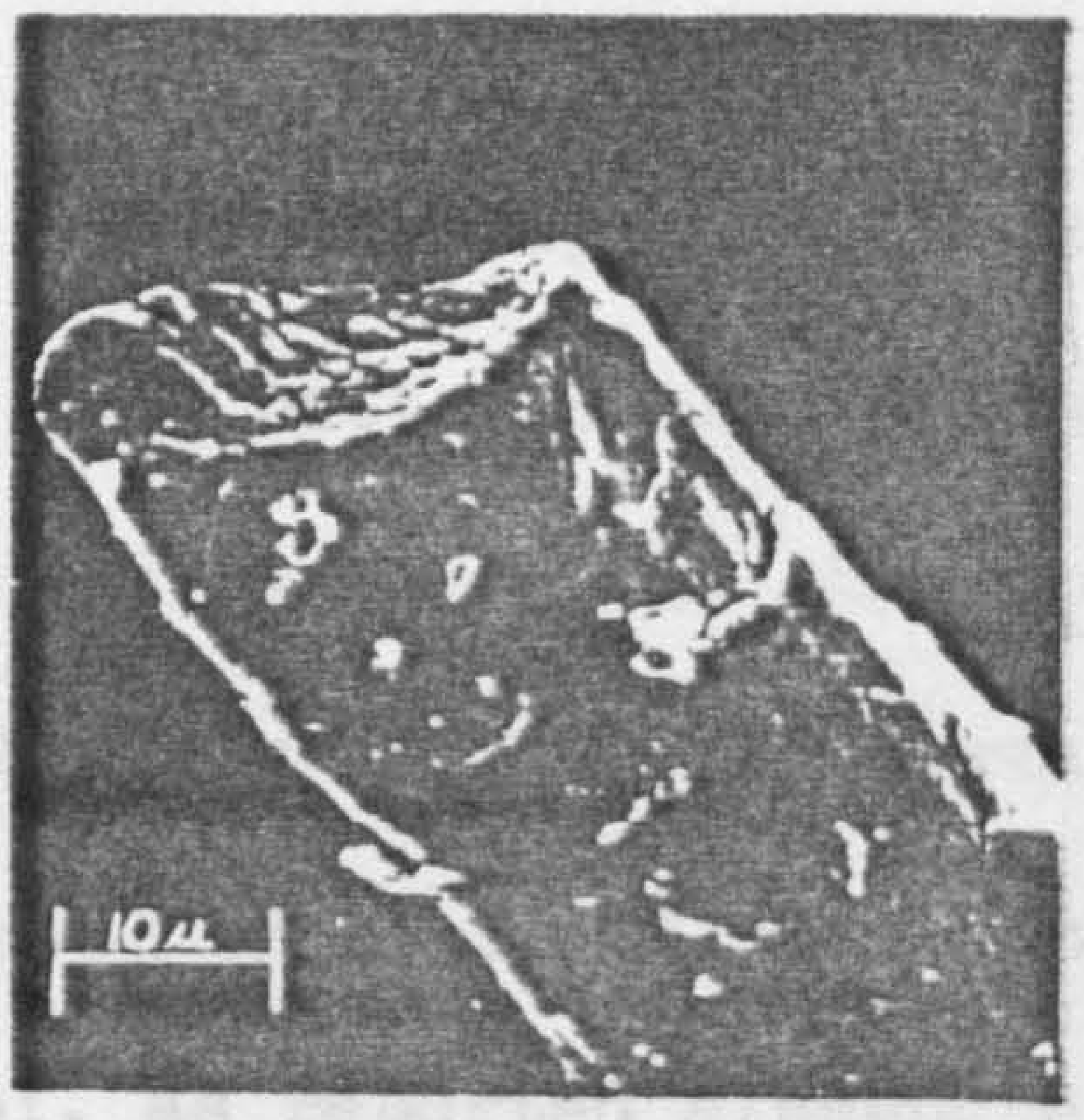


Fig. 6
Transverse fracture
in Stoll Flex test

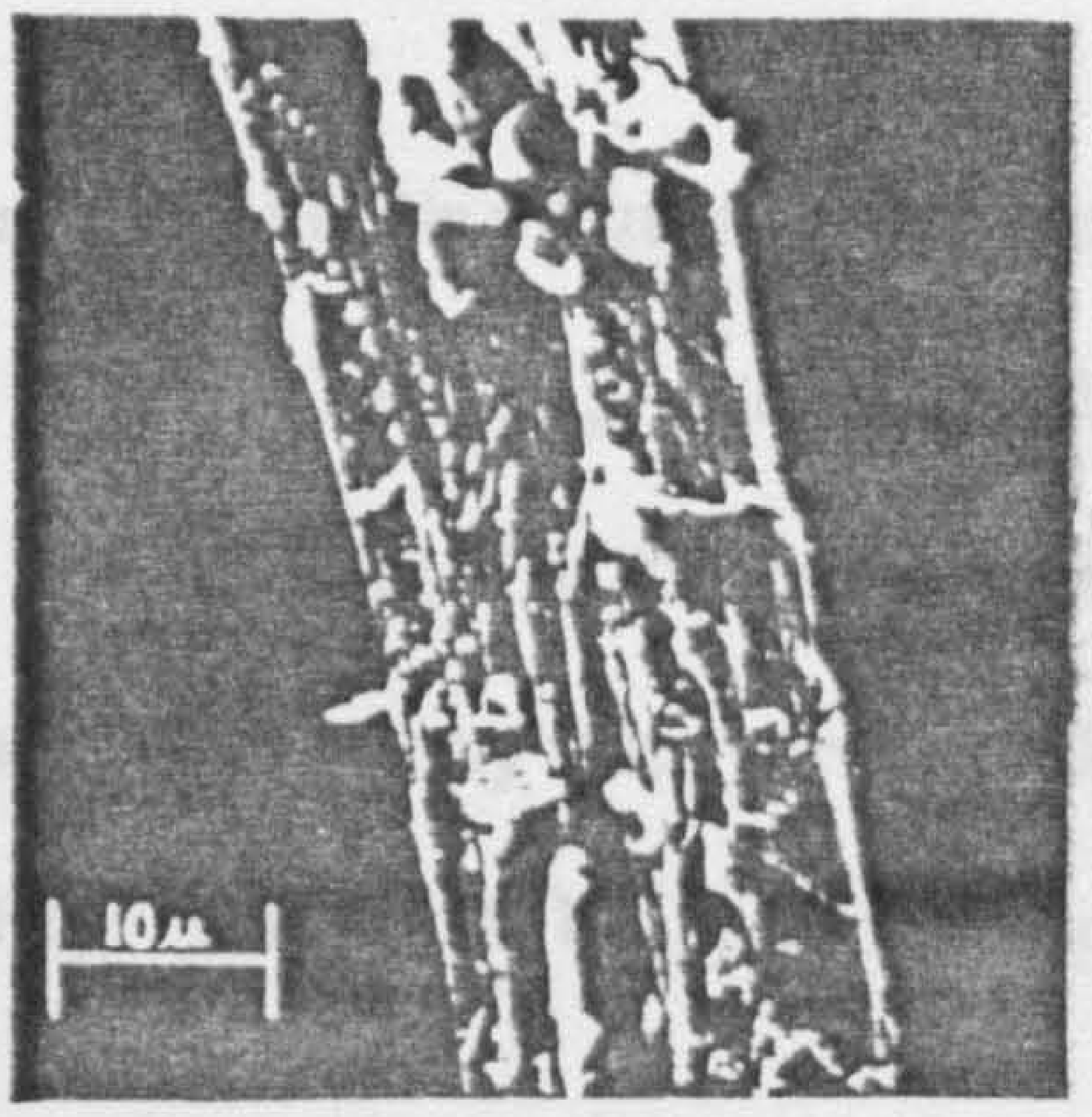


Fig. 7
Longitudinal splitting
in Stoll Flex test

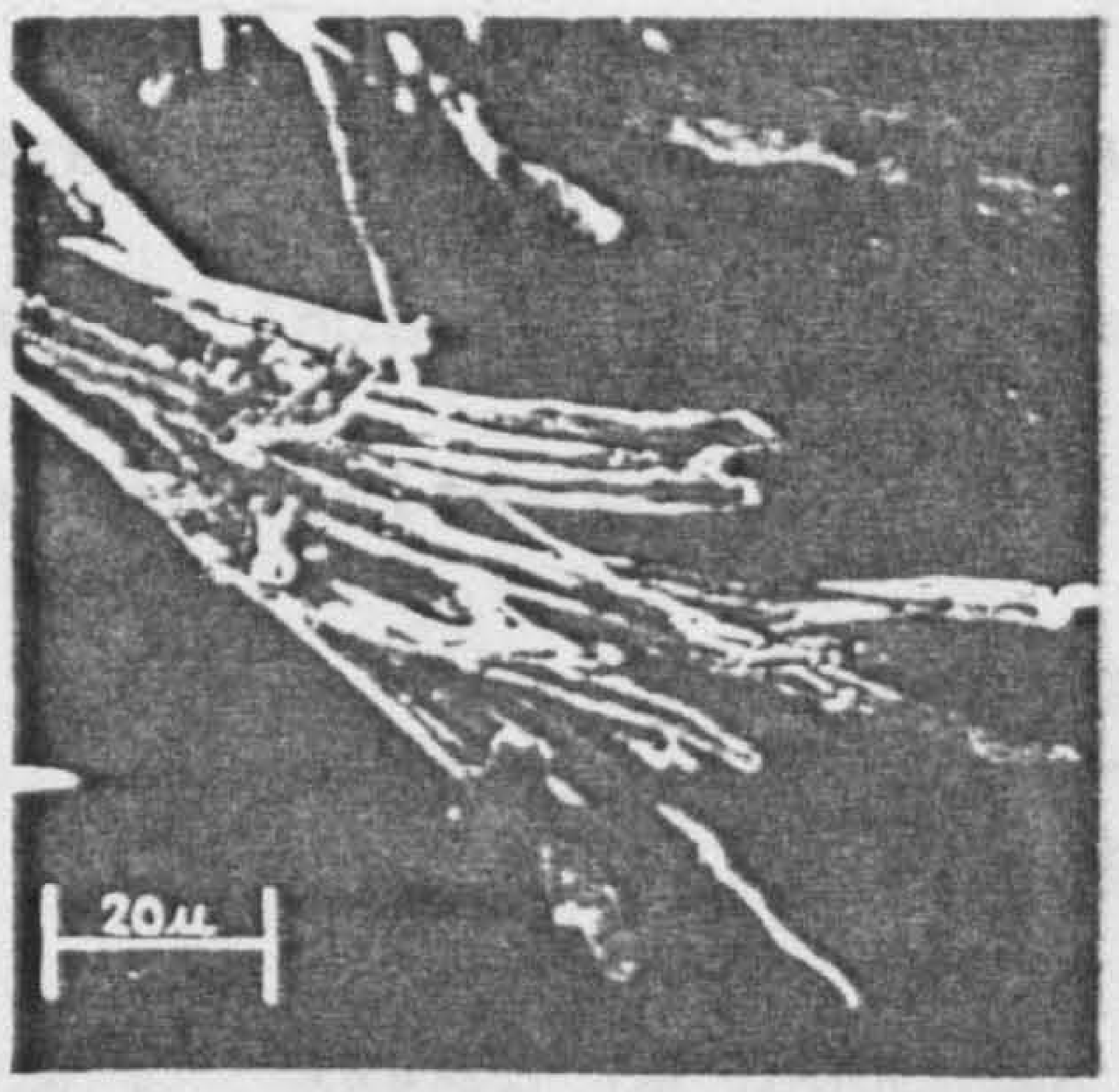


Fig. 8
Fibrillation in Stoll
Flat test

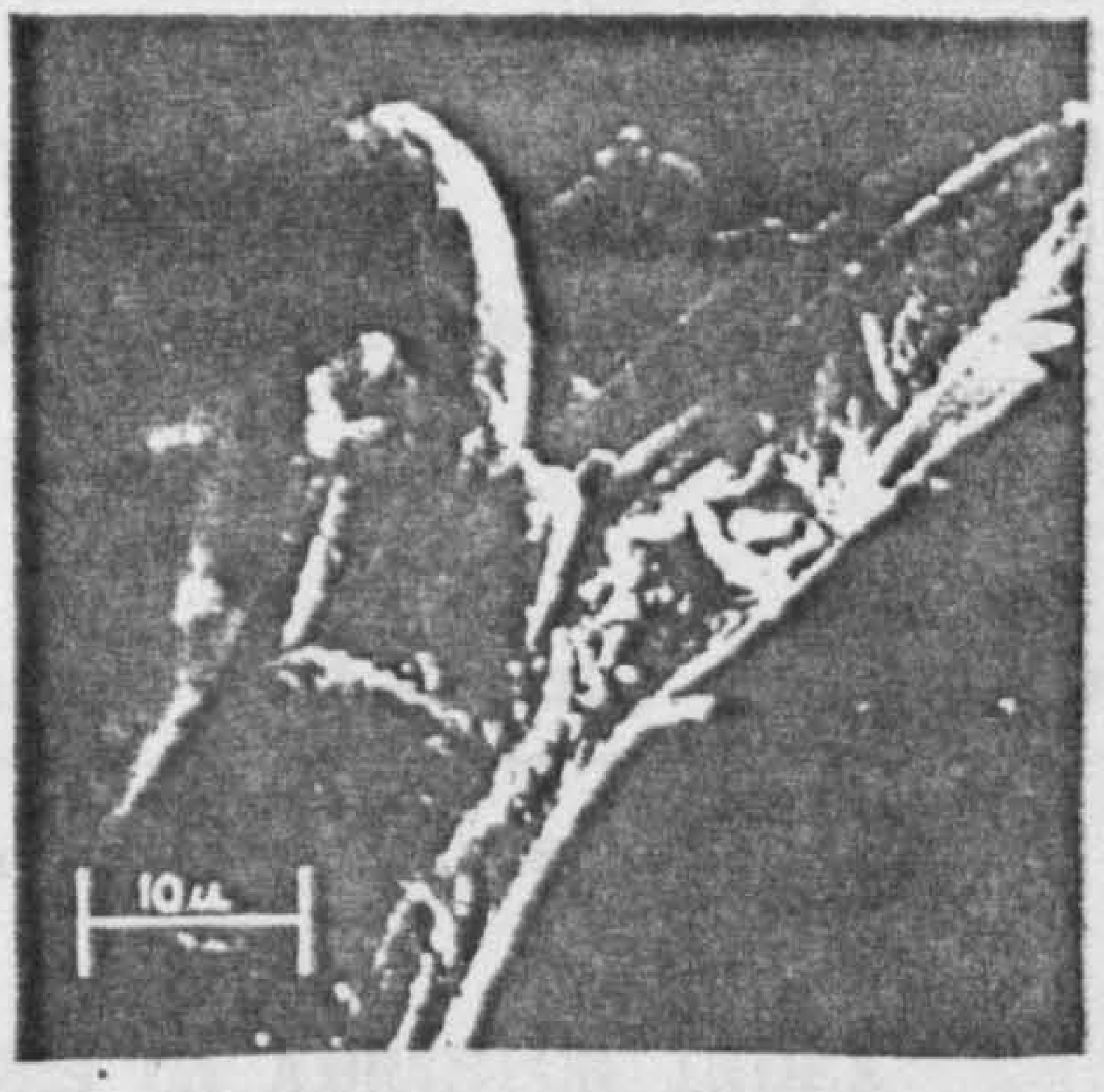


Fig. 9
Fracture in
Accelerotor test

Fig. 10
Fibrillation by abrasion
(Martindale Tester)
against the standard cloth
at 20°C, 65% r.h.

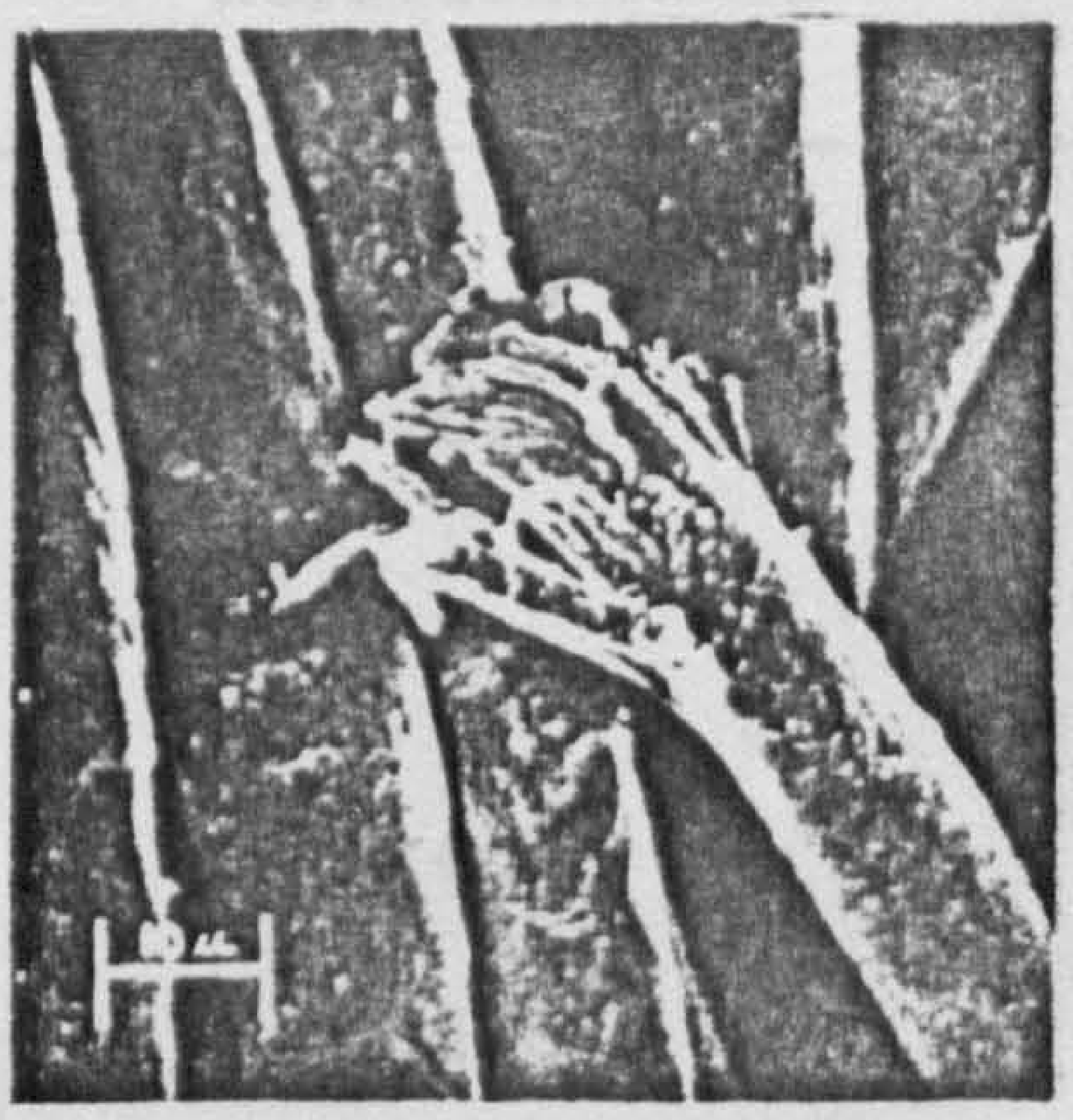


Fig. 11
Fractured fibrils resulting from
abrasion (Martindale Tester) against
the standard cloth at 30°C, 85% r.h.

Scanning electron micrographs of wool fibres damaged in laboratory abrasion-testing machines.

Abrasion against nylon or cotton in the Martindale tester gave the same patterns of cuticle removal, fibrillation, and fibril fracture as occurred with the standard fabric (16). Fabric thinning in the Martindale test, as in normal wear, was caused by the production and removal of short fibre lengths (Fig. 12) and not by powdering the wool, as reported elsewhere (18).

Anderson et al (20) in another study of the abrasion of chemically-modified wool fabrics in the Martindale abrasion tester, observed several other fibre breakdown patterns. Table 1 shows the abrasion index of some chemically-treated fabrics that give different breakdown patterns.

$$\text{Abrasion index} = \frac{\text{Rubs to form hole (end-point) in treated fabric}}{\text{Rubs to end-point in untreated fabric}}$$

TABLE 1 EFFECT OF CHEMICAL TREATMENTS ON ABRASION INDEX

Treatment	Abrasion Index
Untreated	1.0 *
Resorcinol-formaldehyde	0.4
Sodium dodecyl benzene sulphonate (S.D.B.S)	0.3
Trypsin	0.4
o -Chlorophenol	1.8

*Rubs to form hole in untreated fabric = 30,000

The reasons for the different patterns of breakdown during abrasion testing of chemically-treated wool illustrated in Table 1 may be summarised as follows:

(i) Treatment with cross-linking reagents embrittled the cortex and caused the fibre to fracture rather than fibrillate

Fig. 12
Untreated wool 'debris' on abrasion cloth
(in the Martindale abrasion tester)

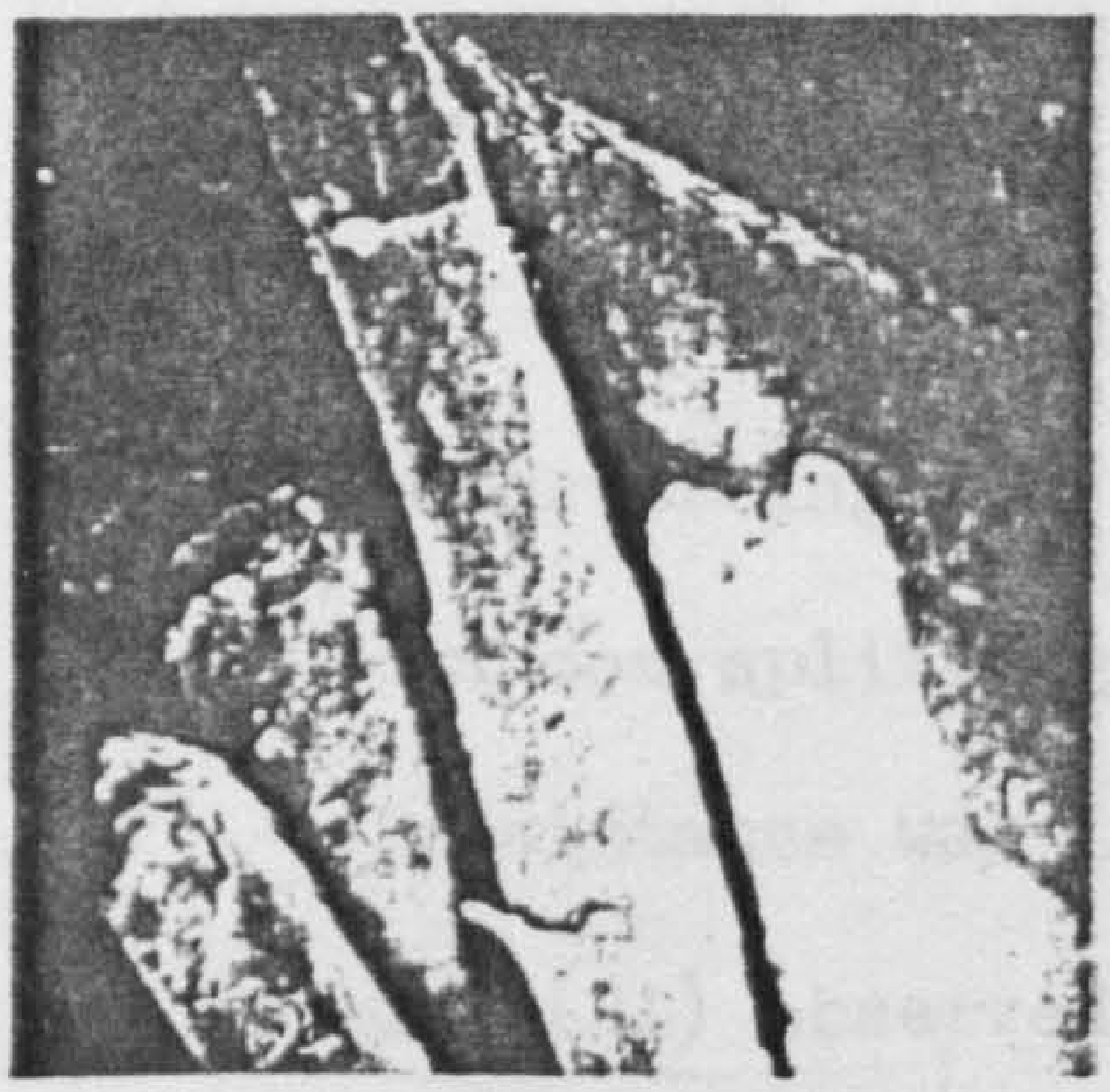


Fig. 13
Resorcinol-formaldehyde treatment.
Shows brittle fracture.

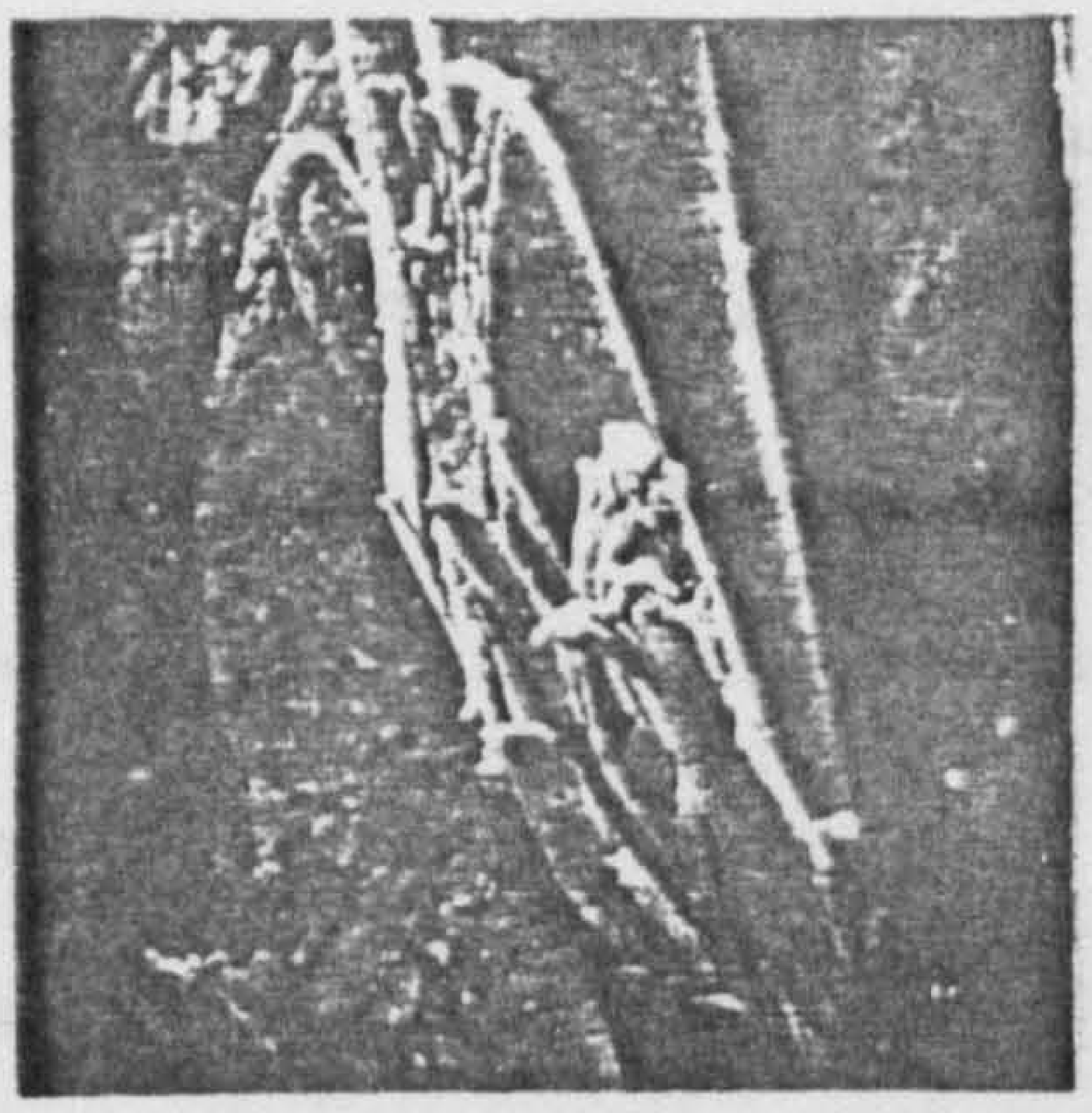


Fig. 14
SDBS treatment. Shows fibrils
of various dimensions.

Fig. 15
Enzyme treatment. Shows
fibrillation at cortical-cell
boundaries.

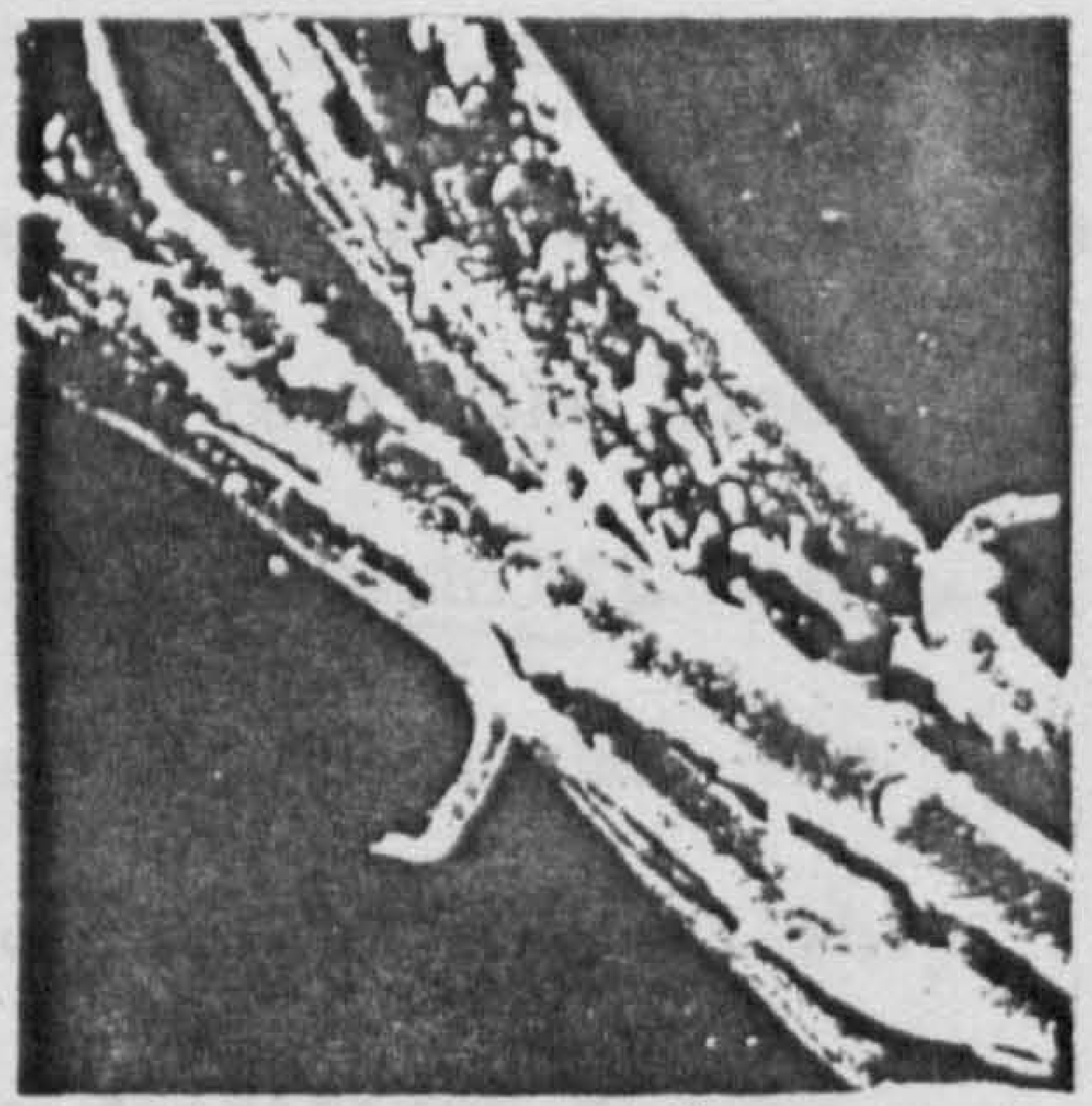


Fig. 16
o-Chlorophenol treatment.
Shows random longitudinal
splitting.

Figures 13-16
Scanning electron micrographs of fibres in chemically treated wool fabrics after abrasion in the Martindale tester.

and hence a poor abrasion resistance resulted (Fig. 13).

(ii) Treatment with an anionic surfactant, caused over-all chemical degradation. The fibrillation and breakdown of the fibres that ensued were similar to, but more rapid than, the corresponding changes in the untreated wool (Fig. 14)

(iii) Treatment with a proteolytic enzyme (trypsin) reduced the abrasion resistance and caused rapid fibrillation of the cortical-cell boundaries probably by preferential attack on the cell-membrane complex (Fig. 15).

(iv) In treatments with o-Chlorophenol apparent stabilization of the usual fission planes takes place without damaging or embrittling the fibre. However fracture occurred after random splitting along the fibre axis, so that the abrasion resistance was in fact increased (Fig. 16).

Reumuth (21) observed a loss of surface fibres, and also of the scale structure leading to the development of polished fibre ends in shiny worsted fabrics. This localised lustre or shine, which is the result of repeated rubbing or gentle abrasion in a garment, is undesirable (22, 23). The areas of a garment that normally receive extensive rubbing during actual wear, i.e. the back, the knee, the cuffs and other edges, are therefore the first to exhibit shine.

In a more recent study (24) it was demonstrated that the morphological changes in the breakdown of wool fibres are highly dependent upon the relative humidity of the conditions during Martindale abrasion testing. The types of fibre fracture during abrasion testing were observed to be as follows:

(i) Completely fibrillated ends (Fig. 17)

(ii) Transversely fractured ends (Fig. 18)

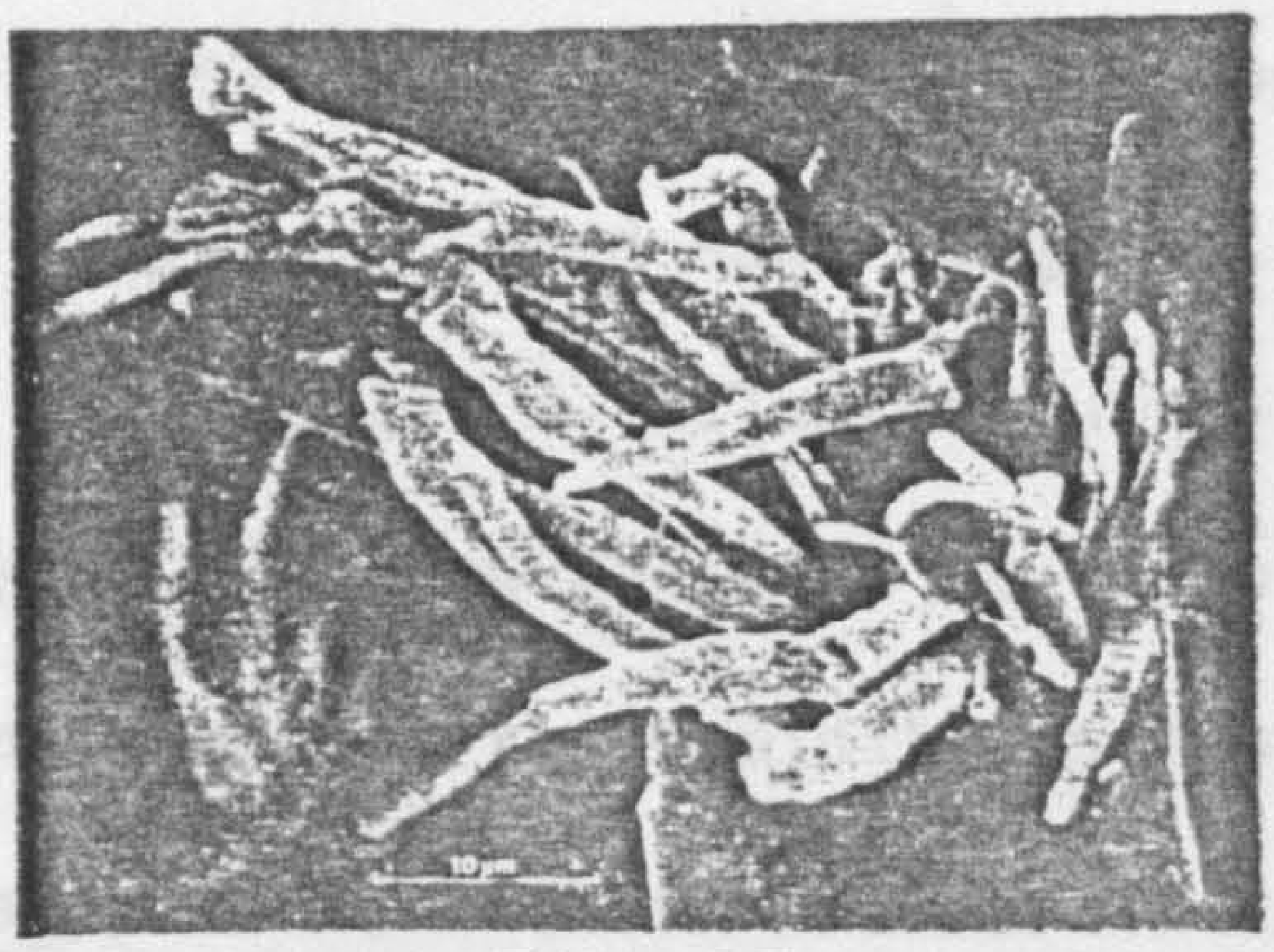


Fig. 17
Completely fibrillated end.

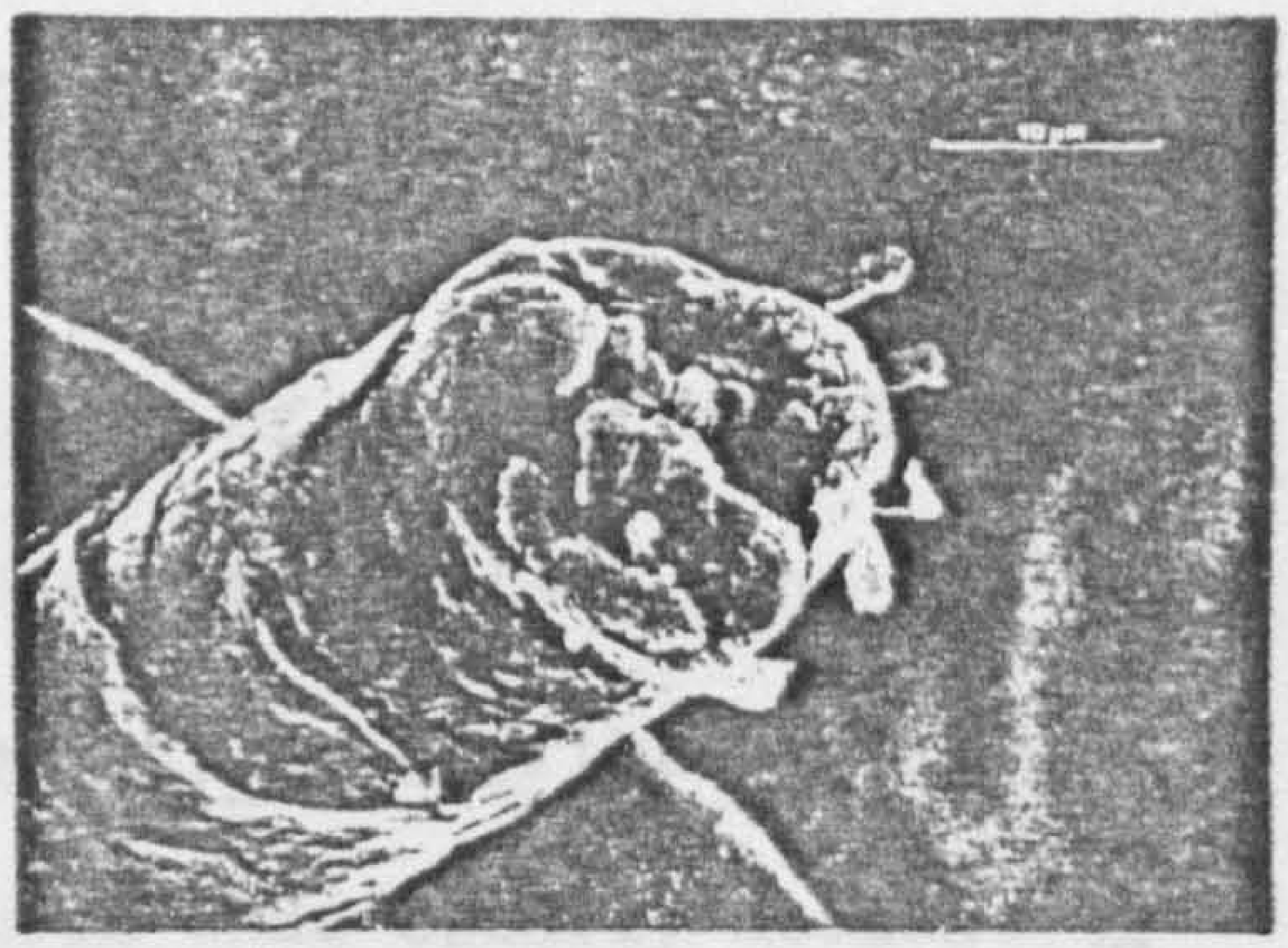


Fig. 18
Transversely fractured end.

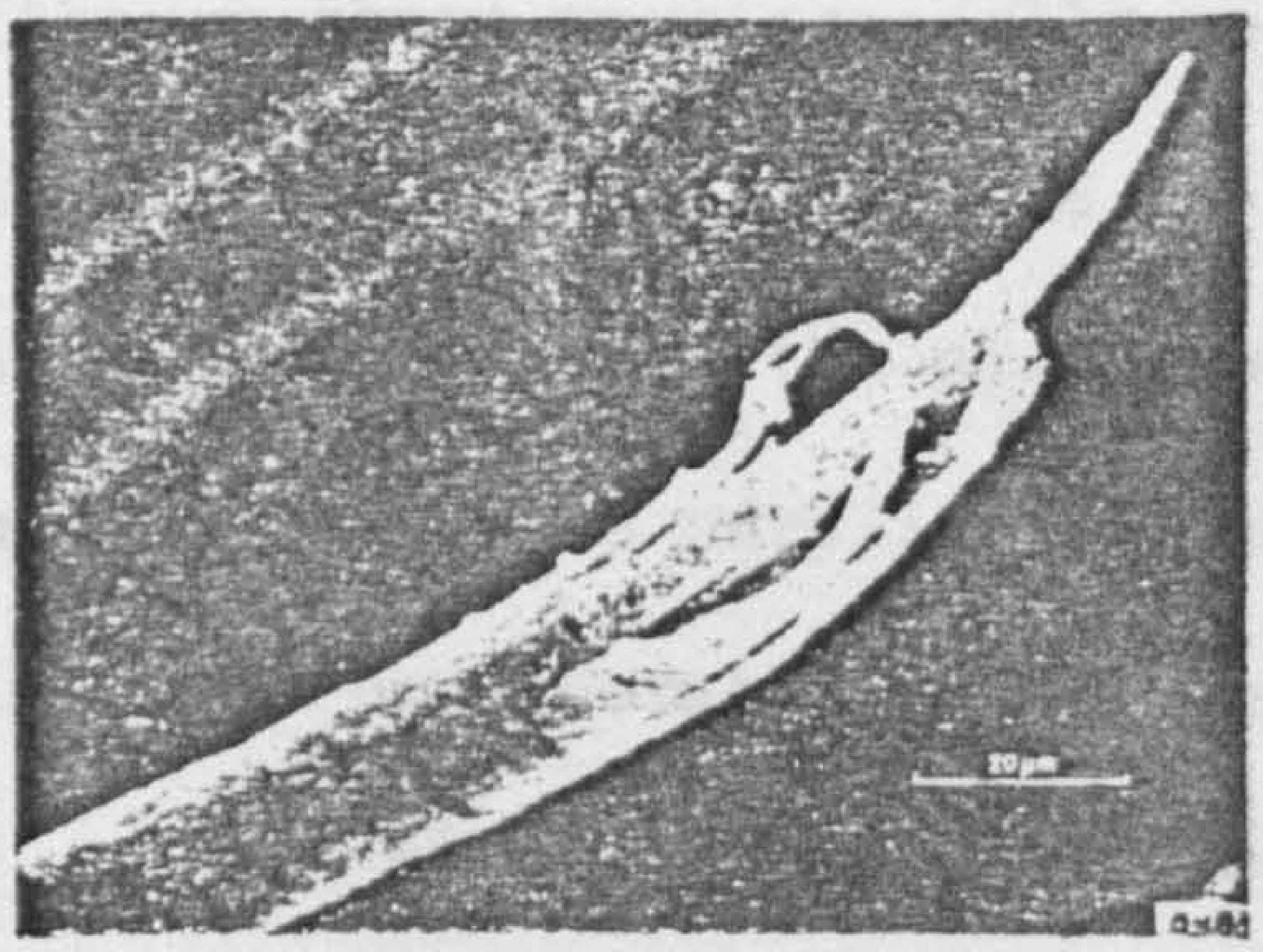


Fig. 19
Longitudinally split end.

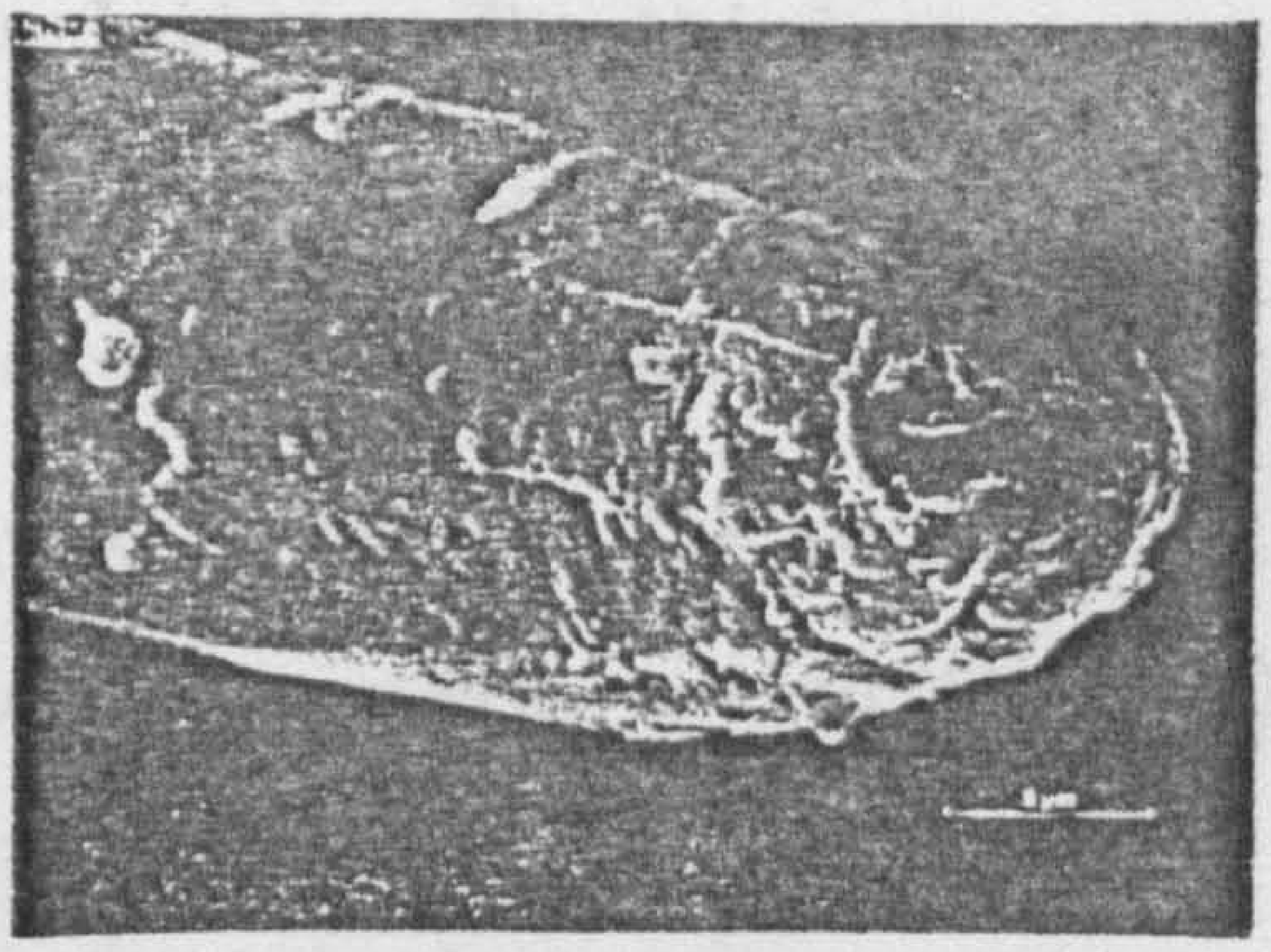


Fig. 20
Rounded end.

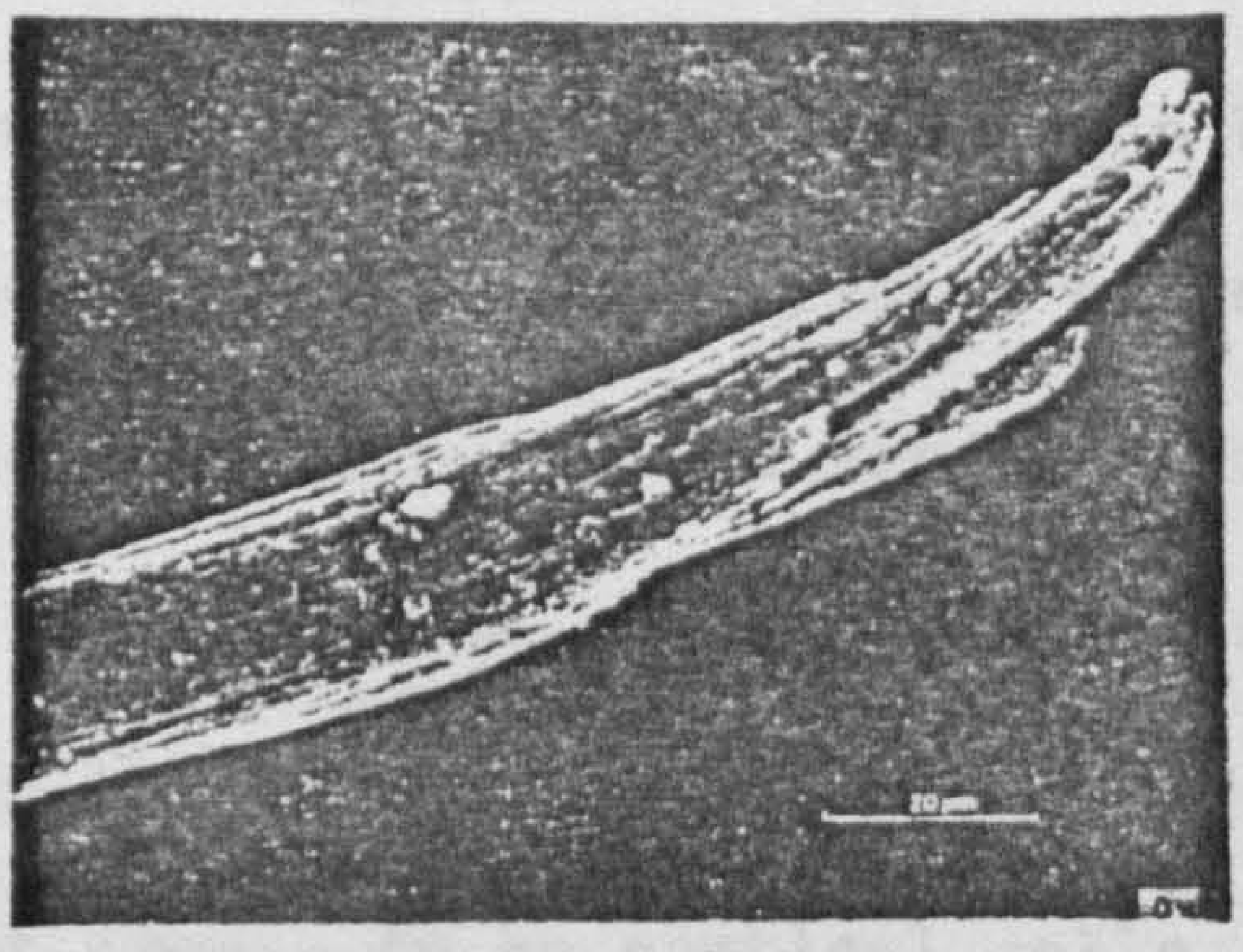


Fig. 21
Fibrillated extended end.

Scanning electron micrographs of abraded wool fibres.
(in the Martindale abrasion tester)

(iii) Longitudinally split ends (Fig.19)

(iv) Rounded ends (Fig.20).

Table 2 illustrates the percentages of the different types of fibre breakage at various relative humidities. The influence of the humidity on the different types of fibre failure is obvious, with the transversely fractured ends clearly dominating the low-humidity region. Both the transversely fractured and the completely fibrillated ends dominated the high-humidity region, although there were generally more of the latter. The third significant type of fracture is the longitudinally split end, which shared almost the same proportion at all humidites. The rounded ends were usually the least frequent type, but the proportion rose considerably at the lowest relative humidity tested (8% r.h.).

Wet abrasion, on the other hand, showed no completely fibrillated ends, but another type of fracture was observed, namely the fibrillated extended end (Fig.21). This together with the longitudinally split ends were the dominating types of fibre failure in wet abrasion on the Martindale abrasion tester. The difference between the completely fibrillated end and the fibrillated extended end are that in the former the cuticle cells are not damaged and the fibrils are numerous, vary in size, but are mostly short and flat with blunted tips. In the latter the cuticle cells are completely removed to reveal what appear to be cortical cells.

1.3 Abrasion Testing

Many methods for assessing the resistance of fabrics to abrasion have been devised; some of the more important methods are listed below:

1) The Linra Wear Tester.

2) The Tabor Machine.

Table 2

Morphology of Fibre Breakdown at Different Humidities[*]

Relative Humidity (%)	Transversely Fractured Ends (%)	Completely Fibrillated Ends (%)	Longitudinally Split Ends (%)	Rounded Ends (%)	Fibrillated Extended Ends (%)	Total Number of Fibre Ends Counted
8	53	10	14	23	0	78
27	60	20	17	3	0	87
48	63	9	19	9	0	67
55	69	19	11	1	0	72
65	51	30	15	4	0	152
70	31	38	23	8	0	105
83	32	40	23	5	0	181
Wet	22	0	34	3	41	104

[*] The figures in the table represent percentage of the total number of fibre ends counted.

3) The Wyzenbeek Abrasion Tester.

4) The Stoll Universal Wear Tester.

5) The T.B.L. Ring Wear Tester.

6) The B.F.T. Abrasion Tester (Courtaulds).

7) The Martindale Abrasion Tester (WIRA Machine).

8) The Schiefer Machine.

9) The Accelerotor.

Of these, the Wyzenbeek abrasion tester, the Martindale abrasion tester and the Accelerotor are generally recognised as among the best. The defects of the earlier testers have been eliminated in the Martindale tester. It allows flat abrasion to be measured rather more accurately than the other test methods. In addition this machine produces morphological changes and types of fibre breakdown which most closely simulate those found in actual wear (16).

1.3.1. The Martindale Abrasion Tester

This abrasion tester is designed in a very compact assembly, four flat fabric samples being abraded simultaneously. The principal object of this type of machine is to avoid preferential rubbing in one direction.

The apparatus consists essentially of an abrading table which is covered with the abradant and a pattern holder which carries the specimen to be tested. The bulk of the apparatus is made up of devices for controlling the abrasive motions, and the pressure between the surfaces.

A general view of this machine is shown in (Fig.22). It consists of a metal plate (P) supported by three pillars A, B, C each of which has a metal cup, with a ground steel horizontal surface inside, containing a steel ball which can move freely in the metal cup.

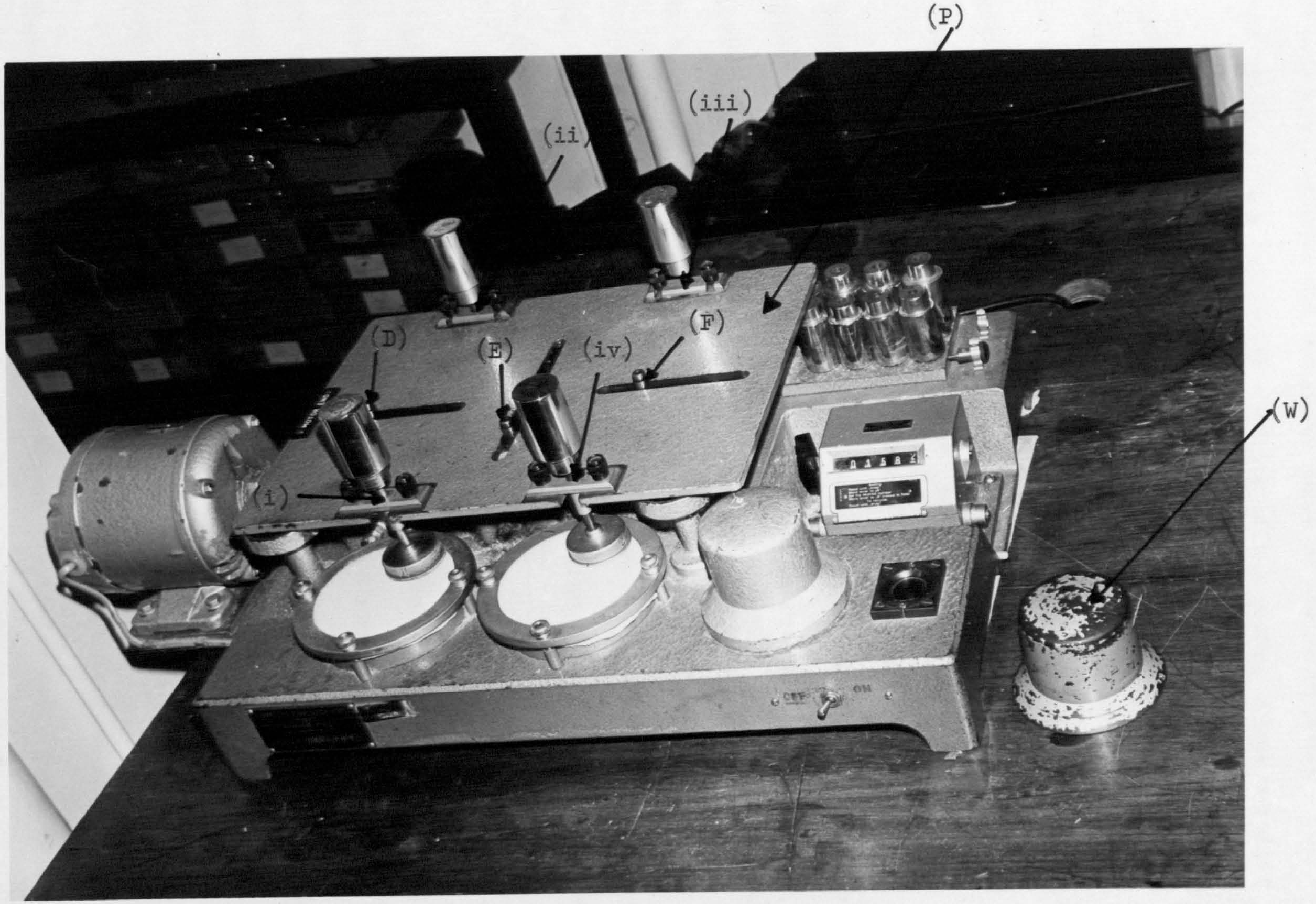


Fig. 22 - General view of the Martindale abrasion tester.

The cups are co-planar and the plate rests on the three balls which result in the horizontal mobility of the plate. Three vertical studs (D, E, F) are fixed each on a separate horizontal wheel. The wheels are driven through gears from an electrical motor in such a way that the two outer studs operate in the length direction at the same number of revolutions per minute, and the centre one operates at right angles at slightly fewer revolutions per unit, which causes the plate (P) to follow a Lissajous path (see Fig.23).

Initially the path followed is a straight line along the diagonal of the figure. Gradually the motion changes through a series of ellipses to a straight line which is now the other diagonal of the figure. As the motion continues, it develops again through the same series of ellipses, which are, however, now described in the opposite direction. This cycle of operation is repeated for as long as desired. This type of motion has the advantage that the pattern under examination is rubbed in all directions.

Four pattern holders (I, II, III, IV see Fig.22) can be bolted to the plate P, in such a way that they are free to move in a vertical direction. Each pattern holder (1.5 in. in diameter) is circular and consists of three parts (A, B, C) as shown in (Fig.24). The sample of fabric is placed over a circular support (B) which fits exactly into a ring (A) which in turn, can be screwed into the main body of the pattern holder (C).

It has been found that, to obtain a satisfactory tension, this operation must be performed by pressing the holder crown against a flat surface. It has also been found that the hardness of the Support specimen (B) allows the abradant to pull the specimen out of the pattern holder, especially when a thin fabric is used. To avoid this

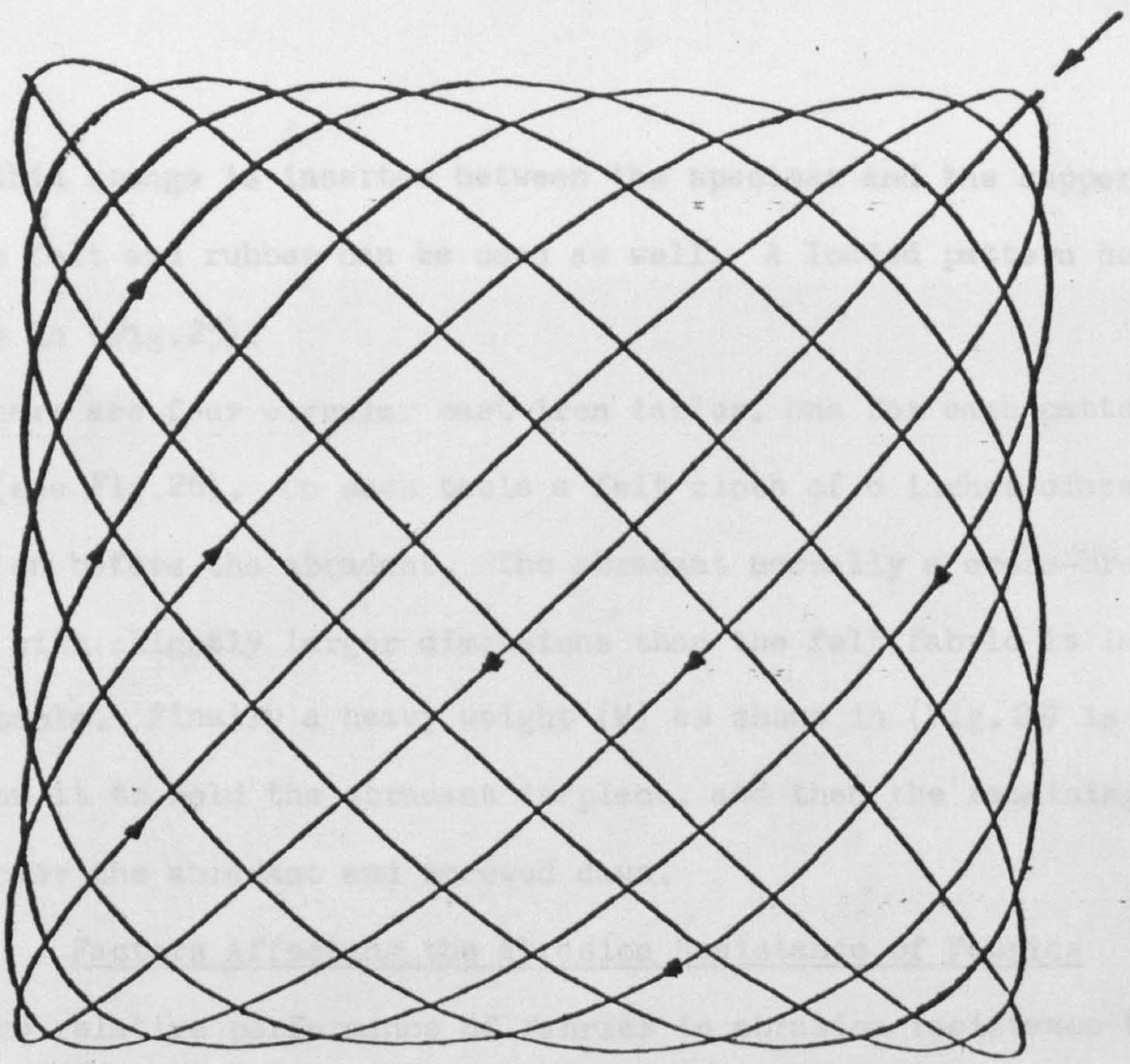


Fig. 23 - Lissajous path traced by plate.

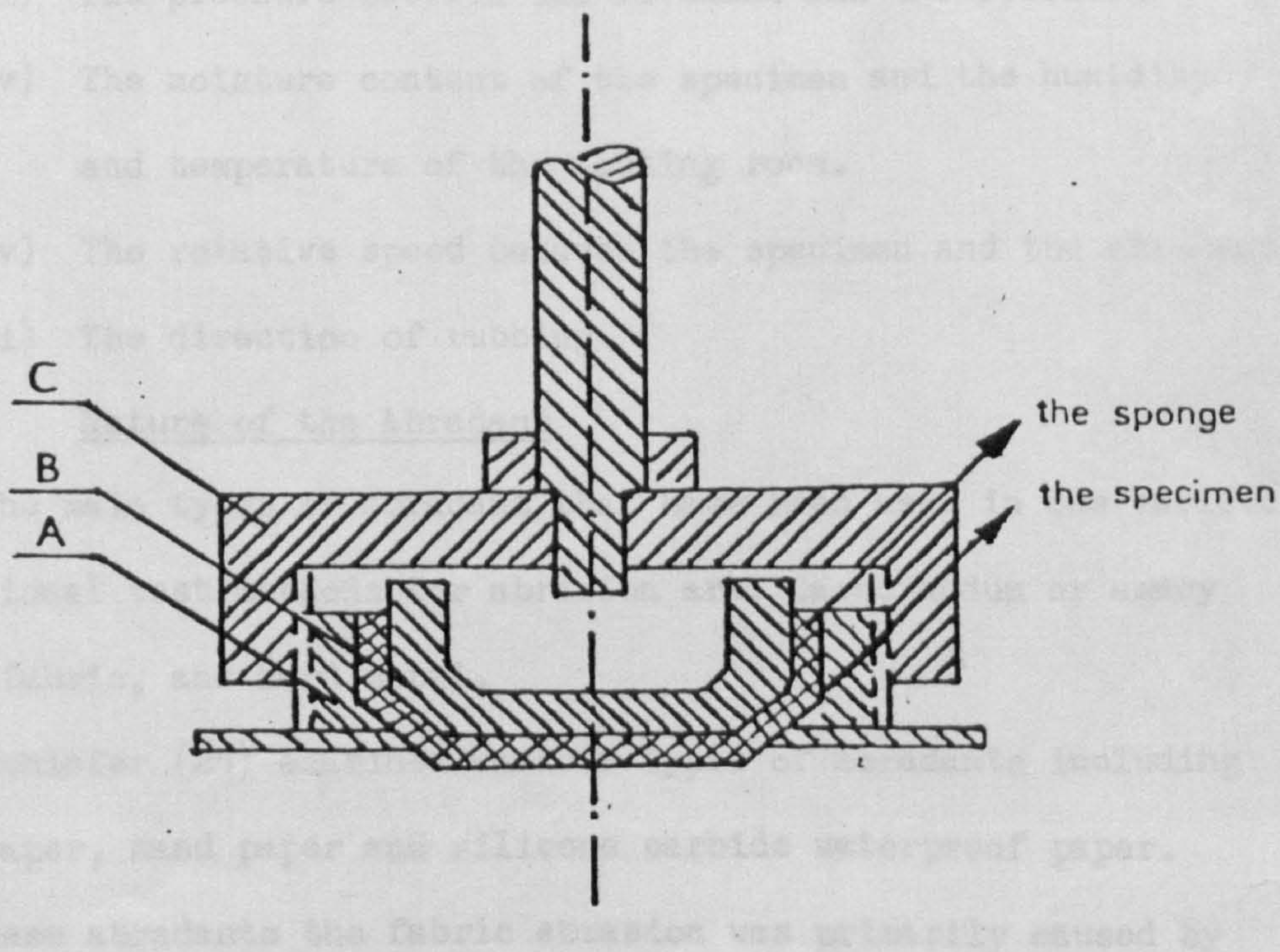


Fig. 24 - The Martindale specimen holder.

a very thin sponge is inserted between the specimen and the support, although felt and rubber can be used as well. A loaded pattern holder is shown in (Fig.25).

There are four circular cast-iron tables, one for each pattern holder (see Fig.26). On each table a felt cloth of 6 inches diameter is laid on before the abradant. The abradant normally a cross-bred wool fabric, with slightly larger dimensions than the felt fabric is laid on the table. Finally a heavy weight (W) as shown in (Fig. 22) is placed on it to hold the abradant in place, and then the retaining ring is put over the abradant and screwed down.

1.3.2 Factors Affecting the Abrasion Resistance of Fabrics

The relative performance of fabrics in abrasion resistance tests depends on the method of assessment. The results depend on:

(i) The nature of the abradant.

(ii) The softness of the reverse side of the specimen.

(iii) The pressure between the abradant and the specimen.

(iv) The moisture content of the specimen and the humidity and temperature of the testing room.

(v) The relative speed between the specimen and the abradant.

(vi) The direction of rubbing.

(i) Nature of the Abradant

The main types of abradant that have been used in the various conventional test methods for abrasion are: Carborundum or emery paper, fabric, and hard metal.

Schiefer (25) examined various types of abradants including emery paper, sand paper and silicone carbide waterproof paper. With these abradants the fabric abrasion was primarily caused by cutting and hence was very fast. These type of abradants are not

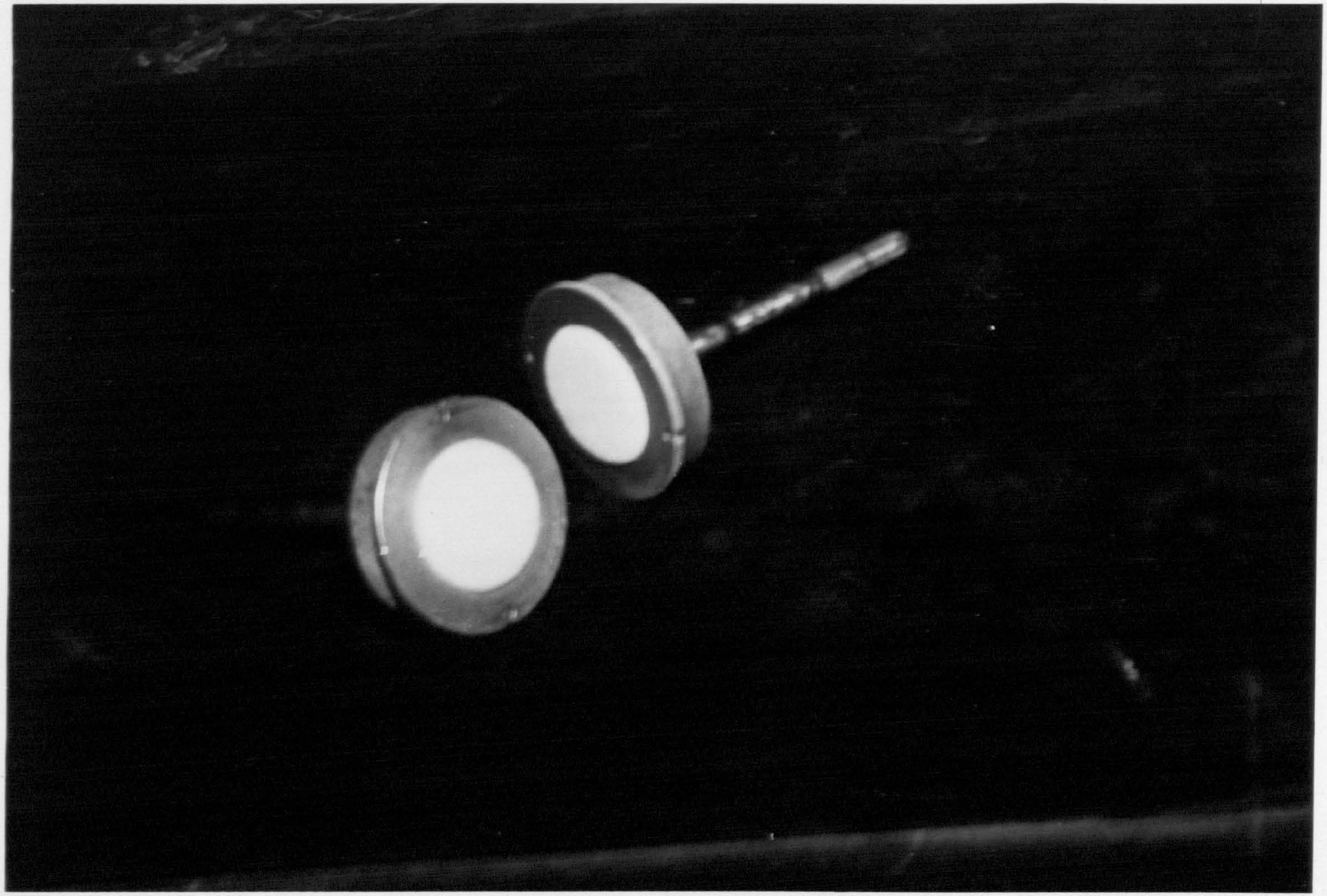


Fig. 25 - Loaded sample holder.

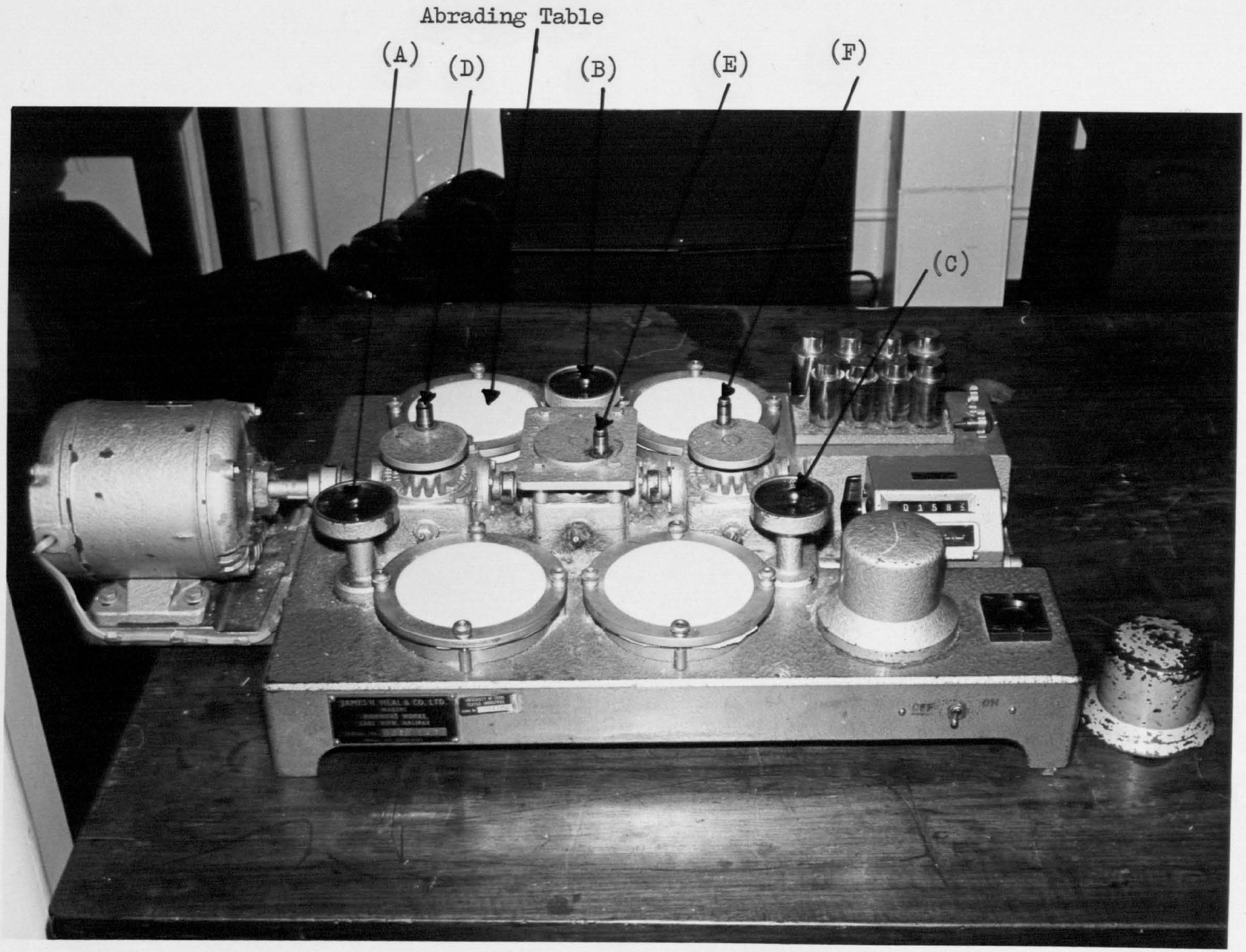


Fig. 26

considered suitable for evaluating the effect of various treatments on the abrasion resistance of textile fabrics except for specialised industrial applications. In addition the abrasive properties of these type of abradants decrease very rapidly during each test.

The use of a standard fabric (a cross-bred wool fabric) as the abradant gives a far better indication of the useful life of the fabric. This type of abradant on the Martindale abrasion tester is shown (16) to produce fairly similar fibre morphological changes to those found in actual wear. This type of abradant was therefore employed in carrying out the present experimental study reported in this thesis.

Hard metal is the most constant form of abradant. Metal abradants are practically constant in action and cause less cutting of fibres during testing than carborundum or emery paper. The metal is of course, far harder than the specimen being tested.

(ii) Softness of the Reverse Side of the Specimen.

The softness of the reverse side of the specimen must also be taken into account, because it can affect the abrasion resistance of the fabric. Different types of sponge, rubber or felt as supports may give different abrasion resistance values. Thus it is essential that the type of support is of the same type and quality throughout the experiment especially for comparative studies.

(iii) Pressure between Abradant and Specimen

The compression of the fabric because of the load applied to the test sample during abrasion testing will also affect the abrasion resistance. For comparative studies, a standard pressure must, therefore, be specified. With an increase in the applied pressure the fibres are fractured rather than worn, while the time required to reach the end-point will be reduced. However this may not simulate the conditions experienced during actual wear.

(iv) Conditions of the Testing Room

The conditions of the testing room must be approximately the same throughout the experiment (relative humidity = 65 ± 2% r.h. temperature = $20^{\circ} \pm 2^{\circ}C$). Changes in these two parameters, especially relative humidity, are very important and it has been shown in the case of wool fabrics (24) to have a considerable effect on the abrasion resistance values.

The specimen must therefore be conditioned for at least 24 h before and after testing, especially when measuring the fabric weight loss.

(v) Relative Speed between Specimen and Abradant

Increased speeds of rubbing may leave insufficient time for the fibres to recover from the deformation, making them more affected by the next stroke of the abradant (26). An increase in the speed of rubbing also generates heat, but it is not known how this affects the abrasion resistance results; for the Martindale machine however, the speed is constant at 50 rubs per min. on the abradant area and uniform abrasion would therefore be expected.

(vi) Direction of Rubbing

When the direction of rubbing is altered with respect to the warp and weft direction major differences in the abrasion resistance of textile fabrics have been noted (27). Yarns which lie in the surface of the fabric, suffer maximum damage when abrasion takes place in a direction perpendicular to their float length (28, 29). However, in the Martindale tester where the preferential rubbing in one direction is avoided, the entire surface of the fabric should suffer the same degree of damage.

1.3.3 Assessment of Abrasion Damage (end-point)

The end-point is the most important aspect for measuring the amount of fabric abrasion. This determination depends upon an accurate method of evaluating the amound of damage which has taken place. It may be influenced by the judgement of the operator, and by the difficulties in obtaining accurate readings during the test.

The methods that may be used (30) to evaluate the amount of abrasion damage include:

(i) The visual assessment or microscopic assessment compared with an unbraded sample.

(ii) The number of cycles required to produce a hole, a broken yarn or a broken strip.

(iii) The loss in fabric weight plotted against the number of cycles.

(iv) The change in thickness e.g. loss in pile weight.

(v) The loss in tensile strength, bursting strength or tear strength.

(vi) Change in other properties e.g. air permeability.

In the present work the appearance of just two broken yarns in the whole of the sample area under test was considered to constitute the end-point of the test. This criterion has been used in other studies (31, 24) and has been shown to yield reproducible results.

1.4 Factors Determining Fabric Abrasion Resistance

The abrasion resistance of a fabric as mentioned earlier, is dependent upon many factors including: fibre properties, yarn and fabric constructions, fabric finishes and the type of abradant (5, 32, 33). For hydrophilic fibres, the amount of moisture present also affects the abrasion resistance (32, 34, 35, 36, 37), and this has been shown to be the case particularly with wool fabrics in recent work by Nhan and Denby (24).

Although these factors significantly affect the abrasion performance it is extremely difficult to place them in a meaningful relative order of importance.

1.4.1 Fibre Properties

1.4.1.1 Fibre dimensions and morphological characteristics

Fibre characteristics, such as cross-sectional shape and surface roughness, fibre dimensions such as length and fineness, can influence abrasion resistance through their effects on the fibre cohesion in yarns (12) and on the magnitude of the stresses and strains developed in the fibres by abrasive forces. Deterioration of yarn structure with poor cohesion will occur because of fibre removal or displacement of even a few fibres (38). Longer fibres are usually more resistant to displacement than short fibres (39, 40, 41), because the longer fibres are firmly held either by adequate twist, or by a closer interweaving of the threads. It has also been shown (39, 40, 41) that fabrics made from filament yarns are more resistant to abrasion than corresponding fabrics made from staple yarn. The longer staple yarn fabrics have better resistance than those containing shorter staple lengths (42). This suggests that fabrics made from combed yarns should be more resistant to abrasion than those made from carded yarns because most of the shorter fibres are removed during the combing operation. In addition, longer fibres make stronger yarns at equal twist and count levels (Fig.27), so that fabrics made from these yarns can withstand the application of periodic stresses more readily (43).

Although fine fibres form stronger yarns, it has been established that, within certain limits (40, 44, 45), the resistance to abrasive wear is better for fabrics composed from coarse fibres. Fibres which are too thin are easily ruptured, because only comparatively gentle forces are needed to develop high levels of fibre stress. However, fibre fracture occurs more readily during the bending of very coarse fibres, because high strains are developed in the outer layer of the bend (46). In addition, a reduction in the number of fibres in the yarn lowers the fibre cohesion which ultimately affects the abrasion resistance.

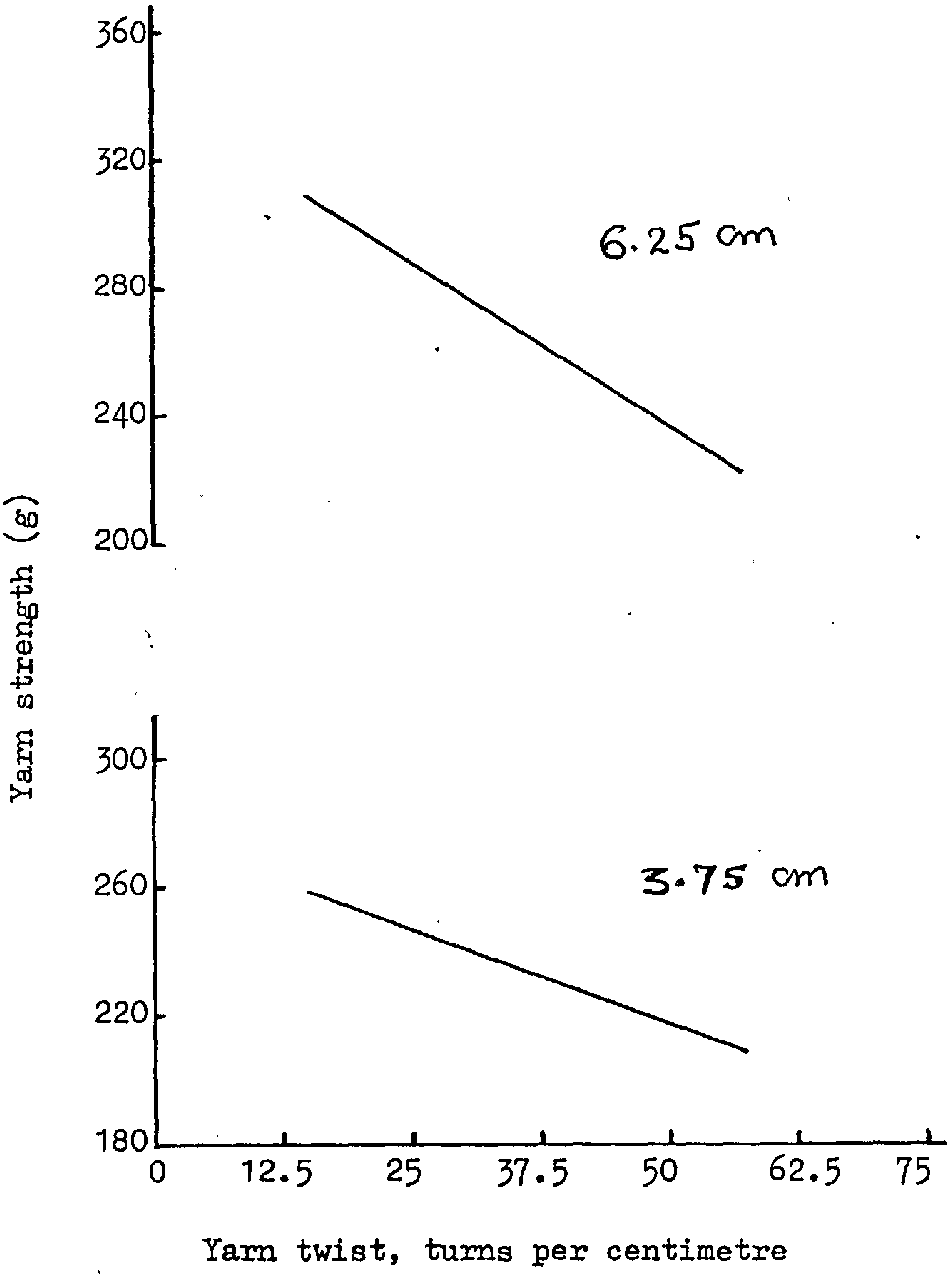
More recent work on wool fabrics made from fibres of widely varying diameter has shown (47) that this parameter has little effect on Martindale abrasion-resistance provided the fabrics are of similar weight and construction.

It has been reported (44, 48, 32) that fibres which have flat, elliptical, or hollow cross-sections favour good resistance to abrasive wear in comparison with fibres of circular cross-section.

1.4.1.2 Mechanical Properties of Fibres in Relation to Abrasion Resistance

Experiments relating abrasion resistance to the mechanical properties of the fibres have been conducted mainly on yarns, to eliminate, as much as possible, the effects of fabric structure. Abrasion performance could thus be related more closely to the fibre

Fig. 27 The effect of staple length of equal twist and count levels of secondary cellulose on yarn strength (43)



material itself which may suffer by the progressive removal of small fragments from its surface, i.e. by attrition, and also by a process of general internal disintegration induced by repeated distortion (28). For filament yarns, this procedure is particularly practical, since the maintenance of the yarn structure depends primarily on the resistance to breakage or damage of individual filaments. However for staple fibres such as wool and cotton, the effects of the yarn structure cannot be eliminated. The abrasion of staple fibre yarns involves not only the rupture or damage of individual fibres but also depends upon factors such as, twist, fibre length and interfibre friction. During the abrasion process, the interfibre friction is very difficult to assess, but it is considered that it would exert an influence on the abrasion resistance.

In spite of these complicating factors, laboratory abrasion studies have shown (32) that tensile, flexural, and shear properties of fibres largely determine abrasion resistance, and of these, the tensile properties are generally considered to be the more important.

1.4.1.2.1 Tensile Properties

In numerous studies it has been suggested that there should be a correlation between the abrasion resistance and wear of different fibres and their mechanical properties and it has been shown that abrasion resistance is higher for fibres which have a greater capacity to absorb work under conditions of repeated stretching (39, 41, 49, 13, 50). This work absorption is measured by the area under the stress-strain curve after "mechanical conditioning" of the fibre, i.e. after it has been repeatedly stressed and allowed to relax over a short period of time. The work absorption after repeated stretching is always lower than that obtained on the first extension, the reduction in work absorption depending upon the fibre elasticity (32). It has been shown that there is little reduction in work absorption for fibres with a high elasticity, while fibres with a poorer elasticity exhibit greater work absorption losses.

Table (3) illustrates the mechanical properties of some mechanically conditioned materials and the corresponding ranking of the fibres in descending order of fabric abrasion resistance (7, 33, 51).

TABLE 3

MECHANICAL PROPERTIES OF MECHANICALLY CONDITIONED MATERIALS

Material	Initial Modulus g/tex	Tenacity g/tex	Extension at break (%)	Work of rupture g/tex	Abrasion resistance min per weight loss (%)
Nylon	120	45	43	3.8	26.0
Terylene	380	33	40	1.9	7.5
Cotton	1200	40	10	1.6	4.5
Viscose	560	24	25	0.6	2.9
Acrylics	270	24	48	0.9	1.5
Wool	270	15	43	0.4	1.5
Polypropylene	160	45	38	3.2	0.8
Acetate	280	12	28	0.4	0.7

Figures 28 (a-c) show the stress-strain curves for several fibres before and after mechanical conditioning.

It can be seen that mechanical

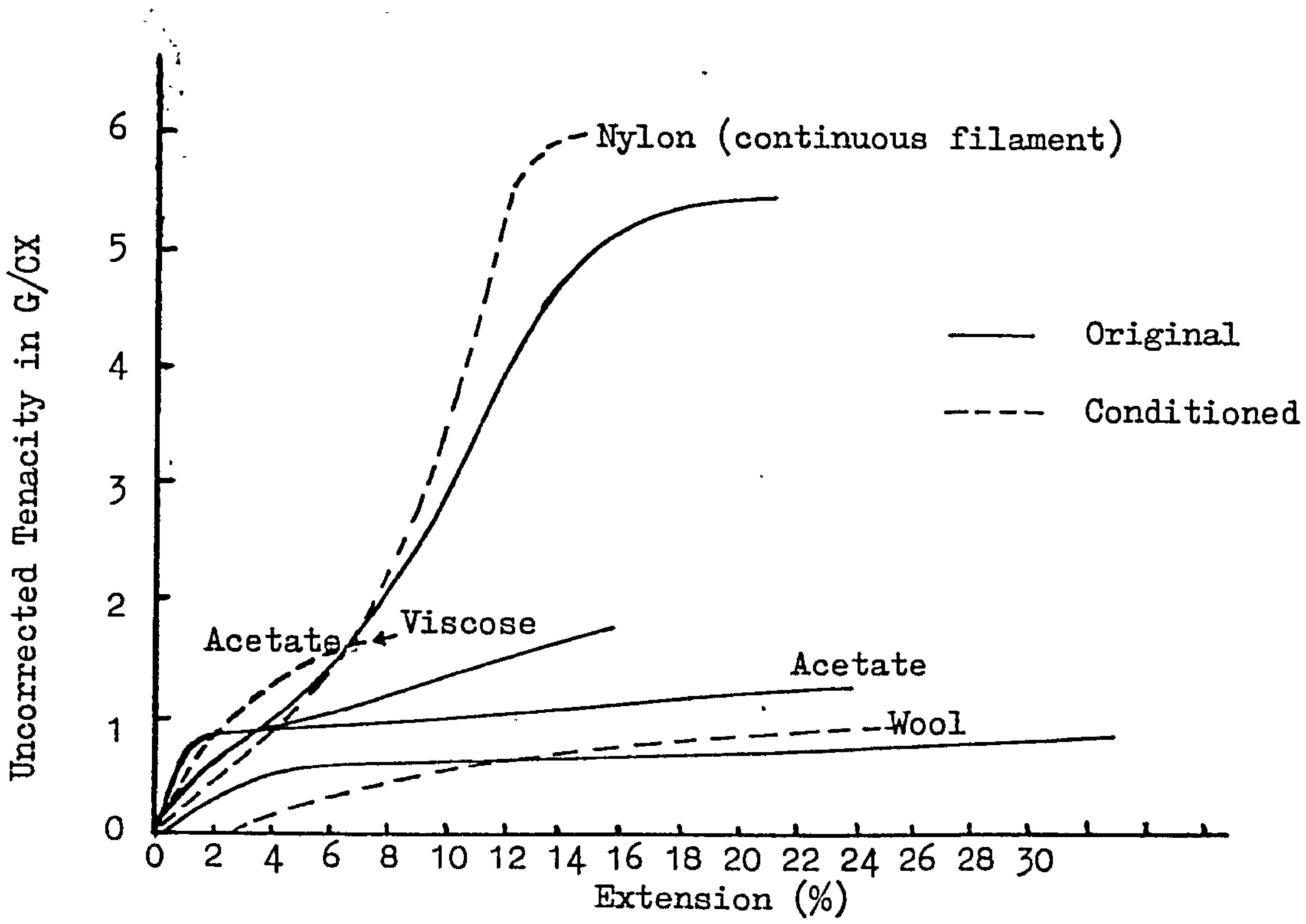


Fig. 28(a) - Stress-strain curves of fibres before and after mechanical conditioning.

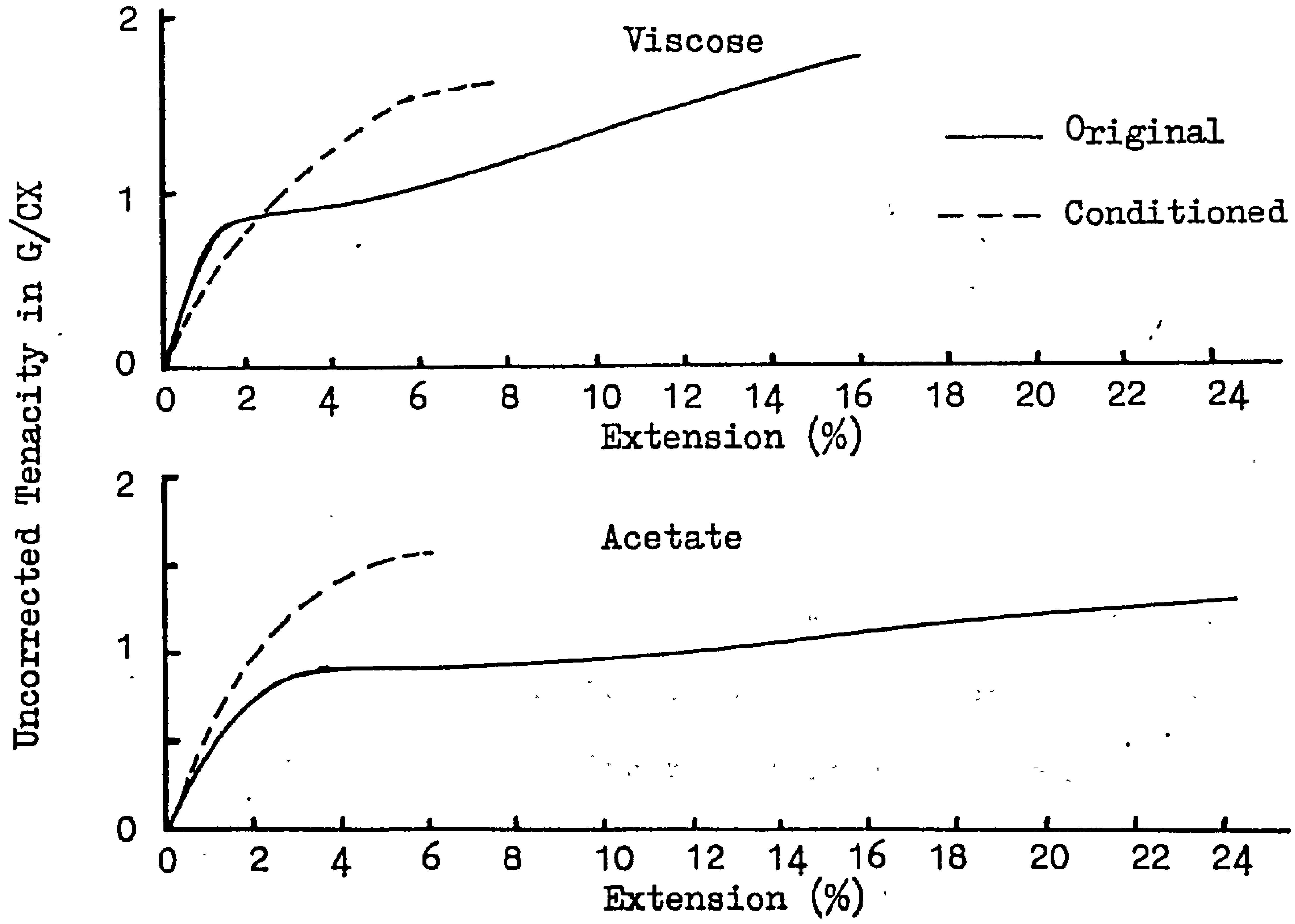


Fig. 28(b), (c) - Stress-strain curves of viscose and acetate before and after mechanical conditioning.

conditioning decreases the initial modulus of elasticity and, indeed the entire stress-strain relationship is altered. Abrasion resistance is related to the area under the broken lines in these figures, representing the work absorption of the mechanically-conditioned fibres.

It has been established (32) that the capacity for work absorption during repeated stretching depends upon: (i) strength, (ii) extensibility, and (iii) elasticity. Fibres deficient in these properties normally exhibit poor abrasion resistance. Extensibility and elasticity appear to be more important than strength, e.g, glass fibres are strong and elastic but, because of their extremely low extensibility, they are easily damaged by abrasion (52).

As can be seen from figures 28b and 28c , the work absorption of viscose and secondary cellulose acetate on first stretching is quite high, but high permanent set associated with the poor elasticity of these fibres considerably reduce their capacity for work-absorption after repeated stretching, and contributes to their relatively low abrasion resistance. Wool, although a weak fibre, has a high extensibility and like viscose and secondary cellulose acetate, exhibits high work-absorption on the first extension. Because of its high elasticity, wool retains most of its ability to absorb work after repeated stretching; hence, its abrasion resistance is quite good despite its low strength. Casein has a similar tenacity and extensibility, to wool, but casein has a much lower elasticity, so that it exhibits a much lower resistance to abrasion than wool (see figures 29 and 30).

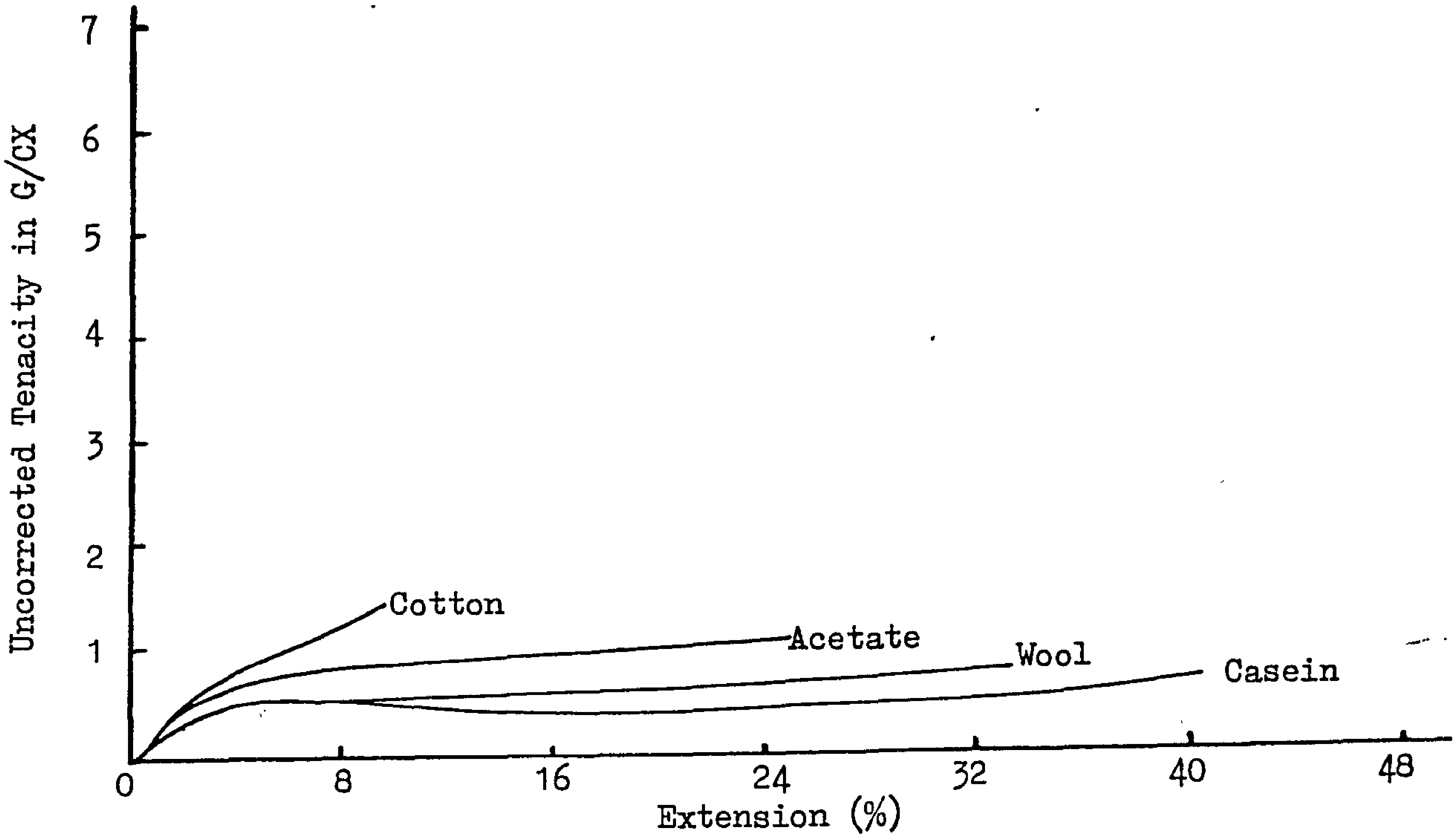

Uncorrected Tenacity in G/CX
7
6
5
4
3
2
1
0
8
16
24
32
40
48
Extension (%)
Cotton
Acetate
Wool
Casein

Fig. 29

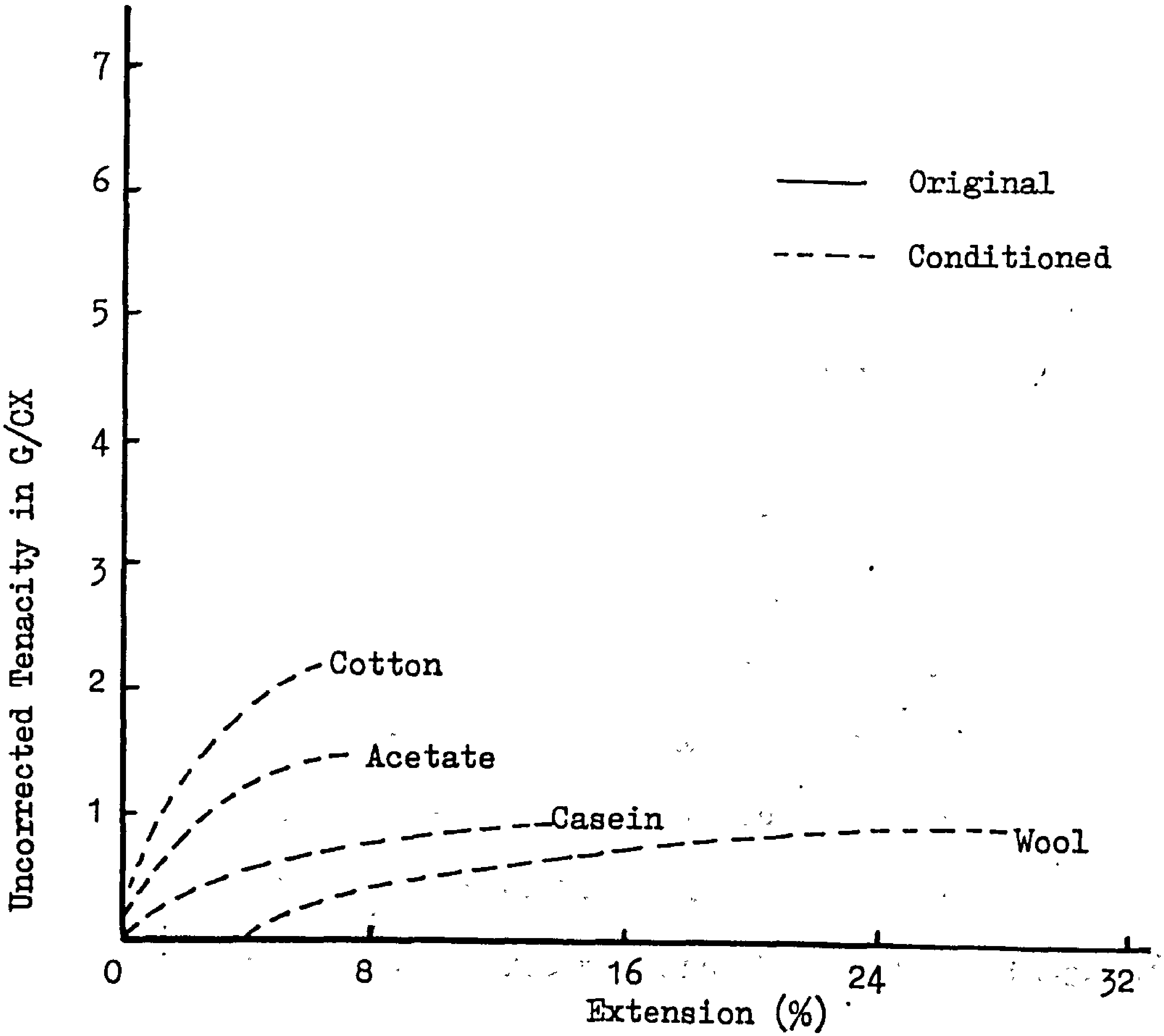

Uncorrected Tenacity in G/CX
7
6
5
4
3
2
1
0
8
16
24
32
Extension (%)
Original
Conditioned
Cotton
Acetate
Casein
Wool

Fig. 30

Mechanical conditioning does not affect the tensile properties of high tenacity multifilament nylon, to any significant degree as may be seen in figure 28a, consequently, if the deformation is repeated, the work-absorption does not diminish significantly. This in part explains the absence of severe destruction of nylon fabric by repeated flex abrasion and is ultimately responsible for its extraordinarily low abrasion damage, i.e. high abrasion resistance.

It has also been shown (41) that a staple nylon yarn which has a lower tenacity and higher extensibility compared with a similar multifilament yarn is greatly affected by mechanical conditioning. This diminishes the energy necessary for rupture after the first deformation. Therefore, the abrasive damage of a staple nylon yarn is higher than that of a nylon multifilament yarn (41).

Although the work absorption of cotton on the first extension is low compared with most other fibres, the absolute reduction in work-absorption after repeated stretching is small compared with that of viscose and secondary cellulose acetate because of its comparatively low extensibility.

On the basis of the stress-strain curves shown in Fig. 29 and 30; wool should be superior to cotton, while secondary cellulose acetate and cotton should have more or less equal abrasion resistance. But, on the contrary, the abrasion performance of cotton is much better than would be expected from its work-absorption capacity. Cotton, moreover exhibits a better abrasion resistance than wool and is far superior to that of secondary cellulose acetate (41). The very high extensibility of both secondary cellulose acetate and wool could be a possible reason for their lower resistance to abrasion compared with cotton. Although the capacity for work-absorption is higher for both fibres than for cotton, the high extensibility reduces the cross-sectional areas of both wool and secondary cellulose acetate fibres, so that concentrated stresses develop from small abrasion forces. This explanation is particularly applicable to secondary cellulose acetate, where a high proportion of the stretch is non-recoverable. The disadvantage of high non-recoverable stretch is also manifested by the abrasion performance of de-crystallized cotton (53). The latter has an increased extensibility but since most of the increased extensibility is non-recoverable, the abrasion resistance of the decrystallized cotton is therefore much lower than that of untreated cotton. In accelerated laboratory testing, cotton fabrics treated with a resin finish normally show a considerable loss in abrasion resistance. The reduction in the abrasion resistance is not a consequence of degradation of the cellulose that occurs when the resin is poorly applied (54). It is considered to be mainly due to the result of changes in the stress-strain properties of the fibres (32). Chemical cross-linking and resin deposition within the fibrils, between the fibrils, and between growth layers of the cotton fibre, hinder relative movement between these structural elements (55, 56). The decreased mobility of cross-linked structural elements decreases the fibre extensibility and increases the elastic recovery, because there is a lower tendency to form new forces of attraction resulting from the movement of the structural elements from their old positions. The strength may be reduced because the fibrils are less free to move into more oriented positions along the fibre axis. Consequently, the capacity for work absorption, and hence the abrasion resistance of the resin-treated fibres is always lower than that of untreated fibres (32).

1.4.1.2.2 Flexural Properties

The development of a resistance to fibre bending, and the tensile stress derived from the inter-fibre friction are two important factors determining the internal abrasion damage resulting from fabric flexing processes (57). Quartermaster tests on the flexing performance of nylon and wool flags indicate the importance of inter-fibre friction (5). Thus while the bending resistance of nylon and wool are equal in performance, the effects of inter-fibre friction tend to be negligible. This results in the improvement of the flex life of the bending of nylon-wool flags. The use of lubricants also suggests that the reduction of inter-fibre friction would also improve the flex abrasion resistance of the fabric (58, 59). Fibres with high elasticity (i.e. recoverable extensibility) show good bending resistance so that the order of inherent abrasion resistance might be somewhat similar to that for flexing endurance (32).

On the basis of flexing endurance, the abrasion resistance of wool should be significantly higher than that of cotton and on a par with that of nylon (58).

1.4.1.2.3 Shear Properties

Shear stress is the result of forces acting perpendicularly to the longitudinal axis of the fibres. The resistance to shear may become important when sudden abrasive forces are applied or fibre movement is restricted (60). It has been argued (61) that a balance between tensile and shear properties is desirable for reasonable abrasion resistance. Moreover, the resistance of cotton to shear as reflected in its excellent knot strength, is said to be a major factor contributing to its low abrasion damage (62). The spiral molecular arrangement in the cotton fibre is believed to contribute to its good shear properties in that the orientation of the fibrils is not completely parallel along the fibre axis (63). Abrasion studies have indicated that excessive lengthwise orientation resulting from "overstretching" of fibres reduces abrasion resistance (41).

Despite these arguments, it is difficult to visualise how shear forces can be applied to a system of twisted fibres. It seems likely that an attempt to apply shear to a twisted fibre would result in changes in the torsional strain rather than in the shear strain.

1.5 Yarn Structure

It is well-known that increasing the diameter of a yarn increases the abrasion resistance (9, 64, 65). Heavier yarns containing more fibres than lighter ones permit a better distribution of the stress for a given load and also require displacement or rupture of a larger number of fibres before attrition is brought about. However, in folded yarns, abrasion resistance is governed by the number of plies as well as the yarn thickness. For example, it has been shown (39) that the abrasion resistance of a 2-ply yarn is roughly five times that of a single yarn of equal count. Increasing yarn ply results in greater fibre cohesion, which leads to a reduction in abrasion damage.

The thickness of the yarns, which are exposed to the rubbing surface, effectively determines the abrasion resistance of the fabrics (66). For example, in sateen cloth, where only one yarn system is predominantly exposed on either surface of the fabric, it is advantageous to use coarser yarns on the surface to be exposed to abrasion, but no advantage is gained if heavy yarns are used in the protected yarn system on the reverse side of the fabric. Heavy yarns may not be effective in increasing abrasion resistance if this is measured solely in terms of changes in surface appearance. Thicker yarns may not necessarily improve the flex abrasion resistance to the same extent as the flat abrasion resistance. Higher strains on fibres in the outside curvature of larger diameter yarns may offset, to some extent, the larger mass to be abraded. It is very important to maintain the uniformity of the yarns, because degradation of individual weak places can cause breakdown of the structure as a whole.

Extensive data on the abrasion resistance of different yarns have been published by many workers (40, 13, 67). Hicks and Scroggie used the Tabor tester for testing yarns and plain weave fabrics, and it was shown that the abrasion life diminishes in the order: nylon > cotton > wool > viscose > secondary cellulose acetate and casein fibres. This finding is based on the results obtained by using different abrasion testing machines and widely varied fabric and yarn samples. Ray (68), in his investigations on wet fabrics, obtained a similar order from flex abrasion tests, by using the Stoll Quartermaster tester. Viscose and secondary cellulose acetate were found to have the lowest resistance to abrasion followed by wool and cotton, Orlon and Dacron, while nylon had the highest abrasion resistance. Matthes (69) used the T.H. Aachen yarn abrasion tester, and found that viscose, cuprammonium and secondary cellulose acetate staple yarns were less resistant to abrasion than the corresponding multifilament yarns. Susich (41) obtained similar results using the Tabor tester for viscose yarns. The reason for this may be that individual staple fibres may project from the yarn surface and may easily be pulled out or cut through. This causes a loosening of the yarn structure which increases the attrition further if torsional and bending forces act up on the yarns.

1.5.1 Yarn Twist

The degree of fibre freedom is influenced by the relative amounts of single and folding twist in yarns. High twist levels restrict fibre movement and low levels decrease fibre security. Thus there should be a optimum twist distribution between these limits for maximum abrasion resistance (40, 42, 66). This is also confirmed by recent work (47) on a series of woven plain weave wool fabrics.

Although there is no evidence that the optimum twist for strength and for abrasion performance are the same, the relationship between abrasion resistance and twist is, therefore, similar to that between tenacity and twist.

Table 4 shows the effect of twist on secondary cellulose acetate yarn strength. The optimum strength is obtained at about eleven turns per inch (t.p.i) beyond which a decrease in strength is obtained.(43).

TABLE 4

The effect of twist on Yarn Strength

Yarn twist (t.p.i) (t/cm)	Yarn strength (g)
11.0 (27.5)	257
15.0 (37.5)	246
19.0 (47.5)	230
23.0 (57.5)	214
27.0 (67.5)	197

(t/cm) = turns per centimetre

This dependence on twist reflects the changes in fibre cohesion. When fibre cohesion is high, the removal or displacement of fibres due to snagging and friction is minimised. No further improvement in fibre cohesion can be achieved if the twist exceeds the optimum value, possibly because the additional twist imposes additional stresses on the fibres (43). The optimum level of twist necessary for a staple yarn is higher than that for a continuous multifilament yarn (40, 66). Moreover, the capacity of the yarn to flatten or to rotate is reduced as the twist level is increased (43). Damage can be reduced if fibres can yield or slip under the surface of a moving abradant. These fibre actions can be obtained by both rotation and flattening of the yarns. If the yarn cannot flatten or rotate, the abrading force is concentrated into a few areas and breakdown occurs more quickly. On the other hand, if the yarn can flatten or rotate, the abrading force is distributed over a much larger area of the yarn, resulting in greater resistance to abrasion.

It is better that the firm binding of the fibres should be achieved by a close weave structure rather than by a high twist level. In fact, if the closeness of the intersections can do all that is required, it is better that the yarn twist should be low rather than high; the reason for this being that the softer the twist, the more readily the yarn can be flattened and so present a larger fibre surface to share in the resistance to the abrasive action (43).

1.5.2 Yarn Crimp

Yarn crimp is one of the important factors determining the abrasion resistance of a fabric. Crimp is calculated by measuring the difference between the projection of the yarn length in the fabric and its length after it has been unravelled from the cloth and then straightened. The amount of crimp present in a yarn determines the extent to which that yarn will rise above the fabric plane. Because abrasive degradation usually occurs first at the surface of a fabric, the projection of a yarn or set of yarns to the fabric surface increases the abrasive damage to those yarns (66). Thus, the balance between warp and weft yarn crimps often determines which set of yarns will be preferentially damaged and to what degree. In a plain woven fabric, the highest degree of abrasion resistance would probably be obtained by having the same yarn size, yarn crimp, and thread count in both warp and weft directions. This type of structure would give the most even stress distribution across the largest number of yarn crowns, thus decreasing the localized load at any one point. When the crimp balance shifts so that one set of yarns contains more crimp than the other, the set containing the most crimp rises further out of the fabric plane and sustains the first, and usually the greatest, amount of damage. The other set of yarns will be protected until the crimp crowns of the first set have been worn down enough for the abradant to come into contact with the protected yarns (66, 70).

Any change in crimp balance between warp and weft yarns during laundering or wear may change both the degree of abrasion and the point of abrasive attack (71, 72).

Slight modifications in fabric construction or weaving conditions, e.g. changes in reed width or warp tension, may considerably change the surface of a fabric by changing the crimp which ultimately change the abrasion performance (73).

If the fabric wear pattern for a particular use indicates that tensile stress will be placed predominantly on one set of yarns (usually the warp), then designing fabrics with a high weft crimp has been found to prolong the wear life of the fabric (66). This improvement in wear occurs because the weft yarns absorb abrasive stresses during wear so that the warp yarns are left relatively undamaged to absorb the tensile stresses.

1.6 Fabric Structure

Yarn formation, threads per centimetre, and weave structure affect abrasion resistance, because they determine the yarn surface area exposed to rubbing,the fibre cohesion in the yarns, the distribution of warp and weft area exposed to abrasion, and the mobility of yarns and fibres needed to prevent damage from the impact of the abrasive forces.

1.6.1 Threads per Centimetre

It has been shown by actual wear and laboratory tests that abrasion resistance improves with increasing numbers of threads per centimetre (63, 66, 74,75). This is probably so because the larger surface area exposed to the rubbing action allows stresses to be distributed more uniformly. The same principle explains the increased abrasion resistance with high pile densities and heights in carpets and with high courses per centimetre in knitted fabrics (46, 76). An increase in the number of threads per centimetre leads to an increase in the number of yarn intersections, increases the fibre and yarn cohesion within the fabric and decreases the probability that fibres will be plucked or slipped out of place within the structure (32, 66).

However, there are limitations on higher fabric setts. The use of too many yarns per centimetre causes rigid areas with restricted mobility of fibre and yarn (66). The very tightly woven structures improve flat abrasion resistance but decrease considerably the flex abrasion (77, 78, 79).

1.6.2 Weave Structure

The influence of weave pattern on fabric abrasion resistance is highly dependent on the type of abradant used, the degree of fabric flexing or bending occurring during abrasion, and the direction of stress application (32, 66, 77, 80). If the abrasion, is flat and multidirectional in nature, plain weaves provide the best fibre binding and, if the yarn count and crimp are balanced, the most equal exposure of warp and weft yarns at the fabric surface. However, modified plain weaves, such as the Oxford or basket weave, can provide greater yarn mobility than do taffeta weaves and thus allow the yarns to absorb the stress by moving away from the abradant. Twill and sateen weaves can provide even greater yarn mobility or alternatively can provide adequate yarn mobility while reaping the advantages of weaving with a higher number of threads per centimetre than is possible with plain weave structures.

Counterbalanced against the advantages of greater yarn mobility in twill and sateen weaves is the increasing vulnerability of the longer floats as they form more and more of the fabric surface. Longer float lengths are also vulnerable to plucking and snagging of both fibres and also entire yarns. However, the yarn floats in twill and sateen weaves can be used to protect the opposite set of yarns from abrasive damage. This becomes valuable when e.g. the warp must withstand the greatest degree of tensile stress during wear and can be protected against abrasive damage by the weft yarn floats in a sateen weave (66). Backer and Tanenhaus (66) reported that in twill and sateen weaves, the maximum abrasion resistance of the float system was obtained when the abrasive stress was applied parallel to the direction of the floats. However, Ruppenicker et al (77) reported that durable press suiting fabrics woven with both twill and sateen weaves exhibited better flex abrasion resistance of the float system when the abrasive stress was applied perpendicular to or across the float than when it was applied parallel to the floats. These authors reported that plain weave fabrics gave better flex-abrasion resistance than did fabrics having Oxford, basket, twill or sateen weaves, although the abrasion resistance order was reversed for simulated trouser cuff edge wear during laundering. Thus high yarn mobility was an important factor in edge wear but was less important than good fibre binding and a balanced distribution of abrasive stress over both warp and weft yarn systems in the flex abrasion tests.

Bajoloni (81) observed that resistance to abrasion increases with increase in sett and with decrease in the float length in a series of twill and sateen weave structures. Similar results were obtained by Saigal (82) and Bhagat (83). Lumb (84) agrees with this general conclusion but he believes that, for twills, the resistance to abrasion increases with increase in float length; for example, a 3/3 twill is more resistant to abrasion than a 2/2 twill.

A more recent analysis (85) of sets of cotton fabrics of different woven constructions made from the same count of yarn indicated that the difference in mechanical properties arise mainly from weave differences. Increase in flex abrasion is compensated by a decrease in tear strength and vice versa. Twill weave fabrics show high tensile strength, while basket weave fabrics give higher tear strength. The plain weave fabrics are best suited for high flex abrasion.

1.6.3. Crown Height

The height of a crown in woven fabrics depends on the weave structure, the yarn thickness, yarn crimp, thread count, and the interaction of these factors in the warp and weft directions. The damage to the fabric depends on the nature and direction of the abradant and the height and number of crowns. The higher the number of crowns, the lower will be the stress concentration per crown (33) and therefore the higher the fabric abrasion resistance.

1.7 Fibre Blending

The changing requirements of the modern way of life both at home and at work, have presented the textile industry with the task of developing fabrics with better and improved performance characteristics such as easy-care properties, durable creasing, improved laundering properties and fabric handle etc.

The introduction of the synthetic fibres opened up a whole new field and made available properties not found in natural fibres. The most important of these properties were high levels of crease recovery, high strength and abrasion resistance and easier laundering and drip-dry procedures. It was realized, however, that for many end-use areas the all-synthetic fabric was not entirely suitable because of problems such as pilling, static build-up, comfort and not least "the synthetic handle" obtained on many fabrics (86).

In order to obtain the required fabric performance the next stage was the development of blended fabrics, where fibres are blended together in an attempt to utilise the best properties of both fibres and to minimise their worst features (86).

When fibre blends were first developed, it was learned that blending stronger fibres with weaker fibres did not always increase the tenacity of the blended yarn over that of an equivalent yarn made entirely of the weaker fibre. For example, blending nylon with cotton to increase abrasion resistance led to a significant loss in yarn strength (87) but blending nylon with wool increased the yarn tenacity (87, 88, 89). Hamburger (90) attributed this phenomenon to the elongation balance between the blended fibres. When two fibres differing in modulus of elasticity and total elongation are blended, both fibres in the yarn extend up to the breaking point of the less extensible fibre (89, 91). After the rupture of these fibres the stress is transferred to the more extensible fibres in the blend. This stress concentration on only part of the fibres in the yarn thus leads to a reduction in the yarn tenacity.

Work on blended fabrics has shown that partial substitution by nylon or polyester fibres improves the abrasion resistance of wool (92, 93, 94, 95), cotton (96, 86), and viscose fabrics (93, 97), whereas the substitution of secondary cellulose acetate or viscose reduces the abrasion resistance of wool fabrics (97, 62). However, blending a more abrasion-resistant fibre with a less abrasion-resistant fibre causes other problems such as frosting and the premature knee burst phenomenon found in jeans (98). Frosting occurs when two fibres differing in both colour and abrasion resistance are combined in a fabric. This results in a gradual and perceptive colour change in the abraded areas, e.g. knees, seats and elbows, when one fibre is preferentially removed from the fabric by abrasion.

1.8. The Effects of Selective Finishing Treatments on the Abrasion Resistance of Wool Fabrics

As discussed in previous sections, there are many factors that may affect the abrasion resistance of a fabric. Fabric production is normally followed by dyeing and finishing processes which improve the desirable properties of the fabric. The finishes applied to obtain these desirable properties and the conditions of application as well as the environmental conditions, such as the relative humidity, often alter the abrasion resistance of the fabrics.

1.8.1 Binding Agents and Lubricants

Binding agents such as starches, gums etc., may be deposited on the fibre or yarn surfaces, because their particle sizes are too large to allow them to penetrate into the fibres. These agents should adhere firmly to the fibre, thus cementing the fibres together and protecting them from abrasion (99, 100). Generally binding agents improve the resistance to flat abrasion, where damage is largely due to surface rubbing without flexing or bending (101, 102, 103), but they do not improve the flex abrasion (104, 105) properties.

Lubricants increase fibre mobility by encasing fibres in smooth films instead of forming a compound within the fibres, or binding and restricting fibre motion. The improvements in flex abrasion resistance obtained with lubricants can be attributed to a reduction in the surface friction and increased fibre and yarn mobilities resulting from reduced interfibre and inter-yarn friction (32, 106, 107). The effects of lubricants on flat abrasion resistance have not been clearly determined, but the use of small amounts of lubricant should improve abrasion resistance as a result of the decrease of surface friction. Syed (108) has shown that solid additives were not successful in this respect.

1.8.2 Moisture Regain

The amount of moisture present in a fabric has little effect on the abrasion resistance of hydrophobic fibres but does affect that of hydrophilic fibres.

Rollins and co-workers (35) and Chippindale (36) reported that wet abrasion of cotton fibres caused extensive fibrillation of the fibres whereas dry abrasion caused more surface erosion, bruising, and mashing. When resin-finished cotton fibres were abraded wet, the fibrils tended to peel off in sheets or strips rather than as individual fibrils. Dry abrasion of cross-linked fibres caused transverse cracks and fractures.

Because water absorption increases both the strength and extensibility of cotton, McNally and McCord (32) theorized that the abrasion resistance of cotton would be higher in the wet state compared with the dry state. However, de Gruy et al (109) found that wetted-out cotton yarn specimens required fewer Stoll flex abrasion cycles to cause rupture than did dry yarns.

Markezich (110) and Reid (37) described various test methods for evaluating abrasive wear in textiles and pointed out differences under wet and dry abrasion conditions in different types of laboratory apparatus utilized for testing fabric wear. They found that in the Accelerotor abrasion test method, cross-linked samples showed a greater weight loss after abrasion than did the untreated control; there was a greater increase in weight loss with decreasing moisture content, while variation in moisture content had a smaller effect on the abrasion resistance of the untreated sample.

Caldwell and Warfield (98) found that viscose fabrics were much less abrasion resistant in the wet state. This is to be expected because of the great loss of fibre strength when wet.

Recent studies (24) on the effects of relative humidity (r.h) on the abrasion resistance of wool fabrics has indicated that changes in relative humidity can significantly affect both the fabric abrasion resistance and the morphology of fibre breakdown.

Figure 31 shows that the abrasion resistance of wool fabrics is very dependent on the relative humidity of the samples. The end-point ranges from 10,750 rubs at 8% r.h., to 58,000 rubs at 83% r.h. The abrasion resistance increases moderately with increasing r.h., whereas, in the high humidity region ($>$65% r.h.), a slight increase in r.h. improves the abrasion resistance of wool fabrics significantly.

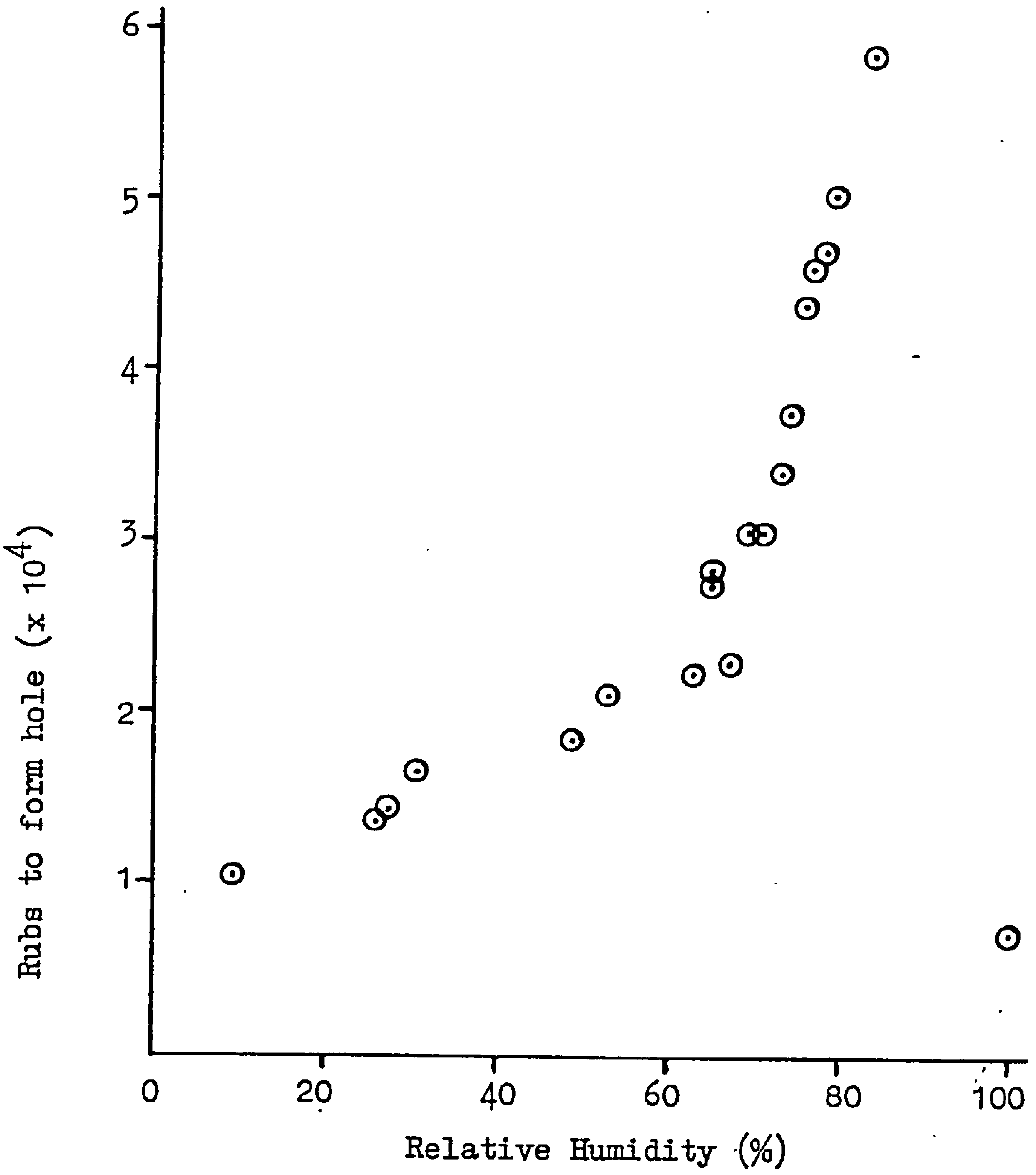
At 100% r.h. (i.e. wet abrasion) the abrasion resistance was decreased, as illustrated in Figure 31 . The results for wet abrasion were also claimed to be substantially the same whether the fabric was shrinkproofed or not.

1.8.3 The Effect of Heat

Thermal treatments are a necessary part of wool processing to produce a finished product with desirable properties, but there must be a balance between the achievement of desirable improvement in the performance of wool products and the loss of performance that is usually associated with thermal degradation.

A high temperature dry heat treatment always causes an appreciable change in the physical chemical and morphological properties of wool keratin (111). The heating of wool to temperatures above 100°C can cause rapid fibre degradation which is accelerated by the presence of water (112). The fibres undergo a variety of chemical

Fig. 31 - Relation between relative humidity and abrasion resistance of wool fabrics.



changes; the nature of these changes depends upon factors such as temperature, time of heating and also pH.

An extensive study of the hydrothermal degradation of wool keratin at temperatures up to 100°C and for higher temperatures has been made by Sweetman (113-114). His reports feature a comprehensive referencing of the earlier literature and give detailed amino-acid analyses for wool after selected treatments. Sweetman also drew comparisons between the effects of liquid water and saturated steam with respect to chemical degradation, and because of the practical interest in setting processes, made some measurements illustrating the chemical degradation of wool at 25% water content. Dry keratinous materials exhibited a much greater resistance to heat (114).

Zahn (115) reported that no degradation occurred in dry horsehair below 150°C, and Mazingue and Van Overbeke (116) reported that heating of wool in the absence of water vapour to temperatures as high as 160°C brought about only slow degradation. Watt et al (117) heated dry wool in vacuo to temperatures as high as 150°C for periods up to 30 min. without weight loss other than water, but heating to temperatures above 160°C for even short periods brought about permanent damage, as indicated by a loss of weight. However, Bull (118) found that moist wool at 105°C readily discoloured and degraded.

Wool fibres in fabric heated slowly to 230°C changed to brown, but showed no surface abnormality (119). Fabric heated for 30 s in silicone oil showed plastic deformation and contraction. Contraction increased rapidly with temperature above 220°C with the maximum near 240°C. Above this temperature the fabric becomes very fragile.

Bell, Hutchinson and Whewell (120) reported that under severe heating conditions, for example, 2 hours at 180°C, wool loses about three-quarters of its strength as measured using single fibre strength data. Treatment with certain metal salts (Zinc or Cadmium Sulphate) leads to an appreciably lower strength loss, though under these conditions it is still high. Table 5 shows the results obtained under these treatments.

TABLE 5

Conditions of heating 180°C in an Atmosphere of Nitrogen

Duration of heating (h)	Breaking Strength (arbitrary units)		
	Untreated	$ZnSO_4$-treated	$CdSO_4$-treated
0	100	-	-
2	40.2	52.3	52.2
3	26.8	30.7	36.5

From torsional properties and other data Menefee and Yee (121) deduced that when wool is heated in vacuo the following succession of events occurs;

(i) Ordinary drying,

(ii) Removal of strongly bound water at 150°C,

(iii) A possible glass transition in the amorphous protein at about 160°C,

(iv) Slow formation of amide crosslinks at 160°C,

(v) Melting of a small part of the ordered wool protein at 215°C, after which

(vi) Amide crosslinks form rapidly,

(vii) Melting of the major ordered part of the wool protein at 235°C,

(viii) Disulphide cleavage between 230 and 250°C and

(ix) General pyrolysis above 250°C.

Therefore, heat treatment of wool at high temperatures should be carried out with great care, with the knowledge that the presence of water, the time of heat treatment, and the pH, oxygen concentration etc., could affect the type and degree of fibre damage and also exert changes in certain fibre properties such as strength, extensibility, elasticity etc. These ultimately are likely to affect the abrasion resistance of the fabric.

1.8.4 The Effect of pH

The practical importance of the effects of acid and alkaline treatments in dyeing and finishing processes has led a number of workers to study the changes occurring when wool is treated in such media (122).

Measurements of the resistance to abrasion of wet wool fabrics have been useful in demonstrating the effects of various acid and alkaline conditions. The resistance to abrasion of fabrics previously treated for one hour over a range of temperatures in solutions of different pH values are shown in Table 6, (123). It is clear that solutions of pH 4.9 - 6.2 have comparatively little effect even at high temperatures, but as the pH progressively rises above pH 6.2, increasing treatment temperatures promote fibre damage presumably due to rupture of the disulphide bonds.

The results shown in Table 7 refer to fabrics which had been soaked in aqueous solutions at various pH values and then wet blown. Maximum resistance to abrasion is obtained when the fabric is processed at pH 6.2, and adverse modification increases with increasing acidity or alkalinity. There is clearly a necessity for pH control in operations such as crabbing and blowing, for not only is the amount of permanent set determined by the pH, but the amount of fibre

TABLE 6

Resistance to abrasion* of fabrics treated for 1h

Liquid pH	Temperature °C								
	18	30	40	50	60	70	80	90	100
1.2	1474	1430	1137	1044	1011	967	858	598	191
1.8	1668	1615	1526	1435	1452	1313	1064	779	464
3.1	1713	1621	1592	1430	1312	1229	1160	1100	859
4.9	1928	-	-	-	1902	-	-	-	1935
6.2	2034	-	-	-	1963	-	-	-	1943
7.2	2073	-	-	-	2028	1937	1855	1650	1318
9.2	1951	1898	1750	1558	1502	1306	1113	782	504
10.8	1892	1764	1395	1189	982	817	494	216	20

* Expressed as one tenth of the number of revolutions of the ring wear tester required to wear a hole. Value for untreated fabric 2034.

TABLE 7

pH	1.3	2.0	2.8	5.5	6.2	9.2	10.4
Resistance* to Abrasion	1342	1390	1754	1982	2066	1187	1036

* Expressed as one tenth of the number or revolutions of the ring wear tester required to wear a hole. Value for untreated fabric 2034.

degradation and colour bleeding increases rapidly at pH values greater than 7 due to disulphide bond breakdown and other factors (124).

Peryman (125) has shown that the damage to wool in boiling aqueous solutions is pH dependent. The effect of pH at the boil on the abrasion resistance of yarn is shown in Figure 32.

It is clear that no change in abrasion resistance has occurred as the results of boiling at pH near 3 but between 3 and 7 increases up to 20% have occurred. Sodium sulphate in concentrations up to 9.2 $g.l^{-1}$ has shown relatively little effect on the wool within pH range 1.7-6.8; but above pH 6.8 the presence of sodium sulphate has caused alkali damage which increases rapidly with increase of salt concentration and rise of pH.

1.8.5. The Effect of Shrink-resist Treatments

While the literature on shrink-resist treatments for wool is extensive (126), only a brief summary will be given here of those treatments which are known to affect the abrasion resistance.

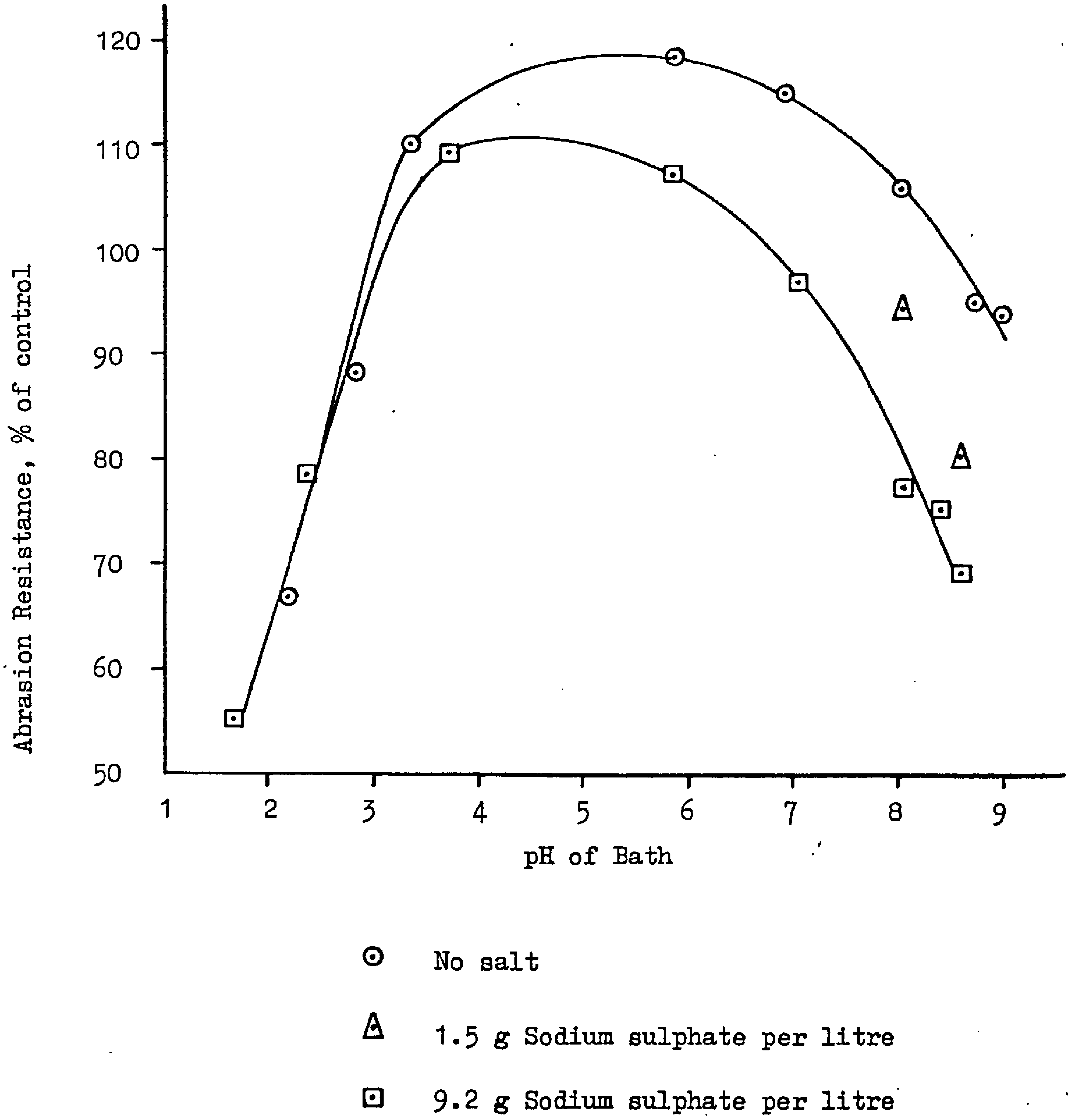
All shrink-resist processes for wool may be broadly classed either as subtractive or additive processes. Subtractive processes are so-called because they involve the loss of a small amount of the weight of wool as a result of the treatment. These processes are mainly oxidative in character.

Additive processes are those in which a polymer is deposited on the surface of the fibres. These usually lead to a small increase in weight, but may involve a preliminary oxidative treatment in order to increase the critical surface tension of the wool and hence improve the adhesion of the polymer to the fibre surface.

1.8.5.1. Subtractive processes

Veldsman and Swanepoel (127) investigated the influence of the rate of chlorination on the shrink-resistance of wool fabric with

Fig. 32 - Effect of pH of boiling on abrasion resistance of yarn.



Dichloro-isocyanuric acid (DCCA). The rate of chlorination of wool with DCCA was varied by changing the pH, temperature, or reagent concentration at which the treatment was carried out. The results show that an increase in the reaction rate, caused by changing the temperature or the reagent concentration, slightly increased the resistance to felting. An increase in the pH on the other hand affected the nature of the chemical reactions involved and reduced the efficiency of the treatment substantially.

TABLE 8

Concn. of DCCA (% O.W.W)	pH of liquor	Time of reaction (min)	Abrasion Resistance (Rubs to hole)	% Area shrinkage (after 120 min. washing)
Untreated	-	-	364	49.8
3	4	16	403	18.2
6	4	8	395	13.3
9	4	7	416	12.4
12	4	4	370	12.6
3	6	30	384	35.2
6	6	18	417	32.7
9	6	14	371	33.8
12	6	8	395	30.1

The results of the abrasion resistance determination are given in Table 8 and show no response to changes in the reaction rate. Further the abrasion resistance values confirm that wool material shrink-resisted with DCCA show increased abrasion resistance.

McPhee (128) studied the reaction of wool with sodium hydroxide in concentrated salt solutions. Wool samples were treated in 1.25 N NaOH solutions for 15 min. at 25°C. The effect of various added salts was studied using both 2M and saturated solutions. It was found that the anions protect wool from alkaline degradation in the order: $S_2O_3^{--} > SO_3^{--} >$ citrate $CO_3^{--} > SO_4^{--} > C_2H_3O_2^{-} > Cl^{-} > Br^{-} > NO_3^{-} > I^{-} > CNS^{-}$ and that cations protect in the order $Li^{+} > Na^{+} > K^{+}$. The protective action of sodium and lithium salts increases with concentration.

The fact that addition of sodium chloride decreases the swelling of wool in aqueous sodium hydroxide (129) suggests that this may be a way of reducing damage, and sodium hydroxide-sodium chloride solutions do lower the feltability of wool (130). Results of practical interest are that wool can be shrink-resisted with minimal damage by treatments with certain aqueous sodium hydroxide solutions and that yellowing of wool in alkaline media can be prevented by the addition of reducing agents, such as sodium bisulphite (128).

Concentrated salt solutions protected wool from oxidative degradation. Oxidising agents produce a higher degree of shrink-resistance when present in concentrated salt solutions than in the absence of salt. Many oxidative treatments followed by reductive treatments shrink-resist wool when the separate treatment alone does not (131).

The properties of wool after treatment in concentrated sodium chloride solution with 2% permonosulphuric acid followed by sodium bisulphite with either 2% potassium permanganate plus sodium hypochlorite containing 2% active chlorine, or 1% peracetic acid plus sodium hypochlorite containing 2% active chlorine, are summarized in Table 9 (132).

Treatment with permanganate/hypochlorite gave the highest weight loss. However, this was the only treatment to soften the handle. Resistance to abrasion was decreased, the least change occurring with acid bromate/salt treatment and the greatest with permonosulphuric acid. The composition of the acid bromate/salt solution was: 0.8% (wt/vol) potassium bromate, 0.75% (vol/vol) Calsolene oil HS and 0.5N acid in 4M sodium chloride.

TABLE 9

Properties of Wool Shrink-resisted by Oxidative Treatments.

Treatment	Weight decrease (%)	Handle	Alkali Solubility	Area Shrinkage	Abrasion Resistance Mg-wt. loss for 5000 rubs
Untreated			12	40	17
Acid bromate/salt 1.5 potassium bromate (% w.o.w.)	0.6	Harsh	17	6	20
4%, permanganate/salt potassium permanganate (w.o.w.)	0.3	Unchanged	18	5	26
Permonosulphuric acid	0	Unchanged	21	7	35
Permanganate + hypochlorite	1.1	Softened	20	5	30
Peracetic acid + hypochlorite	+0.1	Unchanged	20	8	32

1.8.5.2 Additive Processes

One of the main purposes of polymer deposition in and on wool is to make woollen and worsted fabrics shrink-resistant to laundering, dry-cleaning, and tumble drying processes. Other desirable modifications may include increase in abrasion resistance, tensile strength, and resistance to pilling, without affecting the handle, resiliency, wrinkle recovery and the dyeing properties of the fabrics. Additionally, some polymers can impart oil-, water-, and soil-repellency to fabrics.

Depending upon the molecular weight of the product applied, additive treatments can be subdivided into monomer and prepolymer processes.

1.8.5.2.1 Monomer Processes

The approach adopted by early workers towards additive treatments was to apply monomers, usually having a molecular weight of less than 500, to the wool and to polymerize them in situ. The monomers used included anhydrocarboxyglycine (133), diisocyanates (134), silicones (135), acrylic acid esters and related compounds (135) urea-formaldehyde and melamine formaldehyde precondensates (136) and these and related treatments have been described in detail by Moncrieff (137).

This technique produced polymer coatings of low shrink-resist effectiveness, so that high application levels, with a consequent loss of handle, were necessary to give only moderate levels of shrink-resistance.

The interfacial polymerization technique (IFP) has been one successful technique for depositing polymers on the surface of wool fibres. This process masks the natural scales of the fibres, and is the basis of the Wurlan process for imparting shrink-resistance to woollen fabrics and wool tops, without affecting their handle significantly. Uniform films of polyamide resins can be formed readily on wool fibres, and very high levels of shrink-resistance, together with improved fabric physical properties are possible (138). For fabrics, the combination of hexamethylene diamine (HMDA) with sebacoyl chloride is particularly effective. However this process has been superceded by cheaper and more effective treatments.

In general, there is little problem in dyeing the treated material and normally very little shade change occurs if material dyed with fast dyes is treated with the process. The results (Table 10) of abrasion tests on a woollen fabric treated with a polyamide using the Wurlan technique indicate the very great benefits which can be obtained by the use of polymer treatments on wool (139).

TABLE 10

	Stoll flex abrasion cycles (warp)
Untreated-dyed fabric	351
Treated-dyed fabric	461

The Stoll flex abrasion and tensile strength of standard woollen fabric after IFP treatment and dyeing with an acid pre-metallized dye are given in Table 11 (139).

TABLE 11

Abrasion resistance of IFP-treated-dyed and dyed standard flannel

Property	Untreated	Untreated -dyed	IFP-treated-dyed 0.5% HMDA	IFP-treated-dyed 1% HMDA
Stoll flex (warp) cycles.	573	351	484	467
Tensile Strength (lb)				
Cut strip, warp	19.2	18.5	22.4	22.8
weft	18.6	16.4	18.4	20.3

The results show that the tensile strength of the treated-dyed material was greater than that of the untreated control whereas the tensile strength of the untreated-dyed material was lower. This is in marked contrast to many chemical shrink-resist processes which adversely affect the tensile strength during dyeing (140). The Stoll flex abrasion data show an improvement in the treated-dyed material over the untreated-dyed material due to the protective nature of the polymer coating. The fabric properties after Wurlan treatment and after treatment by a mill oxidative process are given in Table 12 (141).

TABLE 12

Comparison of Properties of Fabric after Wurlan and Oxidative Treatments.

Property	Untreated -undyed	Wurlan process -dyed	Mill oxidative process-dyed
Stoll flex, cycles			
warp	573	470	144
weft			
Tensile Strength (lb)			
(Cut strip) warp	19.2	22.8	17.5
weft	18.6	19.5	16.3
Alkali Solubility %	12.5	13.8	21.1
Dye fastness in washing	-	Excellent	poor

The tensile strength of the Wurlan-treated fabric was slightly greater than that of the untreated fabric, whereas that of the oxidative-treated fabric was significantly lower. Of special interest are the low flex abrasion resistance treatments where the alkali solubility of the mill oxidative-treatment sample was high. Although both treated fabrics were dyed with the same formulation, the Wurlan-treated sample was relatively wash fast, whereas the oxidative-treated sample was not.

Evaluation (142) of interfacially formed polyurea coatings as finishing agents by Whitfield indicated that wool fabric modified by an aliphatic polyurea derived from oleic acid dimer diisocyanate (DDI) and ethylene diamine (EDA) had greatly improved handle and reasonably good shrink resistance, but required higher treatment concentrations (up to 6%) of the DDI compared with that required for stiffer aromatic polyureas based on diphenyl methane diisocyanate (MDI), probably due to lower reactivity of the aliphatic isocyanate.

Copolyureas derived from DDI and MDI have been examined in detail (142). It has been shown that relatively small amounts of MDI markedly improve the shrink-resistance of the wool fabric while the aliphatic polyurea yields a considerably softer handle. Excellent shrink-resistance is obtained with fabric modified with copolyureas derived from ethylene and a mixture of DDI and MDI, with improvement in break strength and flex abrasion and without deleterious effects on other textile properties. Data obtained from these treatments on flex abrasion and area shrinkage are shown in Table 13.

TABLE 13

Textile Properties of Polyurea-Modified Wool Fabric.

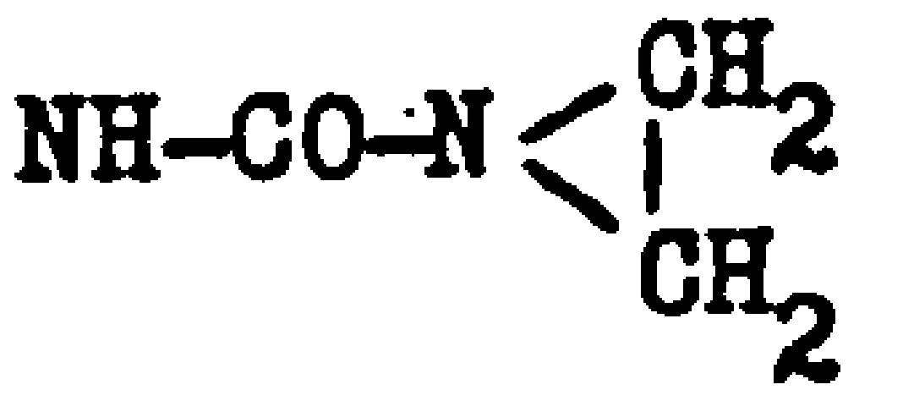
A Polyurea* derived from EDA - Reaction with DDI	MDI	Stoll Flex Abrasion (cycles)	Fabric Area Shrinkage (%) (after 4x75-min washes).
0	0	554	51.3
6	0	757	9.5
0	3	547	0.9
6	3	590	0.3
6	2	583	0.6
6	1	528	0.5
6	0.5	619	2.5
6	0.25	633	3.6

*(EDA - Ethylenediamine (2% in water))
(MDI and DDI, 6% in xylene)

1.8.5.2.2 Prepolymer Processes

The prepolymers currently used in shrink-resist processes for wool usually have a molecular weight of greater than 500, which prevents their diffusion into the fibre, and reactive groups which permit the prepolymer to be polymerized to form a high molecular weight polymer on the fibre surface.

Early prepolymer processes used natural (143) and synthetic rubbers (144, 145) and these have been discussed in detail by Moncrieff (137) who observed that the comparatively high treatment levels applied (10% polymer on weight of fabric) usually had a detrimental effect on the fabric handle.

Various aziridine derivatives have been proposed as shrink-resist agents for wool. It is reported (148) that the effectiveness of aziridines as shrink-resist agents is related to the basicity of the ring nitrogen atoms, so that amino-aziridines provide good shrink resistance while amido-aziridines do not. Use of a polyamide together with an amido-aziridine was suggested to improve the efficiency of finishes containing the amido-aziridine group -  $NH\text{-}CO\text{-}N\left\langle\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\right.$, formed by reaction of an isocyanate and ethyleneimine. It is also reported (146) that amido-aziridine finishes greatly stiffen fabrics and cause severe losses in abrasion resistance. (Table 14).

Wasley and Pittman (147) found that amido-aziridines obtained by reaction of ethyleneimine with poly(butyleneoxide)-based urethane polymers are quite effective as shrink-resist agents. They do not require polyamine additives. They cause little or no loss of abrasion resistance and only slight changes in fabric handle.

TABLE 14

Properties of Aziridine*-treated Fabric

Fabric	Flexural rigidity warp mg-cm	Stoll flex abrasion (warp cycles)	After 5 Washes and tumble drying. Fabric Area Shrinkage(%)	Appearance
Woollen				
Treated	124	840	2	excellent
Untreated	113	870	42	poor
Worsted				
Treated	155	1100	3	excellent
Untreated	141	1160	36	poor
Wool/Cotton 50/50 Blend				
Treated	76	900	2	excellent
Untreated	65	2500	17	poor

*From Adiprene L-100 and ethyleneimine.

Synthappret LKF (Bayer) was the first polypropylene oxide-based reactive prepolymer to be used as a shrink-resist treatment for wool fabrics and garments and this product is still used commercially to a limited extent today. The product is synthesized by reacting the polyol with a diisocyanate to form an isocyanate-terminated prepolymer which is chemically similar to the products used in the manufacture of flexible polyurethane foams (148). The product is usually applied to wool garments from perchloroethylene $CCl_2=CCl_2$ solvent using modified dry-cleaning machines. The treated garments are then stored in ambient conditions and the prepolymer polymerizes to form a high molecular weight polyurea by reaction with atmospheric moisture. The application of the product in this way has been reported by many workers (149-152). Normally 1-1.5% polymer on weight of wool fabric is sufficient to confer an adequate level of shrink resistance. This polymer process has been considered to lead to masking of the scale tips of the fibres and increases the smoothness of the fibre. It also improves the fabric abrasion resistance (148). Interfibre polymer bridges are also formed and thus a reduction in the rate of pilling and an increase in fabric strength would be expected. This process is effective as a shrink-resist treatment for both woven and knitted fabrics but not for loose wool and slubbing (150) because the polymer bridges formed between fibres interfere with subsequent processing of wool into yarn form.

Another method suggested (153) for forming a film of polymer on the wool fibre is to use the phase-boundary cross-linking technique employing polyethylene derivatives such as, Hypalon, a chlorosulphonated polyethylene and Zeset TP (Du Pont), a terpolymer of Ethylene, Vinyl acetate and Methacryloyl chloride. The wool is first padded through an aqueous solution of diamine and then through a solution of Zeset TP or Hypalon in a water-immiscible organic solvent.

It has been shown (153) that relatively small amounts (up to 3%) of Zeset TP or Hypalon are effective with a subsequent improvement in fabric breaking strength and flex abrasion resistance and generally without deleterious effects on other textile properties (see Table 15).

TABLE 15

Properties of Hypalon-and Zeset TP-treated fabrics

Treatment	Stiffness (mg-cm)		Fabric Breaking strength (lb)		Stoll flex abrasion (cycles)		% Area shrinkage after 2 x 75 min. wash.
	warp	weft	warp	weft	warp	weft	
None	146	111	17.9	17.8	660	668	31.5
1.5% Zeset TP	166	169	20.2	19.9	805	766	8.5
3% Zeset TP	245	230	20.6	20.9	773	680	+ 0.2
1.5 Hypalon	171	152	19.3	20.1	718	747	0.5
3% Hypalon	210	217	19.8	19.8	795	854	0.2

+ = increase in fabric area.

Polythiols have also been successful in this respect and relatively small amounts are sufficient for shrink-resist effectiveness (154). The handle of wool fabrics resulting from treatment with Polythiol A2 is considered soft, especially at low levels of treatment and becomes almost indistinguishable from untreated wool after one wash. The flat abrasion resistance of wool (flannel) fabric is increased and the results obtained with various amounts of polythiol A2 applied from aqueous emulsion or perchloroethylene are shown in Table 16.

TABLE 16

Polythiol A2 (% o.w.f.)	Abrasion resistance, (applied from aqueous emulsion)	No. of rubs to hole (applied from perchloroethylene)
0	12,000	-
1	15,670	13,000
2	20,750	14,750
3	19,000	16,250

Studies (155, 156) of wool treated with aqueous dispersions of self-cross-linking polyacrylates indicated that a high level of shrink-resistance, an increase in tensile strength and abrasion resistance and a reduction in tumble drying shrinkage and pilling can be obtained. The softer polyacrylates appear to be generally more useful for wool application than the harder types and the softest acrylate polymer available scarcely changes the handle from that of untreated wool. Treatment with this polymer (Primal K-3) also has no effect of practical significance on the stiffness, tear strength and wrinkle recovery of wool fabrics. In addition, this process gives the highest increase in abrasion resistance for a given weight of polymer, together with a small increase in tensile strength, and is most effective in reducing pilling. Table 17, shows the abrasion resistance of wool fabric treated with various polyacrylates (157).

TABLE 17

Abrasion resistance of a woollen fabric treated with various polyacrylates

Polymer	(% o.w.f.)	(%) Area shrinkage (after severe one hour washing test)	Martindale Abrasion Resistance (rubs to hole).
Untreated		49	8,500
Very 'soft' polyacrylate (primal k-3)	3.5	5	20,200
'Soft' polyacrylate (primal HA-8)	4.1	5	19,200
'Medium' polyacrylate (primal HA-12)	5.2	4	16,400
'Hard' polyacrylate (primal HA-16)	6.5	6	14,700

Feldtman and McPhee (156) have also shown that the effectiveness of polymer treatments as shrink-resist treatments was further increased if the wool was subjected to mildly degradative pretreatment before polymer application.

Polyacrylates are more effective when applied to fabrics made from woollen-spun rather than worsted-spun yarns. This effect, which prevented a greater commercial use of this type of polymer has been attributed (156) to the greater ease with which the polymer emulsion can penetrate the woollen yarn. Furthermore woollen yarns will contain a higher proportion of fibre tips which have been shown (158) to have a higher surface energy than the fibre roots due to the degradation which has occurred in the fleece as a result of natural weathering processes.

A further disadvantage of the self-cross-linking polyacrylates is that the treated fabric has to be heat-cured (e.g. 5 min at 130°C) in the presence of acidic catalysts to effect the cross-linking reaction of the polymer. An exhaustion technique for applying polyacrylates has given promising results (159) but results of industrial trials do not appear to be available.

During the last decade the International Wool Secretariat and Dow-Corning Ltd. initiated the development of a silicone elastomer(DC 109) for prevention of shrinkage in washing with minimum effect on handle, and the work which they carried out has been reported elsewhere (160). Since that time the process has been introduced to industry and is currently being used in production in many countries, mainly for knitwear, although increasing interest is being shown for solvent application to piece goods by either batch treatment or open width padding techniques.

Silicone crosslinking resins can be applied to wool to give a Superwash garment or fabrics, with a minimum of machine modifications. Superwash processes are those generally marketed under the I.W.S. scheme with suitable standards for producing machine-washable wool garments. The mode of action of the cured polymer appears to be by scale masking and interfibre polymer bonding. Such treatments give improved abrasion resistance, wrinkle recovery, and pilling in nearly all cases. for woven woollen and double jersey fabrics (161).(See Table 18).

Another polymer which has been successfully used and is still in commercial application today is the water soluble-epichlorhydrin resin Hercosett 125 (a polyamide resin). Small amounts of resin give a high degree of shrink-resistance. The same amount of resin gives far greater resistance to shrinkage when applied to fabrics pretreated either in bromate/salt or in acid/hypochlorite solution. The pretreatments enhance the results of the resin by allowing the resin to spread more uniformly over the fibre surface (162, 163).

TABLE 18

Fabric Type	Fabric Construction	DC 109 level (%)	Abrasion resistance (rubs to hole) after three weeks. Treated	Untreated
1 Woollen	plain weave	2.8	11,000	8,000
2 Woollen	plain weave	2.8	45,000	2,800
3 Woollen	plain weave	2.8	25,000	18,500
4 Worsted	double jersey	2.5	30,000	36,000

Generally better results on shrink resistance are obtained with given weights of resin on woollen fabrics than on worsted fabrics (164, 162). The properties of resin-treated fabrics are given in Table 19, and it is clear that treatment of wool with a polyamide-epichlorohydrin resin produces shrink-resistance, increases tensile strength and abrasion resistance and reduces the tumble drying shrinkage and pilling. The tear strength is reduced slightly. The treated fabric is stiffer and harsher than the untreated material and the wrinkle recovery is reduced. The magnitude of all these effects depends both on the concentration of resin on the wool and also on the degree of chemical pretreatment. Lankrolan SHR3 (Diamond Shamrock), a Bunte salt-terminated poly-(alkylene)-oxide polymer is also being applied as a shrink-resist treatment for wool fabrics.

The presence of the Bunte salt groups in the polymer makes Lankrolan SHR3 soluble in water and although it can be applied by a pad-dry process the limited stability of the treatment bath and the stiffened handle of treated fabrics (165) have restricted its use in this area. A more interesting property of the product is that it can be applied with reactive dyes to wool fabrics by a cold pad-batch process (166). The presence of sodium bisulphite in the treatment liquor is essential if a shrink-resist effect is to be obtained and it has been suggested (166) that the purpose of the bisulphite is to form thiol groups in the wool which react with the Bunte salt groups of the polymer to form a mixed disulphide.

TABLE 19

Properties of Flannel Fabric after treatment with Polyamide-Epichlorohydrin resin.

Chemical Pretreatment	Concn. resin on wool (%)	Warp tensile strength (Kg)	Extension at break (%)	Warp tear strength	Abrasion resistance No. of rubs to hole.	FAFS (%) after 60 min.
(untreated)	0	(11.8)	(44)	(500)	8,500	49
-	1.5	12.5	41	496	10,000	34
-	2.7	12.8	42	462	14,400	23
-	4.7	13.2	42	437	18,200	12
0.5% bromate/ salt	1.7	13.5	45	440	11,200	15
0.5% bromate/ salt	2.4	13.8	44	448	15,500	4
0.5% bromate/ salt	4.9	15.0	42	458	19,200	0

This process has very little or no effect on the colour fastness of dyed material with reactive dyes which is otherwise normally adversely affected by chlorine-resin treatments (167). Samples treated with Lankrolan SHR3 show much less pilling than untreated and chlorine-resin-treated samples (167).

Synthappret LKF an isocyanate-terminated trifunctional aliphatic polyurethane prepolymer has previously been discussed as an effective shrink-resist agent for wool garments when applied from solvent media (150). Because of the high reactivity of the isocyanate groups to water, stable aqueous emulsions cannot be prepared (168). Conversion to the bisulphite adduct, however, provides a water-soluble product which is extremely stable to prolonged storage, especially at an acid pH. Guise and Jackson (169) have given details of the conversion of Synthappret LKF into a product of this type by reacting it with sodium bisulphite in an ethanol-water solvent mixture.

Rippon and Rushforth (170) have discussed the properties of this compound as a shrink-resist treatment for wool fabrics. The product can be used in admixture with a polyacrylate such as Primal-K-3 (168) or Acramin SLN and this method of shrink-resisting wool fabrics has been referred to as the "Sirolan BAP" process (171). However, it has been shown (172) that there is no technical advantage from the shrink-resist view point in mixing Synthappret BAP with a polyacrylate whereas mixing with an aliphatic polyurethane dispersion such as Impranil DLN or Impranil DLH (Bayer) offers advantages in terms of reduced cost, simplified processing and improved performance (172).

Like most polymer systems Synthappret BAP and Synthappret BAP/acrylate treatments improve the tensile strength and seam slippage properties only slightly (168). Small improvements in abrasion resistance, wrinkle recovery, pilling and snagging properties are also obtained (168).

1.8.6 The Effects of Steam Treatments on the Abrasion Resistance of Wool Fabrics.

Steam treatment is an essential part of wool finishing processes e.g. blowing and fixation of dyes in melange printing. Generally steam is employed at or near atmospheric pressure to prevent damage to the wool which may possibly occur at high temperatures. However, in some cases the use of steam at elevated pressures would considerably reduce the time of treatment and this is essential in such processes as flat setting using pressure decatising machines.

Walde, Barr and Edgar (173) showed that the degradation of plain woven-wool fabric, which had previously been boiled for 1 hour in water and then extracted with anhydrous ether for 18 h, increased with increasing steam pressure or time of steam treatment. The mechanical failure was more rapid than the corresponding losses in fibre weight, nitrogen and sulphur contents.

Humfeld, Elmquist, and Kettering (174) reported that after steaming in moist conditions for 0.5 h in steam at 15 p.s.i.g., bleached all-wool serge showed a loss in strength of 31 per cent.

Haas (175) has reported fibre damage by steaming above atmospheric pressure and suggested that the damage could be minimized by the use of a vacuum treatment prior to atmospheric steaming in place of pressure steaming in order to achieve thorough fabric penetration.

Køpke and Lindberg (176) studied the influence of setting time on the breaking strength of fabrics after steaming in an autoclave at 132°C. They found that the reduction in strength was about 10% after treatment for 20 min., from which it was concluded that a prolongation of the setting time of 8 min. beyond that necessary to obtain a satisfactory degree of setting under the most favourable conditions does not cause unacceptable damage of the fabric.

Elliot, Stevens and Whewell (177) studied the effects of steam pressure and temperature of steaming on the breaking extension and the work required to stretch fibres 30% of their length, and on the values of the Urea-bisulphite (U-B) solubility.

The results are given in Table 20 and 21.

TABLE 20

Breaking Extension of Lincoln Wool Fibres Steamed for 30 min. at Various Pressures.

Steam pressure (p.s.i)	0	5	10	15	20	25
Breaking extension (%)	49.6	48.5	49.2	47.4	46.7	44.8

TABLE 21

% Reduction in work and U-B Solubility of Fibres Steamed at Various Temperatures.

Temperature of Steaming (°C)	% Reduction in Work and U-B Solubility after treatment for (h)		
	0.5	1.0	2.0
100	5.2 (27.3)	8.0 (18.9)	9.9 (16.6)
105	6.1 (23.1)	8.5 (17.0)	10.6 (13.7)
110	9.9 (18.8)	11.6 (14.1)	11.3 (12.5)
120	15.9 (14.8)	16.5 (12.1)	30.7 (11.5)

The Values in the brackets indicate the U-B solubility.

It is clear that on increasing the steam pressure the breaking extension generally decreases. The change in % reduction in work to stretch 30% (R.W) brought about by steaming fibres for various times is little affected by time of steaming if the temperature does not exceed 110°C. At 120°C however the change produced is very time-dependent. Treatment in steam at temperatures above 100°C produces smaller increases in % R.W. than corresponding treatments in water at the same temperature (177).

The U-B solubility of wool fabric treated at high temperatures in steam decreases rapidly with increasing temperature of treatment, the change being dependent on the time of treatment (see Table 21).

Nicholls (178) carried out investigations to ascertain to what extent the presence of alkali or acid in the fibre may influence the degradation caused by treating wool with steam at elevated pressures. The effect of steam up to 12 p.s.i.g. on wool in neutral, alkaline and acid conditions has been ascertained by measuring yarn breaking loads, yarn elongation at break, fabric abrasion resistance, discoloration, alkali solubility, and disulphide content.

It has been shown (178) that wool in a mildly acid state can be treated with steam at a pressure of 12 p.s.i.g. for periods up to 1 h without causing undue damage to the fibres. If, however, residual alkali is present, steam treatments even at atmospheric pressure cause considerable damage. The values given in Table 22 for the loss in weight of treated serge fabric on abrasion resistance are the average of four test samples. Here, the damage produced by steam above atmospheric pressure on wool containing alkali is considerable.

A good correlation was found to exist between certain physical tests and the disulphide-contents, indicating that the damage is mainly due to disulphide bond breakdown (178, 179). As the wool damage increases the disulphide content decreases (179).

TABLE 22

Effect of Steam on Fabric Abrasion Resistance

Steaming Conditions			Loss in Weight (%) for 1000 rubs (Martindale Abrasion Tester).		
Pressure (lb/in^2)	Temp. (^oC)	Time (min)	Acid	Neutral	Alkali
(Control)			2.0	2.0	2.0
0	100	60	2.0	2.2	2.5
4	107	60	2.1	2.1	2.5
8	112	60	2.2	2.5	3.3
12	117	15	2.1	2.1	2.9
12	117	30	2.3	2.5	3.0
12	117	60	2.9	3.5	5.8
12	117	120	4.0	4.3	10.4

1.9 The Effect of Dyeing Processes on the Abrasion Resistance of Wool Fabrics.

The dyeing of wool by exhaustion methods is generally carried out in aqueous solution at temperatures approaching, or even at, the atmospheric boil (100°C). This high temperature together with the associated pH of the dyecloth, has a great influence on the tensile strength and abrasion resistance of dyed wool fabric. Indeed, strength losses of 10-30% can result from conventional exhaustion dyeing procedures (180).

A minimum on the tensile strength loss versus pH curve for high-temperature aqueous treatments occurs in the mildly-acid range at about pH 4. At higher or lower pH values the amount of damage increases markedly, particularly for modified wool fibres. Thus the aim of the dyeing procedure should be to maintain the pH near 4 with the temperature no higher than necessary while the time should be reduced to as short as is practicable to obtain satisfactory levelness, exhaustion and fastness. This can be achieved provided the dyeing starts at a low temperature which is then raised slowly and progressively.

Chrome dyes applied by the mordant or after-chrome methods usually operate with a dyebath considerably more acidic than the optimum pH range mentioned above. The premetallized dyes forming 1:1 complexes are dyed from even more strongly-acid dyebaths. The metachrome method operates with a dyebath which is more alkaline than the optimum pH range. Thus none of these processes, as usually performed,yields the optimum fabric strength and abrasion resistance, but under proper conditions the chrome and metal-complex dyes will give level dyeing at about pH4 by proper control of the rate of temperature rise of the dyebath.

Speakman, Liu and King (181) carried out extensive work on the effects of dyeing with acid and chrome dyes by determining the changes in the reduction in work to stretch single fibres by 30% extension as well as the fabric strength. Their results suggested that dyeing in presence of large amounts of sulphuric acid produced significant adverse modifications as did the afterchrome method of dyeing, although with both the on-chrome and single bath chrome method, only slight reductions in fabric strength were recorded.

Coutie, Lemin and Sagar (182) studied the effects of dyeing wool at high temperatures. Dyeing conditions studied included the following dyebaths containing various reagents:

viz (1) 8% Sulphuric acid;

(2) 3% Sulphuric acid + 10% Glauber's salt;

(3) 3% Acetic acid + 10% Glauber's salt;

(4) 40% Glauber's salt only;

(5) Afterchrome (3% acetic acid + 10% Glauber's salt, exhausting with formic acid and chroming with 1% sodium dichromate);

and (6) Chromate (2% ammonium sulphate + 1% sodium dichromate).

Three different dyeing times were employed:

(i) 60 minutes at 100°C;

(ii) 5 minutes at 120°C;

(iii) 15 minutes at 120°C.

The resistance to abrasion of the treated fabrics was assessed by means of the Martindale Abrasion Testing machine, the abradant being a crossbred tie lining fabric. The results obtained are shown in Table 23.

TABLE 23

Dyeing Method	Abrasion Resistance (dry) (No. of revolutions to hole).	
1	(i)	3,250
	(iii)	1,750
2	(i)	3,750
	(iii)	3,250
3	(i)	5,750
	(iii)	3,750
4	(i)	6,750
	(iii)	4,750
5	(i)	7,500
	(iii)	2,500

Carter (183) pointed out that exhaustion dyeing is the most damaging of all the processes for wool and it normally creates more damage than an oxidative antishrink treatment. Table 24 shows the effects of seven different dyeing procedures on the properties of wool. From the results obtained, the following list of different dyeing techniques was prepared, in the order of increase in degradation of the fibre from (a) to (g), the least degradative effect being with treatment (a):

(a) Afterchrome using acetic acid.
(b) Metachrome mordant method.
(c) Neutral dyeing.
(d) Acid dye with acetic acid.
(e) Acid dye with formic acid.
(f) Acid dye with sulphuric acid.
(g) Afterchrome using sulphuric acid.

The alkali solubility figures obtained (Table 24) were as generally to be expected. The different acid dyeings gave a slightly higher alkali solubility than normal which was most likely due to acid damage. The only surprising result is the large difference between the two afterchrome dyeings (a) and (g). This may be due to the different nature of the two acid treatments. As expected from the high alkali solubility, the afterchrome or sulphuric acid treatments show a large reduction in the work to stretch the fibre by 30%.

In the case of wet abrasion the acid dyed material showed decreased resistance to abrasion, the sulphuric acid dyeing again suffering the greatest reduction. All the other dyeings show an increased wet abrasion resistance, the greatest increase being in the afterchrome method using acetic acid. In the case of the neutral dyeing, however, the increase may be due to the fibres becoming slightly gelatinised by the boiling process, because it has been suggested that a soft fibre will be worn through less readily than a harsh fibre (183). This is supported by the wet abrasion figures for samples boiled in tap water (183).

Peryman (184) has studied the effect of conventional dyeing techniques on wool, using both physical and chemical tests such as yarn breaking load, Martindale abrasion resistance, alkali solubility, urea-bisulphite solubility and cystine content. On the basis of his results, he made the following suggestions for practical dyeing conditions.

(1) Whenever possible, dyeing at the boil should be carried out at pH values near 4.2 (at 100°C) which can be easily attained by the use of acetic acid.

TABLE 24

Dyeing Method	Light or heavy* dyeing	Alkali Solubility	Reduction in work (%)	Wet Abrasion (% of control) (a)	Bursting Strength (% of control) (a)	
					dry	wet
Control (a)		11.2	4.0	100	100	100
Control with boiling	Light	12.3	3.8	123	94	88
	Heavy	11.0	13.3	123	91	81
Acid dye with sulphuric acid	Light	15.6	7.7	68	113	83
	Heavy	15.0	28.2	44	95	92
Acid dye with acetic acid	Light	13.5	4.5	111	98	94
	Heavy	13.4	6.5	77	91	86
Acid dye with formic acid	Light	13.9	3.2	82	102	98
	Heavy	14.1	11.1	73	95	92
Neutral dye	Light	12.8	8.8	142	97	85
	Heavy	12.1	7.9	150	93	84
Metachrome dye	Light	11.0	6.4	164	97	97
	Heavy	10.4	6.7	140	92	80
Afterchrome on sulphuric acid dye	Light	25.2	19.4	147	98	91
	Heavy	23.3	18.9	152	102	84
Afterchrome on acetic acid dye	Light	11.9	1.6	240	95	93
	Heavy	9.8	6.5	252	93	88

* Light dyeing: 30 minute dyeing, Heavy dyeing: 3.5 hours dyeing.

(2) Prolonged boiling in acid solutions of pH values below 3 should be avoided because of the resultent loss of wet strength and abrasion resistance.

(3) Prolonged boiling in liquors of pH values above 5 should be avoided if permanent set, caused by disulphide bond breakdown is undesirable in subsequent processing.

(4) Sodium sulphate should be avoided if the dye liquor is buffered at a pH value greater than the isoionic point (near pH 6.3 at 100°C). If the presence of salt cannot be avoided at pH values greater than this, the time of dyeing should be short and the temperature as low as possible.

(5) The use of dyeing assistants containing acids (or their compounds) with pK (ionization constant) values greater than about 6.5 should be avoided unless ammonia has freely escaped from the liquor or care is taken to prevent the pH from rising above 6.3 (at 100°C).

Lemin and Collins (185) used yarn breaking load and extension at break, and the Martindale abrasion resistance of the fabric as the criteria for determining dyeing methods for producing shades of good fastness to wet treatments on 50/50 blended wool-cotton fabrics. They concluded that reactive dyes, insoluble azo dyes, "Alcian" dyes (solubilized phthalocyanine pigments), and vat dyes could be applied to such materials provided that the concentration of caustic soda did not exceed 4 $g.l^{-1}$, and the temperature did not exceed 40°C. Dyeing with vat dyes resulted in a significant reduction in fabric abrasion resistance, although not in tensile strength. The reduction in tensile strength and extensibility which occurred when applying solubilized vat dyes was judged to be such that these dyes must be considered to be of no practical interest. Very strong oxidising conditions are necessary to develop the final colour of these dyes, and it is at this stage that severe adverse chemical modification of the wool occurs. Similarly, the alkaline reducing conditions necessary when applying sulphur dyes produce much adverse change in the wool (185).

Two general approaches to the problem of dyeing wool without damage (186) are:

(i) The use of effective dyeing assistants which allow dyes normally applied at pH 6-7.5 to be used at about pH 5. Generally these assistants are ethylene oxide derivatives which form complexes with the dyes, and the generally accepted mechanism is that these complexes slowly decompose at or near 100°C. This allows level dyeing to be obtained at relatively low pH values.

(ii) The addition of solvents to the dyebath to obtain complete exhaustion and thorough penetration of fibres by dyes at temperatures well below the boil. In comparison with conventional dyeing processes, solvent-assisted processes improve the quality of wool fibres, shorten the dyeing time, and enable the dyeing temperature to be reduced (187, 188). Moderately soluble solvents, such as n-butanol and benzyl alcohol must be added in relatively high concentrations but emulsified, water-insoluble or very slightly soluble solvents are effective at concentrations as low as 2-3% on the weight of wool (122).

The measurement of the tensile strength of yarn and abrasion resistance of cloth also showed that "solvent-assisted" dyeing at 80°C in presence of benzyl alcohol produced less adverse change than conventional dyeing. Similar improvements in tensile strength, and also in elongation at break of yarn were reported when dyeing was carried out at 90°C (123).

The importance of controlling dyeing conditions to minimise wool damage has thus been well-recognised. This is becoming even more important now with the increasing use of chemical finishing procedures, since dyeing, and also chemical treatments for shrink-resistance and setting, can increase the susceptibility of wool to subsequent degradation as well as cause damage per se (186).

The results in Table 25 indicate the extent to which wool can be damaged by the shrink-resist treatment or by setting after normal dyeing. The damage is at a minimum at pH 4; strongly acid conditions as expected, lead to extensive damage especially below pH 2. Dyeing in strongly acid solutions brings about an increased susceptibility to damage in subsequent treatments, and is probably due to hydrolysis of the peptide bonds. The effects of the mild hydrolysis may be negligible while the disulphide cross-links are essentially intact, but when the wool is then oxidised during a shrink-resist treatment or reduced during setting processes, some stabilising cross-links are broken and this latent damage as a result of hydrolysis is then detected together with any damage due to the chemical treatment alone. Hydrolysis of peptide bonds is much slower at pH 4-6 than at pH $<$ 3, so that damage in chemical treatments after dyeing at these values is still about the same as in treatments on normal wool.

Cookson, Hine and McPhee (189) studied the effects of boiling aqueous solutions on wool oxidised with a variety of reagents. They found that the strength and weight losses for oxidised wool and untreated wool were at a minimum at pH 3-4. Wool that had been treated with hydrogen peroxide to oxidise about 7% cystine was damaged no more

TABLE 25

Damage to Wool in Shrink-Resist Treatment or Flat-Setting after boiling in Aqueous Solutions (186)

			Warp Tensile Strength, kgm wgt			Martindale Abrasion resistance, no. of rubs to hole		
pH of solution	Time of boiling h	Loss in weight %	After boiling	After boiling and shrink-resisting *	After boiling and flat-setting * *	After boiling	After boiling and shrink-resisting *	After boiling and flat-setting* *
(untreated fabric)				(23.9)			(19500)	
1.7	0.5	0.8	20.5	18.5	16.6	14000	9000	4900
1.7	1	1.3	18.0	16.0	14.4	12200	7700	5000
1.7	3	2.9	15.6	13.7	10.5	6100	4000	2000
2.5	0.5	0.3	21.0	20.1	19.0	17000	12400	10000
2.5	1	0.5	18.9	17.9	16.3	15400	11300	8500
2.5	3	1.3	17.0	16.0	14.1	11100	8000	6300
4.0	0.5	0.2	22.5	21.3	21.5	18300	13000	13500
4.0	1	0.3	21.5	20.4	19.6	16800	12600	13000
4.0	3	0.7	21.3	20.0	19.0	14000	10600	10200
6.1	0.5	0.6	21.6	20.6	20.4	17000	13200	12800
6.1	1	1.0	20.4	19.4	18.8	16000	12400	12000
6.1	3	2.2	19.2	18.5	17.2	11800	9000	8200
(Fabric not boiled)				(Shrink-resist treatment only) 22.7	(Flat-set only) 22.2	(Shrink-resist treatment only) 14700		(Flat-set only) 15000

* Shrink-resist treatment was 3% permanganate/salt.

** Flat-setting was with 1% sodium bisulphite solution (fabric pH adjusted to 5.0 before impregnation), steaming time 3 minutes.

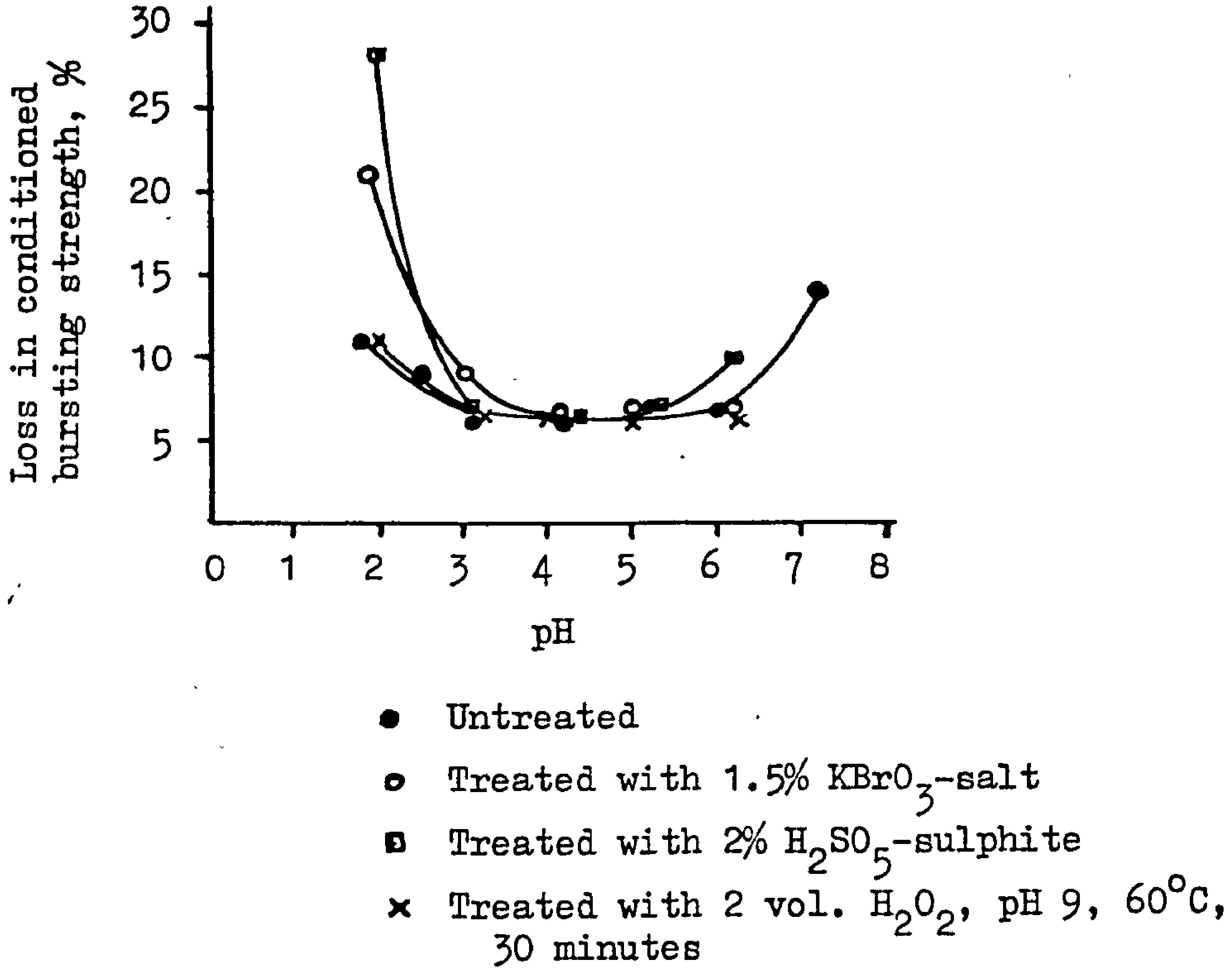
than untreated wool in the boiling solutions, but when treated with a shrink-resist treatment (e.g. acid chlorine, permonosulphuric acid-sulphite or permanganate-salt) was more severely damaged than untreated wool.

They further investigated the dyeing of shrink-resisted wool with milling acid and 1:2 metal-complex dyes. Strength and weight losses were minimised by dyeing at around pH 4 in the presence of non-ionic dyeing assistants at about 85°-90°C. The results of strength tests on the treated and dyed fabrics are given in Table 26 and 27 and clearly show the adverse effects of boiling at pH values outside the optimum range. With permanganate-salt-treated fabrics, damage is severe at pH 1.9 or pH 6.3, whereas bromate-salt treated fabrics are severely damaged at pH 1.9.

Fig. 33 and 34 show the effect of pH of boiling solutions on conditioned and wet-strength loss and Fig. 35 and 36 show the effect of pH at different temperatures on conditioned and wet-strength loss of worsted fabrics treated with permanganate salt. From these results it is clear that the minimum loss in bursting strength occurs at pH 4. The higher the amount of permanganate salt the greater the loss in bursting strength. The higher the temperature of treatment the higher the degradation.

Damage in dyeing after shrink-resist treatment of wool is probably due to oxidation of the cuticle (189). Degradation products of wool, resulting from subsequent attack by boiling solutions, could then diffuse more readily out of the fibres, thereby increasing the rate of degradation.

Fig. 33 - Effect of pH of boiling solutions on strength loss of worsted fabric conditioned at 20°C and 65% r.h.



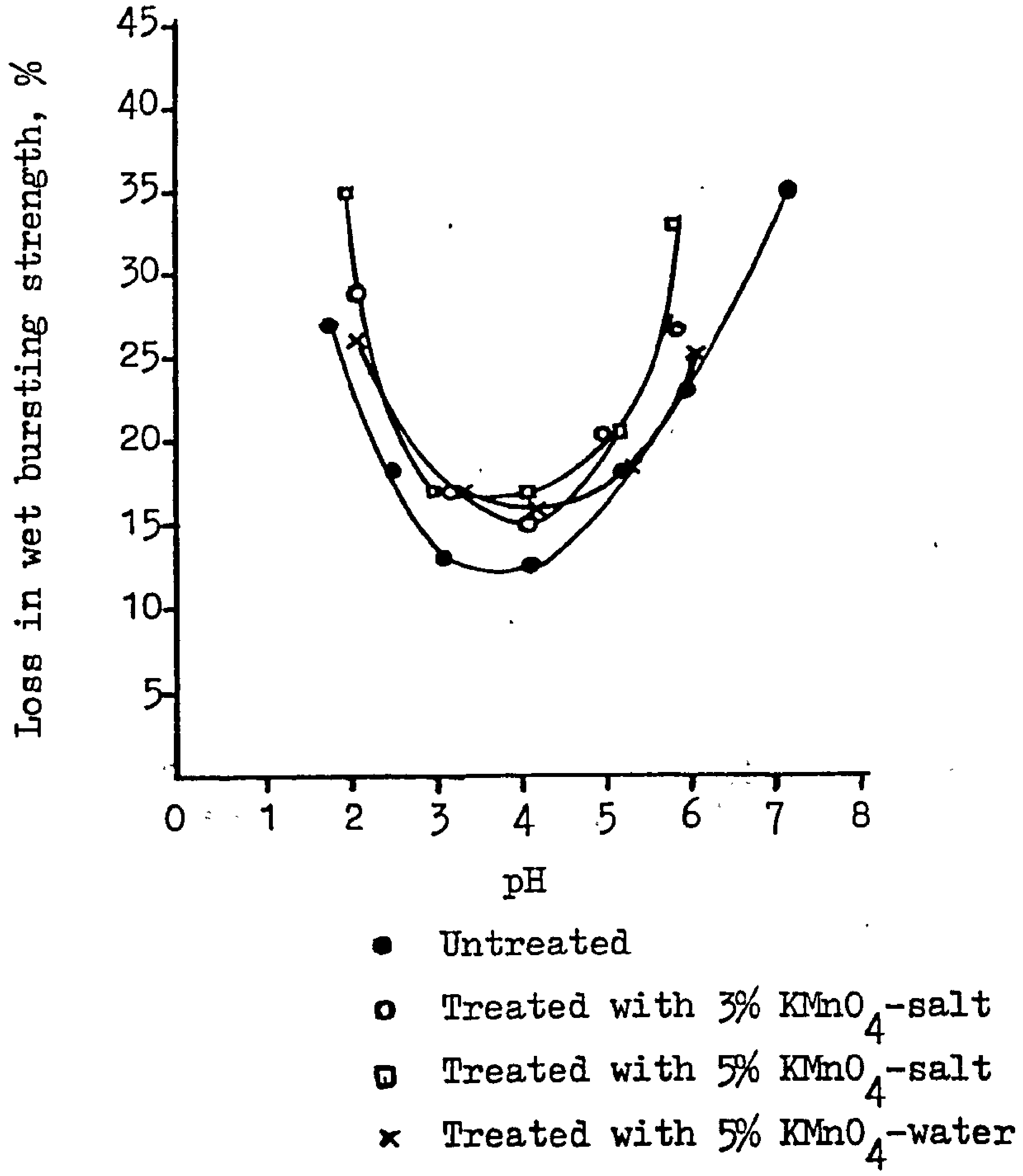


Fig. 34 - Effect of pH of boiling solutions on wet-strength loss of worsted fabric

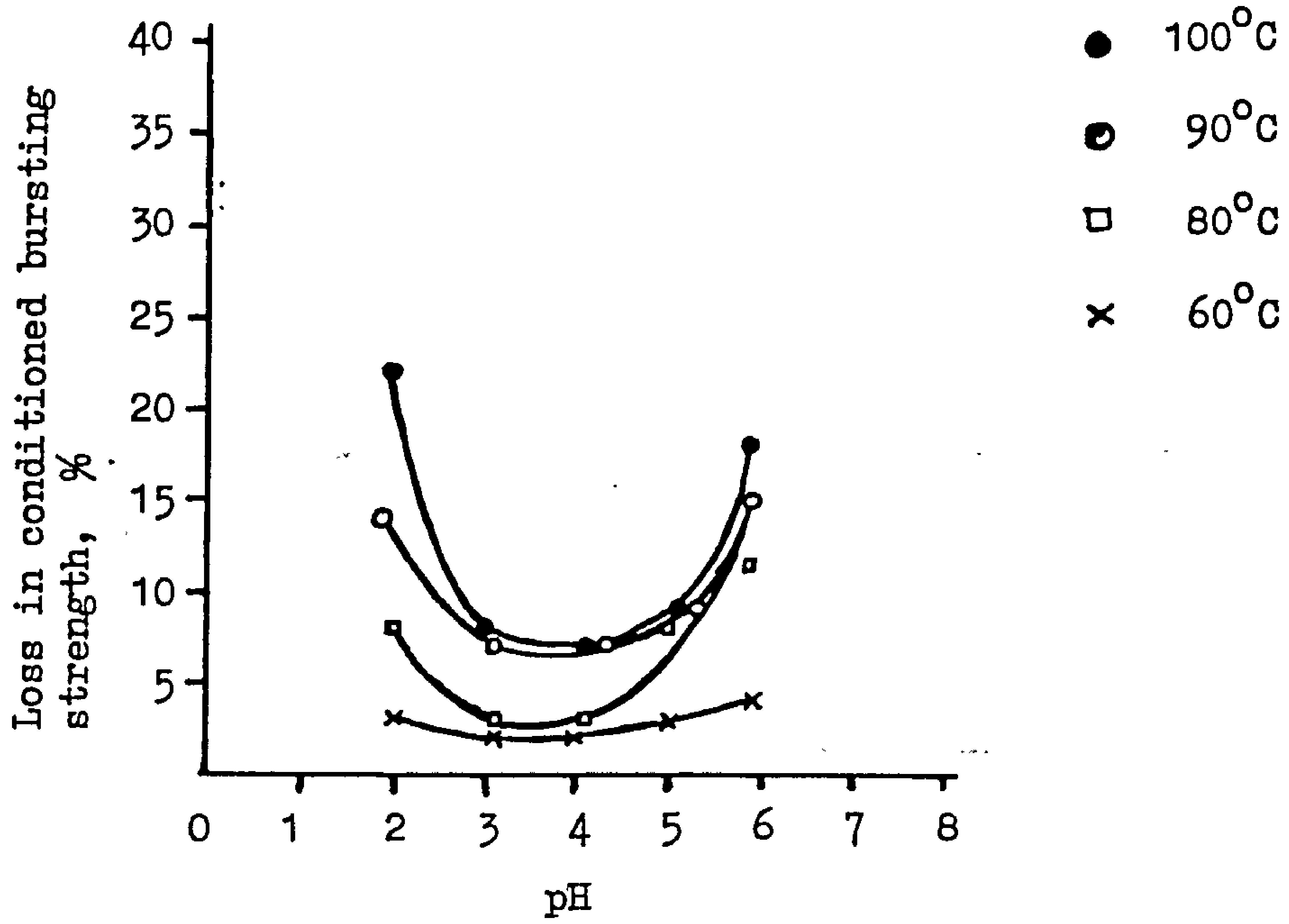


Fig. 35 - Effect of solutions of different pH on strength loss of fabric treated with 5% permanganate-salt and conditioned at 20°C and 65% r.h.

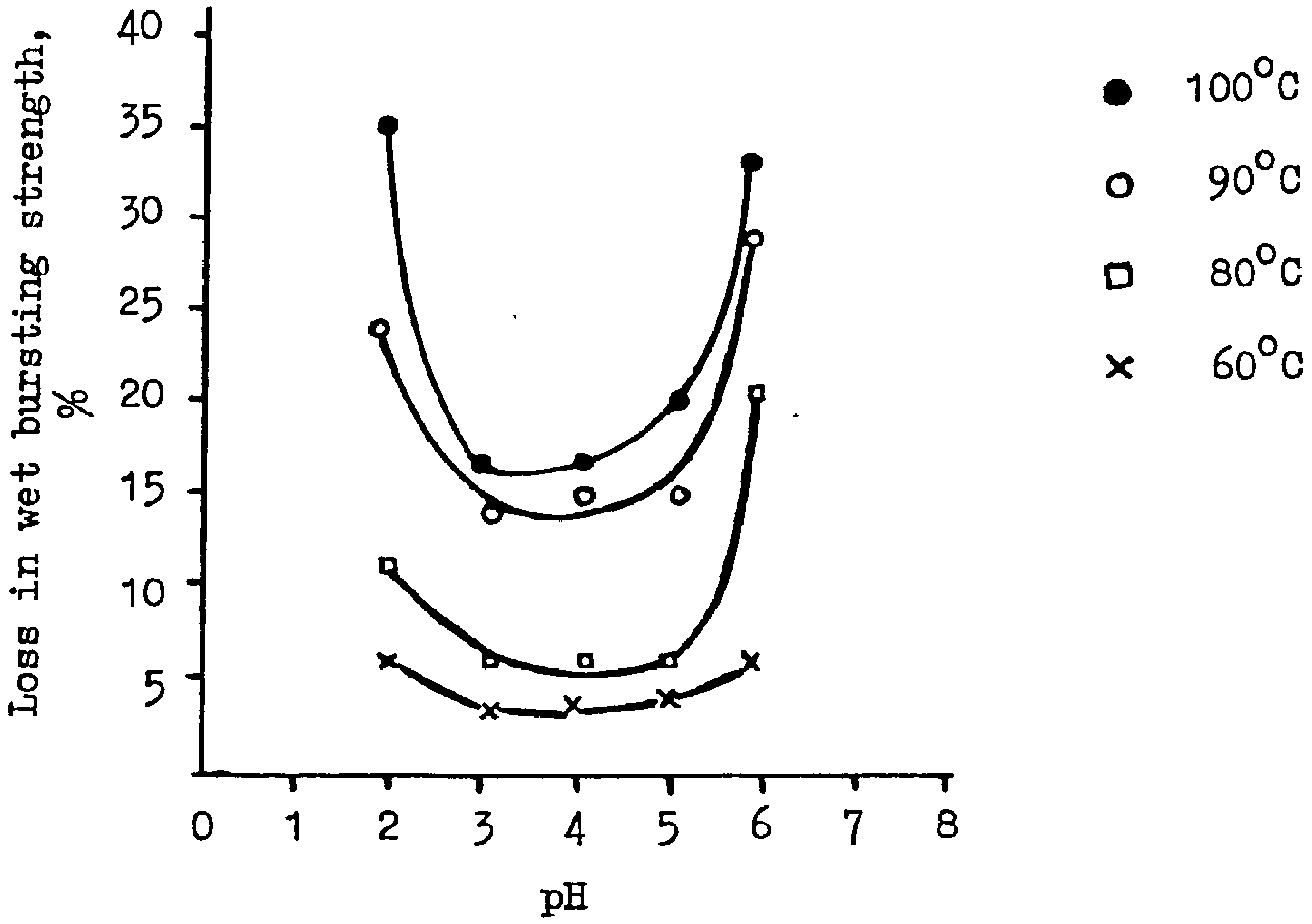


Fig. 36 - Effect of solutions of different pH on wet-strength loss of fabric treated with 5% permanganate-salt.

TABLE 26

Strength of Woollen Fabric after Shrink-resist treatment and boiling.

Shrink-resist treatment	Warp tensile strength (lb-wt) in 1-in. grab tests of fabric after 90 min. at pH			
	(unboiled)	1.9	3.6	6.3
None	25	24	24	23
3% $KMnO_4$-salt	25	21	22	19
5% $KMnO_4$-salt	23	19	20	17
1.2% $KBrO_3$-salt	29	23	26	25
2% $KBrO_3$-salt	30	22	26	25

TABLE 27

Strength of Woollen Fabric After Shrink-resist Treatment and Controlled Dyeing

Shrink-resist treatment		Warp tensile strength (lb-wt) in 1-in grab tests of fabric in solutions brought slowly to boil at	
	Undyed	pH 4	pH 6.5
None	25	24	24
3% $KMnO_4$-salt	25	23	22
5% $KMnO_4$-salt	23	21	19
1.2 $KBrO_3$-salt	29	26	25

The effects of dyeing normal and also shrink-resist treated fabrics under two sets of conditions are shown in Table 28 (190). The dyeing methods are:

(1) A general set of conditions (pH 4, 90°C; 30 min) suggested for minimising damage with all classes of conventional wool dyes, and

(2) A method employed for 1:2 metal complex, and many acid milling dyes (pH 6, 100°C; 1 h).

In all cases, the losses in strength and abrasion resistance are negligible when wool is dyed at pH 4 below the boil. However, losses are significant, especially with the oxidatively-treated wool, when dyed at pH6 at the boil, and these could be even greater if dyed in strongly acid solution.

TABLE 28

Tensile Strength and Abrasion Resistance After Dyeing of Normal and Shrink-resistant, Milled Fabric

Dyeing Conditions	Shrink-resist treatment	acid milled		soap and soda milled	
		Warp-tensile strength (Kg-wt)	Abrasion resistance*	Warp tensile strength (Kg-wt)	Abrasion resistance*
		28.0	36,400	22.6	29,000
(1)	None	28.2	35,500	23.7	27,700
(2)	None	24.9	28,400	21.5	23,200
(1)	3% Very soft polyacrylate	30.6	55,000	26.5	43,000
(2)	3% Very soft polyacrylate	28.7	46,600	25.2	36,500
(1)	1% bromate/salt	29.4	28,200	26.0	23,000
(2)	1% bromate/salt	25.6	22,500	23.0	18,300
(1)	3% permanganate/ salt	26.4	27,000	22.1	21,000
(2)	3% permanganate/ salt	21.6	20,000	18.6	17,200

* Number of rubs to hole on Martindale Abrasion Tester.

CHAPTER 2

The Effects of Polymer Shrink-resist treatments on the Abrasion resistance of Woven Wool fabrics

2.1. Introduction and Objectives

It is clear from many published studies (see Section 1.8.5) that the abrasion resistance of woven wool fabrics can often be improved through the application of polymer treatments. However, the fundamental role played by the polymer in improving the abrasion resistance is not clearly understood. It was with this object in mind that the current experimental work was undertaken.

The experimental work to be described is thus primarily concerned with the fundamental role of polymer treatments in improving the abrasion resistance of woven wool fabrics. Because these treatments are normally applied as shrink-resist processes, a systematic study of the interrelation of the nature of the applied polymer, the polymer add-on level, the method of application and the effects of washing treatments on abrasion resistance and shrink-resistance has been carried out. In this way a more rationalised view of the mechanism of abrasion in woven wool fabrics has been developed. In addition a greater understanding of the nature of synergism for both shrink-resistance and abrasion resistance has been obtained.

The work is preceded by a brief treatment of the mechanism of fabric shrinkage and their prevention utilising polymer shrink-resist and other treatments.

2.2. Shrinkage in Wool Fabrics

At least two types of shrinkage have been recognised (137) in the dimensional changes which occur when wool fabrics are agitated in aqueous liquors. Soaking in warm water or mild agitation in water causes relaxation shrinkage, a property of fabrics made from both natural and man-made fibres or their blends. More severe mechanical action causes felting shrinkage, a property generally associated with the wool fibre and which can be utilized with great effect in the finishing of wool fabrics, yet gives rise to consumer dissatisfaction when it occurs in the finished product.

2.2.1. Relaxation shrinkage

Relaxation shrinkage has been defined (191) as "that shrinkage which occurs without relative longitudinal movement of fibres within yarns". The origins of relaxation shrinkage are in the release of the strains introduced into the fibres during the spinning, weaving or knitting processes. These strains are stabilized by cohesive set, which involves the rearrangement of labile hydrogen bonds (192) and inter-yarn frictional forces. Consequently, conditions which will overcome the cohesive set and the frictional constraints will allow the stresses to relax and cause the fabric to shrink; a combination of such conditions is found in machine washing viz. mechanical agitation in warm water.

One object of the fabric finishing operation is to remove relaxation shrinkage from the fabric. This can be achieved by the general techniques of either stress-relaxation or strain-stabilization.

In stress-relaxation processes the fabric is allowed to relax during the finishing sequence where it is exposed to more severe conditions of relaxation than it will experience in subsequent use. For many fabric structures this will involve normal wet-finishing procedures followed by drying under conditions of minimum tension.

However, it is not always feasible to permit a fabric to relax fully during finishing because this may cause distortion of the fabric surface or especially in the case of double jersey structures may produce an unacceptably narrow fabric. For these reasons, and because it is sometimes not possible to relax all the stresses present in the fabric, it may be necessary to subject the fabric to a strain-stabilization treatment. This utilizes a wool-setting treatment which is capable of rearranging both the non-covalent and covalent cross-links present in the wool fibre, thereby stabilizing the strains present in the fibre. Such treatments commonly used in the fabric finishing operation include boiling water (crabbing), high-temperature steam (decatizing) and reducing agents or alkalis (flat-setting).

Polymers which stabilize felting shrinakge by the formation of inter-fibre bonds are also capable of stabilizing small amounts of relaxation shrinkage (191). However, quite high levels of strain can be stabilized if the fabric is decatized after treatment with a polymer of this type (172). In practice, finish-decatizing is extremely important in the production of machine-washable wool double jersey fabric.

2.2.2. Felting shrinkage - Mechanisms and Theories

Felting has been defined by Makinson (193) as "the process of progressive entanglement of the fibres in an assembly, occurring as a direct result of agitation by undirected external forces". The process have been studied by many workers and inevitably numerous theories have been put forward as each worker sought a unique mechanism for the felting process. This work has been described by

Moncrieff (137) and in various articles (194) (195) (196) (126). It is now believed (193) (126) that depending upon the fabric structure and felting conditions a number of different mechanisms can be operative.

The theories which have found greatest acceptance are those which recognise the presence of the scale structure on the fibre surface as being of prime importance to the felting process.

As early as 1790 Monge (197) observed that the wool fibre has scales which produce a frictional difference between the root-to-tip and tip-to-root directions of sliding; that this difference causes cumulative fibre movement in the rootward direction when an assembly of fibres is agitated, and that imposed deformations, particularly compressions, are locked in by "catching" of the scales, which is accepted by most workers today as an essential part of most of the proposed mechanisms of felting.

Later on Witt (198) and others (199) also considered the mechanism of felting as a rootward migration of wool fibres.

The middle period of activity in the study of the mechanism of wool felting began in the 1920s. Two approaches in particular were emphasized. Shorter (200-202), Arnold (203), Speakman et al (204) and Martin (205) reinstated fibre migration as the principal factor responsible for felting, while Speakman et al (206), and Schofield (207, 208) and Harrison (209) emphasized the role played by recovery of the individual fibres from strain. All these workers were concerned particularly with the felting and shrinkage of wool fabrics. Work on the felting of loose assemblies of fibres was mostly carried out by investigators concerned with the felting of fur (210-213).

The "modern" period of study of felting mechanisms may be said to have begun with the study by Van der Vegt and Schuringa of the felting of wool yarns (214-216). These investigators not only made a systematic study of the factors which influence felting, from which they were able to deduce some features of the mechanism of felting, but also introduced into this field the use of coloured "tracer" fibres. Thus the configuration of such tracer fibres could be observed microscopically by immersing the predominantly white yarn in a liquid of matching refractive index, in which the white fibres were transparent.

Coloured tracer fibres have since been used by Makinson (193, 217-219) in studies of the movements of wool fibres in fabrics and by Flanagan (220) in a study of their movements in a batt of carded wool.

Furthermore a few theories (221-223) have been based on the physicochemical properties of the fibre surface. The surface chemical theory of felting suggests that attractive forces between fibres are a contributory factor in the felting process and there is evidence that repulsive forces between fibres may make an important contribution to the mechanism of some shrink-resist treatments.

2.3. The Control of Felting shrinkage

Speakman *et al* (206) have listed the wool fibre properties which they considered fundamental to the felting process, namely,

i) fibres must possess a surface structure which gives rise to a Differential Frictional Effect (D.F.E.).

ii) ease of fibre extension and deformation.

iii) ability to recover from extension or deformation.

Consequently reducing any of these fibre properties should reduce the felting potential of the wool fabric always assuming that the structure of the fabric permits fibre movement. The rate of felting is known to be decreased as the fabric structure becomes more consolidated, thereby limiting fibre movement (224).

There are several methods by which shrink-resistant wool fabrics can be produced:

(i) By treatments that modify the fibre surface properties, generally referred to as "degradative" processes.

(ii) By treatments that modify the elastic properties of the wool fibres (225, 226).

(iii) By imposing frictional constraints on the fibres by producing tightly constructed fabrics in which fibres will be less able to move (224).

(iv) By applying a polymeric substance to the fabric which covers the fibre scales and therefore modifies the D.F.E. or physically bonds the fibres together and prevents fibre movement. These treatments are referred to as "additive" processes.

(v) Felting properties of wool can also be modified by blending the wool with some other fibre. Several workers (227-229) have studied the effect of blending wool with man-made fibres on the rate of felting of fabrics. With the exception of regenerated protein fibres most man-made fibres reduce the felting rate (227).

In at least one instance, namely the chlorination-Hercosett process, a combination of degradative and additive processes are employed to obtain a satisfactory shrink-resist effect (230).

From the above mentioned methods those which have found greatest commercial application involve the treatment of wool by either a degradative or an additive shrink-resist treatment. These two treatments and most of the reagents used have been described (in section 1.8.5.).

2.4. Preliminary Studies of Polymer Shrink-resist treatments

2.4.1. Introduction and Objectives

The relatively low abrasion resistance of wool fabrics is known to be a frequent cause of consumer dissatisfaction, particularly in pure wool woven suiting fabrics (231, 93). The melt spun synthetic fibres such as nylon and polyester generally have a higher abrasion resistance than wool so that in blends with wool, problems of differential rates of abrasion may lead to undesirable changes in the aesthetic appearance of the fabric (232).

In order to maintain the quality image associated with wool fabrics and to improve their market competitiveness vis-à-vis other fibres, it will be necessary to improve the abrasion resistance of wool fibres and fabrics. In this way improved performance should be maintained on both pure wool and on wool/man-made fibre blend fabrics.

Earlier research work had indicated that polymer treatments applied to wool to improve shrink-resistance can also improve the abrasion resistance (230, 156, 154). Accordingly, the object of the work reported here is to evaluate the effectiveness of various shrink-resist processes for improving the flat abrasion resistance of various woven wool fabrics. In addition relevant fabric parameters have been studied to elucidate more clearly the mode of action of polymer shrink-resist treatments in flat abrasion processes.

2.4.2. EXPERIMENTAL

Materials and Methods

Materials

Fabric Specifications. Three all-wool woven fabrics were used with the following detailed specifications:

Fabric A: A plain weave, light weight worsted fabric with:

conditioned weight per unit area: 112 $g.m^{-2}$
ends per cm : 24
warp count : 23.45 tex
warp twist : 6.8 turns per cm (Z)
picks per cm : 21
weft count : 25.6 tex
weft twist : 6.8 turns per cm (Z)

and a water extract of pH 7.35.

Fabric B: A 2/2 twill worsted fabric with:

conditioned weight per unit area: 178 $g.m^{-2}$
ends per cm : 31
warp count : 36.4 tex
warp twist : 7.4 turns per cm (S folded yarn)
picks per cm : 30
weft count : 23.4 tex
weft twist : 7.6 turns per cm (Z)

and a water extract of pH 6.85.

Fabric C: A plain weave woollen flannel fabric with:

conditioned weight per unit area: 173 g.m^{-2}
ends per cm : 14
warp count : 70 tex
warp twist : 5.6 turns per cm (S)
picks per cm : 14
weft count : 71.4
weft twist : 4.5 turns per cm (S)
and pH of aqueous extract 7.0.

Fabrics B and C were supplied as undyed commercially finished fabrics. Fabric A was scoured in 2% soap solution, rinsed, hydroextracted and allowed to dry at room temperature.

Chemicals

(i) Hercosett 125 (Hercules Inc.) - a cationic polyamide prepolymer supplied as 12.5% w/v aqueous solution.

(ii) Lankrolan SHR3 (Diamond Shamrock) - a Bunte Salt-terminated poly(alkylene)oxide polymer, supplied as a 45% solids solution.

(iii) Impranil DLH (Bayer) - a 40% solids aqueous dispersion of soft polyurethane. This product has a bulk storage life of 6 months and should not be exposed to temperatures below 3°C or above 40°C.

(iv) DC 109 (Dow Corning) - a silicone prepolymer supplied as a 100% concentrated liquid.

(v) DC 109B (Q2-7056) (Dow Corning) - this is a crosslinking agent employed as a catalyst to react with DC 109 to give the silicone polymer.

(vi) Synthappret BAP (Bayer) - a bisulphite adduct of polyurethane, supplied as a yellow viscous liquid containing 50% active constituent and water-soluble. Under normal storage conditions the bulk product is stable for 12 months but this may be reduced to 3 months under tropical conditions.

Chemistry of Polymer shrink-resist treatments

(i) Chlorination-Hercosett process

The resin used is a water soluble cationic polyamide-epichlorohydrin polymer (233). It is prepared (234) (See Fig. 37) by the condensation of adipic acid and diethylenetriamine, to form a polyamide containing secondary amino groups. Epichlorohydrin is then reacted with the amino groups to form a tertiary amino-substituted propylene chlorohydrin. Under alkaline conditions the chlorohydrin forms the corresponding epoxide and cyclic azetidinium chloride.

The commercial resin contains the reactive azetidinium cations which determine the basic character of the Hercosett polymer. It is sold as a 10% solution (Hercosett 57) or 12.5% (Hercosett 125).

In order to apply this polymer to wool tops and fabrics, it is necessary to prechlorinate the wool to increase the surface energy sufficiently to allow the polymer to spread over the fibre surface. Feldtman and McPhee (230) originally showed that the critical surface tension, γ_c, of untreated wool was approximately 40 mN/m, while that of chlorinated wool was 72 mN/m and of the Hercosett resin 55mN/m. More recent studies by Bateup et al (235) have shown that the critical surface tension of untreated wool is 30 mN/m. They also established that the critical surface tension value is dependent upon the liquid used for the test, but comparable values can be obtained using different liquids.

Swanepoel et al (236) have shown that both the chlorination and the antichlor steps play an important role in the polymer absorption and curing process. Chlorination produces anionic groups on the

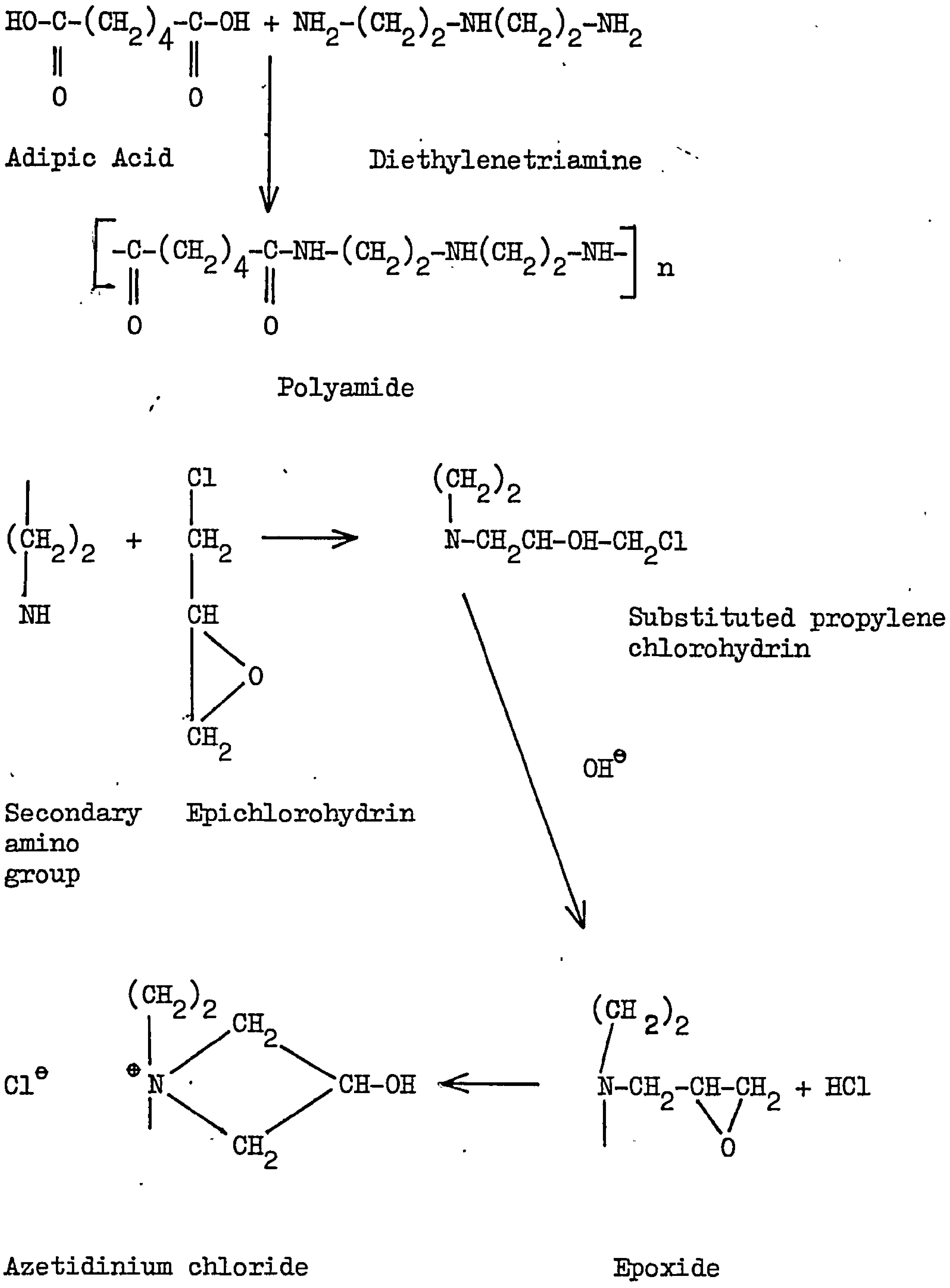
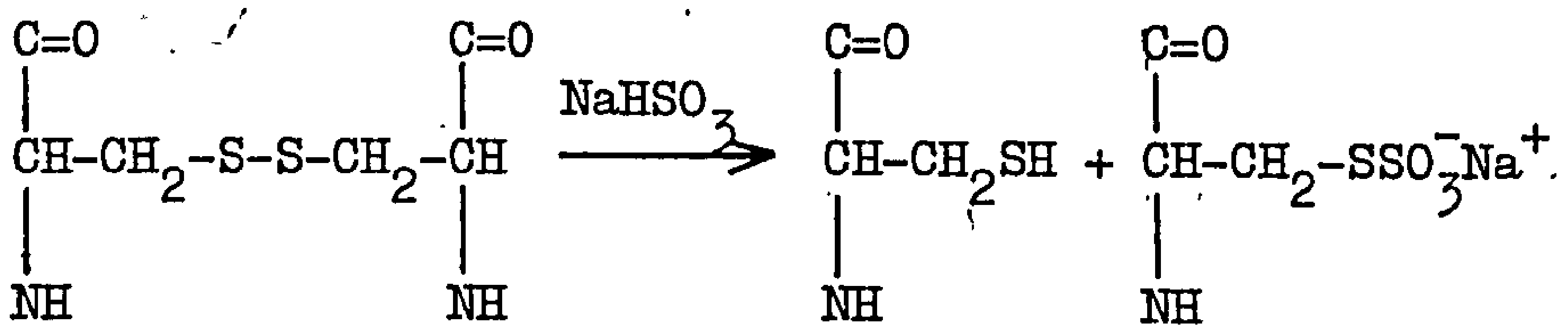


Fig. 37 Preparation of Hercosett resin.

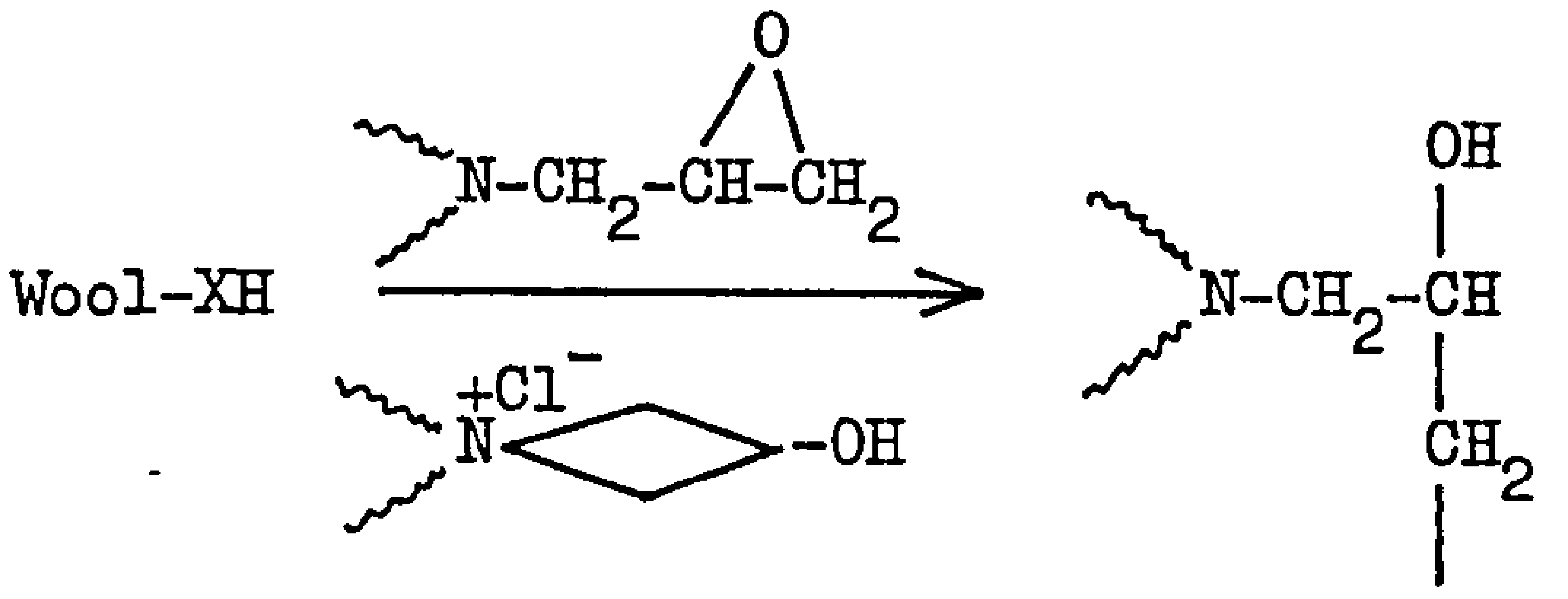
fibre through oxidation of cystine residues to cysteine sulphonic acid residues; these anionic residues confer extra substantivity on the wool for the cationic polymer. Additionally, sodium bisulphite used as the antichlor agent creates further anionic residues in the fibre and also produces more reactive cysteine thiol groups which promote polymer grafting. The following reaction scheme outlines the above reactions of wool with sodium bisulphite.



$$\begin{array}{l}C{=}O \qquad\qquad\quad C{=}O\\ |\qquad\qquad\qquad\quad\;\; |\\ CH{-}CH_2{-}S{-}S{-}CH_2{-}CH\\ |\qquad\qquad\qquad\quad\;\; |\\ NH \qquad\qquad\quad\;\; NH\end{array} \xrightarrow{NaHSO_3} \begin{array}{l}C{=}O\\ |\\ CH{-}CH_2SH\\ |\\ NH\end{array} + \begin{array}{l}C{=}O\\ |\\ CH{-}CH_2{-}SSO_3^-Na^+\\ |\\ NH\end{array}$$

Wool cystine Wool cysteine Wool cysteine-S-sulphonic acid

The thiol groups formed by the above reaction further enhance the curing and fixation of the resin on the wool due to their highly nucleophilic character. Reaction of the resin with the wool following absorption at the surface can be written:



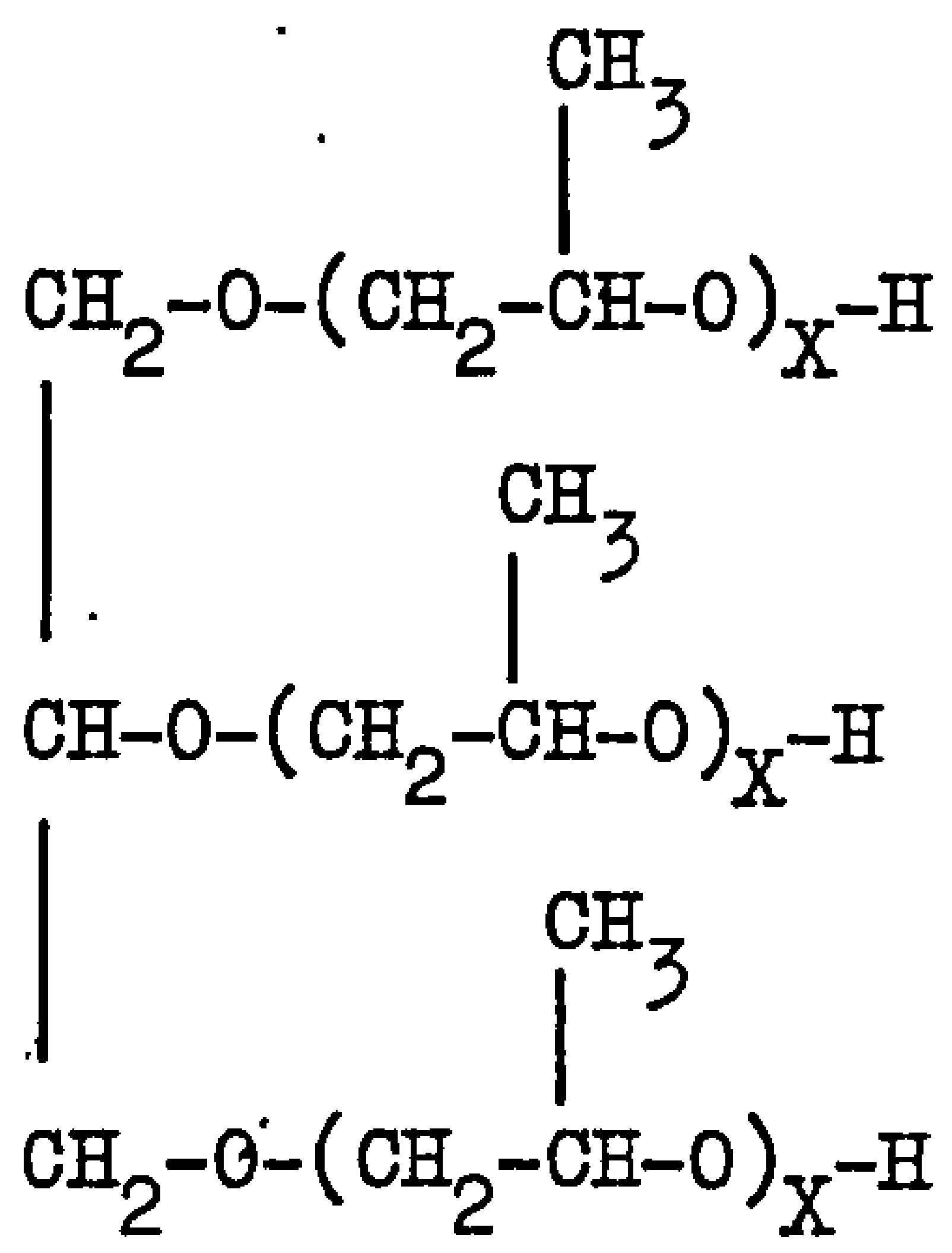
Nucleophilic XH

where ~~~ represents polymer chain

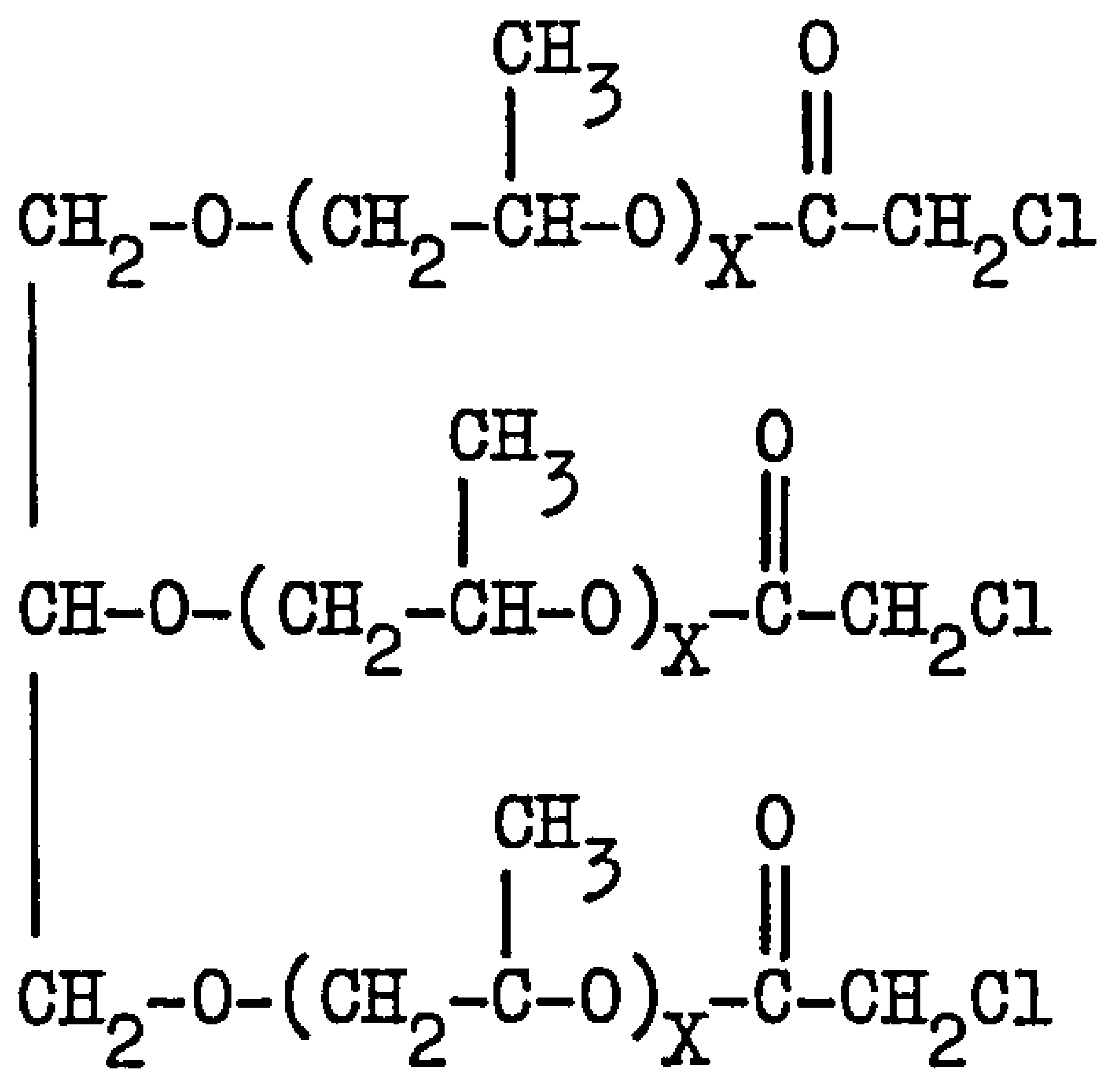
(ii) Lankrolan SHR3

The synthesis of Lankrolan SHR3 has been fully described in other studies (237) and thus it is only given in outline here.

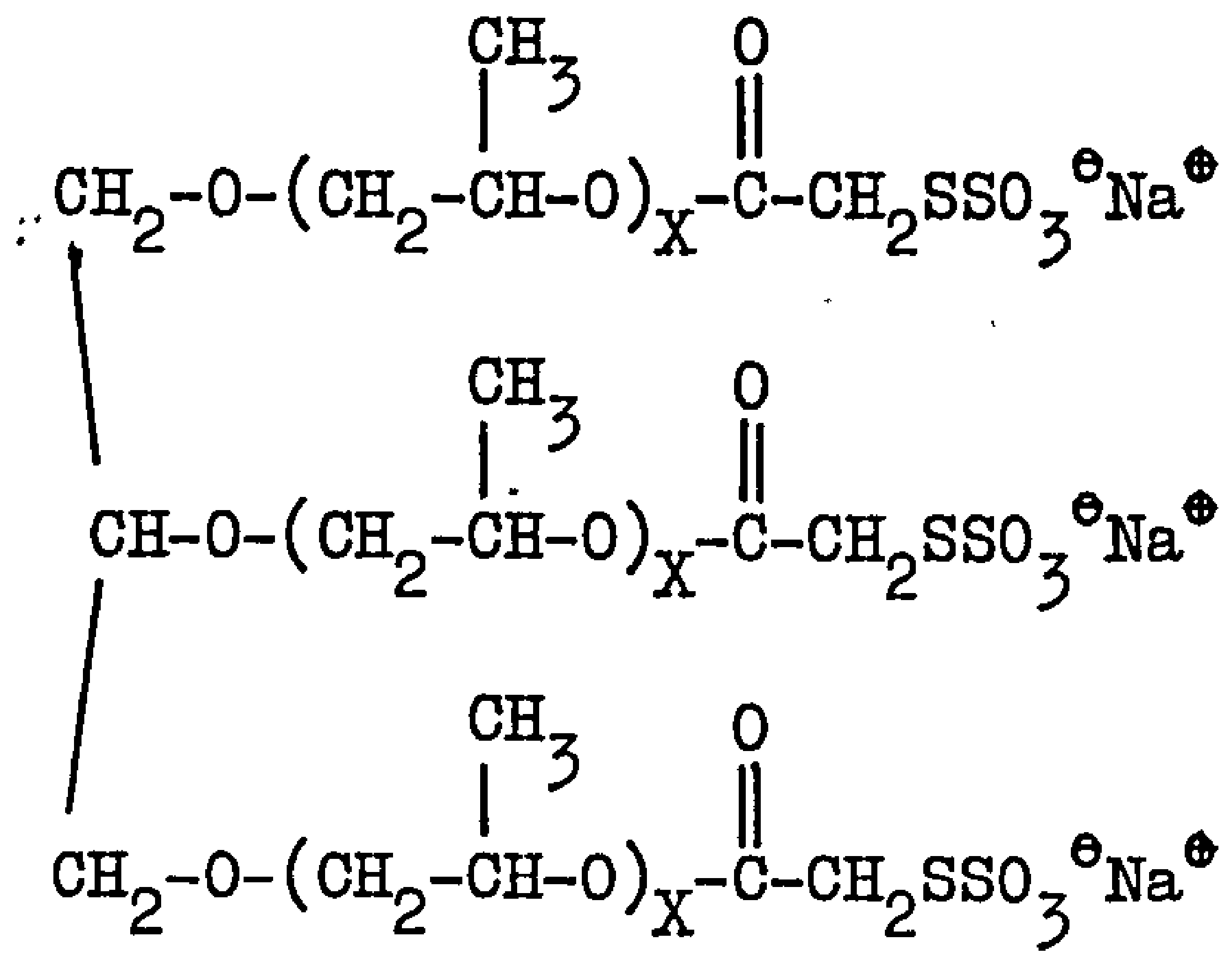
2 The starting material is a trifunctional polyether of general formula:



(where X can be an integer from 5 to 25) which is prepared from propylene oxide and glycerol and has a molecular weight of about 3000. The polyether is reacted with chloroacetic acid to form:



After repeated washing, conversion to the Bunte salt is carried out in iso-propanol by refluxing in the present of sodium thiosulphate where phase separation occurs, leaving the Lankrolan SHR3 resin in the upper phase, viz.



Lankrolan SHR3

The presence of sodium bisulphite in the treatment liquor is essential if a shrink-resist effect is to be obtained and it has been suggested (238) that the purpose of the bisulphite is to form thiol groups in the wool which react with the Bunte Salt groups of the polymer to form a mixed disulphide. Cross-linking is effected when this mixed disulphide rearranges to form a symmetrical disulphide. The proposed reaction sequence is:

$\text{Wool-S-S-Wool} + \text{HSO}_3^{\ominus} \longrightarrow \text{Wool-SH} + \text{Wool-SSO}_3^{\ominus}$

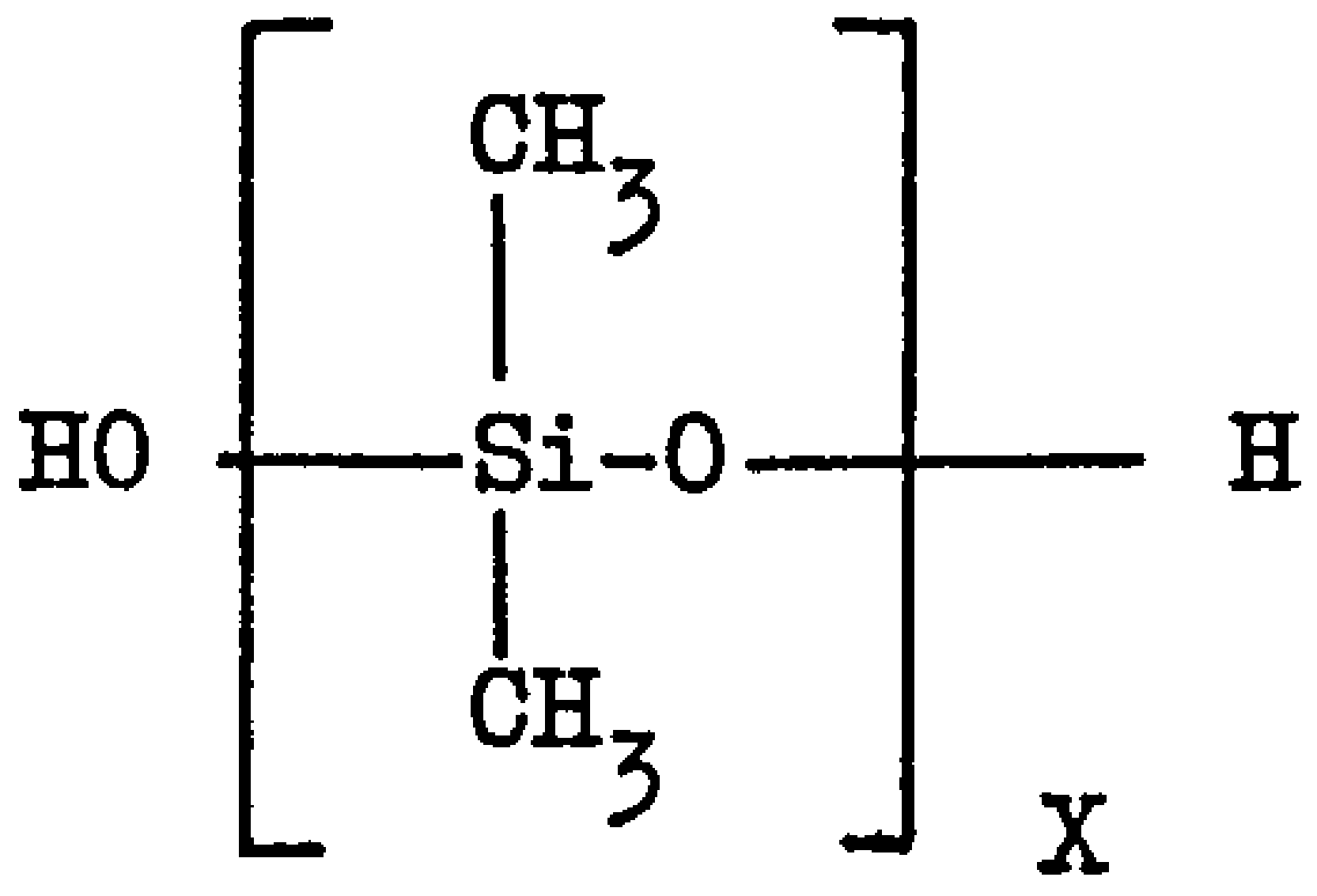
$\text{Wool-SH} + \text{polymer-SSO}_3 \longrightarrow \text{Wool-S-S-polymer} + \text{HSO}_3^{\ominus}$

$\text{2Wool-S-S-polymer} \longrightarrow \text{Wool-S-S-Wool} + \text{polymer-S-S-polymer}$

(iii) DC 109

During the early 1970's, I.W.S. and Dow Corning collaborated in the development of a silicone superwash finish for application from an organic solvent, such as perchloroethylene. The initial work (160) led to the production of a two-pack system based on DC 109 (prepolymer) and DC 109A (catalyst-crosslinking agent).

The prepolymer DC 109 consists (239) of repeat units of the type:



$$HO\left[\begin{array}{c} CH_3 \\ | \\ -Si-O- \\ | \\ CH_3 \end{array}\right]_X H$$

where X is 100-200 (and not 1000-1200 as quoted in 239).

The polymer is hydroxy-terminated, and when crosslinked through these groups with the crosslinking agent produces an elastic polymer by virtue of the long flexible chain-separating reactive sites.

The crosslinker DC 109A can be described as an amino-functional alkoxysilane with potential reactivity towards both the wool and the polymer. The crosslinker, however, can be rendered ineffective in the presence of moisture to an extent that it can no longer crosslink the DC 109 polymer. The DC 109A crosslinker was therefore modified to contain larger alkoxy chains and thereby to have greater water-stability. The resulting crosslinker (Q2 7056) is now the crosslinker recommended (241).

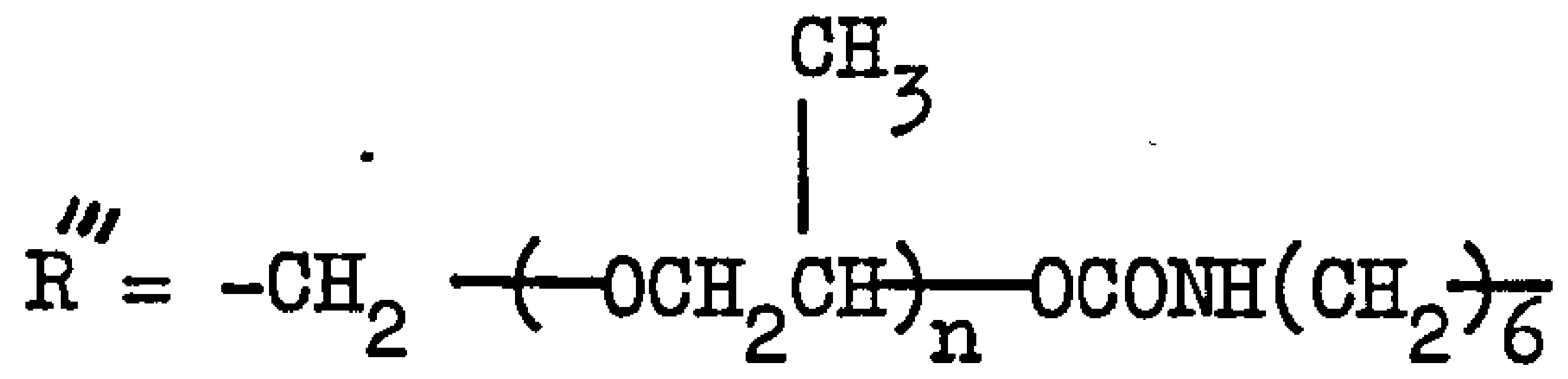
(iv) Synthappret BAP

This is a water-soluble bisulphite adduct of a polyisocyanate (Synthappret LKF-Bayer) (171) and Guise and Jackson (169) have given details of the conversion of Synthappret LKF into a product of this type by reacting it with sodium bisulphite in an ethanol-water solvent mixture.

$$C_2H_5C\left(-R'''NCO\right)_3 + 3NaHSO_3 \longrightarrow C_2H_5C\left(-R'''NHCOSO_3^{\ominus}Na^{\oplus}\right)_3$$

Synthappret LKF
(polyisocyanate)

Bisulphite adduct (BAP)



$$R''' = -CH_2\left(-OCH_2\overset{\overset{\Large CH_3}{|}}{C}H\right)_n OCONH\left(CH_2\right)_6$$

$$n \cong 16$$

The product (Synthappret BAP) can be used in admixture with a polyacrylate such as Acramin SLN 130% (Bayer) and this method of shrink-resisting wool fabrics has been referred to as the "Sirolan BAP" process (171). However, it has been shown (172) that there is no technical advantage in mixing Synthappret BAP with a polyacrylate, whereas mixing with an aliphatic polyurethane dispersion such as Impranil DLN or Impranil DLH (Bayer) offers advantages in terms of reduced cost, simplified processing and improved performance. Impranil DLH has been generally recommended for use with Synthappret BAP (241).

The optimum performance for shrinkage control is achieved by blending the polymers in the ratio of 1 part of Synthappret BAP to 1 part of Impranil DLH dispersion (172). One of the important factors in this process is the fabric preparation. Fabrics intended for treatment with Synthappret BAP should have been scoured to remove processing oils which might otherwise interfere with the adhesion between the polymer and the wool fibres. The pH of the fabric is the most important factor in the whole process (242). It must be greater than pH 5 and ideally should be between pH 6 and 8. Below a fabric pH of 4 curing of BAP is not possible. It is not possible to compensate for excess acidity on the fabric by adding great amounts of alkali to the treatment bath, because excessive addition of alkali reduces the stability through premature reaction of the BAP (243). Consequently the pH of the fabric must be adjusted during wet finishing by running the fabric in soda ash solution.

Methods

Methods of application of shrink-resist treatments

Shrink-resist treatment were applied to the fabrics via typical commercial techniques utilizing either padding or exhaustion processes.

(i) Exhaustion Treatments

(a) Hercosett 125

Wool fabric samples (30 x 30 cm), previously chlorinated with 2% available chlorine (sodium hypochlorite) by wet chlorination, were treated for 5-10 minutes with the appropriate concentration of Hercosett 125 at 35°C (liquor ratio 30:1). The pH was then gradually adjusted to pH 7.5 over a further period of 15 minutes by the addition of sodium bicarbonate. After a further 30 minutes, a cationic softener (Alcamine CA New 13 0.25% (o.w.f.) Allied Colloids) was added and the treatment continued for a further 10 minutes at 35°C. The samples were dried in a low temperature forced-draught air stream and finally cured at 110-120°C for 10 minutes. All samples after treatment were given a 20 s steam treatment on a blowing machine to ensure complete curing of the polymer.

(b) Lankrolan SHR3

The treatment bath was set at 35°C containing 6 g.l^{-1} $MgCl_2.6H_2O$ and 1.5 g.l^{-1} ammonia. The wool fabric was added followed by the Lankrolan SHR3 which was added slowly. The temperature was raised to 50°C over a period of 15 minutes and the wool fabric was treated for 25 minutes at a liquor ratio of 30:1 at 50°C. After hydroextraction the fabric samples were dried at 50-60°C for 20 minutes. All samples were steamed for 20 s on a blowing machine to ensure complete curing of the polymer.

(c) Lankrolan SHR3/Impranil DLH (SHR3/DLH)

A ratio of 4:3 of Lankrolan SHR3 to Impranil DLH was used for the polymer mixture. The two resins were diluted with a small amount of water and the diluted Lankrolan SHR3 solution was added to the dilute Impranil DLH (and not in the reverse order). The liquor to wool ratio was 30:1. The bath was set at 50°C and $MgCl_2 . 6H_2O$ (6 $g.l^{-1}$), wool fabric, and ammonia (1.5 $g.l^{-1}$) were added. The mixture of SHR3/DLH was added to the bath over a period of 15 minutes. After a period of 20-30 minutes total time the bath solution was clear. The treatment was continued for a further 15-20 minutes. The wool samples were removed, hydroextracted and dried in a low temperature over at 50-60°C for 20 minutes. All samples after treatment were given a 20 s steam treatment on a blowing machine to ensure complete curing of the polymer.

(ii) Padding Treatments

DC 109 and Q2 7056 and Synthappret BAP/Impranil DLH were applied by a padding method.

(a) DC 109 and Q2 7056

The recommended formulation of the Dow Corning system is as follows: 9 parts by weight DC 109 superwash wool finish, 1 part Q2 7056 (DC 109B) catalyst. Before making up the stock solution the fabric pick-up was determined and then a table was constructed relating the concentration of ingredients in terms of grams per litre with pick-up and percentage add-on. The required weighed out amounts of DC 109 and Q2 7056 were diluted in separate containers with tetrachloroethylene. The diluted chemicals were transferred to another container and clean tetrachloroethylene was added to make up the final volume required for the treatment. The padding was carried out on a Konrad Peter pad-mangle and then the samples were dried in an air oven at 140°C for 10 minutes. Subsequently the samples were cured in a conditioning room of 65% relative humidity and 21°C for 7 days. Finally the samples were treated with steam for 20 s on a blowing machine to ensure complete polymer curing.

(b) Synthappret BAP/Impranil DLH

As discussed earlier on the fabric pH is the most important factor in this process. The pH of the fabrics used was found to be between the ideal limits (see section 2.4.2.). The fabric pH was measured (244) by shaking 2 g of fabric, cut into small pieces in 100 ml of deionized water for 60 minutes and then testing the pH of the water extract.

As in the case of DC 109, before making up the padding liquor the % fabric pick-up was determined. The weights of Synthappret BAP and Impranil DLH used to give the treatment level required were calculated from the relationship:

$$C = \frac{1000 \text{ x } (\text{treatment level})}{\% \text{ pick-up}}$$

Where $C = g.l^{-1}$ is the concentration of Synthappret BAP and Impranil DLH in the treatment bath. "Treatment level" is expressed in terms of the % on weight of fabric (o.w.f.) total resin solids. All padding liquors contained 3 $g.l^{-1}$ sodium bicarbonate ($NaHCO_3$), which catalyses the curing of the polymers.

Padding liquors were prepared by dissolving the sodium bicarbonate in approximately half the final volume of cold water. The Synthappret

BAP and Impranil DLH were stirred into this solution before adjusting the final volume of the bath by the addition of cold water.

The application was carried out using a two bowl Konrad Peter pad-mangle and then the samples were dried and cured at 140°C in an air oven for 20 minutes.

All samples were given a 20 s steam treatment on a blowing machine to ensure complete curing of the polymer.

Test Methods

In this part of the work four test methods have been used to evaluate the results:

(a) Martindale abrasion tester (WIRA), for flat abrasion.

(b) Martindale tester (WIRA), for rate of fabric weight loss studies.

(c) Shirley Cyclic Bending tester, for cyclic bending hysteresis, and

(d) Instron Tensile tester, for determining the stress-strain behaviour of the fabrics.

All fabric samples were conditioned prior to testing at 65% r.h. and 21°C for at least 48 hours.

Martindale Abrasion Resistance (MAR)

The flat abrasion resistance of fabrics was measured by using the Martindale abrasion tester, which is described in Section 1.3.1.

The Martindale abrasion tester was chosen to determine the flat abrasion resistance of wool fabrics because this machine reproduces fibre fractures closest to those found in wear (16). The specimens, 1.5 in. in diameter, were mounted in the specimen holder with a 3 mm thick polyurethane foam sheet between the fabric and the backing metal plate, to prevent occasional specimen removal. The standard abrasive fabric, a cross-bred worsted, was used as the abradant. It was mounted on felt of about 1.75 mm thickness on the abradant holder. Each specimen holder was loaded with a weight of 595 g.

The rubbing counter was adjusted to zero and the automatic stop was set to a certain number of rubs depending on the type of fabric used. The abradant was changed with every new sample or after 50,000 rubs if the sample had not reached the end-point (245, 246). Samples were removed at various stages, and the condition of each sample was carefully examined. The end-point was reached when there were just two broken yarns in the woven specimen. This criterion is used elsewhere (245, 24) as a suitable end-point.

The mean values of Martindale abrasion resistance (MAR) on three fabric samples are quoted in each case as it was established in preliminary work that one specimen holder gave consistently lower MAR values. Accordingly the latter was not used in this work.

Rate of Fabric weight loss

In this series of experiments the general experimental procedure using the Martindale tester was followed as previously described. Preweighed conditioned fabric specimens were abraded for the requisite number of rubs (e.g. generally fabric A every 2000 rubs, fabric C every 1000 rubs). The specimens were removed, allowed to condition for 24 hours at 65% r.h. and 21°C, weighed and then replaced for further abrasion testing. This was repeated at specified intervals and the mean loss in fabric weight of three specimens as before is quoted in each case.

Fabric Bending Properties

The Shirley Cyclic Bending tester was used in this series of experiments, the flexural rigidity (G_o) and coercive couple (C_o) being determined using the short method of test described in detail elsewhere (247). The mean cyclic bending hysteresis graphs were constructed from the values from three weft-way specimens and G_o and C_o calculated in the normal manner.

Fabric Tensile Properties

The breaking load-breaking extension behaviour of the untreated and polymer-treated samples was measured using an Instron Tensile Tester TM-M Metric Model at 65% r.h. and 21°C. The machine settings were as follows:

Cross-head speed = 10 cm.min.$^{-1}$
Chart speed = 10 cm.min.$^{-1}$
Gauge length = 20 cm

and a "CTM" cell with a load range up to 100 kg.

Three specimens in the weft-way direction were tested for each sample. From the curves obtained the mean breaking load and mean breaking extension were calculated.

2.4.3. Results and Discussion

2.4.3.1. Martindale Abrasion Resistance (MAR)

The results of the Martindale abrasion tests are given in Tables 29-33 and illustrated in Figures 37a-41, in which the change in MAR(%) is plotted against the polymer add-on (% o.w.f.).

In general all the polymer shrink-resist treatments studied increase the MAR of the three woven wool fabrics used in this work.

In the case of the light weight plain weave fabric (fabric A), the increases in MAR are relatively small and for Lankrolan SHR3/ Impranil DLH at 4% polymer add-on and DC 109 at 2 and 3% polymer add-on small decreases in MAR are noted (See Fig. 39 and 40). It has been reported in previous studies that DC 109 can lead to a small decrease in MAR (161). However, the effect is very dependent upon the polymer add-on, while a similar decrease has also been observed

TABLE 29. Martindale Abrasion resistance of fabric treated with Hercosett 125 (by exhaustion) after 2% o.w.f chlorination for 2 min.

Polymer Add-on (% o.w.f)	Fabric A (Worsted)			Fabric B (Worsted)			Fabric C (Woollen)		
	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)
Untreated*	13.0 12.5 10.2	11.9	0	11.9 11.9 11.9	11.9	0	3.6 3.8 3.6	3.7	0
0.5	15.0 16.0 16.0	15.5	30.2	15.0 14.0 11.0	13.3	11.8	4.0 6.0 6.0	5.3	43.2
1.0	13.0 15.0 17.0	15.0	26.0	14.0 11.0 15.0	13.3	11.8	4.25 5.25 6.0	5.2	40.5
1.5	15.0 17.0 18.0	16.5	38.6	13.0 14.0 13.0	13.3	11.8	4.25 6.0 6.0	5.4	45.9
2.0	14.0 14.0 18.0	15.3	28.6	15.0 11.0 14.0	13.3	11.8	4.5 5.5 5.75	5.25	41.9

* For untreated fabric specifications (see section 2.4.2.).

TABLE 30. Martindale abrasion resistance of fabrics treated with Lankrolan SHR3 (by exhaustion).

Polymer Add-on (% o.w.f)	Fabric A (Worsted) Abrasion Resistance ($\text{Rubs} \times 10^3$)	mean	mean increase in MAR (%)	Fabric B (Worsted) Abrasion Resistance ($\text{Rubs} \times 10^3$)	mean	mean increase in MAR (%)	Fabric C (Woollen) Abrasion Resistance ($\text{Rubs} \times 10^3$)	mean	mean increase in MAR (%)
Untreated	13.0 12.5 10.2	11.9	0	11.9 11.9 11.9	11.9	0	3.6 3.8 3.6	3.7	0
1	12.0 13.0 12.0	12.3	3.4	12.5 14.0 14.0	13.5	13.4	6.5 6.0 6.5	6.3	70.3
2	17.0 16.0 16.0	16.3	37.0	15.0 15.0 15.0	15.0	26.0	6.0 6.5 7.0	6.5	75.7
3	18.0 18.0 16.5	17.5	47.0	18.0 18.0 16.0	17.3	45.4	7.0 6.0 7.0	6.6	78.4
4	13.0 14.0 13.0	13.3	11.8	12.0 12.0 12.5	12.2	2.5	6.0 6.0 7.0	6.3	70.3

TABLE 31. Martindale abrasion resistance of fabrics treated with Lankrolan SHR3/Impranil DLH (by exhaustion).

Polymer Add-on (% o.w.f)	Fabric A (Worsted)			Fabric B (Worsted)			Fabric C (Woollen)		
	Abrasion Resistance (Rubs x 10^3)	mean	mean change in MAR (%)	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)
Untreated*	13.0 12.5 10.2	11.9	0	11.9 11.9 11.9	11.9	0	3.6 3.8 3.6	3.7	0
1	12.0 13.0 10.5	11.9	0	12.0 13.0 12.0	12.3	3.4	6.0 6.0 6.0	6.0	62.2
2	18.0 16.5 12.5	15.7	+ 31.9	17.0 16.0 12.0	15.0	26.0	6.75 6.75 7.25	6.9	86.5
3	15.0 15.0 15.0	15.0	+ 26.0	14.5 13.5 13.5	13.8	16.4	6.4 6.4 6.6	6.4	74.3
4	13.0 10.0 10.0	11.0	- 7.6	12.0 12.5 13.5	12.6	5.9	6.0 6.0 6.0	6.0	62.2

* For untreated fabric specifications (see section 2.4.2.)
\+ = increase in MAR, – = decrease in MAR

TABLE 32. Martindale abrasion resistance of fabrics treated with DC109 (by padding).

Polymer Add-on (% o.w.f)	Fabric A (Worsted)			Fabric B (Worsted)			Fabric C (Woollen)		
	Abrasion Resistance (Rubs x 10^3)	mean	mean change in MAR (%)	Abrasion Resistanse (Rubs x 10^3)	mean	mean increase in MAR (%)	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)
Untreated	13.0 12.5 10.2	11.9	0	11.9 11.9 11.9	11.9	0	3.6 3.8 3.6	3.7	0
1	12.5 12.5 12.5	12.5	+ 5.0	14.0 14.0 14.0	14.0	17.6	5.5 6.0 5.0	5.5	48.6
2	11.0 11.0 11.0	11.0	- 7.5	14.0 12.0 12.0	12.6	6.4	6.2 6.5 6.0	6.2	68.4
3	10.0 10.0 8.5	9.5	- 20.1	12.0 13.0 13.0	12.6	6.4	6.0 6.75 6.0	6.2	68.4
4	14.0 14.0 12.0	13.5	+ 13.4	15.0 15.5 15.0	15.2	27.7	7.5 7.5 8.5	7.8	110.8

TABLE 33. Martindale abrasion resistance of fabrics treated with Synthappret BAP/Impranil DLH (by padding).

Polymer Add-on (% o.w.f)	Fabric A (Worsted)			Fabric B (Woollen) Worsted ?			Fabric C (Woollen)		
	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)
Untreated	13.0 12.5 10.2	11.9	0	11.9 11.9 11.9	11.9	0	3.6 3.8 3.6	3.6	0
0.5	14.0 20.0 14.0	16.0	34.5	15.0 17.0 17.0	16.3	37.0	6.25 6.5 7.0	6.5	75.7
1.0	23.0 16.5 16.5	18.5	55.5	17.0 19.0 18.5	18.0	51.3	10.0 10.0 11.5	10.5	183.6
2.0	16.0 24.0 24.0	21.0	76.5	26.0 28.0 26.0	26.7	124.4	15.0 15.0 17.0	15.6	321.6
2.5	18.0 26.0 19.0	21.0	76.5	26.0 28.0 28.0	28.0	135.3	15.0 17.0 16.0	16.3	340.5

Fig. 37a - The effect of Hercosett 125 applied by exhaustion on the Martindale abrasion resistance of wool fabrics

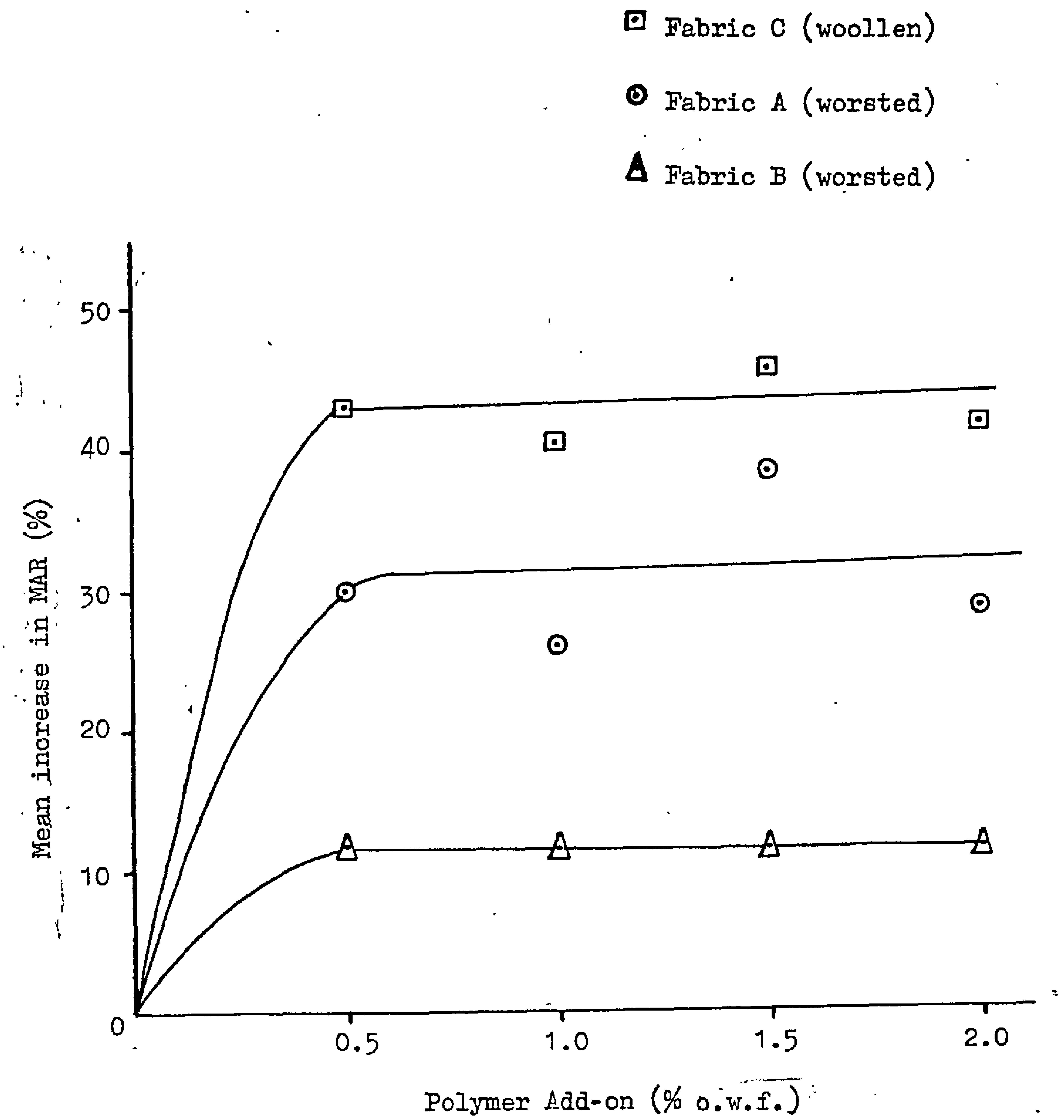


Fig. 38 - The effect of Lankrolan SHR3 applied by exhaustion on the Martindale abrasion resistance of wool fabrics

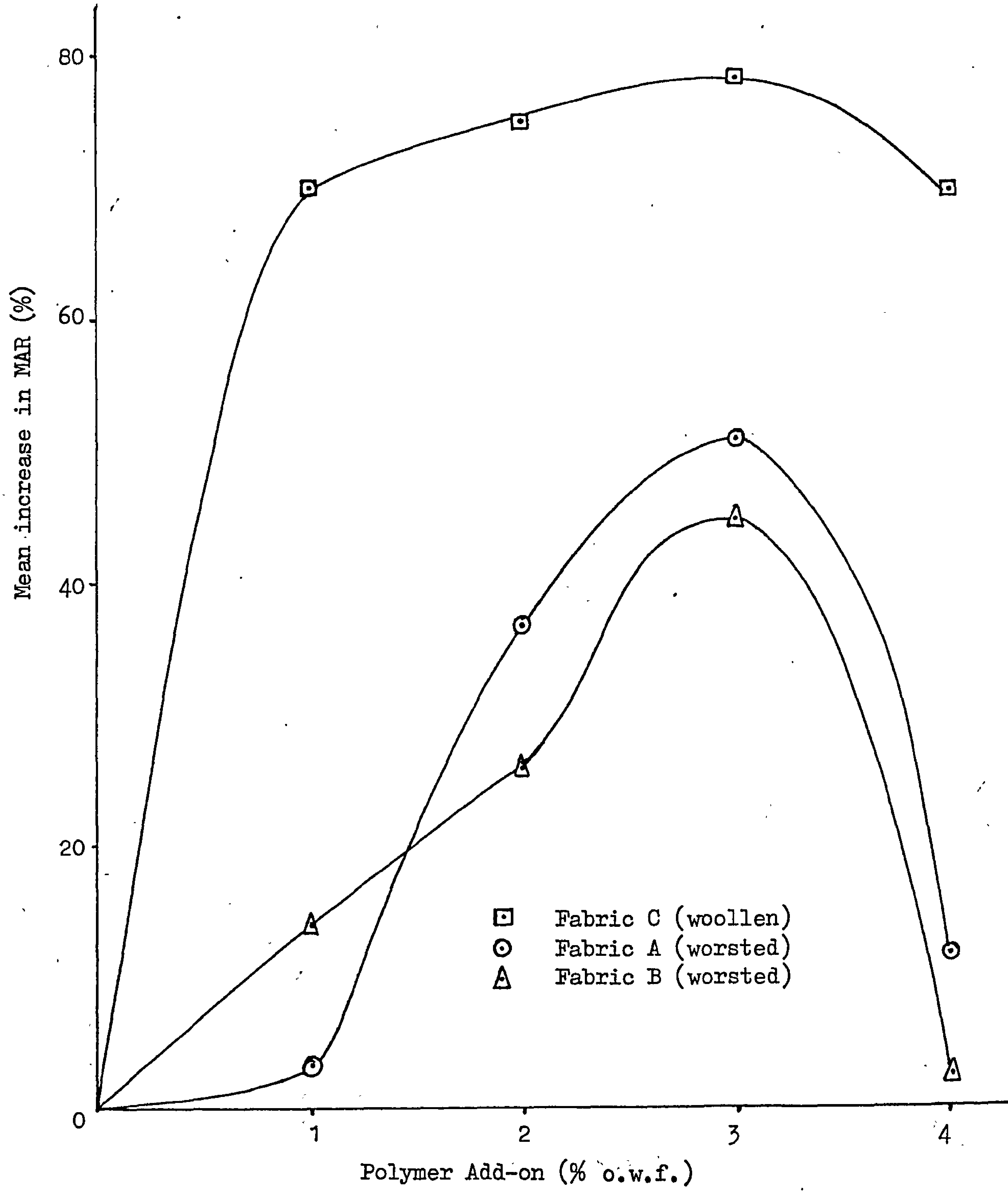


Fig. 39 - The Effect of Lankrolan SHR3/Impranil DLH (exhaustion) shrink-resist finish on the MAR of wool fabrics.

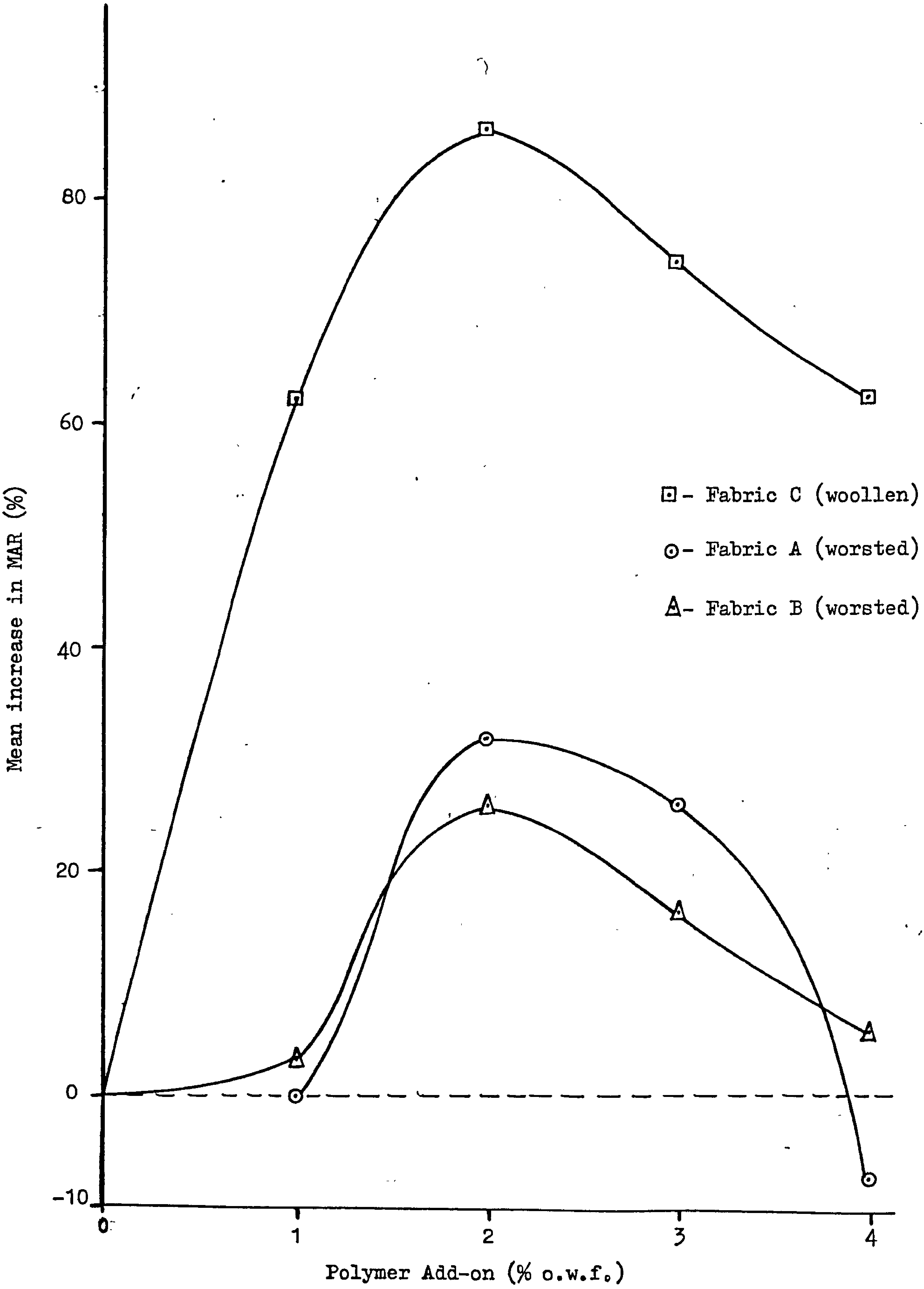


Fig. 40 - The effect of DC-109 applied by padding on the Martindale abrasion resistance of wool fabrics

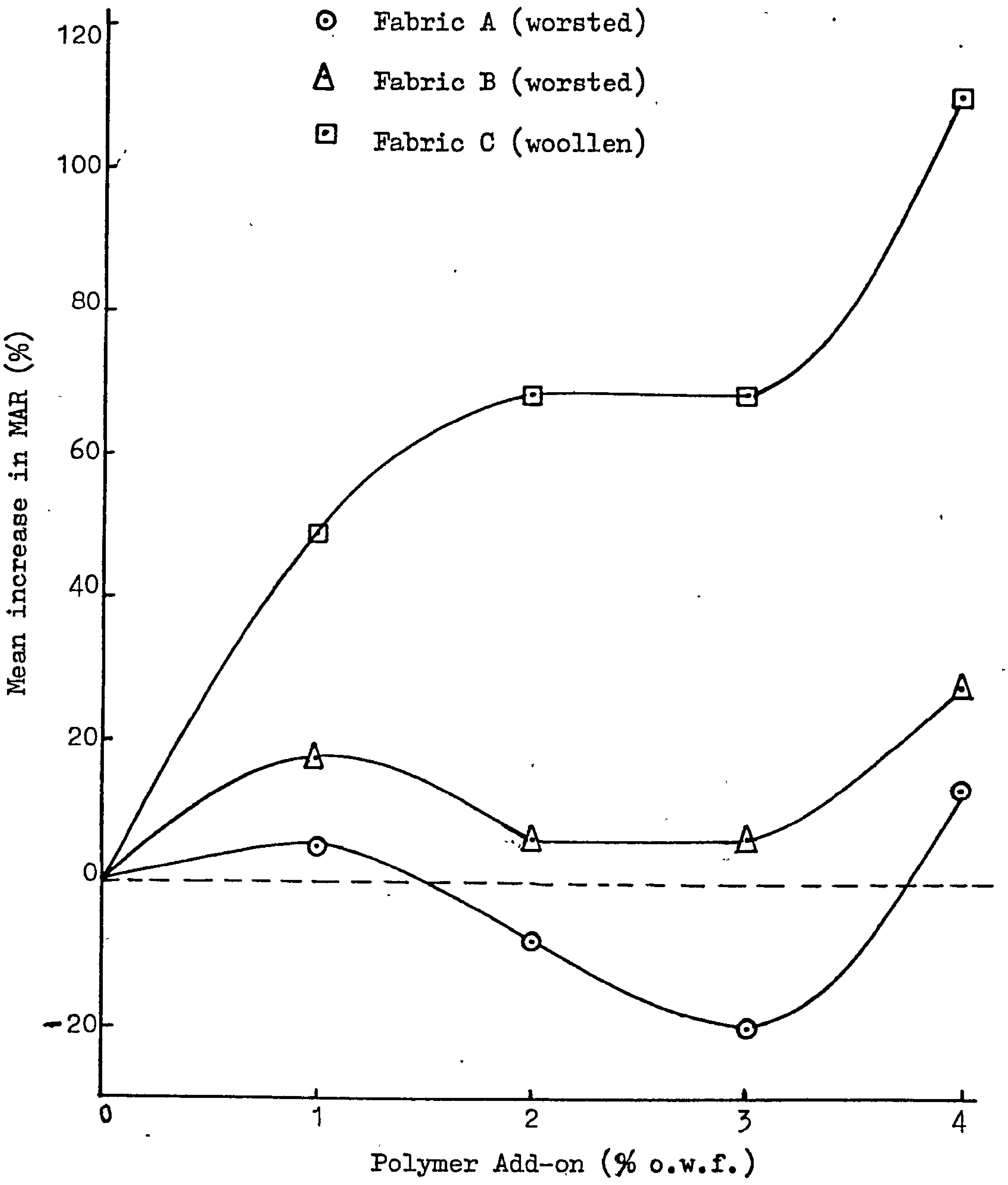
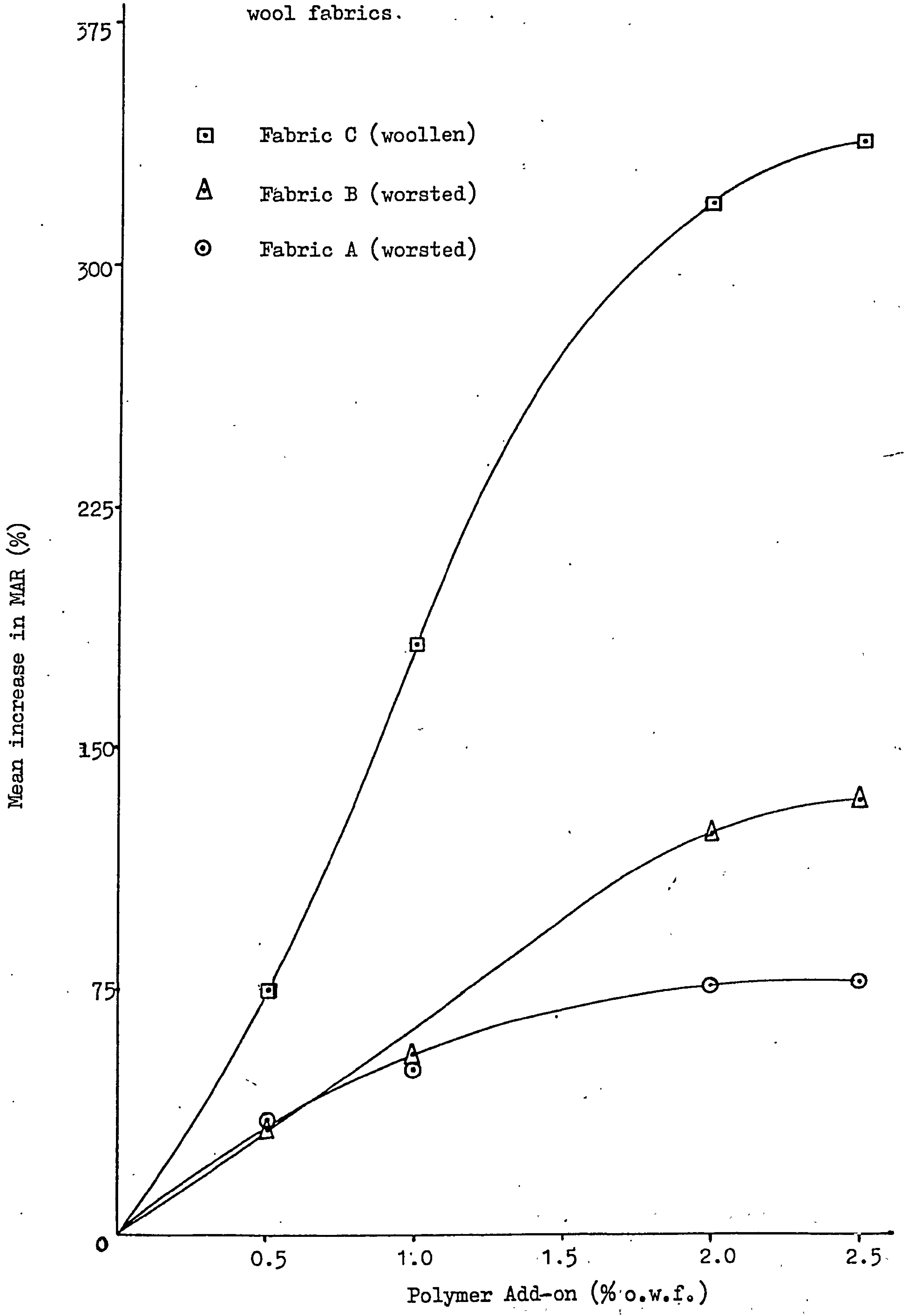


Fig. 41 - The effect of Synthappret BAP/Impranil DLH applied by padding on the Martindale abrasion resistance of wool fabrics.



with a variety of polymers on worsted fabrics (47). The general results are in accord with previous studies on polymer-treated wool fabrics (154, 156, 230).

The most dramatic increases in MAR are demonstrated by Synthappret BAP/Impranil DLH, which on the woollen flannel fabric (fabric C) gave a 340% increase at 2.5% polymer add-on. More moderate increases below 110% are recorded for DC 109, Lankrolan SHR3/Impranil DLH and Lankrolan SHR3, the chlorination-Hercosett treatment in this case yielding somewhat lower abrasion resistance values.

In general, for the padding treatments the order of improvement in MAR is Fabric C > Fabric B > Fabric A, but for the exhaustion treatments the order is Fabric C > Fabric A > Fabric B. It appears therefore that the fabric structure, the nature of the polymer, the polymer add-on and the nature of the method of application of the polymer shrink-resist treatment are of importance in determining the changes in fabric MAR. It would appear that padding treatments probably lead to a greater improvement in the MAR compared with the exhaustion treatments. However, in this preliminary study of the effects of polymer shrink-resist treatments, no direct comparison between padding and exhaustion was carried out using the same polymer. Nevertheless the results obtained on the flannel fabric are significantly higher in each case for all the polymer treatments studied. This is an interesting observation because in other work it was shown that polymer treatments are more effective in promoting shrink resistance in woollen fabrics (156).

In the three exhaustion treatments, the dec increase in MAR is initially rapid with polymer add-on, but thereafter only minor changes are in general to be seen. One exception is Lankrolan SHR3 on fabric

B and fabric A in which the MAR values are reduced as the polymer add-on is increased from 3 to 4%. This phenomenon is also noted in the Lankrolan SHR3/Imprani1 DLH treatment where the MAR value is reduced as the add-on is increased from 2-4% o.w.f. for the three fabrics studied.

The rapid initial rise in MAR could be interpreted in terms of the encapsulation of the fibre by the shrink-resist polymer, but clearly the presence of inter-fibre polymer bridges (so-called inter-fibre bonds) would be expected to significantly modify the MAR value of the fabric. In the treatments applied by padding both polymers could lead to fibre encapsulation and to the production of interfibre polymer bridges. The dramatic improvement in the Synthappret BAP/Imprani1 DLH results may reflect either the intrinsic nature of the polymers or may alternatively be caused by the specific method of application, namely padding. In work to be discussed (in Section 2.5) the effect of the method of application has been studied in detail by applying the same polymer via padding and by exhaustion procedures.

2.4.3.2. Rate of fabric weight loss during abrasion testing

The fabric weight loss results during abrasion testing of selected polymer-treated samples at high and low polymer add-on values for fabric A and fabric C are given in Tables 34-41 and illustrated in Fig. 42-45.

From these results it is clear that for the untreated woollen-spun flannel (fabric C), the rate of weight loss is almost linear and is higher than for any of the polymer-treated samples. In accord with Fig. 37-41 the rate of weight loss is reduced to a greater extent the greater the fabric MAR. In addition, the rate of weight loss

TABLE 34. The effect of Hercosett 125 applied by exhaustion on the weight loss (%) of fabric (woollen flannel).

Number of Rubs $(x10^3)$	Weight loss of flannel fabric treated with Hercosett 125					
	Untreated *		Polymer Add-on (% o.w.f) 0.5		2	
	(%)	mean	(%)	mean	(%)	mean
1	6.41 6.88 5.97	6.4	3.96 4.77 3.77	4.2	3.97 5.59 5.18	4.9
2	12.65 13.41 12.47	12.8	9.92 10.32 11.24	10.5	11.09 11.46 10.60	11.0
3	18.49 21.94 21.37	20.6	14.44 14.58 17.11	15.4	15.97 16.94 15.10	16.0
4	24.73 29.95 27.35	27.3	21.45 20.10 21.95	21.2	22.35 23.16 22.69	22.7
5	—	—	25.50 24.51 26.31	25.4	25.63 26.32 25.87	25.9

* For untreated fabric specifications (see section 2.4.2)

TABLE 35. The effect of Lankrolan SHR3 by exhaustion on the weight loss (%) of Fabric C (woollen flannel).

Number of Rubs (x10^3)	Weight loss of fabric C treated with Lankrolan SHR3					
	Untreated *		Polymer Add-on (% o.w.f) 1		4	
	(%)	mean	(%)	mean	(%)	mean
1	6.41 6.88 5.97	6.4	5.42 5.72 5.17	5.4	5.39 5.55 6.19	5.7
2	12.65 13.41 12.47	12.8	9.44 10.4. 9.80	9.9	9.95 10.51 10.54	10.3
3	18.49 21.94 21.37	20.6	12.33 13.31 12.50	12.7	13.54 13.89 13.80	13.7
4	24.73 29.95 27.35	27.3	14.42 16.06 15.15	15.2	16.87 17.35 17.29	17.2
5	—	—	17.35 18.45 17.92	17.9	20.50 21.11 21.42	21.0
6	—	—	19.36 21.90 20.04	20.4	24.36 26.24 25.62	25.4

* For untreated fabric specifications (see section 2.4.2)

TABLE 36. The effect of DC 109 applied by padding on the weight loss (%) of Fabric C (woollen flannel).

Number of Rubs $(x10^3)$	Weight loss of flannel fabric treated with DC 109					
	Untreated *		Polymer Add-on (% o.w.f) 1		4	
	(%)	mean	(%)	mean	(%)	mean
1	6.41 6.88 5.97	6.4	2.94 3.42 3.26	3.2	2.94 3.59 3.91	3.5
2	12.65 13.41 12.47	12.8	10.40 9.66 10.22	10.1	5.86 6.49 6.26	6.2
3	18.49 21.94 21.34	20.6	15.18 14.09 15.51	14.9	8.20 8.76 8.94	8.6
4	24.73 29.95 27.35	27.3	21.75 18.19 20.89	20.3	9.65 10.58 10.42	10.2
5	—	—	27.77 22.50 26.35	25.5	10.97 12.27 12.19	11.8
6	—	—	32.34 28.58. 31.96	31.0	13.04 14.55 14.13	13.9
8	—	—	—	—	16.43 18.85 17.80	17.7

* For untreated fabric specifications (see section 2.4.2)

TABLE 37. The effect of Synthappret BAP/Impranil DLH applied by padding on the weight loss (%) of Fabric C (woollen flannel).

Number of Rubs (x10^3)	Weight loss of fabric C treated with BAP/Impranil DLH					
	Untreated		Polymer Add-on (% o.w.f)			
			0.5		2.5	
	(%)	mean	(%)	mean	(%)	mean
1	6.41 6.88 5.97	6.4	4.66 4.75 4.11	4.5	3.08 3.13 2.79	3
2	12.65 13.41 12.47	12.8	9.15 9.0 8.99	9.0	5.14 5.14 5.31	5.2
3	18.49 21.94 21.37	20.6	12.43 12.72 12.12	12.4	—	—
4	24.73 29.95 27.35	27.3	16.16 15.80 15.56	15.8	7.04 7.07 7.45	7.2
5	—	—	19.94 20.14 20.31	20.1	—	—
6	—	—	24.18 26.40 24.97	28.2	8.54 8.76 9.15	8.8
8	—	—	—	—	9.77 10.05 10.25	10.0
10	—	—	—	—	11.20 11.62 11.85	11.5
12	—	—	—	—	12.31 12.98 13.11	12.8
14	—	—	—	—	13.30 14.11 14.22	13.9
16	—	—	—	—	14.36 15.40 15.48	15.1

* For untreated fabric specifications (see section 2.4.2).

TABLE 38. The effect of Hercosett 125 applied by exhaustion on the weight loss (%) of Fabric A (worsted).

Number of Rubs ($\times 10^3$)	Weight loss of fabric A treated with Hercosett 125					
	Untreated*		Polymer Add-on (% o.w.f) 0.5		2	
	(%)	mean	(%)	mean	(%)	mean
2	4.65 4.35 4.60	4.5	4.86 4.13 4.88	4.6	4.25 4.39 4.73	4.4
4	6.68 6.23 6.53	6.5	7.0 6.43 7.02	6.8	6.72 7.20 7.06	7.0
6	9.12 8.64 8.93	8.9	9.73 9.19 10.71	9.9	10.02 10.56 10.55	10.4
8	10.82 10.49 10.46	10.6	12.06 10.89 12.45	11.8	10.77 11.66 11.52	11.3
10	13.37 12.93 13.06	13.1	13.66 12.40 14.45	13.5	12.35 13.38 13.36	13.0
12	16.40 15.00 15.46	15.6	16.20 14.51 17.40	16.0	15.23 16.33 16.58	16.0
14	—	—	19.60 17.53 20.95	19.4	16.62 18.05 18.36	17.6
16	—	—	22.26 19.23 23.09	21.5	18.46 20.04 20.28	19.6

* For untreated fabric specifications (see section 2.4.2)

TABLE 39. The effect of Lankrolan SHR3 applied by exhaustion on the weight loss (%) of Fabric A (worsted).

Number of Rubs (x10^3)	Weight loss of fabric A treated with Lankrolan SHR3					
	Untreated *		Polymer Add-on (% o.w.f)			
			1		4	
	(%)	mean	(%)	mean	(%)	mean
2	4.65 4.35 4.60	4.5	3.11 3.48 3.73	3.4	4.45 4.66 4.87	4.7
4	6.68 6.23 6.53	6.5	6.42 6.65 6.50	6.5	8.58 7.66 8.16	8.1
6	9.12 8.64 8.93	8.9	8.60 8.91 8.24	8.6	10.99 9.84 10.38	10.4
8	10.82 10.49 10.46	10.6	10.78 11.37 10.68	10.9	13.85 12.58 13.54	13.3
10	13.37 12.93 13.06	13.1	14.15 15.05 13.58	14.3	17.48 15.33 16.77	16.5
12	16.40 15.00 15.46	15.6	16.58 18.08 16.35	17.0	20.72 18.63 19.09	19.5
14	—	—	20.13 21.96 20.54	20.9	—	—

* For untreated fabric specifications (see section 2.4.2)

TABLE 40. The effect of DC 109 applied by padding on the weight loss (%) of Fabric A (worsted).

Number of Rubs $(\times 10^3)$	Weight loss of fabric A treated with DC 109					
	Untreated *		Polymer Add-on (% o.w.f)			
			1		4	
	(%)	mean	(%)	mean	(%)	mean
2	4.65 4.35 4.60	4.5	5.11 4.63 4.95	4.9	3.37 3.20 3.12	3.2
4	6.68 6.23 6.53	6.5	7.10 7.32 6.99	7.1	4.81 4.31 4.32	4.5
6	9.12 8.64 8.93	8.9	10.80 10.87 10.35	10.7	7.91 7.44 7.30	7.5
8	10.82 10.49 10.46	10.6	12.93 13.47 12.46	12.9	9.56 9.39 8.78	9.2
10	13.37 12.93 13.06	13.1	16.42 16.91 15.96	16.4	13.49 12.73 12.40	12.9
12	16.40 15.00 15.46	15.6	20.93 21.12 20.11	20.7	17.68 16.70 16.86	17.0

* For untreated fabric specifications (see section 2.4.2)

TABLE 41. The effect of Synthappret BAP/Impranil DLH applied by padding on the weight loss (%) of fabric A (worsted).

Number of Rubs $(x10^3)$	Weight loss of fabric A treated with BAP/DLH					
	Untreated *		Polymer Add-On (% o.w.f) 0.5		2.5	
	(%)	mean	(%)	mean	(%)	mean
2	4.65 4.35 4.60	4.5	3.47 3.92 4.20	3.9	2.13 2.05 2.20	2.1
4	6.68 6.23 6.53	6.5	4.68 4.91 5.77	5.1	3.41 3.39 8.83	3.2
6	9.12 8.64 8.93	8.9	7.76 7.97 7.32	7.7	4.48 4.59 4.07	4.4
8	10.82 10.49 10.49	10.6	9.26 9.15 8.35	8.9	5.12 5.65 4.69	5.1
10	13.37 12.93 13.06	13.1	11.37 10.59 10.60	10.8	6.19 6.50 5.93	6.2
12	16.40 15.00 15.46	15.6	13.80 12.56 12.86	13.0	7.68 8.06 7.80	7.8
14	—	—	17.93 15.43 16.00	16.5	—	—
16	—	—	20.01 17.44 18.15	18.5	9.25 9.90 9.31	9.5
20	—	—	—	—	11.31 13.50 11.58	12.1

* For untreated fabric specifications (see section 2.4.2)

Fig. 42 - The Effect of Hercosett 125 and Lankrolan SHR3 applied by exhaustion on the weight loss (%) of fabric C (woollen flannel).

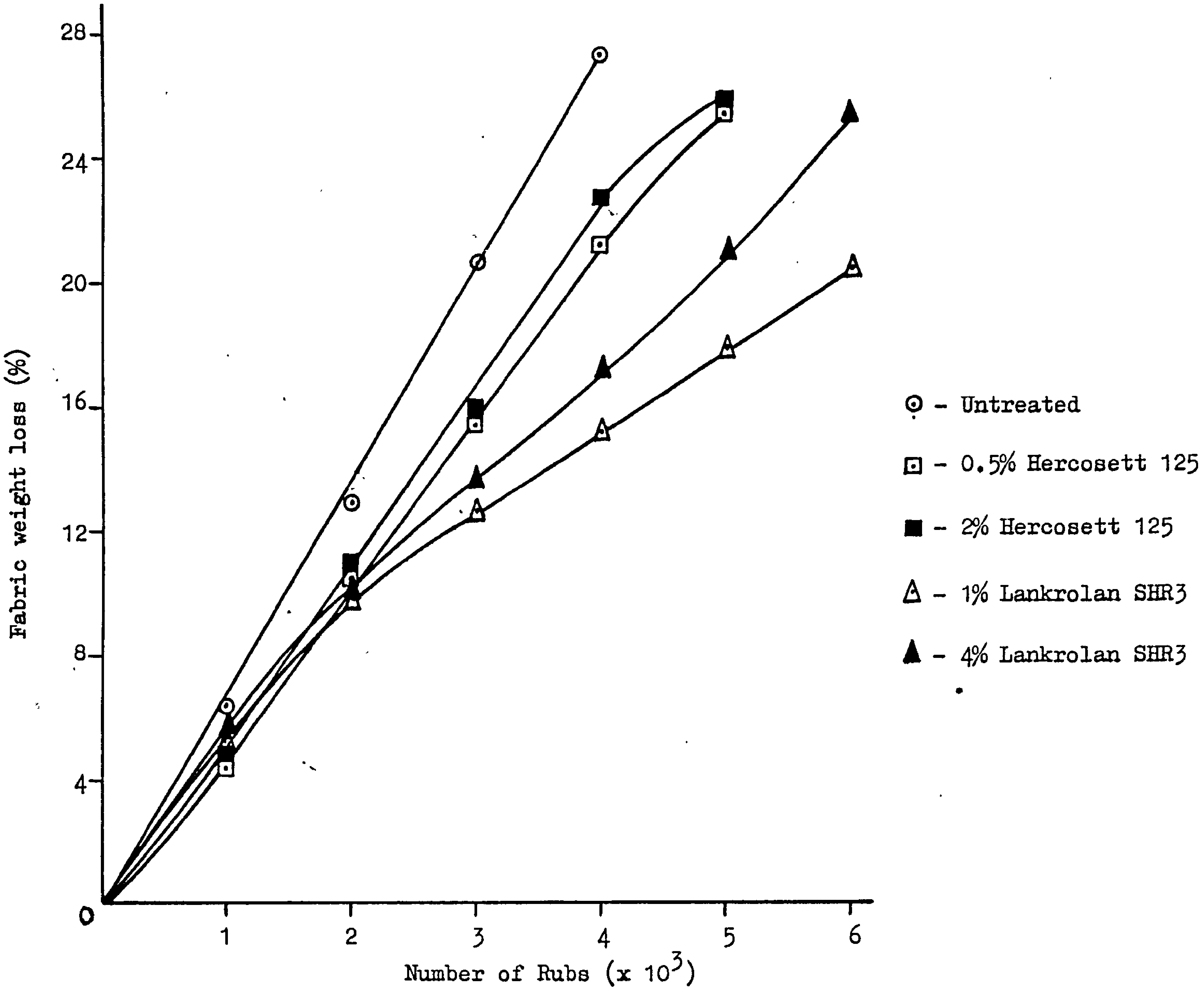


Fig. 43 - The Effect of Synthappret BAP/Impranil DLH and DC 109 applied by padding on the weight loss (%) of fabric C (woollen flannel)

Fig. 44 The Effect of Hercosett 125 and Lankrolan SHR3 applied by exhaustion on the weight loss (%) of fabric A (worsted).

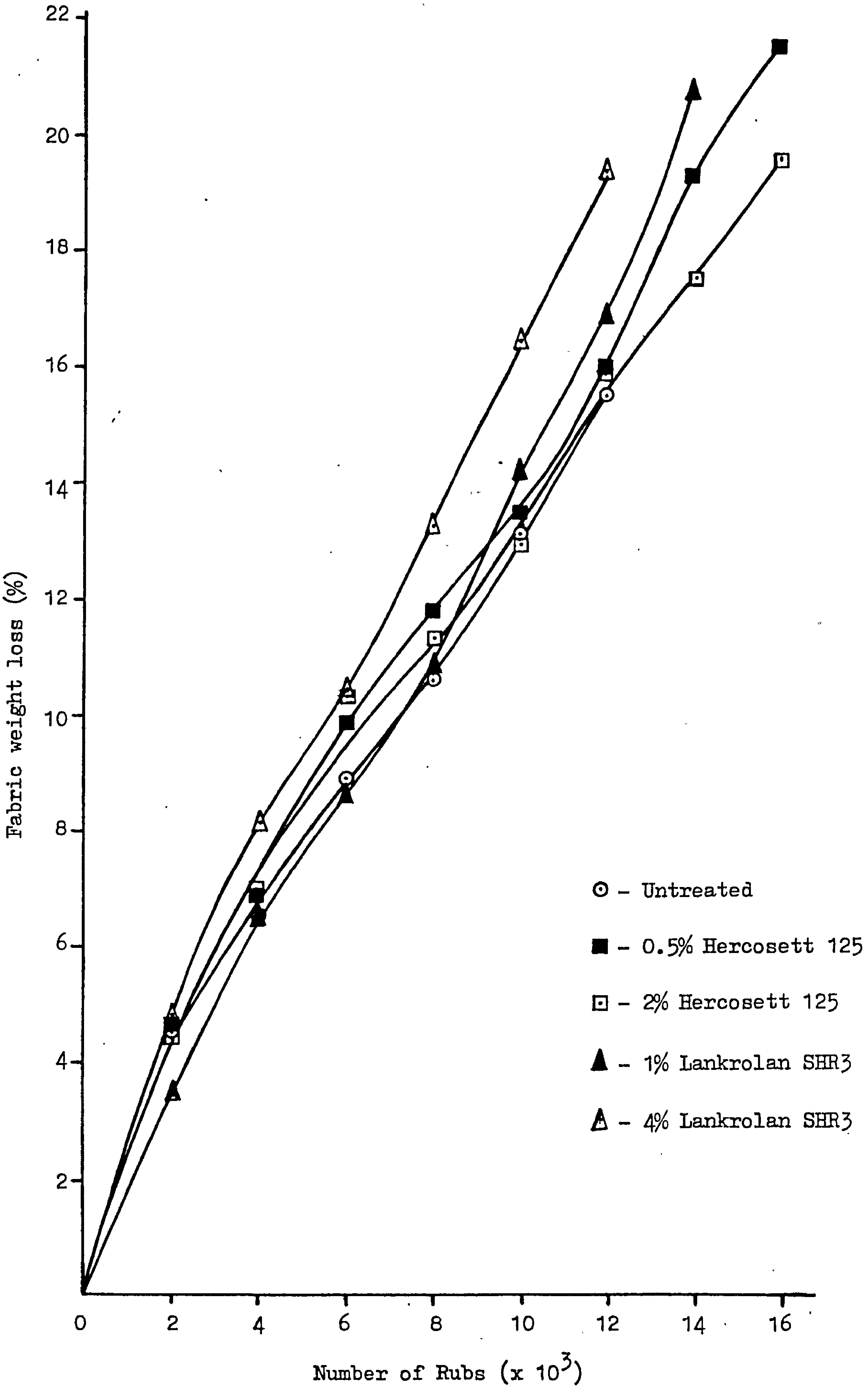
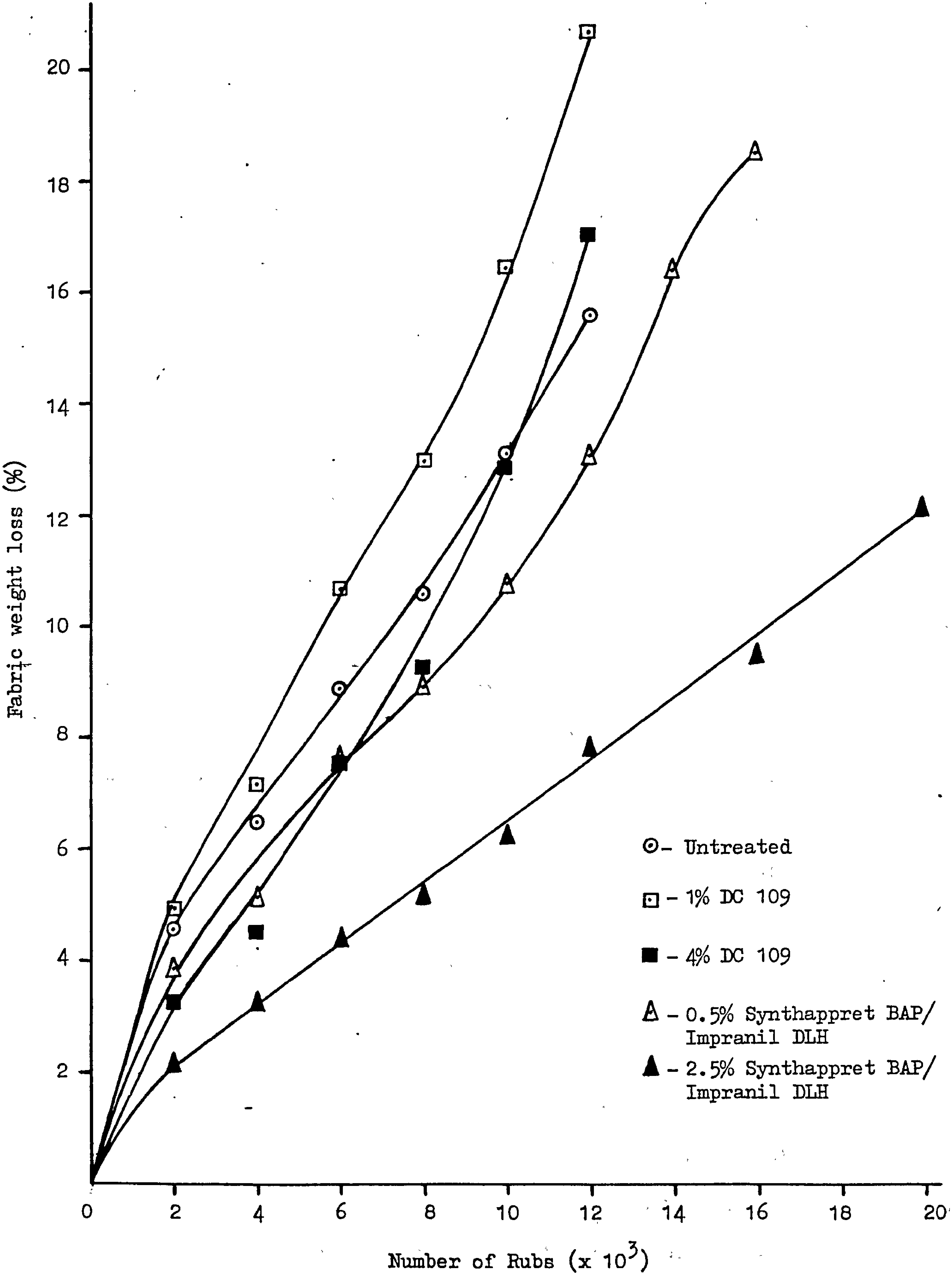


Fig. 45 - The Effect of Synthappret BAP/Impranil DLH and DC 109 applied by padding on the weight loss (%) of fabric A (worsted).



for fabric C, for fabric samples treated with polymers via the padding technique (i.e. Synthappret BAP/Impranil DLH, DC 109) are lower than those treated with polymers applied by exhaustion (i.e. Hercosett 125, Lankrolan SHR3).

In the case of Synthappret BAP/Impranil DLH at 2.5% polymer add-on - the highest abrasion resistance recorded (see Fig. 41) - the rate of weight loss at the end-point is the lowest of all the polymers studied for fabric C and this system is the only treatment which showed a reduction in weight loss at the end-point for fabric A (see Fig. 45).

At the lower polymer add-on value (0.5%) the rate of weight loss is slowed down but there is not much difference in weight loss at the end-point.

A similar picture is obtained with DC 109 on fabric C but the reduction in weight loss is not as pronounced as with Synthappret BAP/ Impranil DLH. In fabric A little change in the rate of weight loss is observed, only a slight increase in weight loss at the end-point. The abrasion resistance at high polymer add-on values is slightly increased, presumably due to load-sharing and absorption of stresses and strains by the polymer.

All the polymers applied by exhaustion slightly reduce the rate of weight loss of fabric C, in accord with the slight increases in MAR values, but exhaustion treatments do not change the rate of weight loss of fabric A and this again correlates with the very small changes in MAR obtained using these polymer treatments. Therefore the fabric structure is a very important factor which controls both the rate of weight loss and the final weight lost at the end-point during abrasion and wear. On woollen-spun fabric, polymer shrink-resist treatments reduce the rate of weight loss during abrasion testing and therefore increase the MAR values, while on worsted-spun fabrics the rate of weight loss is not markedly affected and therefore no large improvements in MAR are obtained.

2.4.3.3. Fabric Bending Properties

The effects of selective polymer shrink-resist treatments on the bending properties of fabric A (worsted spun fabric) and fabric C (woollen spun fabric) are given in Tables 42-45 and illustrated in Fig. 46-53.

The changes in fabric flexural rigidity G_o are characterised by the nature of the polymer and fabric structure, although the general trend for all polymers and the specific method of application are similar. All the polymer treatments appear to behave in a similar fashion, the fabric flexural rigidity (G_o) increasing with polymer add-on. This is in accord with other studies on polymer treatments (248, 249). The most dramatic increases in G_o are observed with the padding treatments, notably with Synthappret BAP/Imprantil DLH treatments followed by DC 109. Increases in G_o in the same order have been observed elsewhere (248, 249).

The increase in G_o is in the order Synthappret BAP/Impranil DLH $>$ DC 109 $>$ Hercosett 125 $>$ Lankrolan SHR3 $>$ untreated for fabric C. A similar order is obtained with fabric A with the exception that little difference between the Hercosett 125 and Lankrolan SHR3 treatments was observed.

The changes in the coercive couple C_o are given in Tables 42-45. C_o is generally increased with increase in polymer add-on. The greater changes are to be observed on fabric C (woollen flannel), while on fabric A (worsted) only marginal changes are exhibited with increase

TABLE 42. The effect of Hercosett 125 (by exhaustion) on the flexural rigidity (G_o) and coercive couple (C_o) of wool fabrics.

Polymer Add-on (% o.w.f)	Fabric A (Worsted)		Fabric C (Woollen)	
	G_o (mg.cm)	C_o (mg.cm)	G_o (mg.cm)	C_o (mg.cm)
Untreated	34.7	8.2	53.0	31.6
0.5	31.0	7.6	61.1	45.8
1.0	32.1	7.6	79	45.8
1.5	34.1	8.1	86.6	43.3
2.0	36.6	8.1	91.7	38.2

The above values represent the mean values of three samples in the weft way direction.

TABLE 43. The effect of Lankrolan SHR3 (by exhaustion) on the flexural rigidity G_o and coercive couple C_o of wool fabrics.

Polymer Add-on (% o.w.f)	Fabric A (Worsted)		Fabric C (Woollen)	
	G_o (mg.cm)	C_o (mg.cm)	G_o (mg.cm)	C_o (mg.cm)
Untreated	34.7	8.2	53	31.6
1	29.5	7.1	61.1	26.5
2	32.6	7.1	63.2	32.6
3	35.7	6.6	63.2	29.5
4	35.1	6.6	65.2	36.6

The above values represent the mean values of three samples in the weft-way direction.

TABLE 44. The effect of DC 109 (by padding) on the flexural rigidity (G_o) and coercive couple (C_o) of wool fabrics.

Polymer Add-on (% o.w.f)	Fabric A (Worsted)		Fabric C (Woollen)	
	G_o (mg.cm)	C_o (mg.cm)	G_o (mg.cm)	C_o (mg.cm)
Untreated	34.7	8.2	53	31.6
1	34.7	6.1	69.3	24.4
2	35.7	8.2	94.2	35.6
3	38.7	8.2	101.9	30.5
4	40.0	10.2	114.6	30.5

The above values represent the mean values of three samples in the weft-way direction.

TABLE 45. The effect of Synthappret BAP/Impranil DLH (by padding) on the flexural rigidity (G_o) and coercive couple (C_o) of wool fabrics.

Polymer Add-on (% o.w.f)	Fabric A (Worsted)		Fabric C (Woollen)	
	G_o (mg.cm)	C_o (mg.cm)	G_o (mg.cm)	C_o (mg.cm)
Untreated	34.7	8.2	53	31.6
0.5	32.6	6.1	75.4	30.6
1.0	35.2	7.1	91.7	33.1
1.5	—	—	142.7	45.9
2.0	54.0	10.2	234.5	71.4
2.5	60.1	10.2	265.0	76.4

The above values represent the mean values of the samples in the weft-way direction.

The Effect of Hercosett 125 (by exhaustion) on the flexural rigidity (G_o) of wool fabrics.

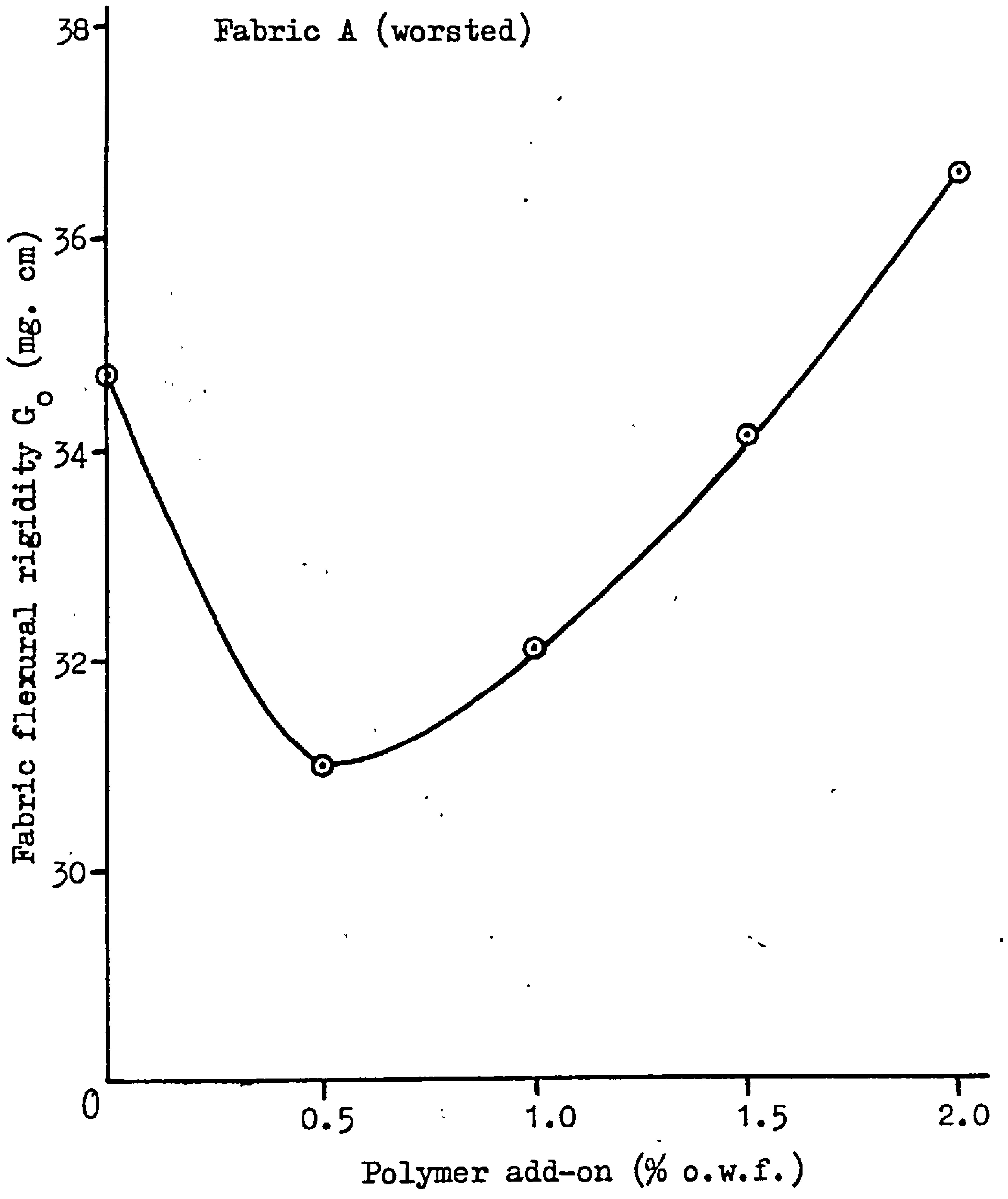


Fig. 46

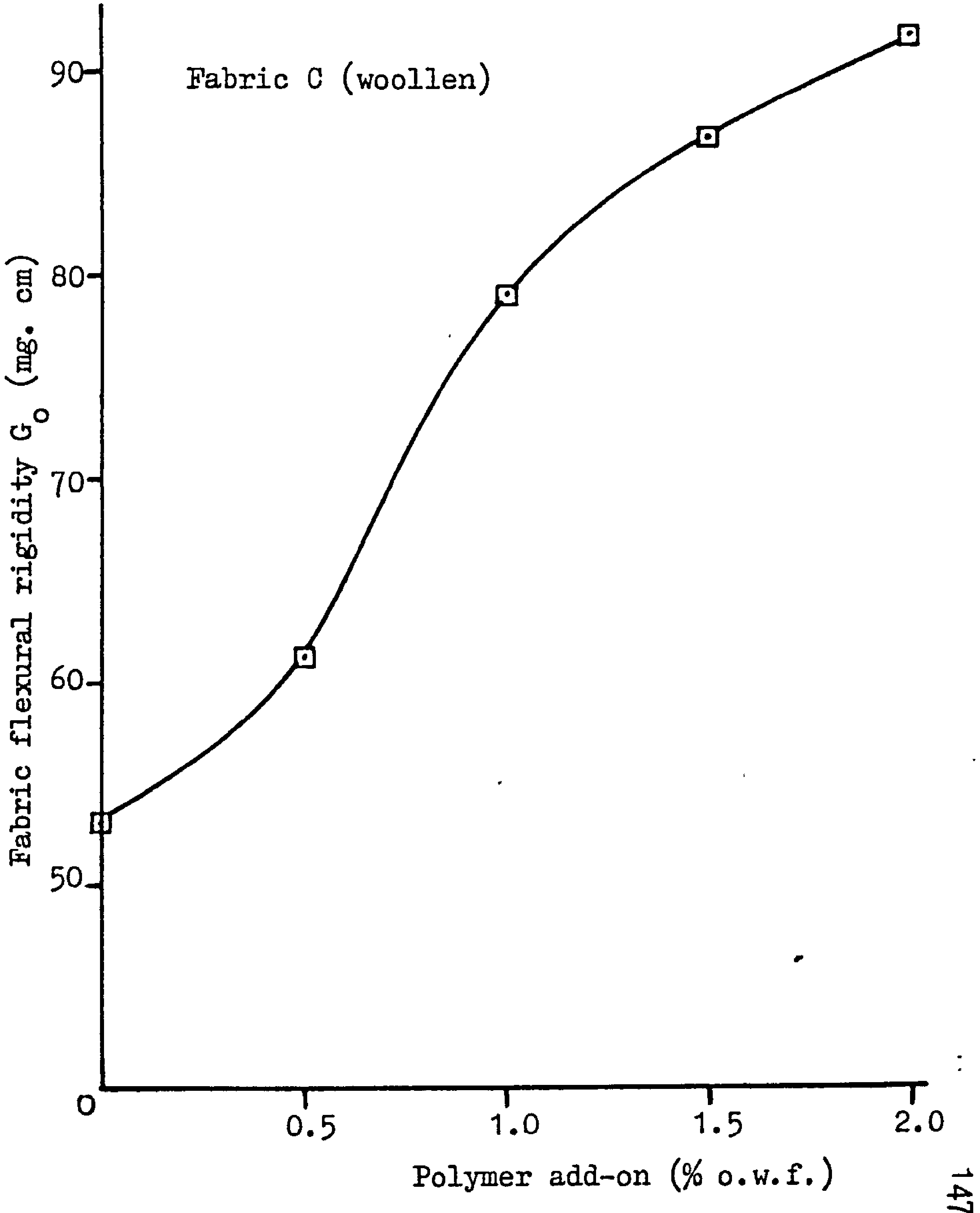


Fig. 47

The Effect of Lankrolan SHR3 (by exhaustion) on the flexural rigidity of wool fabrics.

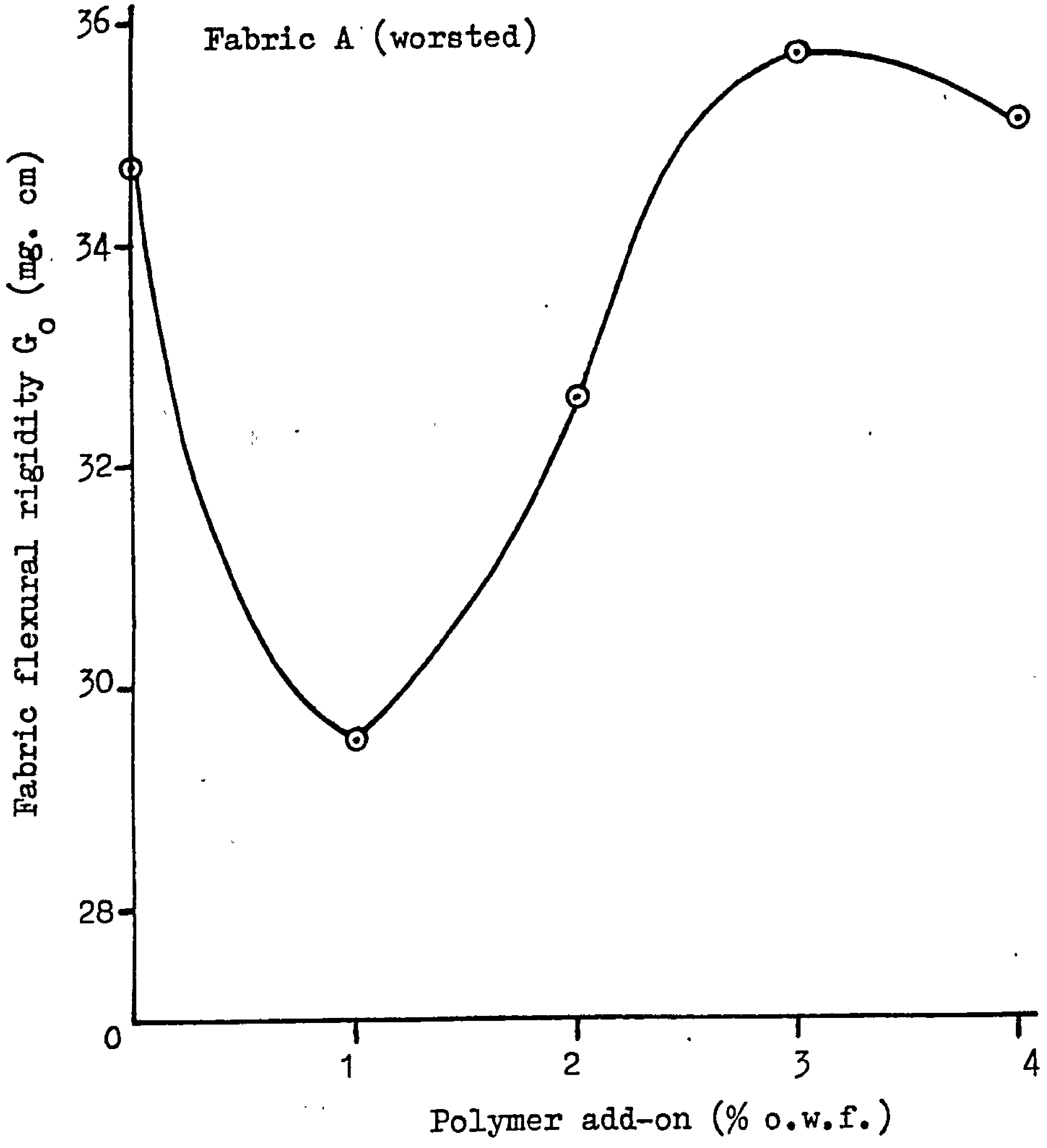


Fig. 48

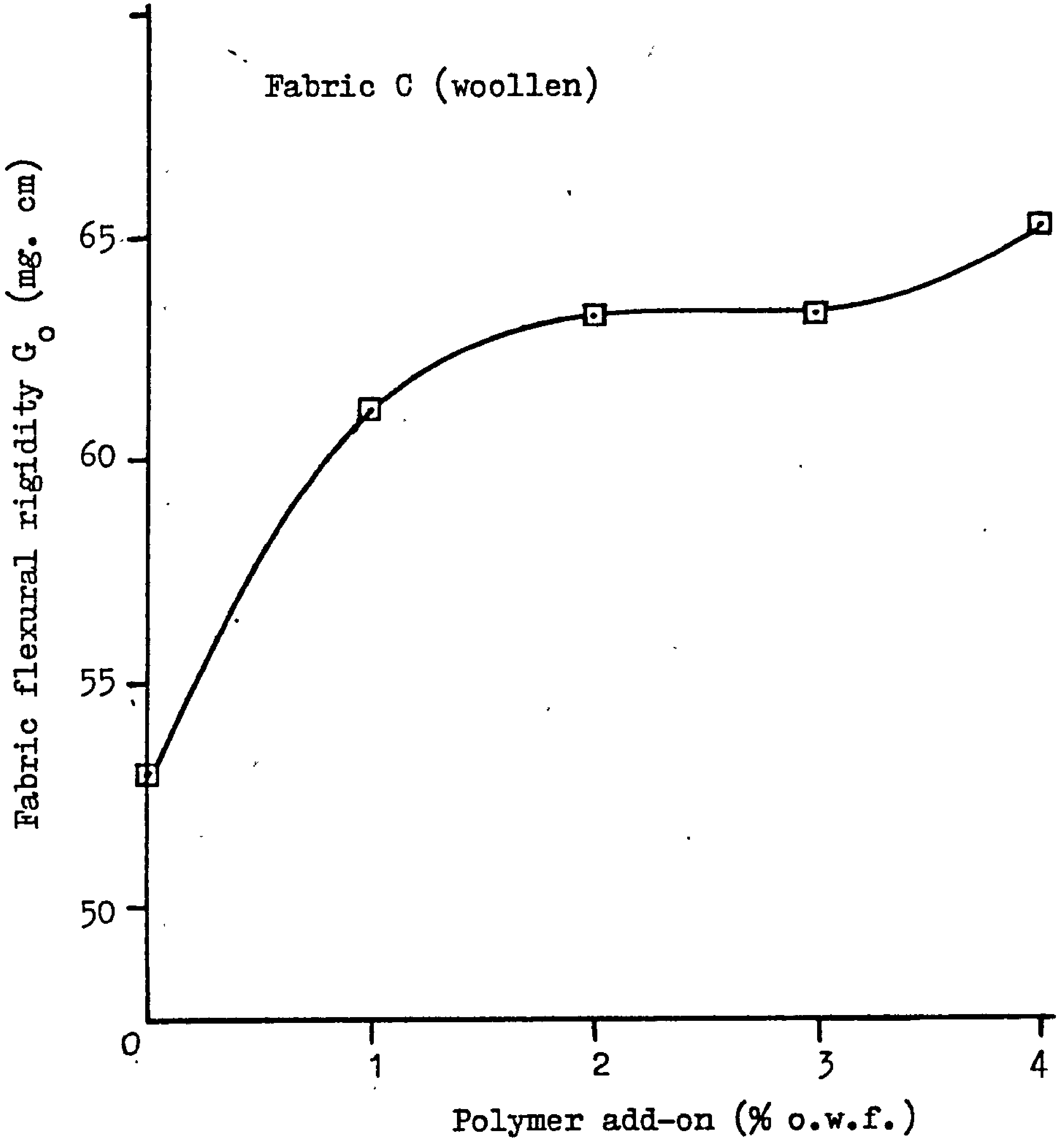


Fig. 49

The Effect of DC 109 (by padding) on the flexural rigidity (G_o) of wool fabrics.

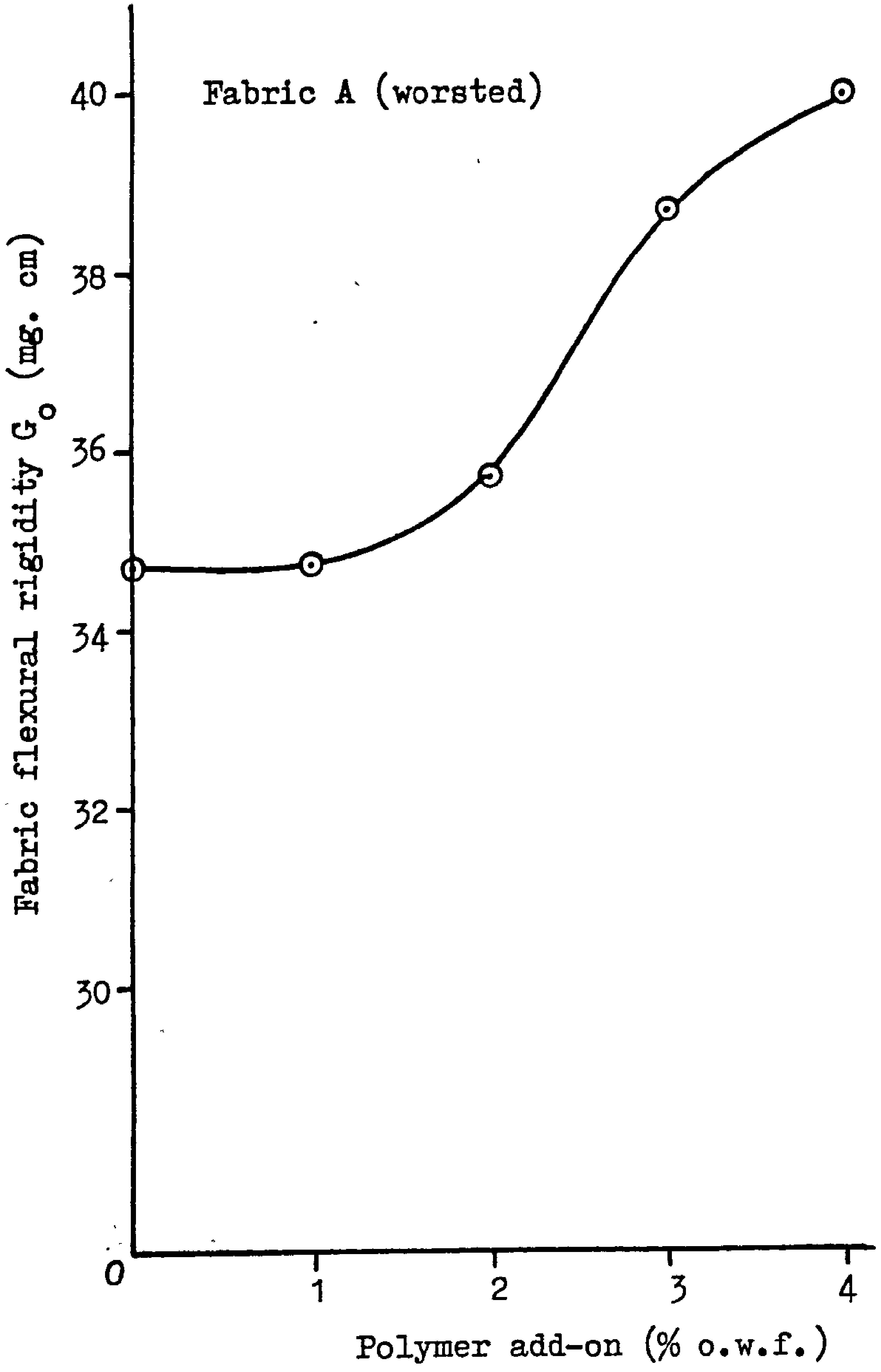


Fig. 50

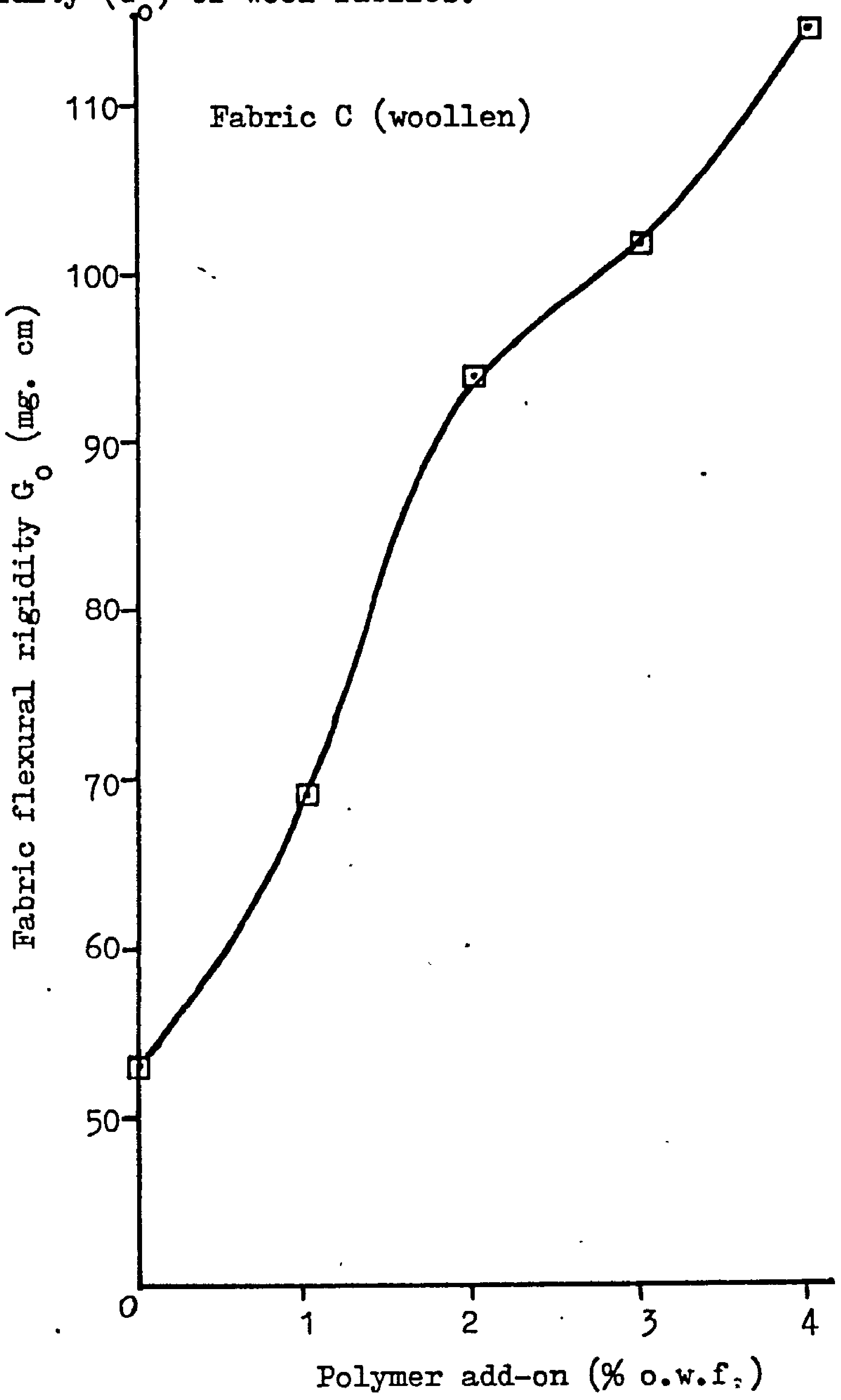


Fig. 51

The Effect of Synthappret BAP/Imipranil DLH (by padding) on the flexural rigidity of wool fabrics.

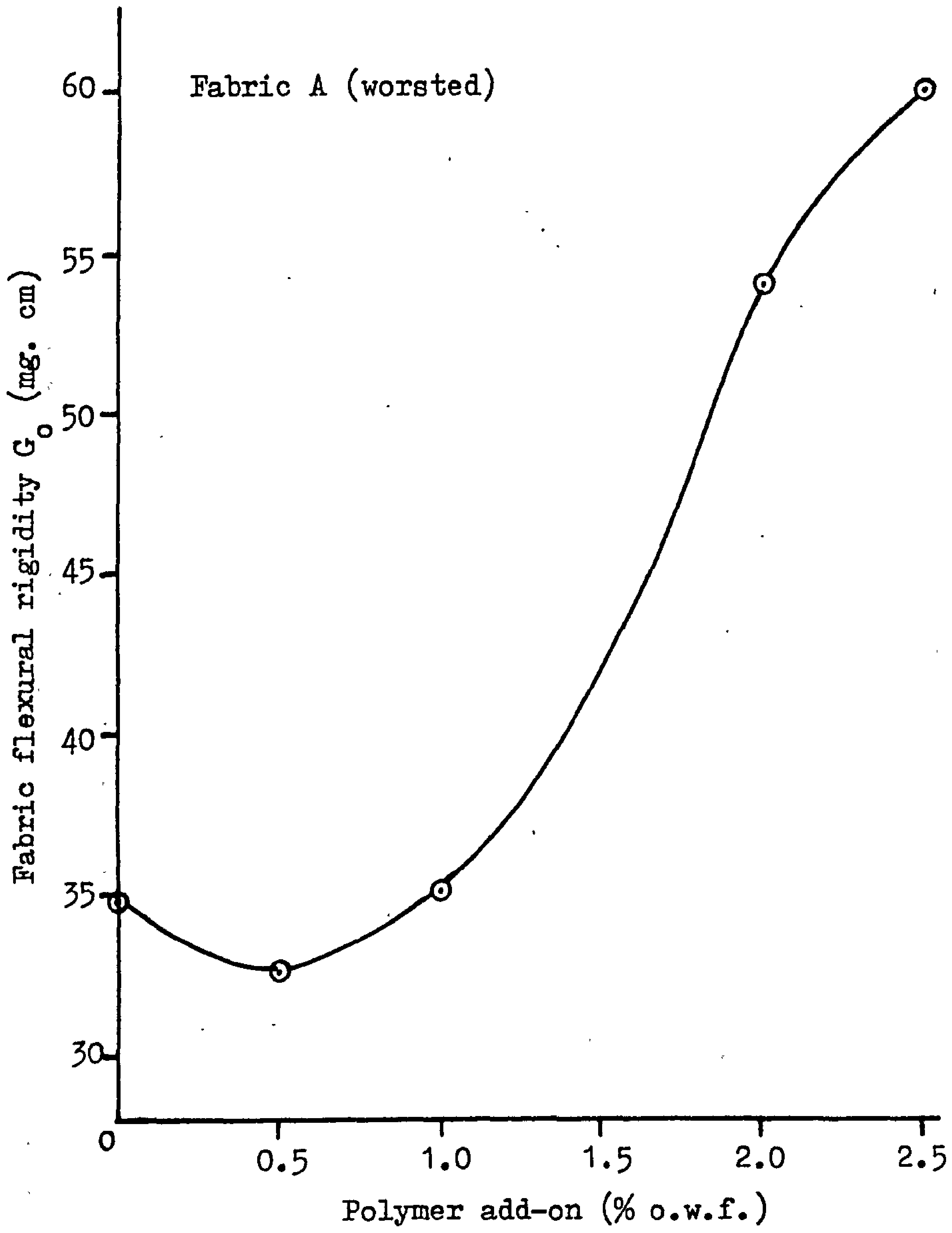


Fig. 52

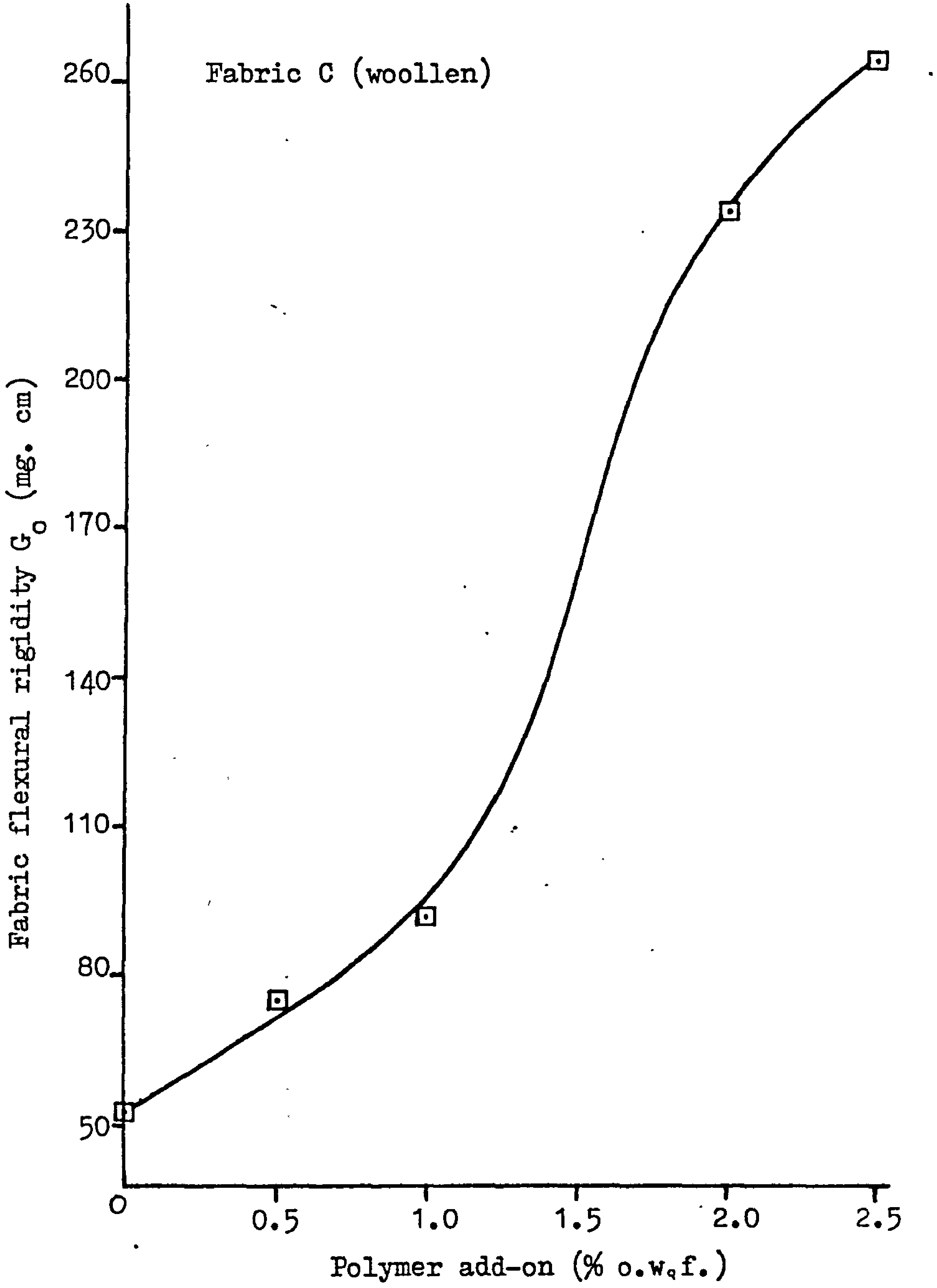


Fig. 53

in polymer add-on. The smaller changes with fabric C are to be observed in the DC 109 and Lankrolan SHR3 treatments while the latter treatment also yields the lowest values with fabric A.

2.4.3.4. Fabric Tensile Properties

The results of the breaking load and breaking extension measurements on untreated and polymer-treated fabrics are given in Tables 46-50.

It can be seen that the breaking load of the wool fabrics is generally increased as a result of the polymer treatments and this is in accord with previous studies on polymer-treated wool fabrics (142, 250-253). One exception is DC 109 where generally a decrease in breaking load was recorded for the three fabrics. A decrease in breaking load was also recorded on fabric C, after treatment with Lankrolan SHR3/Impranil DLH. A decrease in fabric breaking load after the application of polymer shrink-resist treatments to wool fabrics has also been observed elsewhere (254).

The breaking extension values of the polymer-treated fabrics are generally increased, but decreases on fabric A with Lankrolan SHR3 and DC 109 and on fabric B with DC 109 were also recorded.

The general conclusions to be drawn from these results are than an increase in fabric breaking load is normally obtained with increase in polymer add-on. However there are exceptions and this is probably related to the nature of the polymer rather than the method of application.

2.4.4. Conclusions

It has been demonstrated that the changes in MAR, rate of weight loss, bending and tensile properties of a series of woven wool fabrics depend upon:

TABLE 46. The effect of Hercosett 125 (by exhaustion) on the Tensile Properties of Wool Fabrics.

	Fabric A (Worsted)				Fabric B (Worsted)				Fabric C (Woollen)			
Polymer Add-on (% o.w.f)	Breaking Load (Kg)	mean	Breaking Extension (%)	mean	Breaking Load (Kg)	mean	Breaking Extension (%)	mean	Breaking Load (Kg)	mean	Breaking Extension (%)	mean
Untreated	14.3 14.4 13.9	14.2 (0)	36.0 34.0 32.5	34.2 (0)	15.4 15.3 15.5	15.4 (0)	36.0 32.0 30.0	32.7 (0)	8.8 8.8 8.8	8.8 (0)	39.0 34.0 38.0	37.0 (0)
0.5	13.7 15.0 15.0	14.6 (2.5)	39.0 39.0 33.0	37.0 (8.3)	15.6 15.6	15.6 (1.3)	32.0 32.0	33.0 (1.0)	8.9 9.3 9.6	9.2 (4.2)	43.0 43.0 42.5	42.8 (15.6)
1.0	14.3 14.4 14.8	14.5 (2.1)	33.0 39.0 35.5	35.8 (4.8)	15.5 15.5	15.5 (0.6)	36.5 36.5	35.5 (8.7)	8.5 8.3 9.8	8.8 (0)	42.0 41.0 43.0	42.0 (13.5)
1.5	14.8 14.5	14.7 (3.2)	36.5 36.5	36.5 (6.8)	16.3 16.2	16.3 (5.5)	39.0 37.0	36.0 (10.2)	8.7 8.9 9.2	8.9 (1.3)	44.5 41.0 43.0	42.8 (15.8)
2.0	14.6 14.6	14.6 (2.5)	39.0 37.5	38.2 (11.9)	16.3 15.7 15.6	15.8 (2.9)	38.0 33.5 34.5	35.3 (8.1)	8.7 9.2 8.7	8.8 (0)	41.0 45.5 44.5	43.6 (17.8)

The values in parentheses represent the increase (%) in Fabric Tensile Properties.

TABLE 47. The effect of Lankrolan SHR3 (by exhaustion) on the Tensile Properties of Wool Fabrics.

	Fabric A (Worsted)				Fabric B (Worsted)				Fabric C (Woollen)			
Polymer Add-on (% o.w.f)	Breaking Load		Breaking Extension		Breaking Load		Breaking Extension		Breaking Load		Breaking Extension	
	(Kg)	mean	(%)	mean	(Kg)	mean	(%)	mean	(Kg)	mean	(%)	mean
Untreated	14.3 14.4 13.9	14.2 (0)	36.0 34.0 32.5	34.2 (0)	15.4 15.3 15.5	15.4 (0)	36.0 32.0 30.0	32.7 (0)	8.8 8.8 8.8	8.8 (0)	39.0 34.0 38.0	37.0 (0)
1	14.6 15.0 14.3	14.6 (+3.0)	33.5 30.5 32.0	32.0 (-6.3)	16.0 15.1 15.3	15.5 (+0.4)	35.0 36.0 35.0	35.3 (+8.2)	9.2 9.3 9.4	9.3 (+5.3)	46.0 48.0 45.0	46.3 (+25.2)
2	16.3 15.5 15.4	15.7 (+10.7)	34.0 34.0 34.0	34.0 (-0.4)	16.4 15.9 15.5	15.9 (+3.4)	38.0 36.0 36.0	36.3 (+11.2)	9.2 9.9 9.7	9.6 (+8.7)	46.0 44.0 48.0	46.0 (+24.3)
3	15.7 16.5 16.0	16.0 (+13.1)	32.0 38.0 35.5	35.7 (+2.9)	16.4 16.0 16.2	16.2 (+5.2)	38.0 36.0 38.0	37.3 (+14.3)	9.8 10.1 9.3	9.7 (+10.2)	47.0 46.0 46.0	46.3 (+25.2)
4	14.7 15.1 16.0	15.3 (+7.4)	32.5 33.0 31.0	32.2 (-5.8)	16.4 16.2 16.4	16.3 (+6.0)	36.0 35.0 34.5	35.2 (+7.6)	9.5 9.5 9.7	9.5 (+8.2)	46.0 46.0 47.0	46.3 (+25.2)

The values in parentheses represent the change (%) in Fabric Tensile Properties. + = increase, - = decrease.

TABLE 48. The effect of Lankrolan SHR3/Impranil DLH (by exhaustion) on the Tensile Properties of Wool Fabrics.

	Fabric A (Worsted)				Fabric B (Worsted)				Fabric C (Woollen)			
Polymer Add-on (% o.w.f)	Breaking Load		Breaking Extension		Breaking Load		Breaking Extension		Breaking Load		Breaking Extension	
	(Kg)	mean	(%)	mean	(Kg)	mean	(%)	mean	(Kg)	mean	(%)	mean
Untreated	14.3 14.4 13.9	14.2 (0)	36.0 34.0 32.5	34.2 (0)	15.4 15.3 15.5	15.4 (0)	36.0 32.0 30.0	32.7 (0)	8.8 8.8 8.8	8.8 (0)	39.0 34.0 38.0	37.0 (0)
1	14.3 14.7	14.5 (+2.1)	34.0 35.0	34.5 (+1.0)	16.7 16.7 16.6	16.7 (+7.8)	36.0 38.0 39.0	37.7 (+15.3)	9.5 9.3 8.4	9.1 (+2.6)	47.0 46.5 44.5	46.0 (+24.3)
2	15.2 15.1 16.0	15.4 (+8.6)	35.0 36.0 35.0	35.3 (+3.3)	15.8 15.6 15.6	15.7 (+1.7)	33.0 37.0 36.0	35.3 (+8.2)	8.0 8.9 8.8	8.5 (-3.0)	47.0 44.0 47.0	46.0 (+24.3)
3	15.9 14.5 16.3	15.6 (+9.6)	32.5 35.0 35.0	34.2 (0)	16.2 16.6 17.6	16.8 (+9.0)	36.0 38.0 40.5	38.2 (+16.8)	7.9 9.1 8.6	8.5 (-3.0)	47.0 48.0 45.0	46.6 (+26.0)
4	15.8 14.6 15.2	15.2 (+7.0)	35.0 32.0 37.5	34.8 (+2.0)	15.6 15.9 16.2	15.9 (+3.2)	35.5 33.5 33.0	34.0 (+4.1)	8.75 8.45 9.5	8.8 (0)	46.5 42.0 48.0	45.5 (+23.0)

The values in parentheses represent the change (%) in Fabric Tensile Properties. + = increase, - = decrease.

TABLE 49. The effect of DC 109 (by padding) on the Tensile Properties of Wool Fabrics.

	Fabric A (Worsted)				Fabric B (Worsted)				Fabric C (Woollen)			
Polymer Add-on (% o.w.f)	Breaking Load (Kg)	Breaking Load mean	Breaking Extension (%)	Breaking Extension mean	Breaking Load (Kg)	Breaking Load mean	Breaking Extension (%)	Breaking Extension mean	Breaking Load (Kg)	Breaking Load mean	Breaking Extension (%)	Breaking Extension mean
Untreated	14.3 14.4 13.9	14.2 (0)	36.0 34.0 32.5	34.2 (0)	15.4 15.3 15.5	15.4 (0)	36.0 32.0 30.0	32.7 (0)	8.8 8.8 8.8	8.8 (0)	39.0 34.0 38.0	37.0 (0)
1	14.3 14.1 14.1	14.2 (0)	30.0 29.0 31.5	30.2 (-11.7)	14.6 13.7 14.5	14.2 (-7.4)	28.0 25.5 30.0	27.8 (-14.7)	7.4 7.8 8.2	7.8 (-11.1)	37.0 41.0 41.0	39.7 (+7.3)
2	13.5 13.6	13.5 (-4.5)	25.0 34.0	29.5 (-13.6)	—	—	—	—	8.3 8.5 8.1	8.3 (-5.8)	44.0 44.0 38.0	42.0 (+13.5)
3	13.1 13.9	13.5 (-4.5)	26.5 30.5	28.5 (-16.5)	15.2 15.3 15.8	15.4 (0)	32.5 28.0 30.0	30.2 (-7.6)	7.3 7.1 7.5	7.3 (-17.5)	36.5 39.0 41.0	38.8 (+4.9)
4	14.6 14.7 14.3	14.5 (+2.3)	34.0 30.0 30.0	31.3 (-8.3)	14.7 14.8 15.8	15.1 (-1.9)	30.5 32.0 30.5	31.0 (-5.1)	7.8 8.6	8.2 (-6.9)	40.0 39.0	39.5 (+6.7)

The values in parentheses represent the change (%) in Fabric Tensile Properties. + = increase, - = decrease.

TABLE 50. The effect of Synthappret BAP/Inpranil DLH (by padding) on the Tensile Properties of Wool Fabric.

Polymer Add-on (% o.w.f)	Fabric A (Worsted)				Fabric B (Worsted)				Fabric C (Woollen)			
	Breaking Load		Breaking Extension		Breaking Load		Breaking Extension		Breaking Load		Breaking Extension	
	(Kg)	mean	(%)	mean	(Kg)	mean	(%)	mean	(Kg)	mean	(%)	mean
Untreated	14.3 14.4 13.9	14.2 (0)	36.0 34.0 32.5	34.2 (0)	15.4 15.3 15.5	15.4 (0)	36.0 32.0 30.0	32.7 (0)	8.8 8.8 8.8	8.8 (0)	39.0 34.0 38.0	37.0 (0)
0.5	13.6 15.3 14.6	14.5 (2.1)	33.5 32.5 40.0	35.3 (3.4)	15.6 17.2 14.3	16.6 (7.5)	34.0 33.0 34.0	33.3 (2.1)	10.5 9.7 9.9	10.0 (13.6)	44.0 46.0 42.0	44.0 (18.9)
1.0	14.9 14.7 14.6	14.7 (3.7)	39.0 36.0 38.5	37.8 (10.7)	17.3 17.2 16.9	17.1 (11.2)	37.0 41.0 35.0	37.7 (15.3)	11.0 10.5 10.2	10.6 (19.6)	43.0 40.0 46.0	33.0 (16.2)
2.0	16.5 15.1 16.4	16.0 (12.6)	39.5 40.5 45.0	41.6 (21.9)	17.5 18.3 17.8	17.9 (15.9)	40.0 40.0 41.5	40.5 (24.0)	11.3 10.4 10.8	10.8 (22.6)	41.0 42.5 47.5	43.6 (18.0)
2.5	15.7 15.9 16.8	16.1 (13.6)	41.0 42.5 46.5	43.3 (26.8)	18.9 18.6 18.3	18.6 (20.7)	45.8 41.6 42.1	43.5 (33.2)	12.2 11.0 11.7	11.6 (31.7)	44.0 44.0 45.0	44.3 (19.8)

The values in parentheses are the mean increase (%) in Fabric Tensile Properties.

(i) the nature of the applied polymer shrink-resist treatment;
(ii) the polymer add-on;
(iii) the nature of the fabric structure.

The very high improvement in MAR reported for Synthappret BAP/Impranil DLH is believed to arise, at least partly, from the method of application. In most cases there appears to be a limit to the magnitude of improvement in MAR, and in general this level is lower for polymer treatments applied by exhaustion compared with those applied via a padding procedure. However, further study is required (see Section 2.5.) utilising both methods of application for the same polymer treatment in order to establish this unequivocally.

The greatest improvements in MAR were noted for the woven wool flannel which was spun from short wool fibres compared with the lower level of improvement reported for woven worsted-type fabrics.

From the changes in the rate of weight loss on abrasion testing, it is clear that the rate of weight loss is progressively reduced as the MAR value of the fabric is progressively increased. In addition, the rates of weight loss for woollen flannel treated with polymers via the padding technique (i.e. Synthappret BAP/Impranil DLH, DC 109) are lower than those treated with other polymers applied by exhaustion (i.e. Hercosett 125, Lankrolan SHR3).

For worsted spun fabric A there is little change in the rate of weight loss for polymer treatments applied by padding or by exhaustion, with the notable exception of 2.5% Synthappret BAP/Impranil DLH applied by padding where a decrease is observed. Generally the MAR values are slightly increased.

From all these results it must be concluded that the fabric structure is a very important factor in controlling the rate of weight loss during abrasion and wear.

From the changes in fabric flexural rigidity G_o and coercive couple C_o, it is evident that in general polymer treatments increase G_o and C_o, the values increasing with increase in the polymer add-on. The changes are more pronounced in fabric C (woollen-spun) compared with fabric A (worsted-spun). The improvement in tensile properties as a result of the polymer treatments are small and although these might well contribute to the improvement in MAR, the very high levels of MAR obtained in some cases cannot be explained on this basis alone.

2.5. Method of Polymer Application

2.5.1. Introduction and Objectives

It was demonstrated earlier (see section 2.4.3.1.) that shrink-resist treatments are effective in increasing the MAR. The improvement in MAR has been shown to depend not only on the nature of the polymer but also upon the polymer add-on (154, 156, 230) while the fabric structure in addition is considered to play an important role (see section 2.4.3.1.).

An increase in MAR is generally observed with increase in polymer add-on but the level of improvement obtained gradually approached a limiting value which was greater for a woollen flannel than for worsted fabrics (see section 2.4.3.1.). However it has been observed that the MAR may also decrease after polymer shrink-resist treatments applied to worsted fabrics (47). The results of the earlier work described in section 2.4.3.1. also suggested that improvement in the MAR might well be dependent upon the method of application of the polymer shrink-resist treatment.

The object of the experimental work in this section is to investigate the role of the method of application in more detail. Accordingly a range of polymer shrink-resist treatments have been applied to the same fabrics via conventional padding and by exhaustion procedures and the changes in MAR and other fabric properties determined.

2.5.2. Experimental

Materials

Fabric Specifications: Two all-wool fabrics (fabric A and fabric C) were employed. The detailed composition and preparation of the fabrics have been described in detail in section (2.4.2.).

Chemicals: The following chemicals were used in this work:

(i) Synthappret BAP; (ii) Impranil DLH; (iii) Hercosett 125;

(iv) Lankrolan SHR3. Details have been given in (section 2.4.2.).

Methods

Method of polymer application

Padding treatments

(i) Synthappret BAP/Impranil DLH was padded using the procedure described in section (2.4.2.) of this work.

(ii) Hercosett-125. This was applied using a Konrad Peter pad-mangle and a solution containing the amount of polymer required, 0.5% $NaHCO_3$ (o.w.f.) and 2 $g.l^{-1}$ Lissapol N. The polymer was applied to the wool fabric samples (30 x 30 cm) and dried in a laboratory oven at 120°C for 10 minutes. All polymer-treated samples were given a steam treatment for 20 s on a blowing machine to ensure complete polymer curing.

(iii) Lankrolan SHR3. The Lankrolan SHR3 treatments were padded similarly to Hercosett 125 treatments with the addition of 20 $g.l^{-1}$ sodium sulphite, followed by drying at 140°C for 10 minutes. All samples were given a steam treatment for 20 s on a blowing machine to ensure complete curing of the polymer.

Exhaustion treatments

(i) Synthappret BAP/Impranil DLH - The bath is set at a liquor to wool ratio of 40:1 at 50°C with 4 $g.l^{-1}$ $MgCl_2.6H_2O$. The fabric was added and run for 10 minutes adjusting the pH to 7 with either acetic acid or $NaHCO_3$. Synthappret BAP and Impranil DLH were prepared as 10% product solutions. The corresponding volume of 10% Synthappret BAP solution for the required dosage level was added, followed by the addition of the corresponding volume of 10% Impranil DLH, circulated for 20 minutes and the pH maintained at 7 and temperature 50°C. A further 2 $g.l^{-1}$ $MgCl_2.6H_2O$ (diluted with water) was added and the whole bath circulated for a further 15-20 minutes until the bath was clear, (total time 35-40 minutes). A 10% ammonia solution was added to bring the pH to 8 and the bath circulated for 10 minutes. Finally the fabric samples were hydroextracted and dried at 140°C for 10 minutes.

Hercosett-125 and Lankrolan SHR3

Hercosett 125 was applied to prechlorinated wool (2% available chlorine) and Lankrolan SHR3 was applied to untreated wool using the recommended procedures described in detail in section (2.4.2.).

Finally all the polymer-treated samples were blown for 20 s to ensure polymer curing and conditioned at 65% r.h. and 21°C for at least 7 days prior to testing.

Test Methods

(i) Martindale Abrasion Resistance (for experimental method see section 2.4.2.).

(ii) Rate of Weight Loss Studies (For experimental method see section 2.4.2.).

(iii) Stereoscan Electron Microscopical Examination Fabric samples were coated with a thin layer of gold to provide a conducting layer and examined on a Cambridge Mark II SEM at an accelerating potential of 20 kV.

(iv) Pilling During the rate of weight loss experiments on fabric C the number of pills on the abraded surface of the specimen was recorded by visual examination. The rate of pilling on fabric A was insignificant and zero pilling was, in fact, registered for this fabric.

(v) Fabric Bending Properties (For experimental method see section 2.4.2.).

(vi) Fabric Tensile Properties (For experimental method see section 2.4.2.).

2.5.3. Results and Discussion

2.5.3.1. Martindale Abrasion Resistance (MAR)

The results of the effects of polymer shrink-resist treatments on the MAR applied by padding and by exhaustion techniques on fabric C and fabric A are given in Tables (51 and 33), (52 and 29), (53 and 30). The mean increase in MAR (%) is plotted against polymer add-on (% o.w.f.) for the systems Synthappret BAP/Impranil DLH, Hercosett 125 and Lankrolan SHR3 in Fig. 54-56 respectively. In agreement with the previous work (see section 2.4.3.1.), the MAR is increased by the presence of the shrink-resist polymers, and for those treatments applied via the padding technique significantly higher levels of MAR are achieved.

The MAR values obtained from wool fabrics treated with the same polymer thus differ according to the original method of application, namely, padding treatments lead to higher MAR values than exhaustion treatments. This confirms the original suggestion advanced in section (2.4.3.1.) in which a variety of polymer systems were studied, but results by padding and exhaustion on the same polymer had not been obtained. In this study the order of improvement in MAR for polymer padding treatments was in the order Synthappret BAP/Impranil DLH > Hercosett 125 > Lankrolan SHR3 for the same polymer add-on, and all values were greater than that for the untreated fabric.

For the treatments applied via exhaustion the order of improvement is generally Synthappret BAP/Impranil DLH > Lankrolan SHR3 > Hercosett 125 for the same level of polymer add-on and the values are

TABLE 51. Martindale Abrasion Resistance of fabric C (woollen flannel) treated with Synthappret BAP/Impranil DLH (by exhaustion).

Polymer Add-on (% o.w.f.)	Fabric C (woollen)		
	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)
Untreated	3.6 3.8 3.6	3.7	0
0.5	6.2 6.2 6.5	6.3	70.3
1.0	7.0 7.0 7.5	7.2	89.2
1.5	7.0 7.0 7.5	7.2	89.2
2.0	7.2 7.0 7.2	7.2	89.2
2.5	9.0 8.5 8.5	8.6	134.2

TABLE 52. Martindale Abrasion Resistance of fabrics A and C treated with Hercosett 125 (by padding).

Polymer Add-on (% o.w.f.)	Fabric A (worsted)			Fabric C (woollen)		
	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)
Untreated	13.0 12.5 10.2	11.9	0	3.6 3.8 3.6	3.7	0
0.5	17.0 18.0 18.0	17.7	48.4	5.5 5.5 5.5	5.5	48.6
1.0	19.5 20.0 17.0	18.8	58.0	6.2 6.0 6.7	6.3	70.0
1.5	16.5 17.0 15.0	16.2	35.8	7.2 8.0 8.0	7.7	109.4
2.0	17.0 19.5 17.0	17.8	49.8	9.0 9.0 9.0	9.0	146.0

TABLE 53. Martindale Abrasion Resistance of fabric C (woollen flannel) treated with Lankrolan SHR3 (by padding).

Polymer Add-on (% o.w.f.)	Fabric C (woollen)		
	Abrasion Resistance (Rubs x 10^3)	mean	Mean Increase in MAR (%)
Untreated	3.6 3.8 3.6	3.7	0
1	6.7 6.0 6.0	5.8	57.6
2	6.7 6.5 6.2	6.5	75.7
3	6.7 6.5 7.0	6.7	82.4
4	7.5 7.5 7.7	7.6	105.0

Fig. 54 - The effect of Synthappret BAP/Impranil DLH on the Martindale abrasion resistance of wool flannel

Fig.55 - The effect of Hercosett 125 on the Martindale abrasion resistance of wool flannel

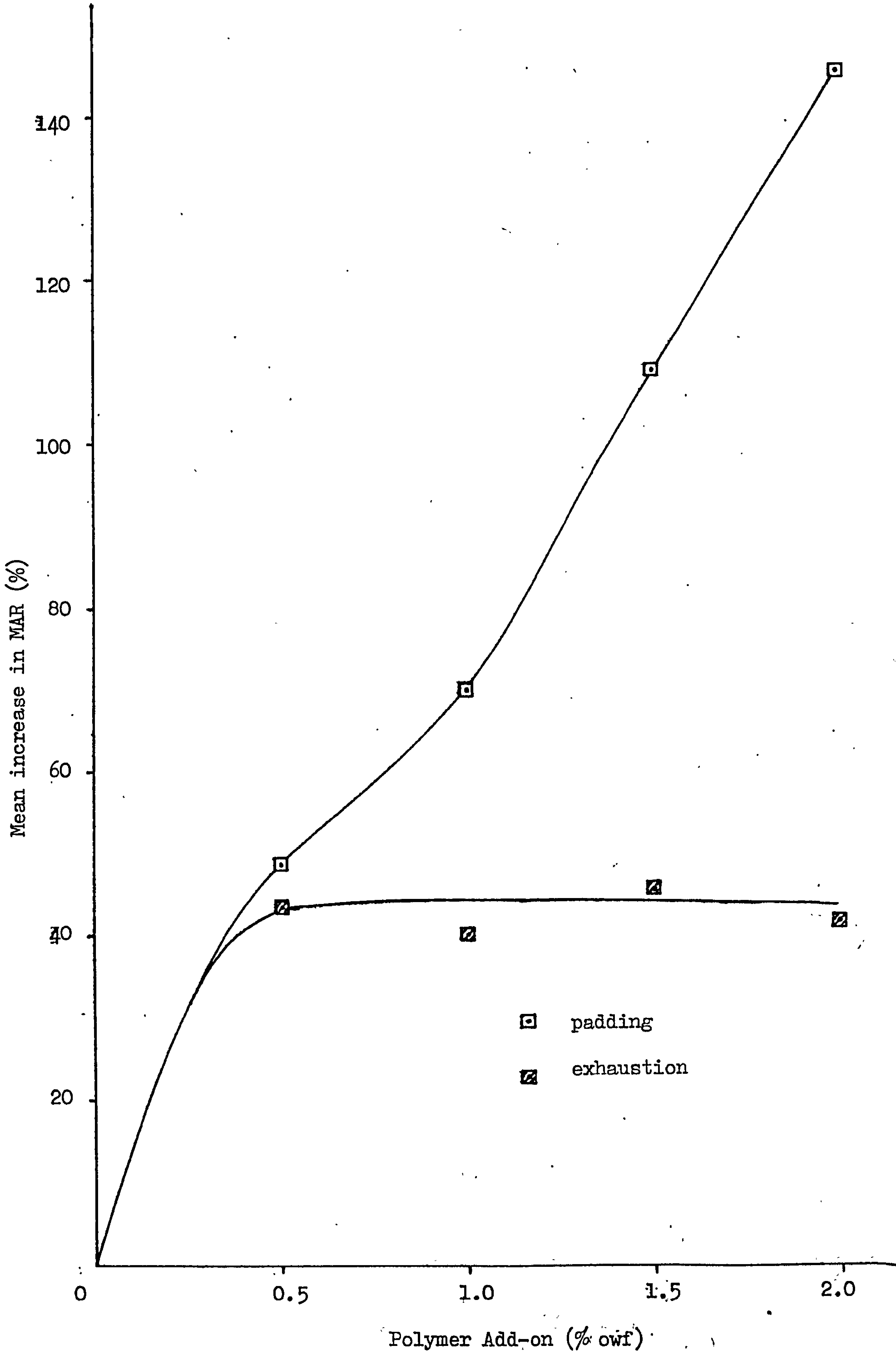
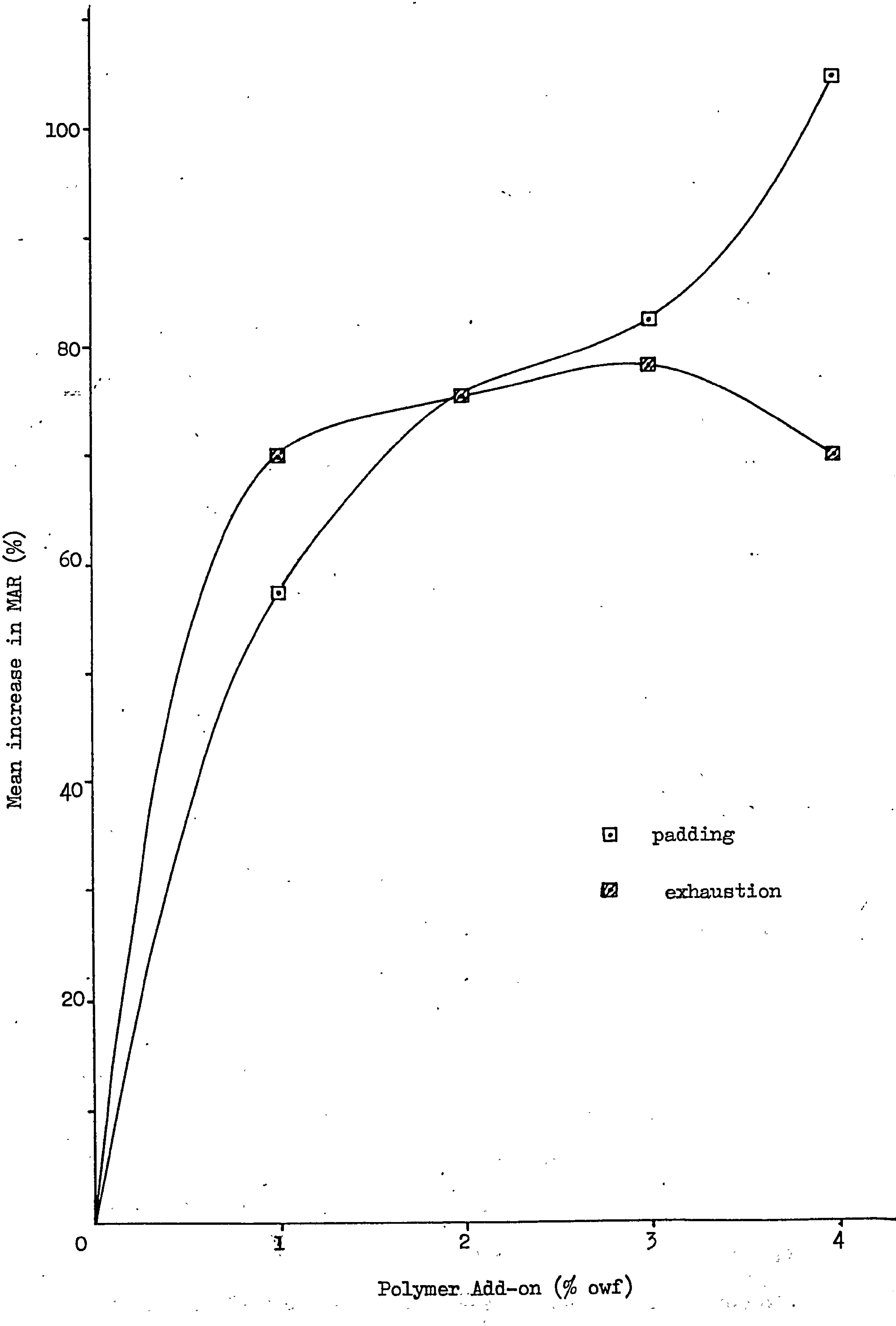


Fig. 56 - The effect of Lankrolan SHR3 on the Martindale abrasion resistance of wool flannel



again higher than that for the untreated fabric. However, it is clear from Fig. 54-56 that after an initial increase in MAR, little further change takes place with polymer add-on in the range studied. Thus the level of improvement obtained tends towards an equilibrium or limiting value. Only in the Synthappret BAP/Impranil DLH treatment is there a suggestion of any further increase in MAR as the polymer add-on is increased beyond the 2% level.

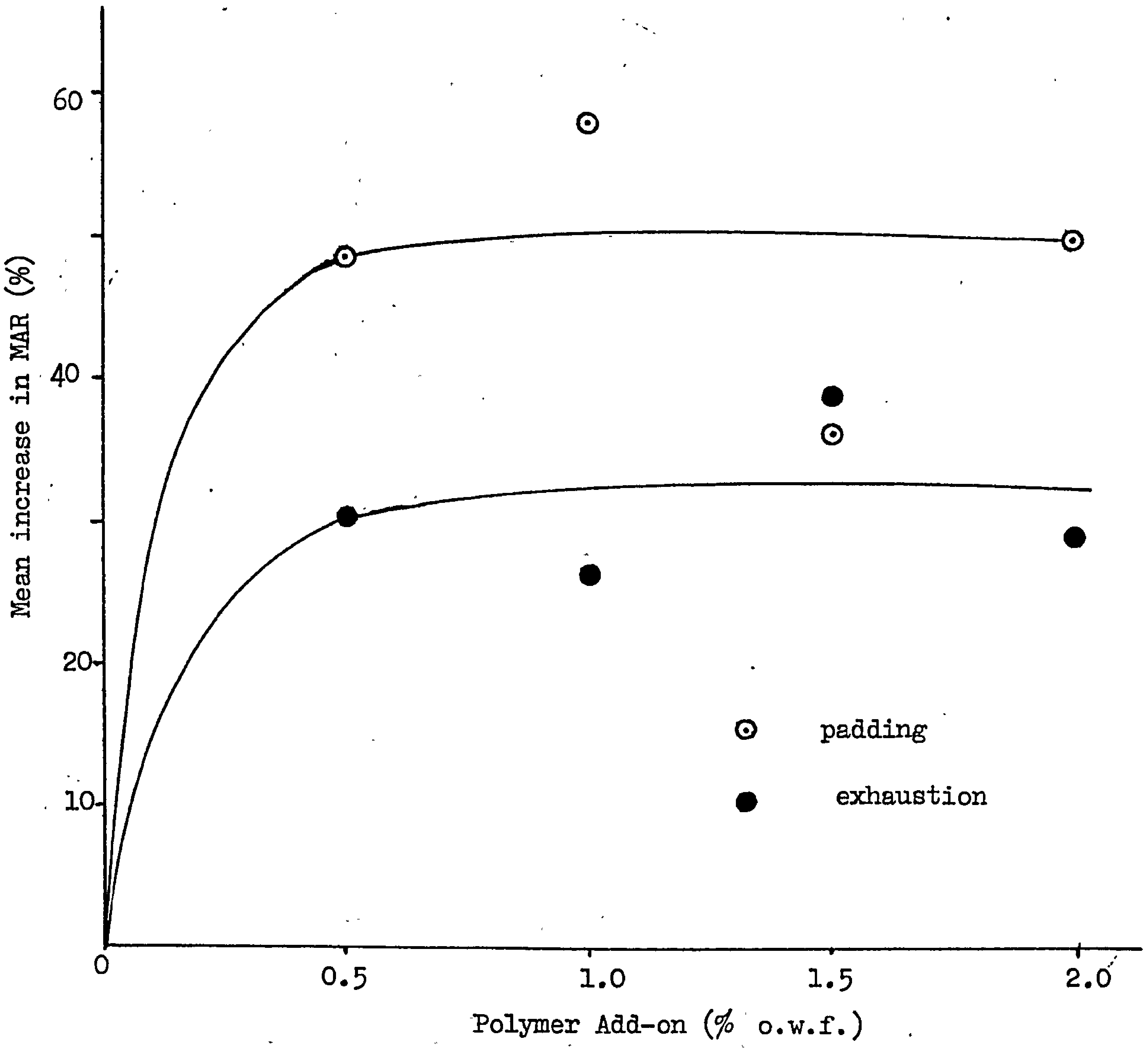
Comparison of Fig. 57 (fabric A) with Fig. 55 (fabric C) illustrates the observation previously made that the fabric structure exerts a subtle influence upon the MAR. Thus in the woollen-spun flannel there is a marked improvement in flat abrasion resistance with polymer add-on obtained by padding, whereas the values obtained by exhaustion approach a limiting value (~ 45%). For the light-weight worsted-spun fabric A, while the padded polymer values are greater than the values obtained by exhaustion, both treatments suggest that a limiting value is approached, the level of which is around 50% for the padding treatments and 30% for the exhaustion treatments respectively. Thus only in the padding treatments is there evidence of a dramatic change in the response of the polymer-treated fabric to abrasion. In those fabric treatments applied by exhaustion, similar low levels of improvement in flat abrasion resistance are to be noted.

Thus in the experimental work described here greater emphasis has been placed on the woollen-spun flannel (fabric C) because of the much greater levels of improvement reported. In this manner an explanation for the experimental observations was obtained.

2.5.3.2. Rate of Fabric Weight loss during Abrasion Testing

In order to quantify the results of Fig. 54-57 in greater detail, the rate of loss of fabric weight was measured against the number of

Fig. 57 -The effect of Hercosett 125 on the Martindale abrasion resistance of worsted fabric (fabric A).



rubs on the Martindale Abrasion Tester for both fabric C and fabric A.

The results for selected polymer add-on values for all the polymer treatments applied via padding and by exhaustion on Fabric C (woollen-spun flannel) are illustrated in Fig. 58-60 and 42 and given in Tables 54 and 37 , 55 and 34 , 56 and 35 . For the untreated woollen-spun flannel, the rate of weight loss is almost linear and is larger than any of the polymer-treated samples. In accord with Fig. 54-57, the rate of weight loss is dramatically reduced the greater the MAR value of the fabric while, in addition, the rates of weight loss for the fabrics treated via the padding technique are significantly lower than those obtained by exhaustion. This is particularly noticeable with the higher polymer add-on values and more specifically in the case of Synthappret BAP/Impranil DLH at 2.5% polymer add-on, where the highest MAR value is recorded (see Fig. 54). In the padded series of samples, the rate of weight loss at high polymer add-on values shows evidence of falling into two distinct stages, namely an initial stage, where the rate of weight loss is higher, followed by a slow and almost linear increase in weight loss in the case of Synthappret BAP/Impranil DLH and also for Lankrolan SHR3.

At the lower polymer add-on value of 0.5%, there appears to be little to choose between the results obtained via either the padding or the exhaustion technique. It may also be noted that at the high polymer add-on values for the padding-treatments, the weight loss at which the end-point (breakage of two yarns in the fabric surface) was recorded is decreased significantly below that for the untreated fabric.

For comparison purposes, similar results on the worsted-spun

Fig. 58 - The effect of Synthappret BAP/Impanil DLH on the weight loss of woollen flannel during abrasion testing

Fig. 59 - The effect of Hercosett 125 on the weight loss of woollen flannel during abrasion testing

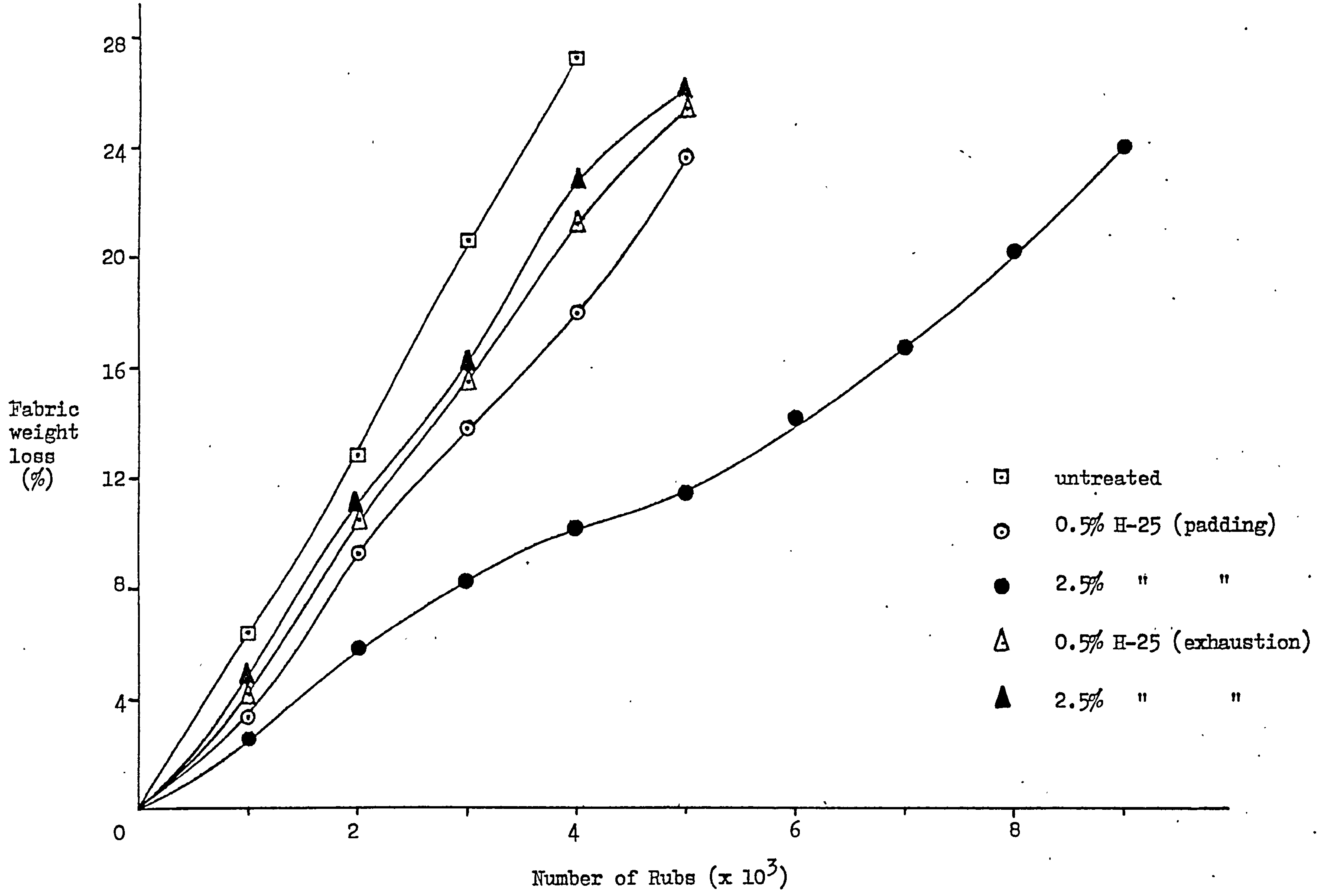


Fig. 60 - The effect of Lankrolan SHR3 applied by padding on the weight loss of woollen flannel during abrasion testing

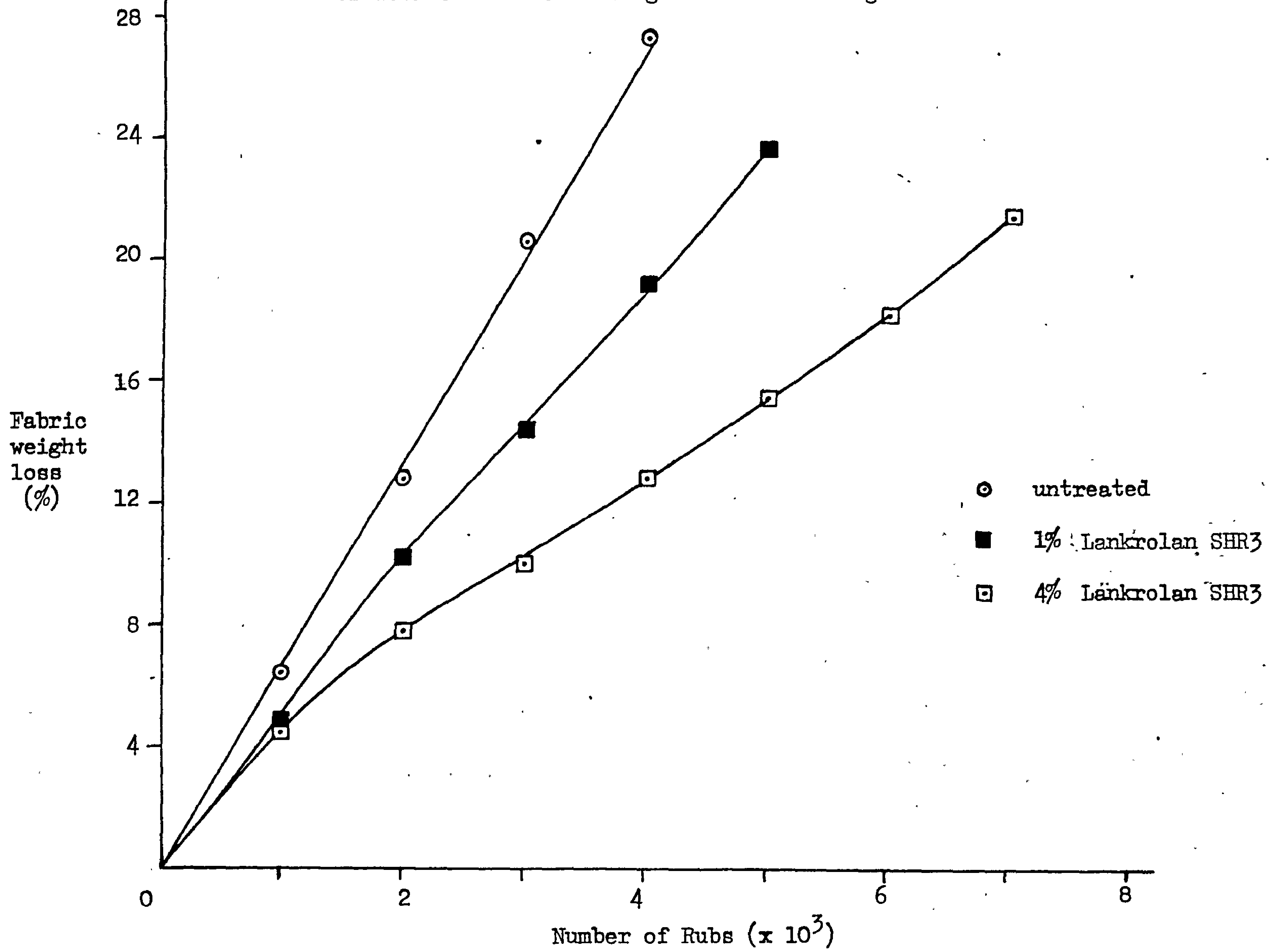


TABLE 54. The effect of Synthappret BAP/Impranil DLH applied by exhaustion on the weight loss (%) of fabric C (woollen)

Number of Rubs ($x10^3$)	% Weight loss of fabric C treated with BAP/DLH					
	Untreated *		Polymer Add-on (% o.w.f) 0.5		2.5	
	(%)	mean	(%)	mean	(%)	mean
1	6.41 6.88 5.97	6.4	4.64 5.0 4.42	4.7	3.37 3.34 3.37	3.4
2	12.65 13.41 12.47	12.8	8.74 8.47 8.03	8.4	6.30 5.92 6.17	6.1
3	18.49 21.94 21.37	20.6	12.50 12.38 11.48	12.1	9.25 8.78 9.38	9.1
4	24.73 29.95 27.35	27.3	15.94 16.09 14.42	15.5	11.76 11.21 11.70	11.5
5	—	—	19.97 20.97 18.14	19.7	14.53 13.83 14.19	14.2
6	—	—	25.27 25.70 21.50	24.1	17.00 16.30 16.76	16.7
7	—	—	—	—	19.91 19.46 19.37	19.6
8	—	—	—	—	23.60 22.80 22.47	22.9
9	—	—	—	—	28.10 27.60 26.20	27.3

* For untreated fabric specification (see section 2.4.2)

TABLE 55. The effect of Hercosett 125 applied by padding on the weight loss (%) of fabric C (woollen flannel).

Number of Rubs ($x10^3$)	% Weight loss of fabric C treated with Hercosett 125					
	Untreated *		Polymer Add-on (% o.w.f) 0.5		2	
	(%)	mean	(%)	mean	(%)	mean
1	6.41 6.88 5.97	6.4	3.70 3.12 3.20	3.3	2.90 2.63 2.31	2.6
2	12.65 13.41 12.47	12.8	9.58 8.86 9.43	9.3	6.14 5.77 5.69	5.9
3	18.49 21.94 21.37	20.6	14.14 13.12 14.20	13.8	8.57 7.87 8.21	8.2
4	24.73 29.95 27.35	27.3	18.24 17.76 18.27	18.1	10.41 9.91 10.15	10.1
5	—	—	23.86 23.46 23.66	23.7	12.07 11.21 10.98	11.4
6	—	—	—	—	15.15 13.60 13.95	14.2
7	—	—	—	—	17.92 15.91 16.30	16.7
8	—	—	—	—	22.14 18.75 19.60	20.2
9	—	—	—	—	26.70 22.75 22.61	24.0

* For untreated fabric specifications (see section 2.4.2)

TABLE 56. The effect of Lankrolan SHR3 applied by padding on the weight loss (%) of fabric C (woollen flannel).

Number of Rubs ($\times 10^3$)	% Weight loss of fabric C treated with Lankrolan SHR3.					
	Untreated *		Polymer Add-on (% o.w.f) 1		4	
	(%)	mean	(%)	mean	(%)	mean
1	6.41 6.88 5.97	6.4	4.94 4.91 4.27	4.7	4.44 4.44 4.78	4.5
2	12.65 13.41 12.47	12.8	9.67 11.00 9.93	10.2	7.73 7.50 8.12	7.8
3	18.49 21.94 21.37	20.6	13.62 15.56 14.02	14.4	10.00 9.55 10.43	10.0
4	24.73 29.95 27.35	27.3	17.65 20.99 19.04	19.2	12.68 12.54 13.28	12.8
5	—	—	22.34 25.23 23.43	23.7	14.94 15.90 15.71	15.5
6	—	—	—	—	17.57 18.84 18.13	18.2
7	—	—	—	—	20.81 22.31 21.40	21.5

* For untreated fabric specifications (see section 2.4.2)

light weight fabric (fabric A) are shown in Fig. 61 and 44 and Tables 57 and 38 for Hercosett 125 applied by padding and by exhaustion respectively. It is immediately apparent, in contrast to the results on fabric C in which large improvements in MAR are obtained that while the rate of weight loss is reduced slightly by the presence of the polymer in the padded series, the values obtained by exhaustion lie within the same narrow band of values. In corroboration of the work in section 2.4.3.1. only slight improvements in MAR are obtained and this is in accord with the minor changes in the rate of weight loss with number of rubs and illustrates once more the fact that the fabric structure, per se, is of great importance in determining both the level of MAR obtained in untreated fabric and also the degree of improvement to be gained through the use of polymer shrink-resist finishes.

Thus in the case of fabric A, while the rate of weight loss is not markedly dissimilar to that of the untreated fabric, it will be noted that the level of weight loss at the end-point is greater for the polymer shrink-resist treatments and that these are very similar for the padding and exhaustion methods of application for Hercosett 125-treated samples. For these treatments, the end-point would, therefore, appear to depend upon the same mode of fabric abrasion as the untreated fabric, except that the end-point is retarded by the presence of the polymer shrink-resist treatment.

These results are in accord with work on other polymers in which similar results were obtained by padding or by exhaustion (see section 2.4.3.2.). The only exception noted was Synthappret BAP/Impranil DLH applied by padding at 2.5% polymer add-on, where the end-point was displaced to lower weight loss values in a similar manner to that

Fig. 61 - The effect of Hercosett 125 applied by padding on the weight loss of worsted fabric during abrasion testing

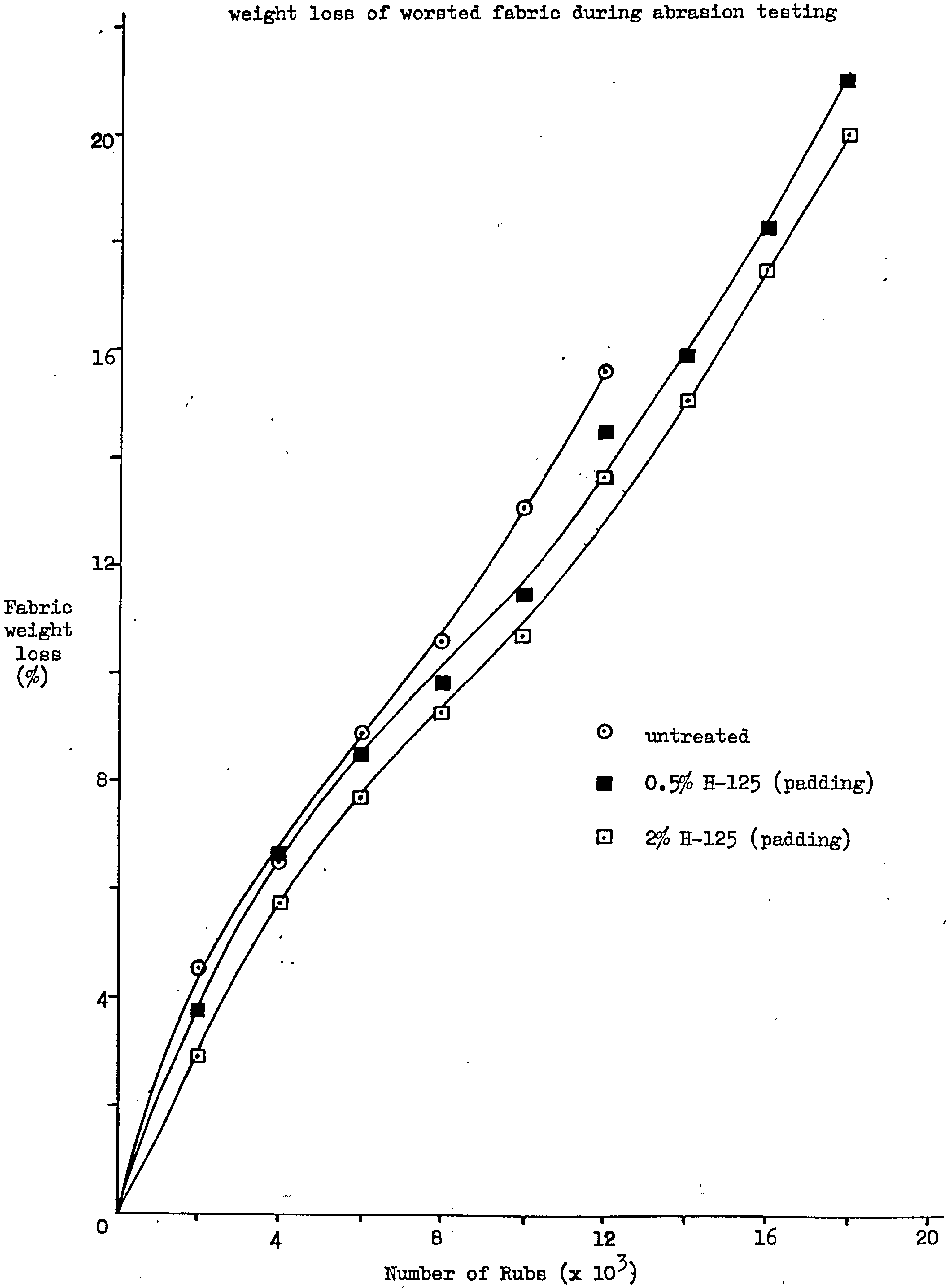


TABLE 57. The effect of Hercosett 125 applied by padding on the weight loss (%) of fabric A (worsted).

Number of Rubs ($\times 10^3$)	% Weight loss of fabric A treated with Hercosett 125.					
	Untreated *		Polymer Add-on (% o.w.f)			
			0.5		2	
	(%)	mean	(%)	mean	(%)	mean
2	4.65 4.35 4.60	4.5	3.35 3.78 3.90	3.7	2.84 2.72 3.25	2.9
4	6.68 6.23 6.53	6.5	6.03 6.88 6.92	6.6	5.48 5.52 6.28	5.8
6	9.12 8.64 8.93	8.9	8.05 8.63 8.84	8.5	7.70 6.99 8.45	7.7
8	10.82 10.49 10.46	10.6	9.46 9.61 10.46	9.8	9.69 8.39 9.90	9.3
10	13.37 12.93 13.06	13.1	11.10 11.20 12.16	11.5	11.25 9.37 11.49	10.7
12	16.40 15.00 15.46	15.6	14.38 14.31 14.96	14.5	14.46 12.31 14.38	13.7
14	—	—	15.72 15.62 16.51	16.0	15.53 13.43 16.40	15.1
16	—	—	17.80 17.94 19.30	18.3	18.37 15.38 19.07	17.6
18	—	—	20.64 20.36 22.40	21.1	21.29 17.20 21.74	20.1
20	—	—	22.95 22.48 24.68	23.4	23.20 19.90 23.65	22.2

* For untreated fabric specifications (see section 2.4.2)

described for fabric C, although the effects were less marked.

2.5.3.3. SEM Studies of Polymer-treated Fabrics

Some typical SEM photographs are shown in Fig. 62-63 for the woollen flannel which had been treated with Synthappret BAP/Impranil DLH by padding and by exhaustion at a polymer add-on of 2.5% o.w.f. It is clear from these observations that the padding treatment leads to a greater proportion of inter-fibre polymer bonding compared with the same treatment applied by exhaustion. Indeed fibre bonding has been advanced as the major mechanism of shrink resistance in polymer-treated wool fabrics produced by pad-dry processes (255, 256). This observation is perhaps to be expected in terms of the deposition and spreading of the concentrated polymer solution as a result of the padding and drying process (255). Hydrostatic tension forces will help to maintain the polymer in film form in between closely aligned fibres and yarns and the high viscosity, which will increase further as the polymer film gels, will aid in forming bridges of cured polymer in between adjacent fibres in the absence of other external applied forces as well as coating or encapsulating the fibre surface.

In a similar manner it has been postulated (257) that at low levels of retention during the dewatering of wool fabrics, water is held as pendular drops clinging to individual fibres but menisci will form predominantly at points of fibre contact or crossovers. Thus if sufficient water is present, drops may bridge between adjacent pairs or groups of fibres. A similar situation no doubt appertains in the case of polymer treatments applied via the padding route.

In the exhaustion treatment, however, the high liquor:fibre ratio will lead predominantly to coating of the wool fibre surface with a thin polymer film. The possibility of forming inter-fibre polymer

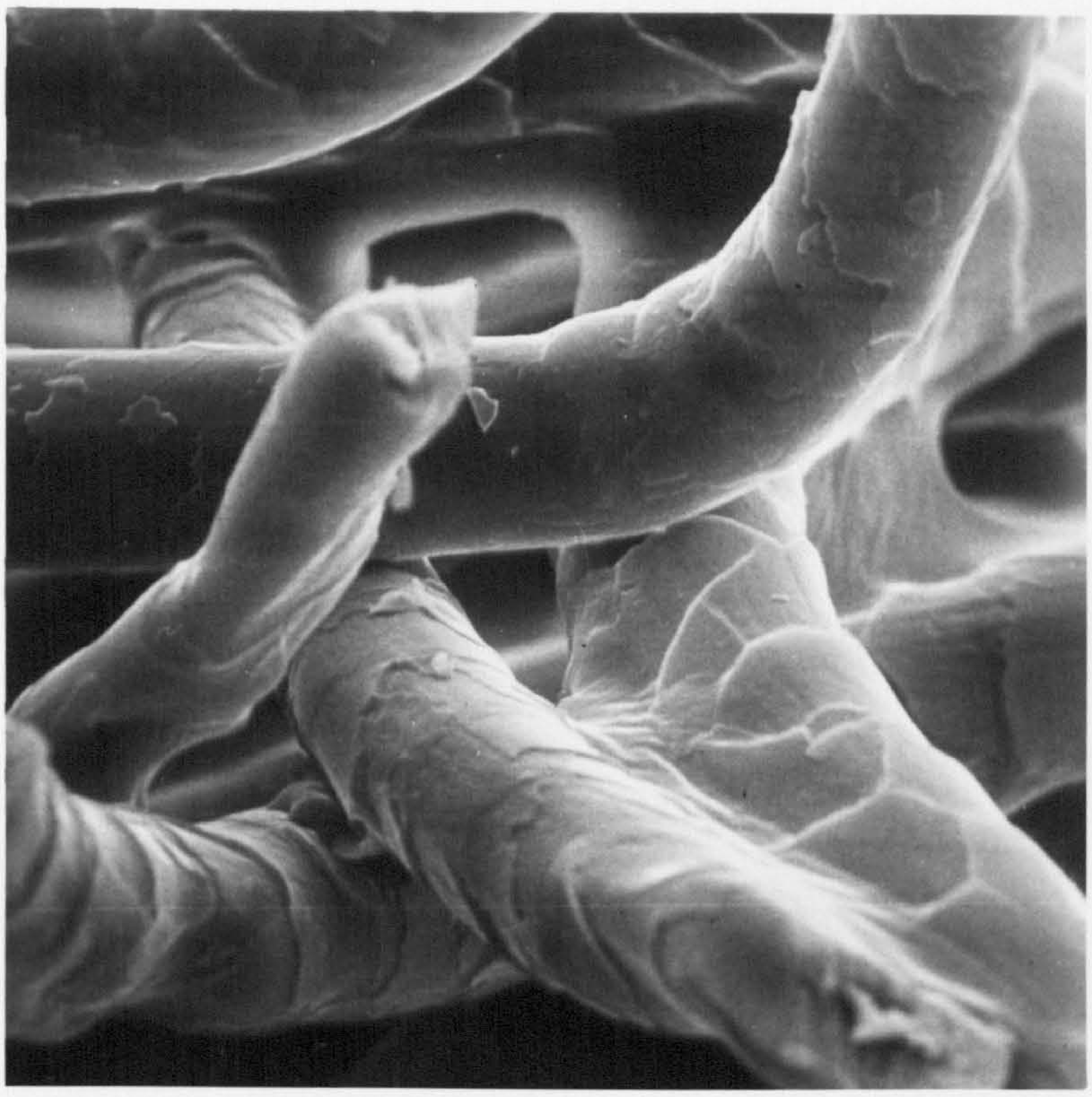


Fig. 62 Woollen flannel - 2.5% Synthappret BAP/Impranil DLH by padding.

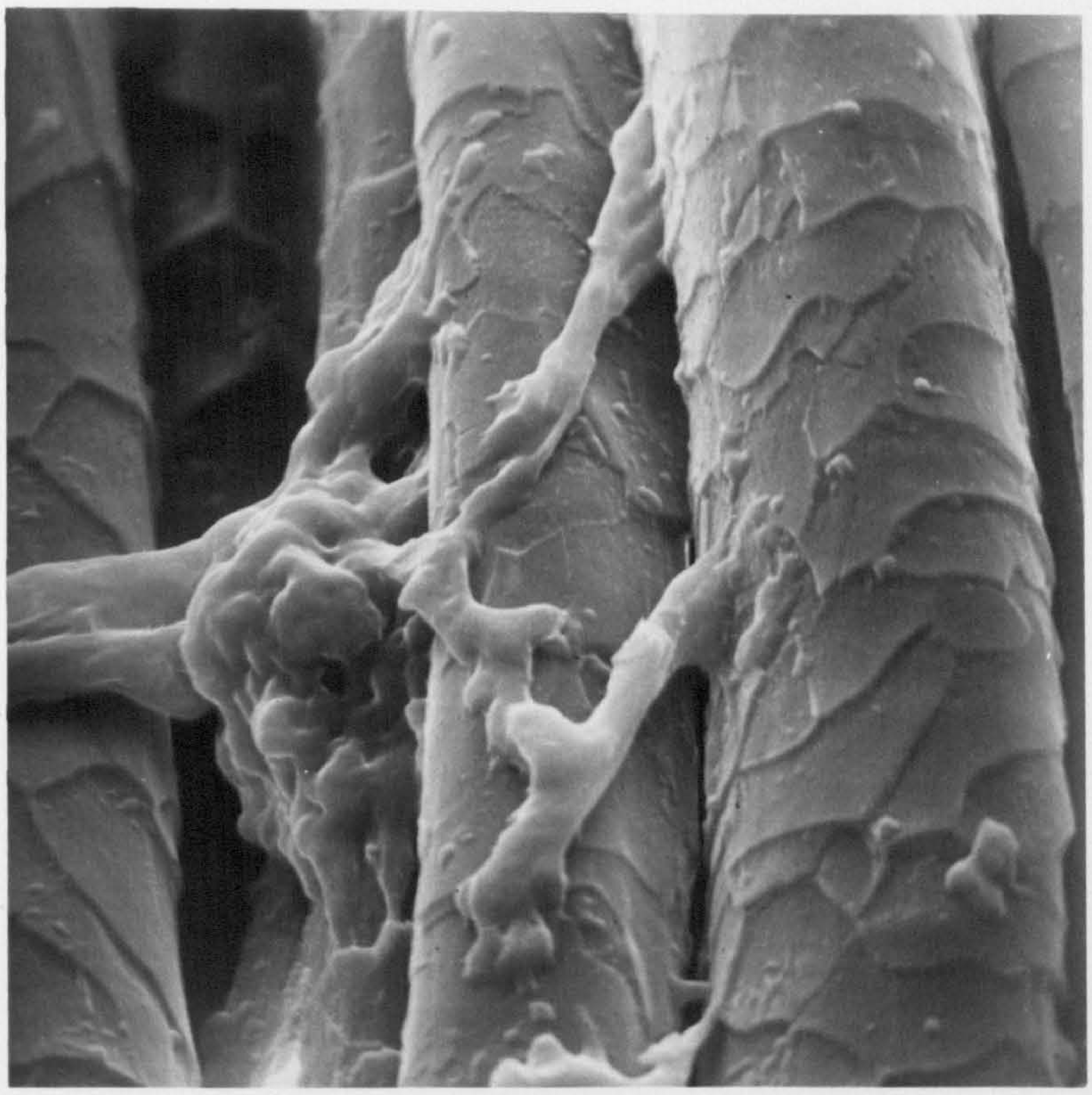


Fig. 63 Woollen flannel - 2.5% Synthappret BAP/Impranil DLH by exhaustion.

bridges is much lower not only because of the less viscous nature of the solution, but also because of the influence of hydrodynamic and mechanical forces upon the fibres within the fabric structure during the treatment. The mechanical agitation of the fabric thus leads essentially to encapsulation of the fibre surface by the polymer treatment with few inter-fibre polymer bridges (126).

Allanach _et al_ have recently demonstrated in SEM studies that Synthappret BAP/Impranil DLH by exhaustion showed frequent local concentrations of polymer but almost a complete absence of inter-fibre bonds in the fabric (258). In this particular case it was postulated that the major mechanism of shrink-resistance was the "stand-off mechanism" originally proposed by Makinson and Lead (259). This phenomenon is shown in Fig. 63.

In the chlorination-Hercosett treatments a similar picture emerges (see Fig. 64-65), but in this case, as has been noted in other studies (255), the charged nature of the chlorinated wool fibre promotes very uniform fibre encapsulation using the exhaustion method of application Fig. 65 . Nevertheless, application via the padding technique does appear to lead to the formation of inter-fibre polymer bridges as well as fibre encapsulation Fig. 64 .

These observations are believed to be of crucial importance in any explanation of the effects of polymer treatments on the MAR of wool fabrics, for clearly the presence of inter-fibre polymer bridges will exert a marked restraining influence upon the capacity of the fabric structure to be disorganised or otherwise disrupted by the application of abrading forces. This influence would be expected to be greater than that obtained purely through the fibre encapsulation mechanism or the stand-off mechanism, as the loss of fibres from the fabric under

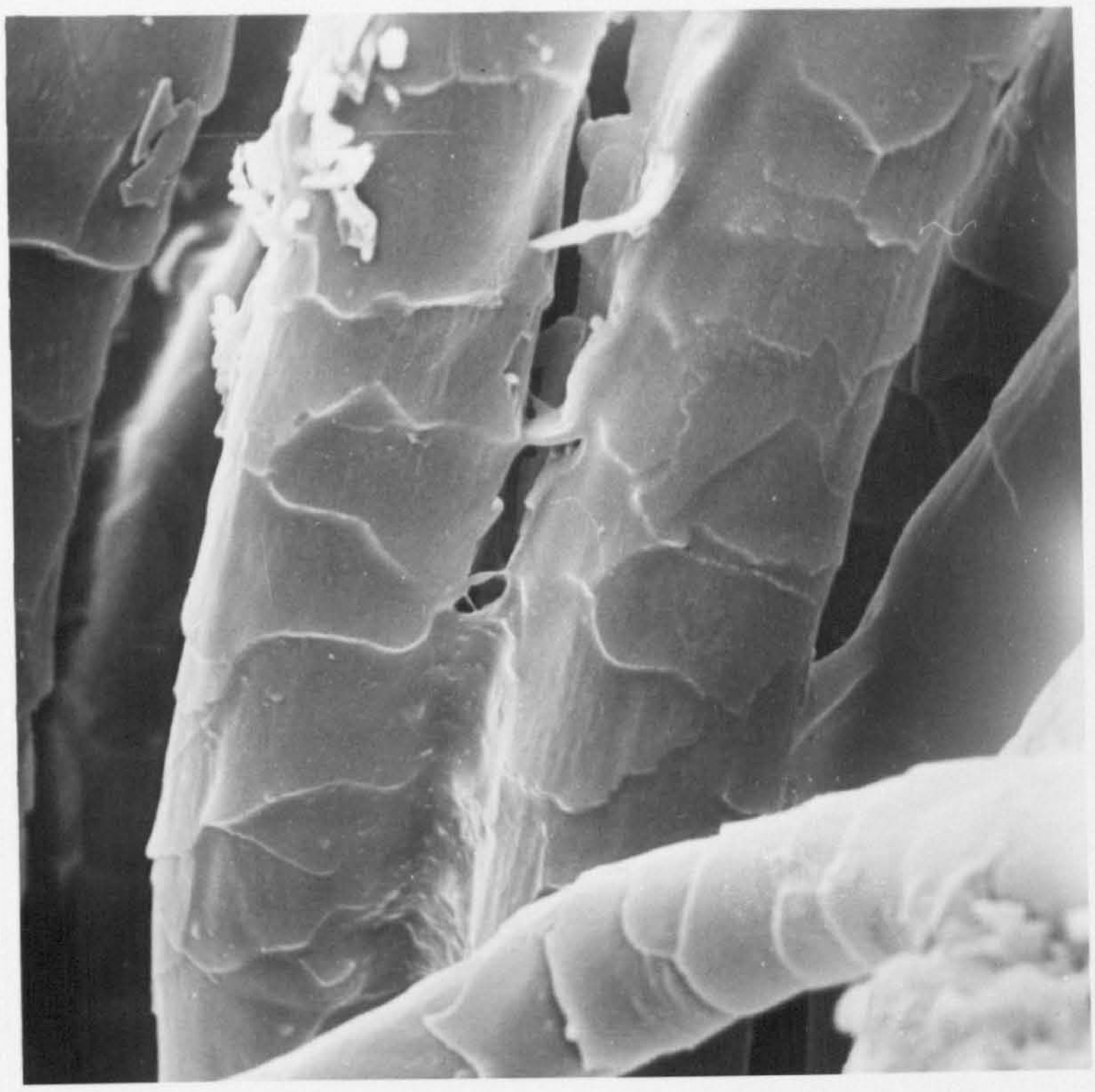


Fig. 64 - Woollen flannel - 2% Hercosett 125 applied by padding.

Fig. 65 - Woollen flannel - 2% Hercoestt 125 applied by exhaustion.

the action of the forces applied during abrasion testing would be expected to be considerably lower in the presence of such inter-fibre polymer bridges.

The presence of inter-fibre polymer bridges should be manifested in the changes of the fabric properties, and for this reason, fabric samples subjected to either the padding or the exhaustion treatment have been studied for a number of polymers and the effects of increase in polymer add-on, etc., on the increased formation of inter-fibre polymer-bonds during shrink-resist finishes evaluated. The changes in the fabric properties have been related to the changes in the MAR of the wool fabrics.

2.5.3.4. Fabric Pilling-mechanism of fabric wear

In Tables 58-60 the number of pills formed after every 1000 rubs on the Martindale Abrasion Tester are recorded for various polymer shrink-resist treamtnets applied by the padding and exhaustion method.

In the case of Lankrolan SHR3 applied at 4% o.w.f. polymer add-on, it can be clearly seen from Table 58 that the application of the polymer by exhaustion leads to a slight reduction in the rate of pilling after the first 1000 rubs. Thereafter the rate of pilling decreases and remains at a uniformly low level compared with the untreated fabric. In the specific case of the same conditions applied by padding the pilling is dramatically reduced even within the first 1000 rubs and thereafter pilling is not noted until near the end-point. These differences are very marked, and further striking confirmation is to be seen in Table 59 for Hercosett 125 in which again the initial rate of pilling is reduced by exhaustion, but the greatest reduction on pilling is to be observed in the padded fabric.

TABLE 58. Pill formation on Lankrolan SHR3 - Treated Wool Flannel (fabric C).

Number of Rubs ($\times 10^3$)	Number of pills on fabric C treated with Lankrolan SHR3					
	Untreated * fabric		By Exhaustion		By Padding	
			Polymer Add-on (% o.w.f) 4		4	
	Pills	mean	Pills	mean	Pills	mean
1	33 28 30	30	33 31 30	31	14 5 14	11
2	24 17 20	20	20 10 16	15	0 0 0	0
3	15 20 17	17	2 7 9	6	0 0 0	0
4	13 18 20	17	1 8 1	3	0 0 0	0
5	-	-	3 6 1	3	0 0 0	0
6	-	-	9 5 4	6	0 0 0	0
7	-	-	-	-	1 1 0	1

* For untreated fabric specifications see section 2.4.2.

TABLE 59. Pill formation on Hercosett 125 - treated wool flannel (fabric C).

Number of Rubs (x 10^3)	Number of pills on fabric C treated with Hercosett 125					
	Untreated * fabric		By Exhaustion		By Padding	
			Polymer Add-on (% o.w.f)			
			2		2	
	Pills	mean	Pills	mean	Pills	mean
1	33 28 30	30	23 12 8	14	1 4 5	3
2	24 17 20	20	13 3 17	8	0 0 0	0
3	15 20 17	17	16 2 5	8	0 0 0	0
4	13 18 20	17	12 7 12	10	0 0 0	0
5	-	-	Too joined	many and together	0 0 0	0
6	-	-	-	-	0 0 0	0
7	-	-	-	-	-	-
8	-	-	-	-	0 0 0	0
9	-	-	-	-	0 0 0	0

* For untreated fabric specifications see section 2.4.2.

TABLE 60. Pill formation on Synthappret BAP/Imypranil DLH - Treated Wool Flannel (fabric C).

Number of Rubs (x 10^3)	Number of pills on fabric C treated with BAP/DLH									
	Untreated fabric		By Exhaustion				By Padding			
			Polymer Add-on (% o.w.f)							
			0.5		2.5		0.5		2.5	
	Pills	mean	Pills	mean	Pills	mean	Pills	mean	Pills	mean
1	33 28 30	30	32 28 36	32	32 28 28	30	28 29 24	27	4 2 5	4
2	24 17 20	20	17 13 14	15	11 11 14	12	13 13 12	13	0 0 0	0
3	15 20 17	17	9 9 10	9	6 5 8	6	13 8 6	9	-	-
4	13 18 20	17	5 10 11	9	7 1 2	3	8 8 9	8	0 0 0	0
5	-	-	15 12 9	12	3 4 5	4	6 8 8	8	-	-
6	-	-	-	-	6 5 7	6	9 8 9	9	0 0 0	0
7	-	-	-	-	8 5 4	6	-	-	-	-
8	-	-	-	-	9 7 4	6	-	-	0 0 0	0
10	-	-	-	-	-	-	-	-	0 0 0	0
12	-	-	-	-	-	-	-	-	0 0 0	0
14	-	-	-	-	-	-	-	-	0 0 0	0
16	-	-	-	-	-	-	-	-	0 0 0	0

These results suggest that the migration of fibres to the fabric surface to form pills is reduced to a greater extent by the padding treatment than by the exhaustion treatment. It must be further concluded that the essential difference between the fabric samples lies in the different proportion of inter-fibre polymer bridges introduced as a result of the method of application of the polymer. The results are thus in accord with the SEM studies in that the greater reduction in fabric pilling will be associated with greater numbers of interfibre polymer bridges.

A further demonstration of the phenomenon may be seen in Table 60 for Synthappret BAP/Impranil DLH-treated fabric in which the higher polymer add-on value, which should give rise to a greater proportion of interfibre polymer bridges, doesin fact give rise to very much lower rates of pilling. However, in agreement with the general hypothesis, the treatments applied by exhaustion still exhibit pilling during abrasion testing, whereas at the higher level of polymer add-on (2.5% o.w.f.) the padded samples do not exhibit pilling. The greater number of interfibre polymer bonds formed at the higher polymer add-on level is in accord with the more viscous nature of the polymer applied to the fabric during padding, because of the greater concentration of polymer in the solution at a low liquor:fibre ratio. In exhaustion treatments the corresponding changes will be small and the effect on the number of interfibre polymer bridges will accordingly be small, but noticeable.

2.5.3.5. Fabric Bending Properties

The effects of the various polymer shrink-resist treatments on the bending properties of the wool flannel (fabric C) are illustrated in Fig. 66-68 (see Tables 61-63 and 42, 43, 45). The

Fig. 66 .- The effect of Lankrolan SHR3 on the flexural rigidity of woollen flannel

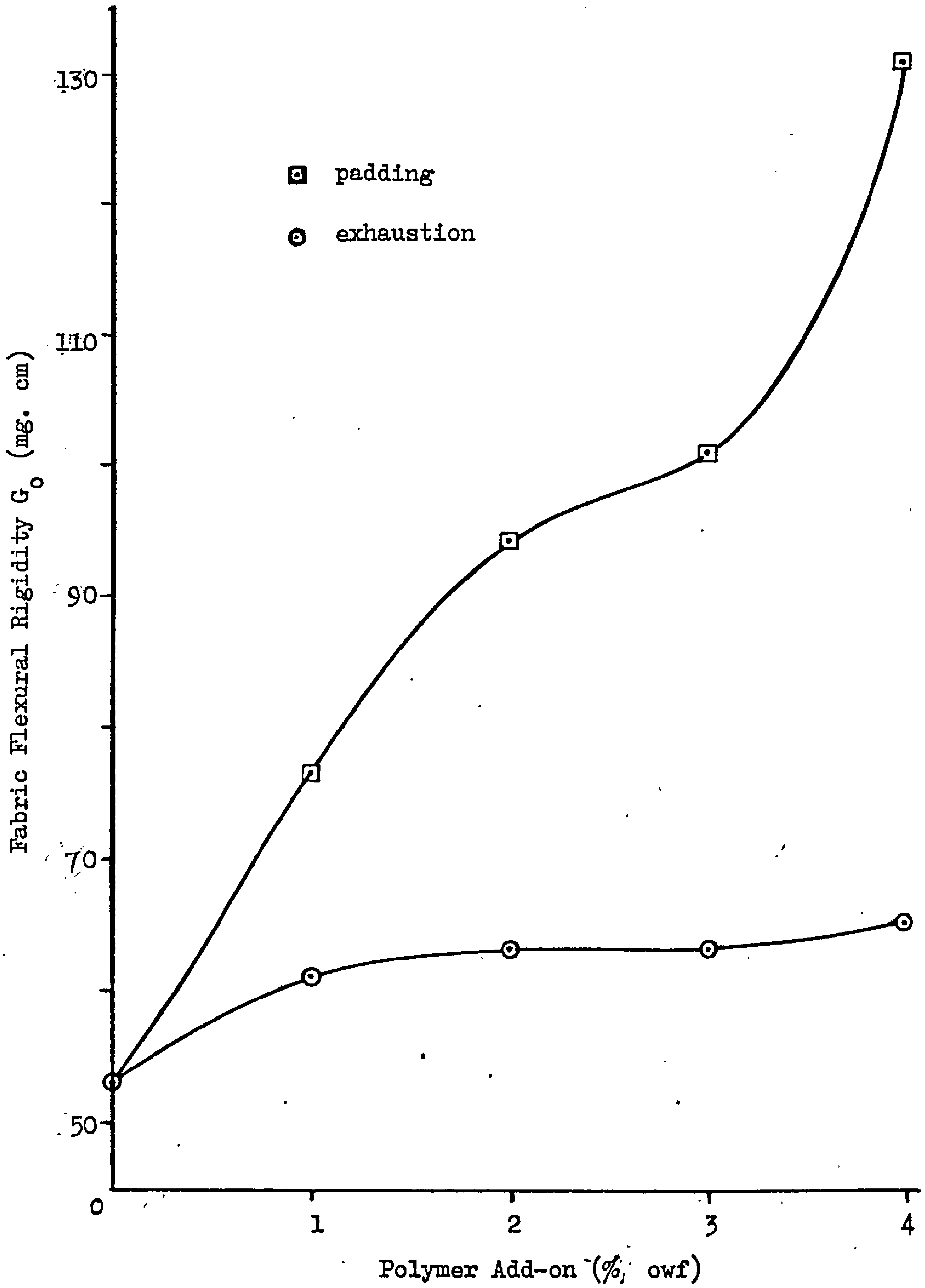


Fig. 67 - The effect of Hercosett 125 on the flexural rigidity of woollen flannel

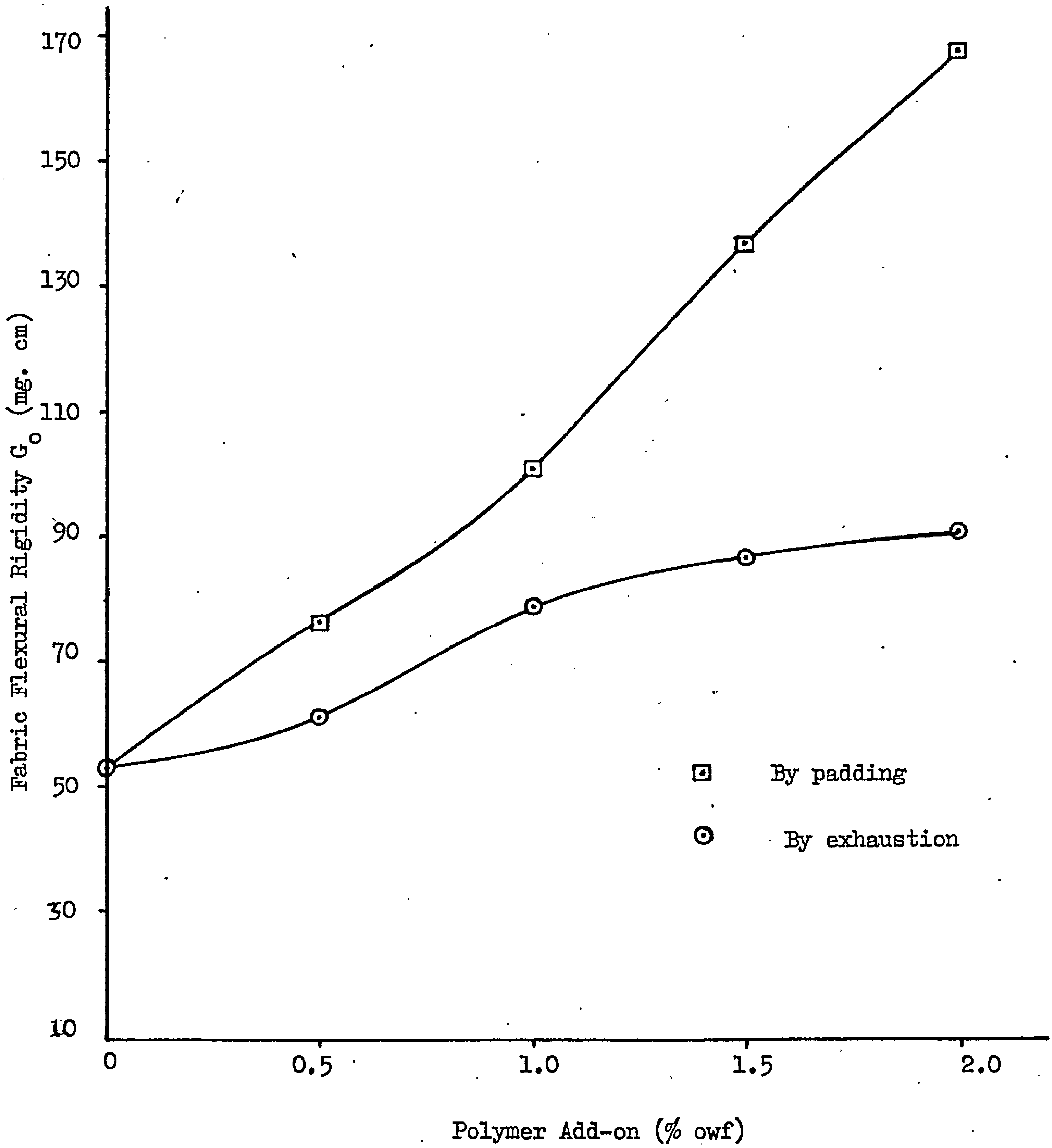


Fig. 68 - The effect of Synthappret BAP/Impranil DLH on the flexural rigidity of woollen flannel

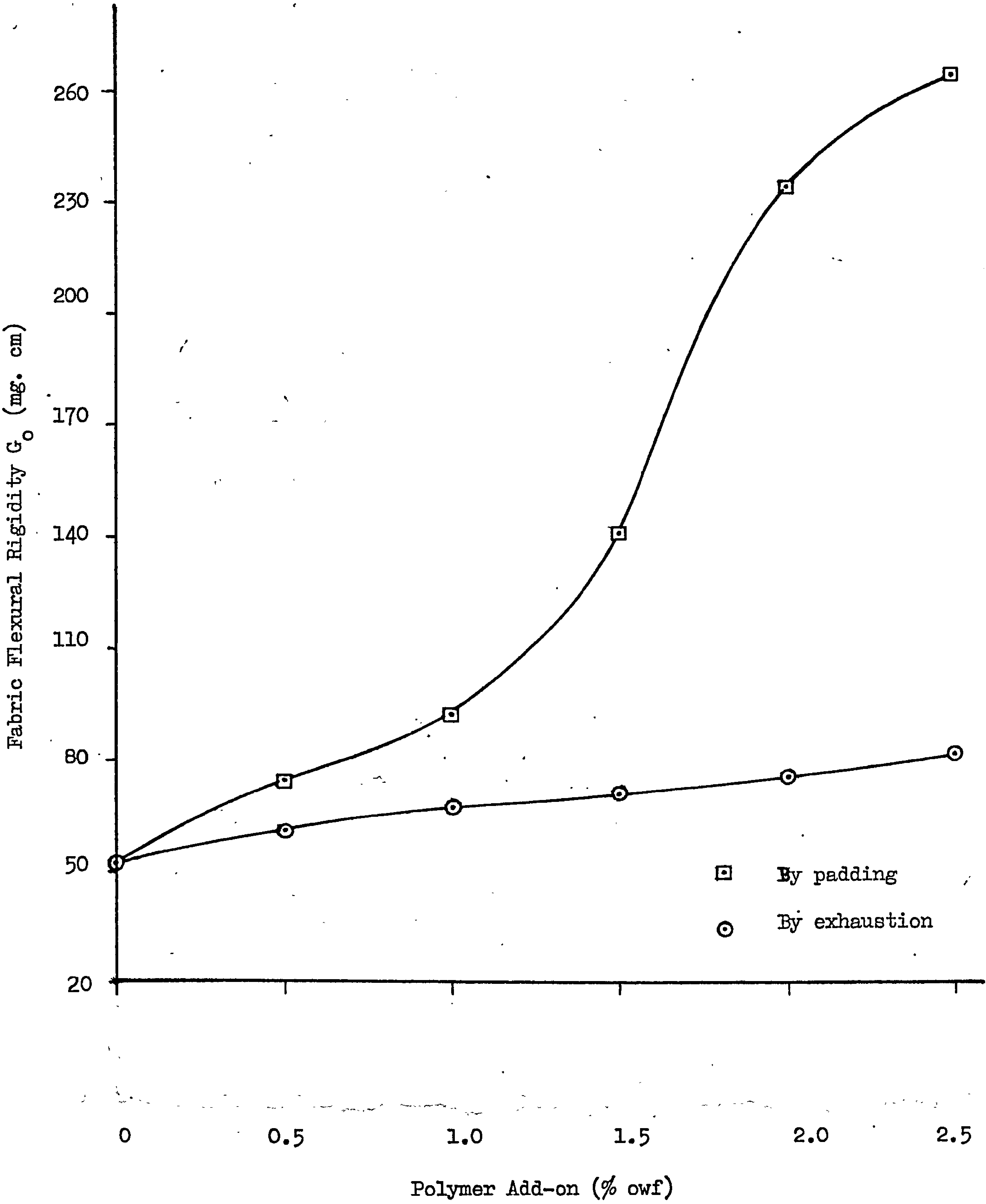


TABLE 61. The effect of Lankrolan SHR3 (by padding) on the flexural rigidity G_o and Coercive couple C_o of flannel fabric (Fabric C).

Polymer Add-on (% o.w.f.)	Fabric C (Woollen)	
	G_o (mg.cm)	C_o (mg.cm)
Untreated	53.0	31.6
1	76.9	35.6
2	94.2	40.7
3	101	40.7
4	131	40.7

The above values represent the mean values of three samples in weft-way direction.

TABLE 62. The effect of Hercosett 125 (by padding) on flannel rigidity G_o and Coercive couple C_o of wool fabrics.

Polymer Add-on (% o.w.f.)	Fabric A (Worsted)		Fabric C (Woollen)	
	G_o (mg.cm)	C_o (mg.cm)	G_o (mg.cm)	C_o (mg.cm)
Untreated	34.7	8.2	53.0	31.6
0.5	33.6	10.1	76.5	51.0
1.0	44.8	10.1	101.9	56.0
1.5	44.8	10.1	137.6	66.0
2.0	47.9	13.2	168.2	76.4

The above values represent the mean values of three samples in weft-way direction.

TABLE 63. The effect of Synthappret BAP/Impranil DLH (by exhaustion) on flexural rigidity G_o and Coercive couple C_o of flannel fabric (Fabric C)

Polymer Add-on (% o.w.f.)	Fabric C (Woollen)	
	G_o (mg.cm)	C_o (mg.cm)
Untreated	53.0	31.6
0.5	61.2	26.5
1	67.3	30.6
1.5	71.4	30.6
2	75.4	31.6
2.5	81.5	32.6

The above values represent the mean values of three samples in weft-way direction.

increases in flexural rigidity (G_0) are characterised by significantly greater changes as a result of padding compared with application by exhaustion. All three polymer shrink-resist processes behave in a similar manner, the fabric flexural rigidity increasing with polymer add-on and all values being greater than for the untreated fabric. However, the increase in G_0 is in the order Synthappret BAP/Impranil DLH > Hercosett 125 > Lankrolan SHR3 for the padded series while in the exhaustion series the order is Hercosett 125 > Synthappret BAP/Impranil DLH > Lankrolan SHR3. Increase in G_0 with increase in polymer add-on has previously been reported elsewhere (248, 249), and all the polymer treatments yield higher G_0 values than the untreated fabric.

In a general way these changes are mirrored by the improvements in MAR reported in Fig. 54-56 and it is considered that these observations are in accord with the other findings in this work. Namely, that the padding process leads to a higher incidence of inter-fibre polymer bridges which will in turn promote a larger increase in the fabric flexural rigidity values. By comparison, the increases in G_0 for the exhaustion treatments are indicative of the lower proportion of inter-fibre polymer bridges formed as a result of this treatment. The interrelation of these results with MAR is clear, in that the exhaustion values lead to lower levels of increase in MAR compared with the padding treatments. These results are corroborated by the changes in the coercive couple C_0 which yield a similar pattern of results, indicating that the restraint to fibre bending and movement within the fabric is more greatly promoted by the padding process. The values of C_0 for the exhaustion series of treatments exhibit only marginal changes with increase in polymer add-on. The smallest changes are to be seen in the Synthappret BAP/Impranil DLH exhaustion treatment.

The changes in G_o reported in Fig. 69 and 46 and Tables 62 and 42 for fabric A again demonstrate the greater increase in G_o obtained in the padding treatment using Hercosett 125. The most marked changes in G_o occur above a polymer add-on of 0.5% o.w.f. applied by padding, but in fabric A the subsequent increase in G_o with polymer add-on is not as pronounced as those obtained using fabric C (see Fig. 67) and this is considered to reflect the differing nature of the fabric composition and structure in each case.

The values of the coercive couple C_o in general reflect the trends previously reported for fabric C, but again the changes are of a lower order of magnitude on fabric A. Padding treatments lead to greater increases in C_o than exhaustion treatments using the same polymer, while in general the values of C_o increase with polymer add-on.

2.5.3.6. Fabric tensile properties

The results of the breaking load (kg) and breaking extension (%) measurements on untreated and polymer-treated fabrics are given in Tables 64-67 and 46, 47, 50.

It can be seen that the breaking load of the fabric is generally increased as a result of the polymer treatment. The trend of the results indicates an increase in breaking load with polymer add-on in both the padded and the exhaustion series of treatments for both the wool flannel (fabric C) and the light weight worsted fabric (fabric A).

The exception is Hercosett 125 applied by padding. All treatments applied via padding or exhaustion on both fabrics appear to increase the breaking extension. However, the breaking extension values

Fig. 69 - The Effect of Hercosett 125 on the flexural rigidity of fabric A (worsted).

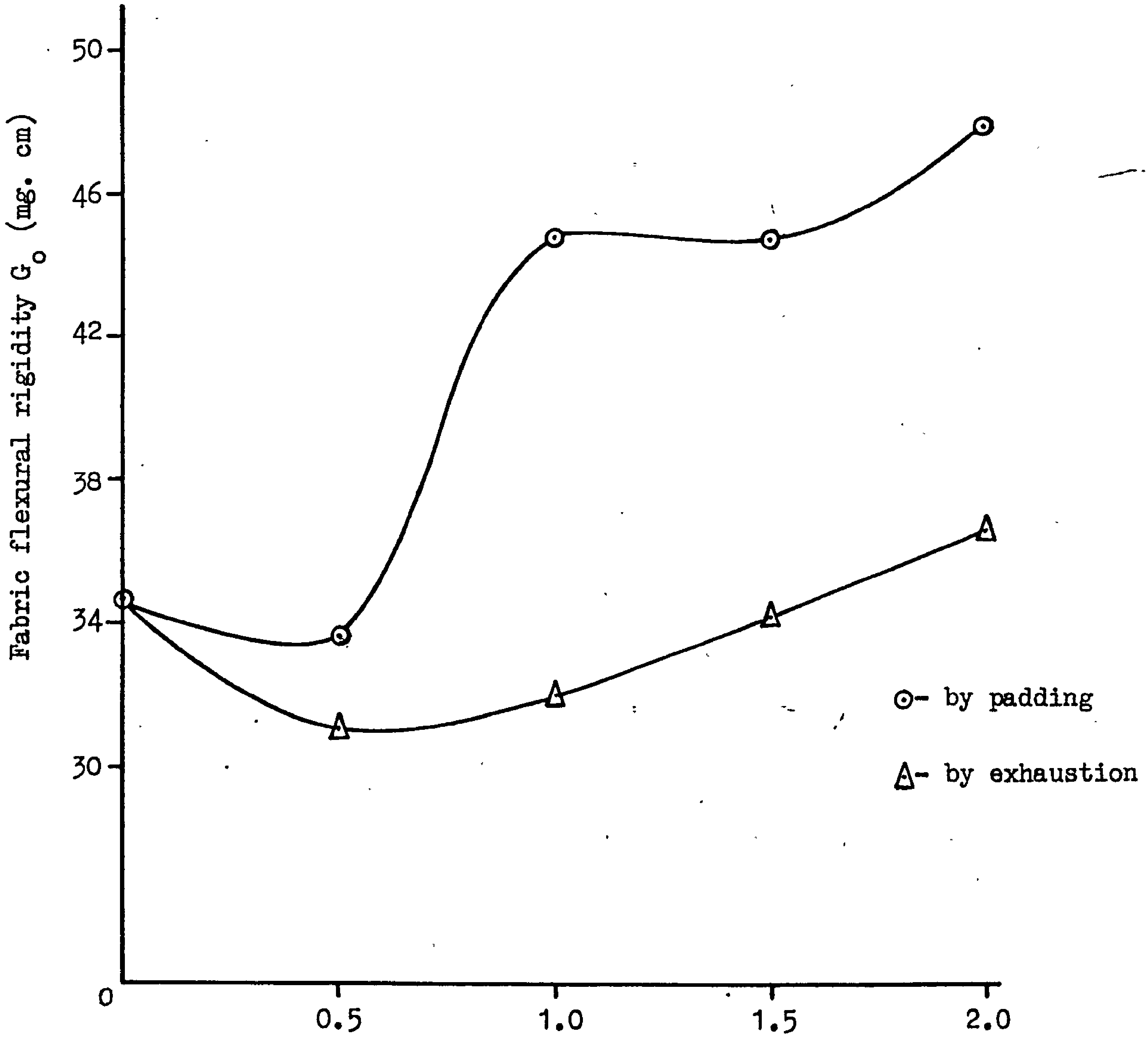


Table 64. The effect of Synthappret BAP/Impranil DLH (by exhaustion) on the tensile properties of fabric C (woollen flannel).

Polymer Add-on (% o.w.f.)	Fabric C (woollen flannel)			
	Breaking Load		Breaking Extension	
	(Kg)	mean	(%)	mean
Untreated	8.8 8.8 8.8	8.8	39.0 34.0 38.0	37.0 (0)
0.5	10.8 10.8	10.8 (22.3)	40.0 42.0	41.0 (10.8)
1.0	10.0 10.5	10.2 (16.1)	39.0 39.0	39.0 (5.4)
1.5	10.8 11.1	10.9 (24.0)	39.0 42.0	40.5 (9.5)
2.0	11.0 11.0	11.0 (24.6)	41.0 42.0	41.5 (12.2)
2.5	11.3 11.3	11.3 (28.0)	43.0 43.0	43.0 (16.2)

The values in parentheses represent the mean increase (%) in Fabric Tensile Properties.

TABLE 65. The effect of Lankrolan SHR3 (by padding) on the tensile properties of fabric C (woollen flannel).

Polymer Add-on (% o.w.f.)	Fabric C (woollen flannel)			
	Breaking Load		Breaking Extension	
	(Kg)	mean	(%)	mean
Untreated	8.8 8.8 8.8	8.8 (0)	39.0 34.0 38.0	37.0 (0)
1	10.5 10.3	10.4 (17.8)	45.0 44.0	44.5 (20.3)
2	9.6 9.8	9.7 (9.9)	41.0 46.0	43.5 (17.6)
3	9.3 9.2	9.2 (4.8)	38.0 40.0	39.0 (5.4)
4	10.4 10.1	10.2 (16.1)	45 43.0	44.0 (18.9)

The values in parentheses represent the mean increase (%) in Fabric Tensile Properties.

TABLE 66. The effect of Hercosett 125 (by padding) on the tensile properties of fabric C (woollen flannel).

Polymer Add-on (% o.w.f.)	Fabric C (woollen flannel)			
	Breaking Load		Breaking Extension	
	(Kg)	mean	(%)	mean
Untreated	8.8 8.8 8.8	8.8 (0)	39.0 34.0 38.0	37.0 (0)
0.5	10.9 11.5	11.2 (26.8)	33.0 31.0	32.0 (15.6)
1.0	11.4 10.6	11.0 (24.6)	35.0 31.0	33.0 (10.8)
1.5	13.1 13.3	13.2 (49.5)	33.0 32.0	32.5 (12.2)
2.0	13.0 12.3	12.6 (43.3)	37.0 34.0	35.5 (4.1)

The values in parentheses represent the mean increase (%) in Fabric Tensile Properties.

TABLE 67. The effect of Hercosett 125 (by padding) on the tensile properties of fabric A (worsted).

Polymer Add-on (% o.w.f.)	Fabric A (worsted)			
	Breaking Load		Breaking Extension	
	(Kg)	mean	(%)	mean
Untreated	14.2 14.3 13.9	14.2 (0)	36.0 34.0 32.5	34.2 (0)
0.5	17.7 16.1	16.9 (+19.0)	33.0 31.0	32.0 (- 6.3)
1.0	16.8 18.1	17.4 (+22.9)	37.0 37.0	37.0 (+ 8.3)
1.5	16.0 18.1	17.0 (+20.1)	35.0 35.0	35.0 (+ 2.5)
2.0	16.7 17.1	16.9 (+19.0)	33.0 33.0	33.0 (- 3.4)

The values in parentheses represent the mean change (%) in Fabric Tensile Properties. + = increase, - = decrease.

obtained for the exhaustion treatments are generally greater than the comparable padded treatment values for the same polymer add-on. An increase in tensile properties has been reported for other polymer shrink-resist treatments on wool fabrics (142, 156, 230, 250-253). However, the increases reported for these treatments are relatively small and could not therefore account for the large increases in MAR recorded in Fig. 54-57 . Nevertheless, there may well be some contribution to the improvement in MAR, but this must operate at a lower order of magnitude compared with the other changes induced in the fabrics as a result of the polymer shrink-resist treatments.

2.5.4. Conclusions

The results of this work are in agreement with the hypothesis advanced in the studies in section (2.5.3.1.) that the MAR of woven wool fabrics is increased by polymer shrink-resist treatments, and that the level of improvement depends upon the type of polymer, the polymer add-on and particularly on the method of application.

Padding treatments lead to a significantly higher level of MAR compared with application by exhaustion for the same polymer and same add-on level. These results are consistent with the view that in padding processes the formation of a greater number of inter-fibre polymer bridges is promoted as well as fibre encapsulation. In exhaustion processes the predominant mode of action would appear to be through fibre encapsulation, i.e. surface coating, with few if any inter-fibre polymer bridges. This has been confirmed in SEM studies of polymer-treated fabrics.

The changes in the rate of weight loss on abrasion testing have been correlated with pill formation in the wool flannel (fabric C) in that a greater rate of pill formation is associated with a greater rate of weight loss. Thus in short fibre fabrics, e.g., woollen-spun wool, the preferential formation of inter-fibre polymer bridges in padded polymer-treated fabrics leads to a reduction in the rate of loss of weight through loss of pills from the fabric surface. It is for this reason that padding treatments give rise to a greater improvement in MAR, compared with that obtained by exhaustion techniques in which fibre encapsulation would appear to be the main operative mechanism by which shrink-resistance is obtained.

These conclusions are substantiated by the fabric bending results which lead to greater changes in the padded fabric series and it has also been demonstrated that the improvements in fabric tensile properties are small and of a magnitude not sufficient to explain the dramatic improvement obtained in padding treatments.

2.6. Synergism in Abrasion resistance and Shrink-resistance

2.6.1. Introduction and Objectives

Previous work on the Martindale Abrasion Resistance (MAR) of woollen and worsted woven fabrics has demonstrated that polymer shrink-resist treatments can effect significant improvements in MAR (154, 156, 164, 230, see also section 2.4.3.1.). It has been clearly shown that this improvement is dependent not only on the nature of the applied polymer and the polymer dosage level, but that the method of application can equally well exert a dramatic effect upon the magnitude of the improvement obtained (see section 2.5.3.1.).

As a result of extensive work, it was proposed that the application of polymer shrink-resist treatments via padding techniques gave rise to a more beneficial improvement than in application by exhaustion processes (see section 2.5.3.1.). This effect was clearly greater on woollen-type fabric than on worsted fabrics. The mechanism of improvement of MAR was considered to be dependent upon the reduction in the rate of loss of fibres from the fabric during abrasion processes as a result of the polymer shrink-resist treatment.

It is well-established that the reduction in felting of wool fabrics is caused by the reduction in the D.F.E. of the wool fibre and by the reduction in the freedom of the fibres to migrate within the fibrous assembly (126). Application of polymer shrink-resist processes via exhaustion techniques are believed to lead predominantly to fibre encapsulation, whereas it has been established in stereoscan microscopic studies that padding treatments additionally provide inter-fibre polymer bridges (so-called fibre-fibre bonds) which provide increased restraint to fibre movement within the fabric (255, 256, 260). It is the latter factor which is believed to be of paramount importance in reducing the rate of weight loss from the fabric during abrasion testing particularly in short fibre (i.e. woollen-spun type) fabrics.

It has been reported that synergistic improvements in shrink-resist effectiveness may be obtained using mixtures of Synthappret BAP with Impranil DLH (172, 242). It was therefore considered of interest to establish whether a synergistic improvement in both shrink-resistance and in MAR could simultaneously be obtained using this polymer system.

Accordingly the work described in this study has been concerned with the inter-relationship between shrink-resist effectiveness and improvement in MAR on woollen-spun fabrics. Other relevant fabric properties have also been studied.

2.6.2. Experimental

Materials

Fabric: Only the plain weave woollen flannel (fabric C), described in detail in section (2.4.2.) was used in this study.

Chemicals: (1) Synthappret BAP (Bayer)
(2) Impranil DLH (Bayer)

The detailed nature of the above two chemicals has been given in section (2.4.2.).

Method of Application of Polymers

Synthappret BAP and Impranil DLH were applied either separately, or together on a 1:1 weight basis of the commercial products, using a Konrad Peter mangle and adjusting the fabric pick-up to give the desired polymer add-on. All pad liquors contained 3 $g.l^{-1}$ sodium bicarbonate to catalyse the subsequent curing process, while in the application of Synthappret BAP and Impranil DLH a wetting agent, Lissapol N, was employed. The fabric samples (30 x 30 cm) were padded, dried and cured in a hot air oven at 140°C for 20 minutes. All samples were given a 20 s steam treatment on a blowing machine to ensure complete curing of the polymer. The samples were then subsequently conditioned at 65% r.h. and 21°C for at least three days prior to testing.

Test Methods

The general experimental methods employed were as follows:

(i) Abrasion Resistance (see section 2.4.2.).

(ii) Rate of Weight loss during Abrasion Testing (see section 2.4.2.).

(iii) Pilling (see section 2.5.2.).

(iv) Fabric Tensile Properties (see section 2.4.2.).

(v) Fabric Bending Properties (see section 2.4.2.).

(vi) Shrink-Resistance The mean fabric area felting shrinkage (F.A.F.S.) results for the samples under test were determined according to I.W.S. Test Method 185 using a 50-l International Cubex machine with 12.5-l of liquor (261).

(vii) Flex Abrasion Resistance The flex abrasion resistance was measured by using the Stoll flexing and abrasion tester described in detail elsewhere (262).

Three test specimens (8 x 1.5 in.) wide in the weft direction were used, the samples being taken from different weft sections. The folding bar was loaded with 1.5 lb. weight and no weight was used on the pressure plate. These were found from initial trials to be the optimum conditions for avoiding vibration of the pressure plate and rippling of the fabric during the operation. Rippling of the fabric may be caused by excessive loading of the pressure plate (262).

2.6.3. Results and Discussion

2.6.3.1. Abrasion Resistance

The results of testing on the Martindale abrasion tester are plotted against the polymer add-on (% o.w.f.) in Fig. 70 (see Tables 68 and 33). It is clear that the number of rubs required to produce a hole in the fabric decreases in the order Synthappret BAP/ Impranil DLH > Synthappret BAP > Impranil DLH > Untreated. The combination of Synthappret BAP with Impranil DLH for padded fabric also gives improved results compared with the additive curve obtained by adding the individual results of Synthappret BAP and Impranil DLH together (see Fig. 70). Thus the combination of Synthappret BAP/ Impranil DLH applied by padding gives rise to a synergistic improvement in MAR for wool fabric of the woollen flannel type. In an analogous fashion to the results of flame retardant experiments, synergism may be defined as an effect which is greater than the additive effect (263).

These results parallel the results obtained in other studies (154), (see also sections 2.4.3.1. and 2.5.3.1.) which have demonstrated conclusively that the MAR increases with increase in polymer add-on and that application via a padding procedure can give rise to substantial improvement in MAR on woollen flannel (see section 2.5.3.1.).

The synergistic improvement in the specific case of the Synthappret BAP/Impranil DLH combination must presumably arise as a result of either interaction between the two polymers and/or from their distribution and mode of adhesion to the fibres within the fabric. It is known from earlier studies that the presence of inter-fibre polymer bridges (so-called fibre-fibre bonds) arising from the nature of the padding process leads to a dramatic improvement in MAR

Fig.70 - The effect of Synthappret BAP and Impranil DLH applied by padding on the Martindale abrasion resistance of woollen flannel

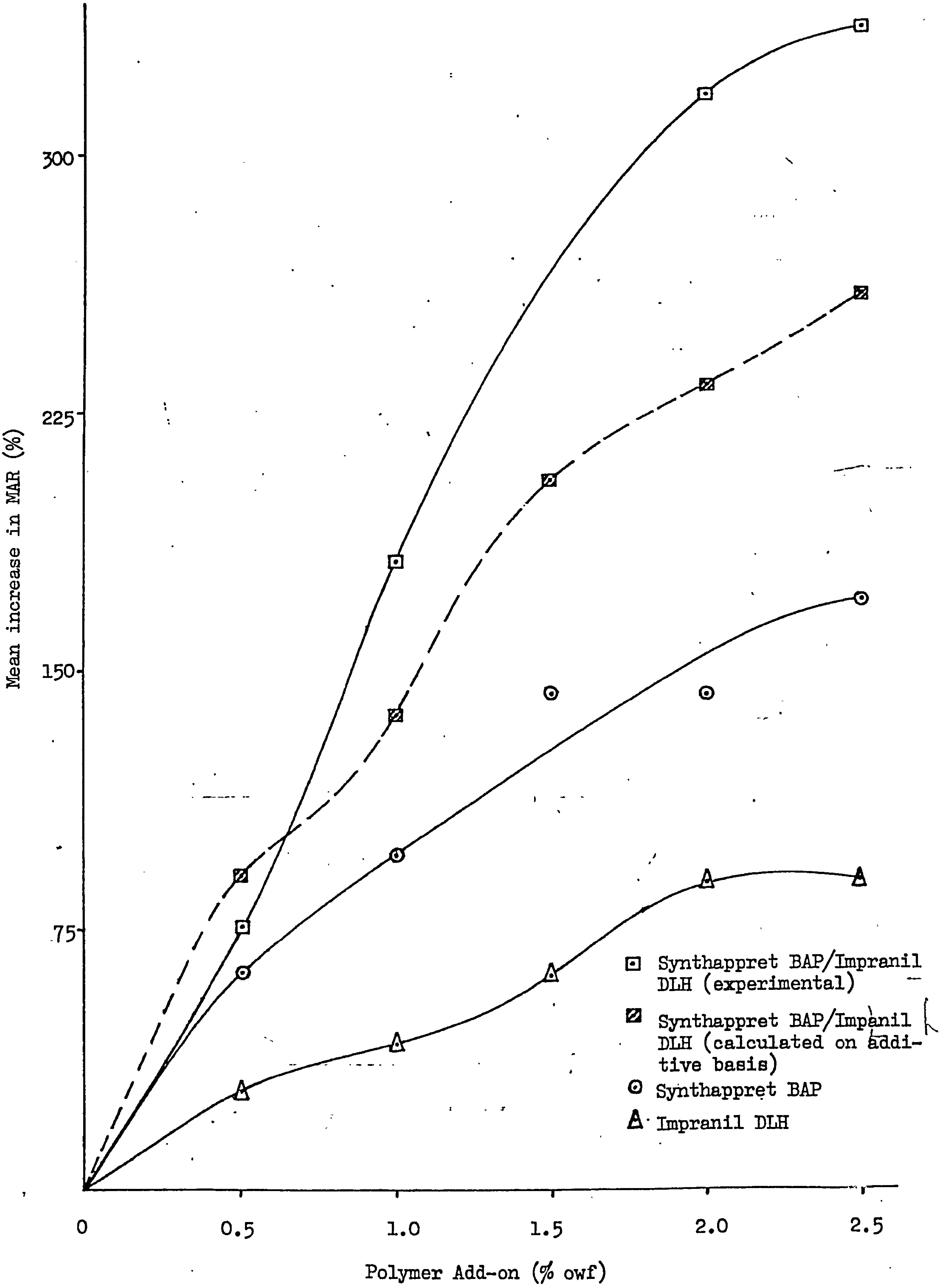


TABLE 68. Martindale Abrasion Resistance of fabric C (woollen flannel) treated with Synthappret BAP and Imprănil DLH (by padding).

Polymer Add-on (% o.w.f)	Synthappret BAP			Imprănil DLH		
	Abrasion Resistance (Rubs x 10^3)	mean	mean increase (%)	Abrasion Resistance (Rubs x 10^3)	mean	mean increase (%)
Untreated	3.6 3.8 3.6	3.7	0	-	-	-
0.5	6.0 6.0 6.0	6.0	62.2	4.5 4.5 5.2	4.7	28.4
1.0	7.0 7.7 7.0	7.2	95.9	5.5 5.5 4.7	5.2	41.9
1.5	8.5 9.2 9.2	9.0	143.2	6.0 6.0 6.0	6.0	62.2
2.0	8.5 9.0 9.5	9.0	143.2	7.5 7.5 6.5	7.2	89.2
2.5	10.0 11.0 9.0	10.0	170.3	7.5 7.0 7.0	7.2	89.2

of woollen flannel (255, 256, 260, see also section 2.5.3.1.).

Thus the nature of the polymer interaction between Synthappret BAP and Impranil DLH may improve the quality of the fibre-fibre bonds by increasing the capacity for absorbing stresses and strains within the fibrous assembly. This could arise from the formation of Type B fibre-fibre bonds rather than Type A fibre-fibre bonds as defined by Cook (264). Alternatively, the wetting, spreading and flow properties of the resultant polymer may differ substantially, leading to a greater number of interfibre bonds.

It has been demonstrated that the prevention of felting shrinkage in the polymer-treated wool fabric is closely related to the degree of spreading (162, 163), the distribution of polymer and its adhesion to the fibre surface (265-267), together with the mechanical properties of the polymer (135, 268).

It has also been reported that for interfibre bonding to act as a shrink-resist mechanism not only the quantity but also the quality in terms of adhesive and cohesive strength are two very important factors in determining the efficiency of a polymer as a shrink-resist treatment (172).

Qualitative support for the hypothesis that Synthappret BAP/ Impranil DLH gives rise to tougher and more elastic films was obtained by casting thin films on a microscopic slide of the two polymers separately and of the combination Synthappret BAP/ Impranil DLH. Subjectively Impranil DLH gave a more brittle film, while Synthappret BAP was still brittle but gave a more elastic film. The combination of Synthappret BAP/Impranil DLH (which is very similar to Synthappret BAP) appeared to yield a very elastic tough film with good work-recovery properties (264, 269). Thus it is considered that part of the improvement, at least, stems from the superior physical properties of this specific combination of polymers studied in this work (269).

It has been pointed out that the level of shrink-resistance can be increased by improving the adhesion between the polymer and wool to the point where cohesive failure of the polymer becomes the dominant mode of failure (267). A tough but highly flexible film such as that produced by Synthappret BAP/Impranil DLH and other synergistic combinations of polymers may, therefore, point the way towards the formulation of polymer shrink-resist treatments that impart superior shrink-resistance and abrasion resistance to wool fabrics.

2.6.3.2. Rate of Fabric weight loss

The rates of weight loss for the untreated and the polymer-treated fabrics are given in Tables 69, 37 and illustrated in Fig. 71. The weight loss in the initial stages of the abrasion test generally appears to be linear, but for those polymer treatments which incorporate Synthappret BAP at higher add-on levels, the rate of weight loss is slowed down appreciably compared with the other treatments. It is noticeable that the weight loss at the end-point is lower for the Synthappret BAP/Impranil DLH combination even though the MAR in terms of the number of rubs to hole is dramatically improved. This suggests that the evenness of fabric treatment leads to a lower and more uniform rate of weight loss compared with the other treatments, and this may indeed be a reflection of the improved physical properties of the polymer film in relation to interfibre bonds.

In accordance with other work (section 2.5.3.2.) the rate of weight loss decreases as the polymer add-on is increased, and in addition padding treatments as opposed to exhaustion generally yield

TABLE 69. The effect of Synthappret BAP and Impranil DLH applied by padding on the weight loss (%) of fabric C (woollen flannel).

Number of Rubs $(\times 10^3)$	Weight loss of fabric C treated with BAP, DLH									
	Untreated fabric*		Polymer Add-on (% o.w.f)							
			Synthappret BAP				Impranil DLH			
			0.5		2.5		0.5		2.5	
	(%)	mean	(%)	mean	(%)	mean	(%)	mean	(%)	mean
1	6.41 6.88 5.97	6.4	2.92 2.99 3.09	3	3.32 3.18 3.04	3.2	4.07 4.01 4.09	4.0	4.0 4.24 3.06	3.7
2	12.65 13.41 12.47	12.8	8.8 8.47 8.21	8.5	6.90 6.84 6.30	6.7	9.54 8.91 10.49	9.6	8.18 9.01 7.05	8.1
3	18.49 21.94 21.37	20.6	12.5 11.97 11.98	12.1	8.45 8.41 7.33	8.1	12.59 11.50 13.19	12.7	11.07 11.88 9.05	10.6
4	24.73 29.95 27.35	27.3	16.14 15.40 15.71	15.7	10.42 10.79 9.46	10.2	16.86 15.47 18.76	17.0	14.71 15.26 12.28	14.1
5	-	-	19.92 19.78 19.56	19.7	12.0 12.49 10.71	11.7	21.45 19.99 23.27	21.6	17.72 18.92 15.07	17.2
6	-	-	24.34 24.74 24.0	24.4	13.35 14.34 12.15	13.3	-	-	21.40 24.03 18.63	21.3
7	-	-	-	-	-	-	-	-	24.35 25.93 20.97	23.7
8	-	-	-	-	16.95 18.21 15.85	17.0	-	-	-	-
10	-	-	-	-	22.02 24.84 20.63	22.5	-	-	-	-

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* For untreated fabric specifications see section 2.4.2.

Fig. 71 - The effect of Synthappret BAP and Impranil DLH applied by padding on the fabric weight loss during abrasion testing

less linear and lower rates of weight loss. Further, it has also been noted that as the MAR of the fabric is improved by polymer padding treatments, the weight loss at the end-point appears to be decreased. This has been presumed to arise as a result of a change in the mode of abrasion. Thus fibre shedding is the predominant mechanism for untreated, low polymer add-on treated fabrics by padding and for polymer-treatments applied by exhaustion procedures. As the polymer add-on is increased above 0.5% o.w.f. by padding, the mode of abrasion progressively changes to a gradual process of attrition and wear of the fabric.

2.6.3.3. Fabric Pilling

The results of the effects of the polymer treatments on the pilling of the woollen flannel fabric at selective polymer add-on values are given in Tables 70 and 60 . It is clear that, at the 0.5% polymer add-on level there is little change in the pilling propensity of the treated fabrics compared with the untreated fabric. This indeed is in agreement with the weight loss studies previously discussed (see section 2.6.3.2.) for the migration of fibres to form pills in the fabric surface, which are subsequently removed from the fabric, is considered to be an essential feature of the fibre shedding mechanism. This mechanism is considered to be the predominant mechanism determining the flat abrasion resistance in fabrics spun from short fibre, relatively low twist yarns, e,g, spun on the woollen system.

At the 2.5% o.w.f. polymer add-on level the pilling is dramatically reduced as previously demonstrated for padded polymer-treated woollen flannel with a high level of MAR (see section 2.5.3.4.). However, pilling is still evident within the first 1000 rubs, but thereafter

TABLE 70. Pill formation on Synthappret BAP and Impranil DLH - Treated Wool Flannel (fabric C).

Number of Rubs ($x 10^3$)	Number of pills on fabric C treated with BAP, DLH									
	Untreated fabric		Polymer Add-on (% o.w.f)							
			Synthappret BAP 0.5		2.5		Impranil DLH 0.5		2.5	
	Pills	mean	Pills	mean	Pills	mean	Pills	mean	Pills	mean
1	33 28 30	30	32 30 32	31	24 17 18	20	28 30 26	28	27 20 20	22
2	24 17 20	20	19 22 19	20	3 0 0	1	14 12 19	15	13 9 8	10
3	15 20 17	17	10 13 10	11	0 0 0	0	14 8 16	13	5 5 6	5
4	13 18 20	17	13 11 10	11	0 0 0	0	12 11 13	12	4 8 5	6
5	-	-	15 15 13	14	0 0 0	0	7 13 17	12	8 7 5	7
6	-	-	13 15 11	13	0 0 0	0	-	-	7 8 8	8
7	-	-	-	-	-	-	-	-	7 8 7	7
8	-	-	-	-	0 0 0	0	-	-	-	-
10	-	-	-	-	0 0 0	0	-	-	-	-

Pills from 2.5% Impranil DLH were smaller in size compared with those of 0.5%.

decreases essentially to zero for Synthappret BAP and Synthappret BAP/ Impranil DLH. Clearly the initial pilling must be associated with the entanglement of protruding surface fibres, and Impranil DLH treatment, by itself, does not appear to halt pill formation. The role of Synthappret BAP must therefore be significant in the prevention of initial pill formation.

The overall pilling decreases in the order Synthappret BAP/ Impranil DLH > Synthappret BAP > Impranil DLH > Untreated, which is indeed the order of improvement in MAR. It was noted that the pills formed at high polymer add-on values were smaller than those correspondingly formed at low polymer add-on values.

These results confirm that the primary mode of fabric abrasion in the woollen flannel studied in this work is due to the removal of fibres from the fabric, i.e. by fibre shedding, as a result of fibre migration, pilling and the resultant removal of the pills from the fabric surface. The role of polymer treatments applied by the padding technique would thus appear to depend upon the promotion and formation of numerous strong and elastic interfibre bonds which prevent fibre movement within the fabric. Pilling as a result is dramatically decreased so that the mode of abrasion then reverts to a process of gradual erosion or attrition of the surface fibres until a hole is created. The greater work-absorption capacity of the Synthappret BAP/ Impranil DLH treatments is considered to lead to the lowest rates of pilling, fibre shedding and fibre attrition and hence to the greatly improved MAR.

2.6.3.4. Fabric Tensile Properties

The tensile properties of the untreated and polymer-treated samples are illustrated in Tables (71 and 50). It is clear that the

TABLE 71. The effect of Synthappret BAP and Impranil DLH applied by padding on the tensile properties of fabric C (woollen).

Polymer Add-on (% o.w.f.)	Synthappret BAP				Impranil DLH			
	Breaking Load		Breaking Extension		Breaking Load		Breaking Extension	
	(Kg)	mean	(%)	mean	(Kg)	mean	(%)	mean
Untreated*	8.8 8.8 8.8	8.8 (0)	39.0 34.0 38.0	37.0 (0)	-	-	-	-
0.5	10.7 9.5	10.1 (14.4)	43.0 40.0	41.5 (12.2)	10.0 9.5	9.7 (10.4)	40.0 40.0	40.0 (8.1)
1.0	11.2 9.7	10.4 (18.3)	44.0 44.0	44.0 (18.9)	11.3 10.1	10.7 (21.2)	44.0 44.0	44.0 (18.9)
1.5	11.0 10.0	10.5 (18.9)	45.0 40.0	42.5 (14.8)	11.0 9.9	10.5 (18.9)	41.0 42.0	41.5 (12.2)
2.0	10.2 10.2	10.2 (15.5)	41.0 41.0	41.0 (10.8)	10.2 10.2	10.2 (15.5)	44.0 44.0	44.0 (18.9)
2.5	10.2 10.8	10.5 (18.9)	40.0 43.0	41.5 (12.2)	11.2 10.9	11.05 (25.1)	43.0 43.0	43.0 (16.2)

The values in parentheses represent the mean increase (%) in Fabric Tensile Properties.

tensile properties of Synthappret BAP/Impranil DLH do not exhibit a synergistic improvement in either fabric breaking load or breaking extension compared with the additive results for the individual polymers. Indeed while the fabric breaking load values are improved compared with the other polymers, the improvement is less than that expected on the additive basis. The fabric breaking extension values exhibit little change between polymer treatments, but both the breaking extension and the breaking load are generally improved as the polymer add-on is increased and the values are greater than that of the untreated fabric.

For these reasons it is considered that the improvement in the tensile properties of the polymer-treated fabrics must reflect the tensile properties of the polymer films, and particularly the properties of the interfibre bonds. However, it is equally clear that synergism, as demonstrated by the MAR results, must depend also on some other factor. It is considered that the type, number and distribution of interfibre bonds left after the padding and drying process must also contribute to the synergistic improvement in fabric properties and performance (126, 172, 255, 256, 264).

Thus factors which effectively control the number, type and distribution of the interfibre bonds will be of crucial importance in the design of future improved abrasion-resistant finishes for woollen spun fabrics. Clearly the ease of fibre wetting, polymer spreading and polymer adhesion to the fibre will be ultimately interrelated with such factors as the tensile properties of the resultant film and the rate of curing when the interfibre bonds are initially formed. It is perhaps relevant to point out that while Synthappret BAP and Impranil DLH applied independently require a wetting agent, the combination of both polymers may be applied satisfactorily without a wetting agent.

2.6.3.5. Fabric Bending Properties

The results of the flexural rigidity (G_o) and coercive couple (C_o) determinations are given in Tables 72, 45. The values of the flexural rigidity G_o are plotted in Fig. 72 where it can be seen that above a level of 1.5% o.w.f. polymer, Impranil DLH yields higher values than obtained using Synthappret BAP alone. Synthappret BAP/Impranil DLH-treated samples exhibit much larger changes in G_o, and it would appear that the values for G_o are greater than those calculated on the purely additive basis of the values for the separate components at the same polymer dosage level. For example the additive value at the 1% o.w.f. level for Synthappret BAP plus Impranil DLH is 198.7 mg-cm compared with a value of 234.5 mg-cm for 2% o.w.f. Synthappret BAP/Impranil DLH. It is to be expected on the basis of these treatments that a stiffer fabric will be produced compared with the untreated fabric, and this was particularly noticeable at the higher polymer add-on levels used in this work. Similar effects have been noted in other work in other polymer shrink-resist systems (248, 249).

The combination of Synthappret BAP/Impranil DLH however does not lead to changes in C_o as marked as those observed with G_o. Impranil DLH increases the values of C_o at a much greater rate with polymer dosage level than does Synthappret BAP, but surprisingly the combination of both polymers leads to a lower value of C_o than that expected on the purely additive basis.

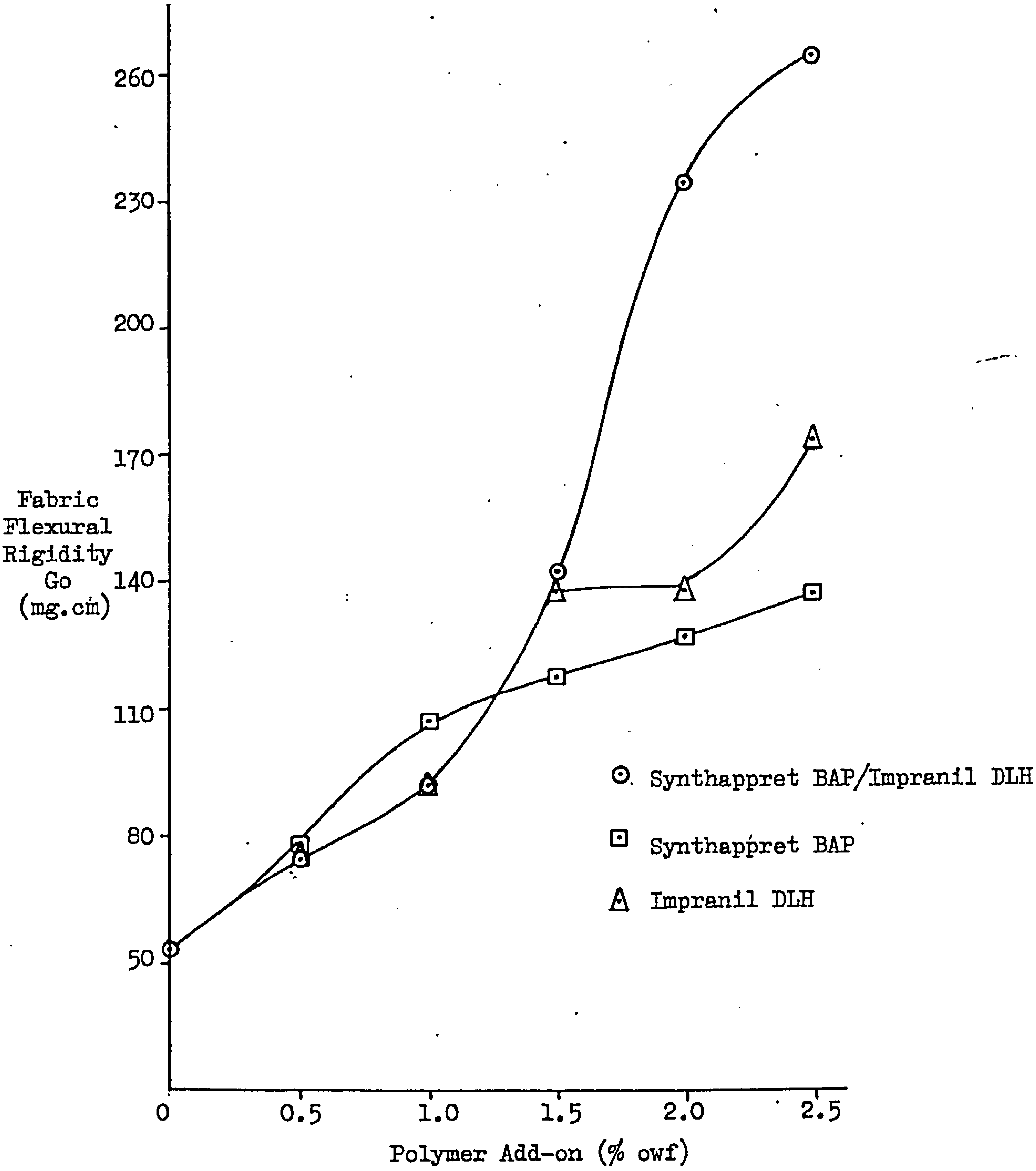
One interpretation of these results is that all the treatments lead to an increase in G_o and C_o with increase in polymer dosage

TABLE 72. The effect of Synthappret BAP and Impranil DLH (by padding) on the bending properties of woollen flannel(Fabric C)

Polymer Add-on (% o.w.f)	Synthappret BAP		Impranil DLH	
	G_o (mg.cm)	C_o (mg.cm)	G_o (mg.cm)	C_o (mg.cm)
Untreated	53.0	31.6	-	-
0.5	77.5	30.6	76.5	40.8
1.0	107.0	45.9	91.7	51.0
1.5	117.2	53.5	137.6	76.5
2.0	127.4	45.9	137.6	76.5
2.5	137.6	45.9	173.3	81.5

The above values represent the mean values of three samples in the weft direction.

Fig. 72 - The effect of Synthappret BAP and Impranil DLH applied by padding on the flexural rigidity of woollen flannel



level as a direct result of the formation of interfibre polymer bridges and fibre encapsulation. The larger increases reported for G_o in the case of Synthappret BAP/Impranil DLH are perhaps more suggestive of the improved strength of the interfibre polymer bridges which, in turn, are more elastic in character, as evidenced by the results for C_o. By contrast, the results for Impranil DLH alone would suggest that the stiffness of the polymer film relative to Synthappret BAP is greater and that the interfibre polymer bridges formed would then be less able to withstand the forces experienced during shrink-resistance and abrasion testing. Thus the effectiveness of the Synthappret BAP/ Impranil DLH treatment would be related to its stress-sharing and work-absorption capacity, which in turn would be higher than for Synthappret BAP or for Impranil DLH.

The effectiveness of Synthappret BAP/Impranil DLH is no doubt intimately related to the physical properties of the interfibre polymer bridges for it has been demonstrated elsewhere that excessively brittle or rubbery polymers give rise to weak points in the fabric and hence to unsatisfactory levels of shrink-resistance (135). In addition it may be that the number of interfibre polymer bridges formed in the case of Synthappret BAP/Impranil DLH treatment is greater than that obtained by the individual polymers alone.

2.6.3.6. Shrink-Resist Effectiveness and Abrasion Resistance

The fabric area felting shrinkage (F.A.F.S.) (%) results are given in Table 73 for Synthappret BAP/Impranil DLH, Synthappret BAP and Impranil DLH all applied via the padding technique. The F.A.F.S. values after 3hours washing in the cubex are plotted against the polymer add-on and the % increase in Martindale abrasion resistance in Fig. 73 and 74 respectively.

<u>TABLE 73</u>. The effect of Synthappret BAP and Impranil DLH (by padding) on the fabric area felting shrinkage (FAFS) of woollen flannel (fabric C).

Polymer Add-on (% o.w.f.)	Synthappret BAP/Impranil DLH				Synthappret BAP				Impranil DLH			
	FAFS (%) after washing for				FAFS (%) after washing for				FAFS (%) after washing for			
	0.5 h	1 h	2 h	3 h	0.5 h	1 h	2 h	3 h	0.5 h	1 h	2 h	3 h
Untreated	22.0	35.3	45.0	52.2	-	-	-	-	-	-	-	-
0.5	2.5	4.1	12.1	19.7	2.5	6.5	16.0	24.1	12.9	26.3	39.2	45.6
1.0	0	0	0	0	0	0	1.7	3.3	12.1	26.3	39.2	45.6
1.5	0	0	0	0	0	0	0	0.8	7.4	17.5	33.3	40.6
2.0	0	0	0	0	0	0	0	0	5.7	12.9	26.3	34.0
2.5	0	0	0	0	0	0	0	0	5.7	12.1	23.4	34.0

Fig. 73 - The effect of Synthappret BAP and Impranil DLH on the fabric area felting shrinkage of woollen flannel after 3 h. Cubex testing.

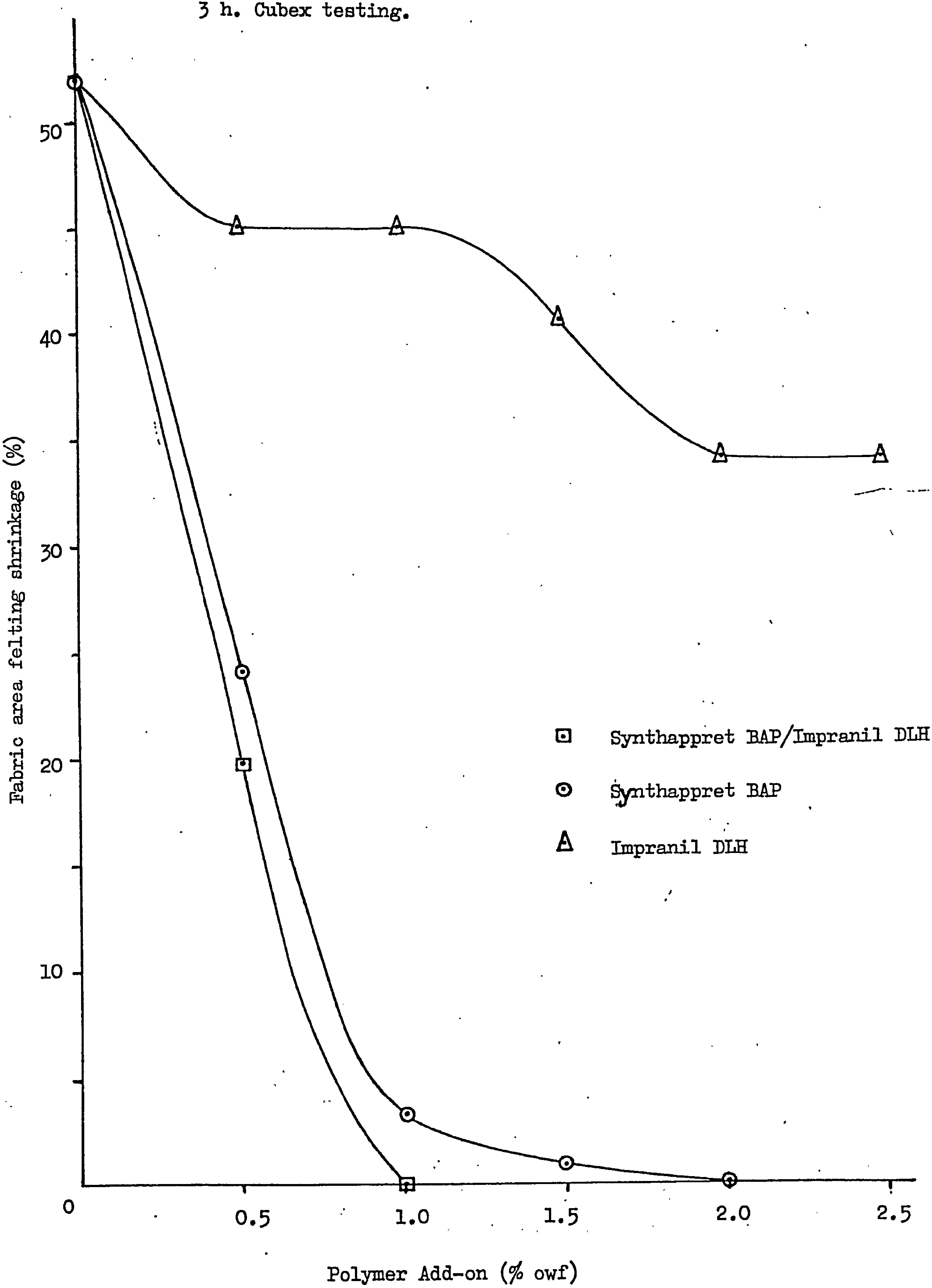
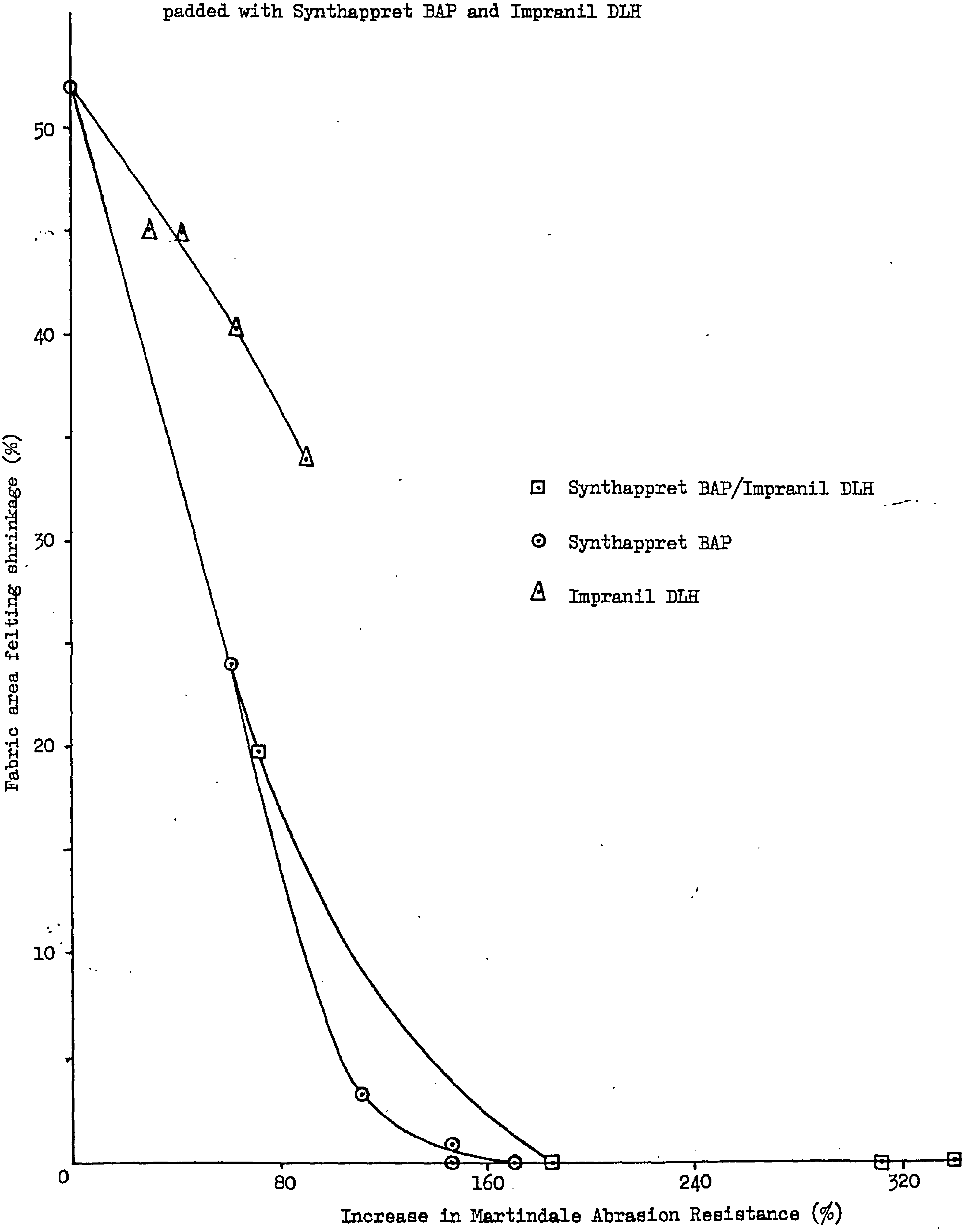


Fig. 74 - The relationship between fabric area felting shrinkage (%) and increase in Martindale Abrasion Resistance for woollen flannel padded with Synthappret BAP and Impranil DLH



A comparison of Fig. 73 with Fig. 74 clearly shows that an increase in shrink-resist effectiveness as measured by the reduction in fabric area felting shrinkage (F.A.F.S.) (cubex 3 hour test) is paralleled by an increase in MAR. The synergistic improvement in shrink-resist effectiveness previously reported (172, 241) for Synthappret BAP/Impranil DLH is confirmed in Fig. 73 and Synthappret BAP is clearly vastly superior to Impranil DLH in terms of its shrink-resist effectiveness at the same polymer add-on. Impranil DLH applied alone via padding is relatively ineffective as a shrink-resist treatment.

These results are a striking confirmation of the hypothesis that in woollen-spun fabrics composed of low twist yarns and short fibres, the predominant mechanism of fabric abrasion consists in fibre migration to the fabric surface to form pills, followed by the loss of fibre from the yarn structure. This leads to high rates of weight loss and hence to low values of MAR.

It must be concluded, therefore, for woollen-type fabrics that a synergistic improvement in shrink-resist effectiveness is accompanied (in the case of Synthappret BAP/Impranil DLH applied by padding) by a synergistic improvement in MAR. This is a very significant phenomenon which suitably exploited in this, and in other polymer shrink-resist treatments, could lead to higher performance levels and possibly a wider range of end uses for woollen-type fabrics.

The relation between MAR and shrink-resist effectiveness is further explored in Fig. 74 where the dramatic improvement in MAR is marked by a steep decline in the F.A.F.S. value. The values for Synthappret BAP and for Synthappret BAP/Impranil DLH are closely spaced together whereas the Impranil DLH values over the same polymer add-on range are clearly much less effective both in terms of shrink-resistance and abrasion resistance. An important point is that when the F.A.F.S. value reduces effectively to zero at a particular polymer add-on level, very high increases in MAR are subsequently obtained with higher polymer add-on values, especially in the case of Synthappret BAP/Impranil DLH.

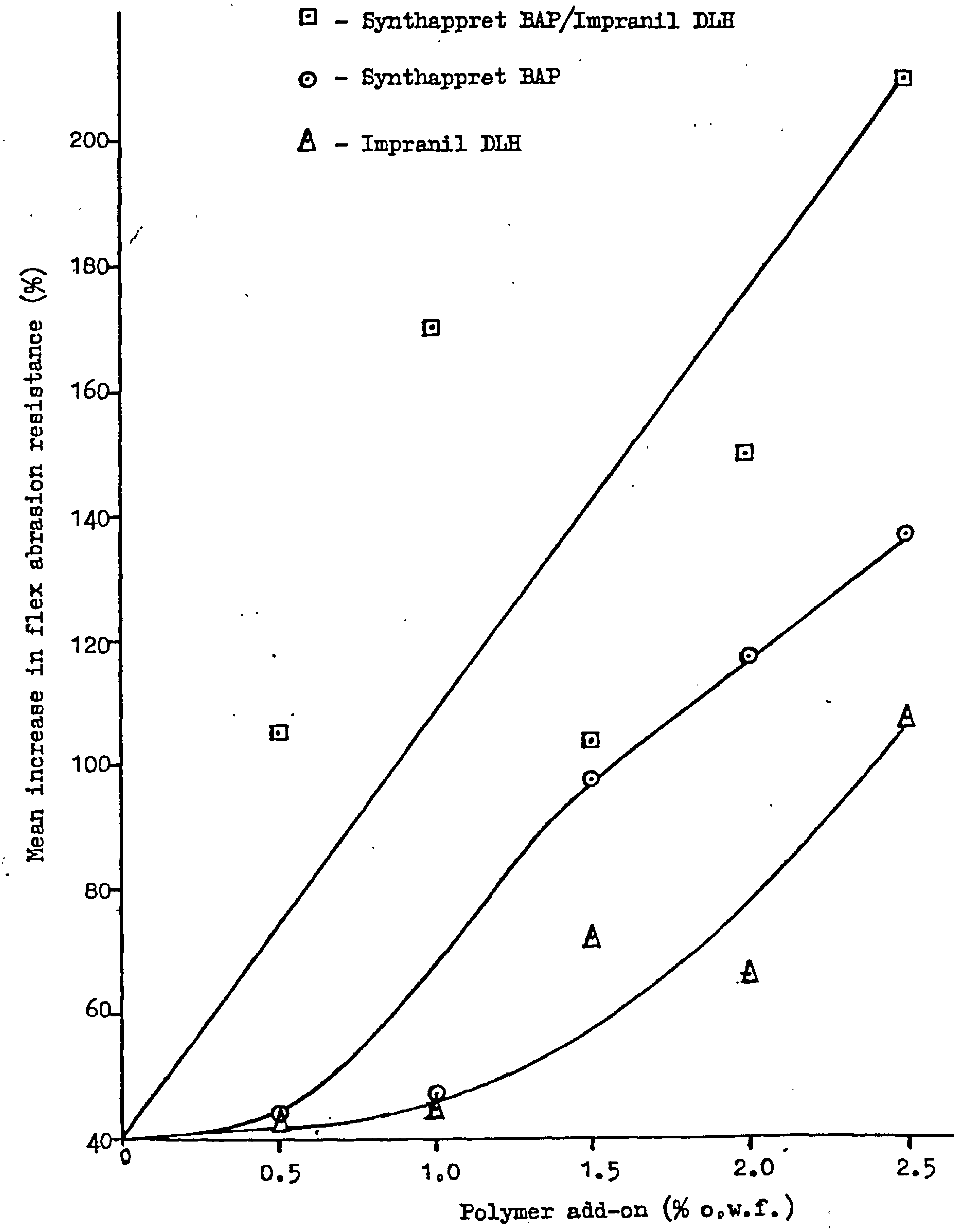
It must be concluded therefore that the elimination of fibre migration or felting within the fibrous assembly is a key factor in the improvement in MAR and that once this condition is attained, high levels of MAR will result. It considered that this arises primarily through the beneficial action of the interfibre polymer bridges formed as a result of applying the shrink-resist polymer treatment via a padding process.

2.6.3.7. Flex Abrasion Resistance

The results of testing on the flexing and abrasion tester for fabrics treated with Synthappret BAP/Impranil DLH, Synthappret BAP, Impranil DLH are plotted against the polymer add-on (% o.w.f.) in Fig. 74a and given in detail in Table 74 .

It is clear that the number of cycles required to rupture the polymer-treated fabric samples at the same polymer add-on decreases in the order Synthappret BAP/Impranil DLH > Synthappret BAP > Impranil DLH for all polymer add-on levels and all the values are greater than for the untreated sample. These results, in accord with the results obtained in the Martindale abrasion tester (see section 2.4.3.1., 2.5.3.1. and 2.6.3.1.), demonstrate that the flex abrasion resistance generally increases with increase in polymer add-on. Although the synergistic improvement obtained in MAR (see section 2.6.3.1.) and shrink-resist effectiveness (see 172, 241 and section

Fig. 74a - The Effect of Synthappret BAP and Impranil DLH (by padding) on the flex abrasion resistance of fabric C (woollen).



<u>TABLE 74</u>. The effect of Synthappret BAP and Impranil DLH (by padding) on the flex abrasion resistance (FAR) of Fabric C (Woollen).

Polymer Add-on (% o.w.f)	Synthappret BAP/Impranil DLH			Synthappret BAP			Impanil DLH		
	Flex Abrasion Resistance cycles	Flex Abrasion Resistance mean	mean increse in FAR (%)	Flex Abrasion Resistance cycles	Flex Abrasion Resistance mean	mean increase in FAR (%)	Flex Abrasion Resistance cycles	Flex Abrasion Resistance mean	mean increase in FAR (%)
Untreated	160 165 175	167	0	-	-	-	—	—	—
0.5	390 335 300	342	104.8	238 250 230	240	43.7	285 210 225	240	43.7
1.0	480 445 430	452	170.7	240 255 240	245	46.7	265 220 240	242	44.9
1.5	370 330 320	340	103.6	330 330 330	330	97.6	280 295 285	287	71.9
2.0	350 455 445	417	149.7	410 360 320	363	117.4	260 300 225	278	66.5
2.5	510 545 500	517	209.6	390 420 373	395	136.5	350 350 340	347	107.8

2.6.3.6.) was not observed in the case of flex abrasion resistance, it is evident that the combination of Synthappret BAP/Impranil DLH yields better flex abrasion values compared with Synthappret BAP or Impranil DLH applied separately. Some of the reasons for not obtaining synergism in the flex abrasion resistance are believed to be the more severe nature of the flexing test and the complex mode of flexing and abrasion imparted to the fabric. This may be one reason for the greater variability in the results for Synthappret BAP/ Impranil DLH treatments which yield the highest improvements in performance at all polymer add-on levels studied. Nevertheless using the Stoll flexing and abrasion tester neither synergism nor additivity of the results is observed, although there is an undoubted improvement in performance using the Synthappret BAP/Impranil DLH treatments.

2.6.4. Conclusions

For the same polymer add-on level applied via a padding treatment, the order of improvement in Martindale abrasion resistance has been shown to be Synthappret BAP/Impranil DLH > Synthappret BAP > Impranil DLH > Untreated for a woollen flannel. The synergistic improvement using Synthappret BAP/Impranil DLH is considered to arise from the quality and the quantity of the interfibre polymer bridges (interfibre bonds) formed which effectively restrict fibres migration within the fabric. Thus the rate of loss of fibre from the fabric via pilling and shedding is dramatically reduced and the Martindale abrasion resistance significantly improved.

Synthappret BAP/Impranil DLH applied via padding leads to an appreciably stiffer fabric handle and this is reflected in the progressive increases in the fabric flexural rigidity (G_o) with increasing polymer add-on. The increases reported for C_o (the coercive couple) are of a lower order of magnitude although these also increase progressively with increase in polymer add-on. It is considered that these changes reflect the improved quality of interfibre bonding resulting from the use of Synthappret BAP/Impranil DLH applied by padding, for padding leads to the formation of greater numbers of interfibre bonds as well as fibre encapsulation. The latter is most probably the predominant mode of action resulting from polymer treatments applied via exhaustion techniques.

The flex abrasion resistance is also increased in a similar order to that obtained for MAR i.e. Synthappret BAP/Impranil DLH > Synthappret BAP > Impranil DLH > Untreated. The synergistic effect observed in shrink-resist effectiveness and MAR is not observed in the flex abrasion results and the reasons for this are believed to be the more severe nature of the flexing test and the complex mode of abrasion imparted to the fabric.

It is clear that future research in wool finishing should be directed to the exploitation of novel and improved polymer shrink-resist treatments that are applied by methods that promote the formation of interfibre bonds which are numerous, strong and flexible. While the situation is less clear for the improvement in MAR for worsted fabrics the use of such treatments for short fibre (woollen-spun) materials will thus lead to a significant improvement not only in shrink-resistance but also in abrasion resistance. In this manner the goal of improved quality for such fabrics vis-à-vis man-made fibre fabrics should be attained and the marketing competitiveness of wool fabrics improved.

2.7. The Effects of Cubex Testing

2.7.1. Introduction and Objectives

The Martindale abrasion resistance (MAR) of woven wool fabrics has been shown to be markedly dependent upon the presence of polymer shrink-resist treatments (154, 156, 164, section 2.4.3.1.). The nature of the polymer (154, 156, 164, section 2.4.3.1.), the polymer add-on level (154, 156, 164) and particularly the method of application of the polymer treatment are of considerable importance in determining the level of MAR obtained (see section 2.5.3.1.). The role of the fabric structure and in particular its interrelation with the number and physical properties of interfibre polymer bridges formed have been examined in some detail for woollen-spun fabrics and a possible mechanism for improvement in MAR has been proposed. Thus the prevention of fibre migration and felting in short fibre low twist woollen-spun fabrics leads to dramatic improvements in the Martindale abrasion resistance test. It has been considered that this arises from the reduction in propensity to pill and loose fibre from the fabric during abrasion testing, for loss of fibres is believed to be the primary cause of low MAR of such fabrics, although a different mode of abrasion is considered to apply to worsted-type fabrics.

In previous work (see sections 2.4. and 2.5.) the effects of polymer type, polymer add-on and method of application were studied and a synergistic improvement in shrink-resist performance and MAR (see section 2.6.) were reported. A noticeable feature of washed fabrics was the softer handle and more fuzzy surface appearance after a 3 hour Cubex wash test. Because of this effect on padded fabrics, this work has now been extended to study the effects of

Cubex washing tests on such polymer-treated fabrics in order to establish whether the improvement in abrasion resistance is retained after washing. Studies have accordingly been carried out on shrink-resist treated fabrics in which no area shrinkage was observed after a 3 hour Cubex washing test.

2.7.2. Experimental

Materials

Fabric: The plain weave woollen flannel (fabric C) described in detail in section 2.4.2. was used in this study.

Chemicals: (1) Synthappret BAP (Bayer)
(2) Impranil DLH (Bayer)

The detailed nature of the above chemicals have been given in section (2.4.2.).

Methods

Method of Application of Polymer shrink-resist Treatments

Synthappret BAP was applied either separately, or together with Impranil DLH on a 1:1 weight basis of the commercial products by typical conventional padding or exhaustion procedures described in detail in section 2.5.2.

All samples were in addition subjected to a 20 s treatment with steam on a blowing machine to complete the curing of the shrink-resist treatments.

Test Methods

(i) Martindale Abrasion Resistance (see section 2.4.2.).

(ii) Shrink-resistance Testing (see section 2.4.2.).

(iii) Fabric Thickness This was measured using a Reynolds and Branson fabric thickness tester under an applied pressure of 5 $g.cm^{-2}$.

(iv) Fabric Bending Properties (see section 2.4.2.).

(v) Fabric Crease Recovery Angle This was measured generally in accordance with BS 3086, 1972, using a Shirley Crease Recovery tester (270). At least 4 weftwise samples were measured in each case, the fabric sample being held between glass plates under a load of 1 kg for 2 minutes, followed by 1 minute recovery and measurement of the crease recovery angle.

2.7.3. Results and Discussion

2.7.3.1. Shrink-resist Effectiveness

The fabric area felting shrinkage (F.A.F.S.) (%) results are given in Tables 73, 75 for Synthappret BAP/Impranil DLH applied via padding and by exhaustion and also for Synthappret BAP applied via padding. The F.A.F.S. values after 3hours washing in the Cubex are illustrated in Fig. 75 . It is clear that the padding treatments for Synthappret BAP/Impranil DLH and Synthappret BAP alone are superior to Synthappret BAP/Impranil BLH applied via the exhaustion method.

The nature of this dramatic improvement has been discussed earlier (see sections 2.4.and 2.5.) in which it was concluded that padding treatments promote a greater number of interfibre polymer bridges (interfibre bonds) than normally obtained in exhaustion treatments. This is again confirmed in this study and the quality of the interfibre polymer bridges, as denoted by the physical properties, e.g. strength, elasticity and resilience of the polymer films, are also considered to be of importance. Indeed the addition of Impranil DLH to Synthappret BAP functions in this way to promote a synergistic improvement in both the shrink resistance and MAR.

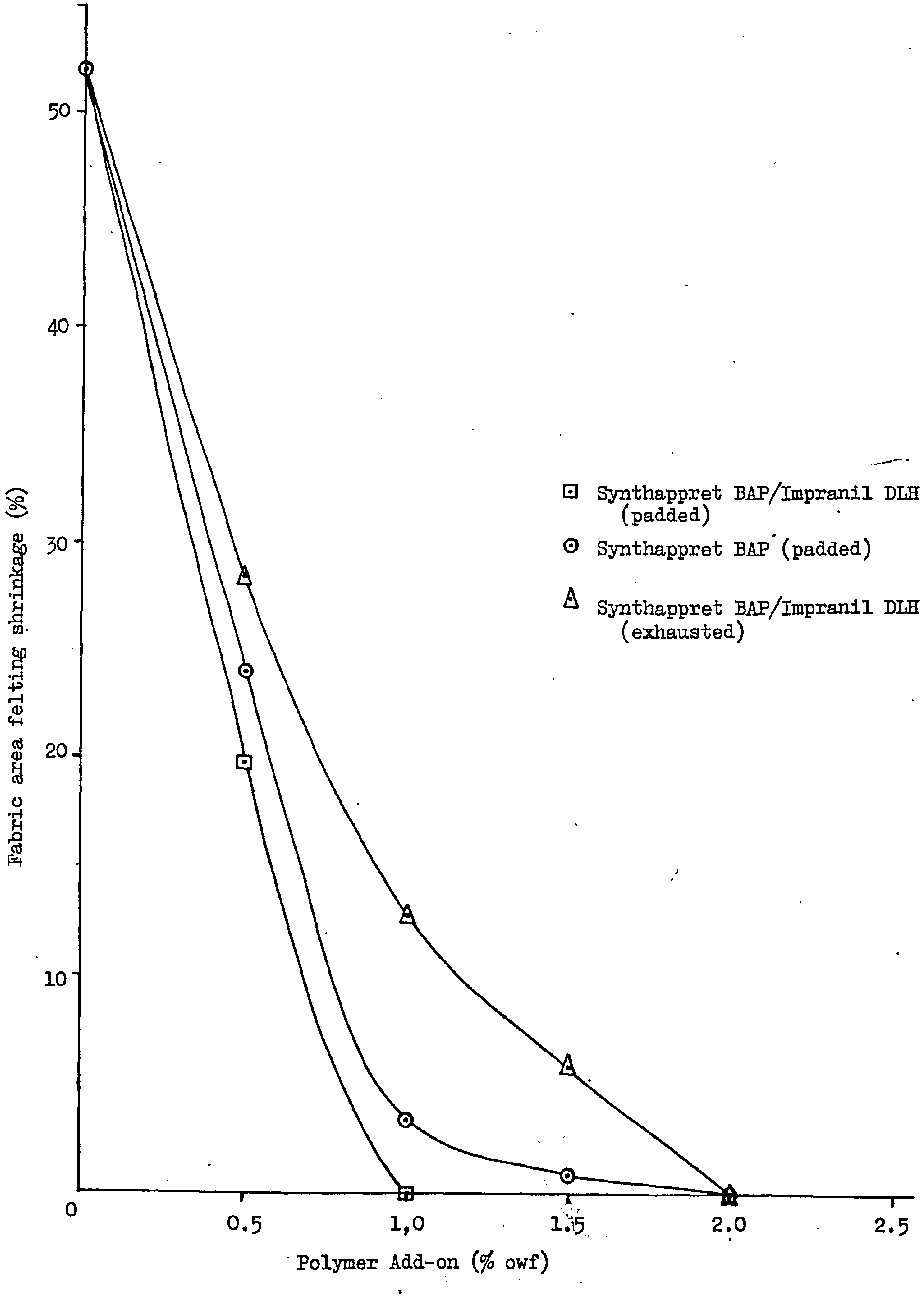
These conclusions are of especial relevance to woollen-spun wool fabrics in which fibre migration and felting must be prevented

TABLE 75. The effect of Synthappret BAP/Impranil DLH (by exhaustion) on the fabric area felting shrinkage (%) of fabric C (woollen)

Polymer Add-on (% o.w.f.)	Fabric C (woollen)			
	FAFS (%) after washing for			
	0.5 h	1 h	2 h	3 h
Untreated*	22.0	35.3	45.0	52.2
0.5	4.1	6.5	12.3	28.5
1.0	1.7	2.5	7.4	12.8
1.5	0	0.8	3.3	5.75
2.0	0	0	0	0
2.5	0	0	0	0

* For untreated fabric specifications see section 2.4.2.

Fig. 75 - The effect of polymer add-on on fabric area felting shrinkage (%) for woollen flannel



as the first step, from giving rise to surface fibres, pilling and subsequently loss of fibres through shedding during abrasion and wear. Worsted-spun fabrics behave somewhat differently because the mode of fabric abrasion is different and hence the improvements in MAR as a result of polymer treatments are of a lower order of magnitude (see sections 2.4.3.1. and 2.5.3.1.).

One interesting observation to be gathered from Fig. 75 is that the polymer dosage level to attain completely shrinkproof fabric after 3 hours treatment in the Cubex differs markedly according to the method of application of the polymer. Thus Synthappret BAP/Impranil DLH applied by exhaustion requires twice the polymer add-on compared with that required using the padding technique for polymer application. These results are clearly of great relevance in the promotion of high levels of shrink-resistance with minimum modification of the fabric handle and indeed this phenomenon has been noted by Allanach et al (259) in recent work who found the same ratio of 2:1 in polymer add-on terms when comparing exhaustion with padding.

2.7.3.2. Martindale Abrasion Resistance (MAR)

The Martindale abrasion resistance results for the various polymer shrink-resist treatments at 2.5% o.w.f. are illustrated in Table 76 . All samples had been given a 3 hour wash test in the 50 l Cubex machine followed by conditioning at 65% r.h. and 21°C for at least 3 days prior to abrasion testing.

It is clear from Table 76 that the increase in MAR previously reported (see sections 2.5. and 2.6.) for these polymer treatments is maintained and even improved after 3hours washing in the 50 l Cubex machine. These fabric samples were chosen specifically because they did not shrink in the wash test so that changes in area shrinkage

TABLE 76. The effect of Cubex washing for 3 h on the Martindale abrasion resistance of woollen flannel shrinkproofed using Synthappret BAP and Impranil DLH

2.5 (% owf) Polymer Add-on	Woollen Flannel		
	Abrasion Resistance (Rubs x 10^3)	mean	Mean Increase in MAR (%) after washing
Synthappret BAP/ Impranil DLH (padded)	18.7 19.0 19.2	19.0	413.5 (340.0)
Synthappret BAP/ Impranil DLH (exhausted)	9.5 9.2 9.2	9.3	152.0 (134.0)
Synthappret BAP (padded)	12.0 10.0 10.5	10.8	193.0 (170.3)

The above % values are calculated on the untreated value (100%)

The values in parentheses represent the mean increase in Martindale abrasion resistance after padding but before washing.

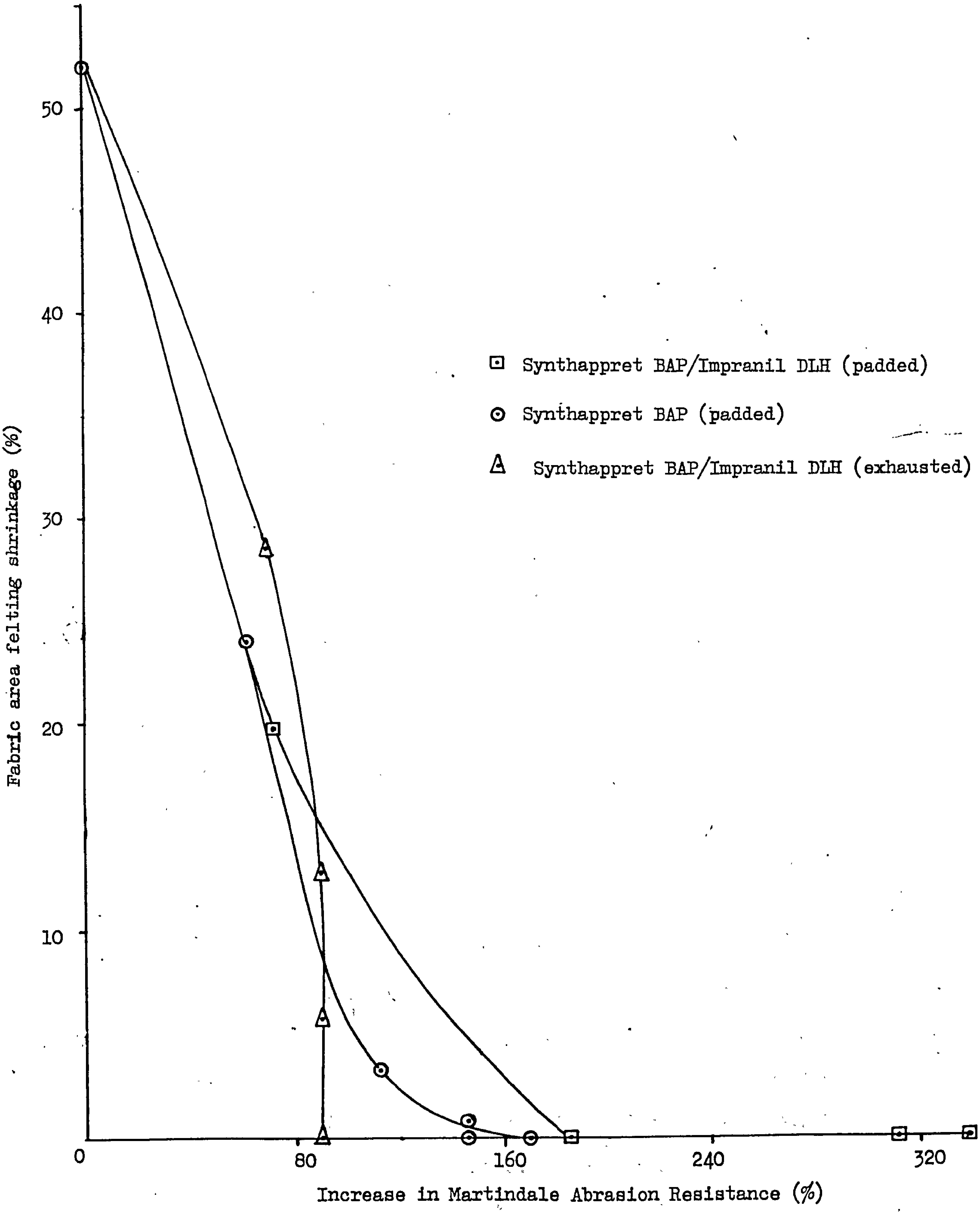
could not introduce any complicating side effects. All the percentage increase values quoted are expressed relative to the value for untreated, unwashed conditioned fabric (100%).

From Table 76 it can also be seen that the two polymer padding treatments are superior to the exhaustion treatment both before and after washing. These results are important because they demonstrate that provided a satisfactory level of shrink-resistance can be obtained, then an accompanying increase in the MAR results can also be obtained, and that the preferred method of treatment is via padding rather than exhaustion. In addition the improvement in MAR appears to be increased slightly after a 3 hour Cubex wash test. This is more noticeable in the case of the Synthappret BAP/Impranil DLH padding treatment.

One possible interpretation of the improvement in MAR after washing is that the wet agitation experienced in the Cubex test leads to the removal of any unfixed polymer and additionally it may sever some of the interfibre polymer bridges. The net result is thus to produce a more flexible polymer-treated fabric in which the capacity of the fibre polymer network to absorb the energy imparted to it during abrasion testing is increased, i.e. the fibre-polymer network approaches a new and higher equilibrium position in terms of its work-absorption capacity.

The physical properties of the polymer film are naturally of great importance and in Fig. 76 it is seen that superior shrink-resistance and MAR are obtained from the Synthappret BAP/Impranil DLH-treatment applied via the padding technique. As previously discussed the physical properties of Synthappret BAP are improved by the addition of Impranil DLH and as a result the synergistic

Fig. 76. - The relationship between fabric area felting shrinkage (%) and Martindale abrasion resistance for woollen flannel



effect is noted.

In accord with the improvement in fabric shrink-resistance obtained by padding vis à vis exhaustion, the improvement in MAR is shown in Table 76 to be even greater than the factor of 2:1 reported for shrink-resist effectiveness. This has also been discussed in section 2.5. of this work.

2.7.3.3. Changes in Fabric Properties as a result of 3 hour washing test

(i) Fabric Thickness

The changes in fabric thickness reflected in Table 77 demonstrate the marked compression of the fabric as a result of the padding process. While all the polymer-treated fabrics were subsequently blown to ensure satisfactory curing of the polymers, the main reduction in fabric thickness can be seen to emanate from the padding treatment, the reduction being much greater than for the corresponding polymer exhaustion treatment. Indeed the order of dimensional stability with regard to F.A.F.S. values mirrors the changes in fabric thickness. The greatest change in thickness corresponds to the greater dimensional stability and the order of stability thus decreases in the series 2.5% Synthappret BAP/Impranil DLH (by padding) > 2.5% Synthappret BAP (by padding) > 2.5% Synthappret BAP/Impranil DLH (by exhaustion) > Untreated.. Similar conclusions may be drawn for the same series of fabrics in the washed state (3 hour Cubex).

It is notable, however, that the fabric thickness increases as a result of wet agitation treatments and the untreated sample has clearly felted considerably (see Table 78). The MAR values are higher after washing treatment (Table 76) and while the F.A.F.S. values are zero, the recovery of the fabric after washing from the compression imposed by previous treatments is almost the same

TABLE 77. The effect of washing on the thickness of woollen flannel (fabric C)

STATE OF FABRIC	THICKNESS OF FABRIC C (mm)			
	Untreated	2.5% Synthappret BAP/ Impranil DLH (padded)	2.5% Synthappret BAP/ Impranil DLH (padded)	2.5% Synthappret BAP (padded)
Untreated	1.245	-	-	-
Blown	0.786	0.855	1.029	0.94
Washed*	3.25	1.332	1.501	1.447

* During washing only untreated fabric shrank

TABLE 78. The effect of various treatments on the thickness of woollen flannel (fabric C).

Treatment	Fabric Thickness (mm)					
	Untreated	Untreated Blown	Polymer treated ‡ and blown samples Add-on (% o.w.f.)			
			1	1.5	2.0	2.5
Before washing	1.25	0.79	0.95	0.92	0.92	0.86
After washing	3.25*	-	1.41	1.39	1.35	1.33

* Fabric felted in Cubex Washing Test

‡ Polymer Treatment - Synthappret BAP/Impranil DLH applied by padding

irrespective of the method of application for Synthappret BAP/ Impranil DLH. The order of fabric compression after washing is padded > exhausted, but the net increase in the fabric thickness is almost identical for both samples, e.g. padded 0.477 mm, exhausted 0.472 mm.

The increase in fabric thickness for the polymer-treated fabrics takes place with the formation of a considerable amount of surface fuzz which protrudes from the body of the fabric. This must contribute towards the softer handle of the fabrics, which have not shrunk otherwise, and leads to a greater initial degree of surface pilling during the Martindale Abrasion Testing. However, this does not lead to the formation of large pills and dramatic losses in fibres through shedding because the polymer film in the padded fabrics appears to be largely in the form of interfibre polymer bridges which prevent fibre migration and shedding.

(ii) Fabric Bending

Fabric stiffness has previously been shown to be an important component of fabric handle (271) and is markedly affected by the type of polymer and the treatment conditions (249). The results shown in Fig. 77 (see Table 79) demonstrate in accord with previously published work (248, 249) that washing treatments reduce the values of the fabric flexural rigidity (G_0). Padding clearly leads to a much stiffer fabric than that obtained by comparable exhaustion procedures (see section 2.5.3.5.). The higher compression of the fabric during padding and blowing must change the nature of the woven fabric structure considerably. As a result constraints are imposed on the fabric during bending primarily as a result of the increase in yarn/yarn interactions.

Fig.77.- The effect of Synthappret BAP/Impranil DLH on the flexural rigidity of woollen flannel

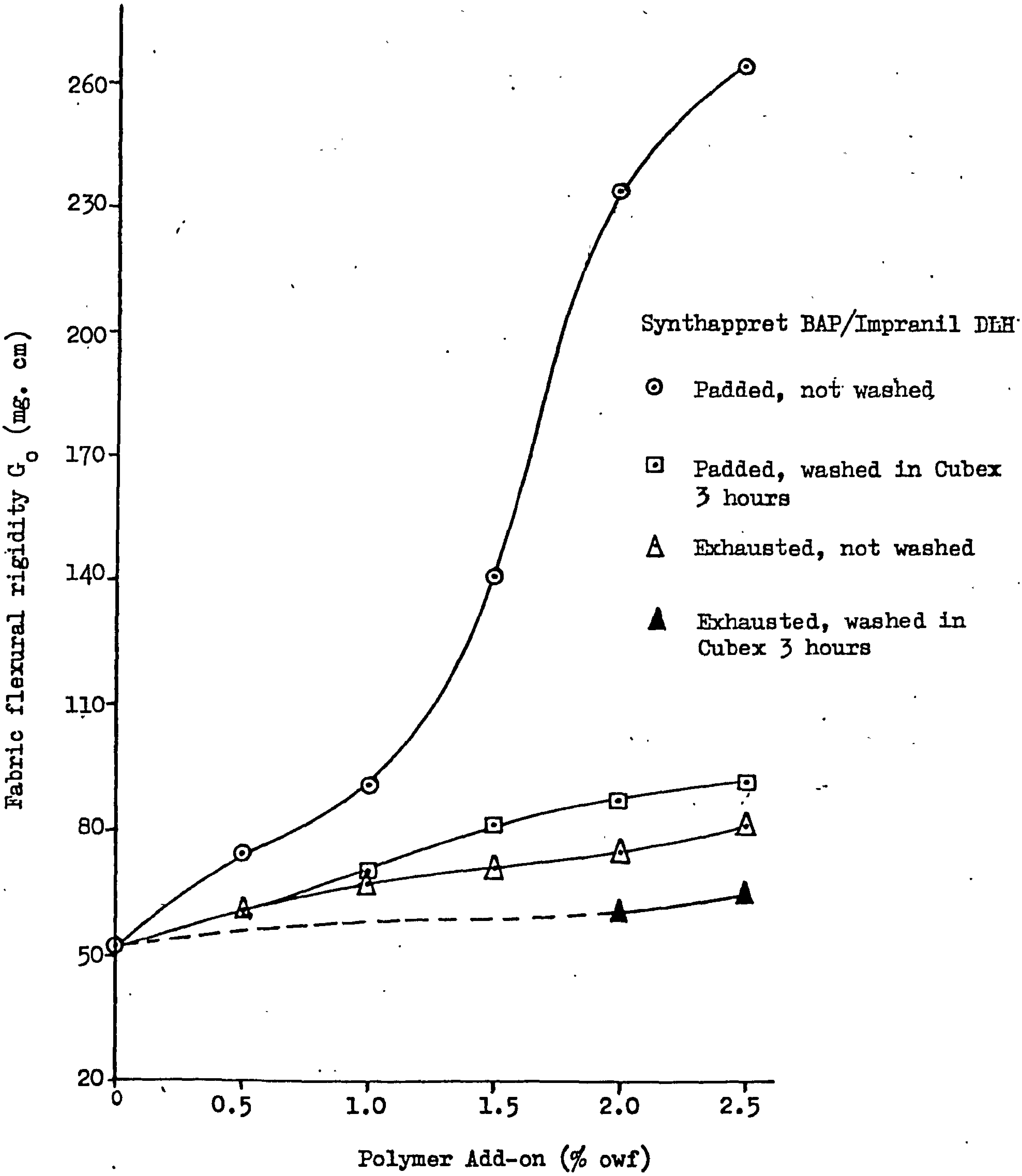


TABLE 79. The effect of washing in Cubex (3 h) on the flexural rigidity (G_o) and Coercive couple (C_o) of fabric C.

Polymer Add-on (% o.w.f.)	Padded		Exhausted	
	G_o (mg.cm)	C_o (mg.cm)	G_o (mg.cm)	C_o (mg.cm)
Untreated	53.0	31.6	-	-
1.0	69.3	30.6	-	-
1.5	81.5	32.6	-	-
2.0	86.6	38.2	61.2	30.6
2.5	91.7	35.6	65.2	30.6

The above values represent the mean values of three samples in weft-way direction.

However, it is notable in Fig. 77 that the values of G_o for padded fabrics are substantially reduced after washing, almost to the levels obtained in the exhaustion treatments before washing, but above 1% o.w.f. the values for the padded and washed fabrics are still slightly higher. This is considered to reflect the influence of the changes in the fabric structure and relaxation of yarn/yarn interactions that occur during washing, and the stiffer nature of the interfibre polymer bridges, i.e. the polymeric network within the fabric.

The polymer exhaustion treatments create smaller increases in G_o compared with the untreated fabric, and again, the values increase with increase in polymer add-on. The effect of washing in the Cubex for those samples that did not felt (i.e. $>$ 2% o.w.f. in this study) while reducing G_o, as previously observed with the padded samples, only leads to relatively minor changes. This is considered to reflect the mode of action of the polymer as a result of the exhaustion treatment, where the fabric is not compressed and fibre encapsulation is the major shrink-resist mechanism. Any changes imparted by the blowing treatment appear to be rapidly minimised by the Cubex treatment, for there are few, if any, interfibre bonds that can help in retaining the compressed state, and hence exert a marked influence on G_o. For the same reasons the C_o values for polymer-exhausted samples after washing are virtually the same as those for the untreated fabric and lower than those for the padded washed samples at the same polymer add-on. The reduction in yarn/yarn interactions is also to be seen in the dramatic reduction in C_o in the padded samples after washing, but the retention of the interfibre bonding leads to a higher C_o value compared with the untreated fabric.

Exhaustion treatments lead to a less stiff type of handle which is often considered desirable. However, washing padded fabric creates a very similar type of handle in this case and such aftertreatment would clearly be of importance in commercial treatments.

Discussion of Fabric Thickness and Bending Studies

The changes in fabric thickness as a result of the polymer padding treatment, followed by blowing for 20 s clearly demonstrate that the thickness decreases with increase in polymer add-on. Cubex washing treatments, however, relax the fabric so that while the effect of polymer add-on is still to be seen (see Table 78) the values have increased to a higher level. The changes in thickness after washing are fairly constant for the polymer-treated fabrics and moreover are believed to take place without extensive rupture of the interfibre polymer bridges.

These changes in fabric thickness are considered to contribute towards the reduction in G_o and to the accompanying improvement in fabric handle, which is markedly less stiff. Relaxation of the fabric structure during Cubex washing could also lead to some degree of improvement in MAR by virtue of the creation of a more uniform distribution and absorption of the abrasive forces during abrasion testing. Similar improvements have been noted in other relaxation treatments such as the action of organic solvents (see section 3.3.2.1.) and in scouring treatments (47).

The possibility also exists that removal of loose polymer within the fabric during washing could lead to a reduction in the frictional forces within the fabric, thereby leading to an improvement in the MAR. However, it seems more feasible that the mechanical action exerted in washing treatments is more likely to lead to a considerable reduction in the yarn/yarn interactions and to the rupture of a small number of interfibre polymer bridges. The resultant stress distribution and work-absorption within the washed fabric may as a consequence be more uniform in nature, leading to a small but measurable improvement in MAR.

2.7.3.4. The effects of blowing on the abrasion resistance and pilling of woollen flannel

The MAR of woollen flannel is improved slightly as a result of the 20 s blowing treatment (see Table 80). In addition the rate of pilling is slightly reduced compared with a similar fabric which had not been blown. These minor changes are considered to reflect the effect of decreasing the fabric thickness as a result of blowing, thereby producing a fabric with a more planar surface. However, the changes are small and do not materially affect the conclusions drawn in this work (section 2.4.4., 2.5.4. and 2.6.4.).

2.7.3.5. Crease Recovery Angle (CRA)

The results of the crease recovery angle (CRA) measurements are illustrated for different polymer add-on levels in Table 81.

Irrespective of the method of application, it is clear that the Synthappret BAP/Impranil DLH treatment improves the CRA of woven woollen flannel and this is in accord with the published results for other polymer shrink-resist treatments which improve the wrinkle recovery of wool fabrics (272, 273).

Nevertheless, Table 81 illustrates the differing nature of the results obtained at the same polymer add-on level by padding and by exhaustion treatments. For the exhaustion treatment the CRA is increased to 156.3° at 0.5% o.w.f. add-on and thereafter only minor

TABLE 80. The effect of blowing on the pilling during abrasion of flannel fabric (Fabric C)

NUMBER OF RUBS $(\times 10^3)$	No. of pills formed on woollen flannel during abrasion after blowing for 20 s.			
	Untreated Fabric		Untreated Blown Fabric	
	Pills	Mean	Pills	Mean
1	33 28 30	30	30 28 24	26
2	24 17 20	20	21 16 18	18
3	15 20 17	17	18 12 13	14
4	13 18 20	17	18 14 13	15

Untreated Fabric - Martindale Abrasion Resistance 3700 rubs
Untreated Fabric after Blowing - Martindale Abrasion Resistance 3900 rubs

TABLE 81. The effect of Synthappret BAP/Impranil DLH treatments on the crease recovery angle of woollen flannel

	Crease Recovery Angle (degrees)			
Polymer Add-on (%)	Applied by Padding	After Washing	Applied by Exhaustion	After Washing
0.5	155.3 (1)	*	155.3 (0.8)	*
1.0	157.3 (1.7)	156.3 (0.6)	156.5 (0.6)	*
1.5	157.8 (0.6)	157 (0.5)	157 (0.5)	*
2.0	160 (0.9)	158 (0.9)	156.5 (0.8)	156.5 (0.8)
2.5	161 (0.5)	161.8 (0.6)	156.8 (0.8)	156.3 (0.6)
Untreated	147.5 (1.1)			

* Samples not measured because of shrinkage during washing.

Values in parentheses are coefficients of variation (%).

changes take place even though the polymer add-on is increased to 2.5% o.w.f. In contrast, while the results at the 0.5% o.w.f. add-on level applied by padding yield the same level of improvement observed by the exhaustion treatment, the CRA continues to rise slowly with increase in polymer add-on to 161^{0} at 2.5% o.w.f. This is a significant improvement over the values for the untreated fabric (147.5^{o}) and a smaller, though no less significant, improvement over the values observed for the polymer exhaustion treatments.

Washing for 3 hours in the Cubex exerts hardly any noticeable effect upon the CRA of the polymer-treated fabrics studied, whether applied by exhaustion or by padding (see Table 81). However, it can be seen from Fig. 77 that there is a considerable reduction in the fabric flexural rigidity (G_o) after washing which leaves the fabric flexural rigidity slightly above the value for the polymer exhaustion treatment.

The explanation of the results of the crease recovery and flexural rigidity measurements is considered to be dependent upon the mechanical agitation of the fabric during the washing treatment in the Cubex. The major component of the fabric stiffness in padded fabric is considered to arise from the nature of the yarn/yarn interactions as a result of the compression of the fabric structure that occurs during padding and is retained by the fabric after curing (see section 2.7.3.3.). Mechanical forces applied to the fabric break down these interactions in the same manner that mechanical softening treatments reduce the fabric stiffness and this must be aided by fibre swelling and relaxation processes. Fabric stiffness has been demonstrated to be an important factor in determining the handle of wool fabrics (271). For these reasons the fabric which is compressed and stiff after padding and curing becomes softer and more pliable in handle after washing treatments. In addition the fabric thickness has been shown to increase after washing by approximately the same amount, irrespective of the polymer add-on for the samples studied in this work (see section 2.7.3.3.).

In polymer exhaustion treatments it has been demonstrated that the predominant mode of action is through encapsulation of the fibre surface by the polymer or by the stand-off mechanism. There is little evidence to support the proposition that interfibre bonds are formed. In addition, the fabric thickness is not compressed as in the padding process, and so the untreated fabric thickness is essentially retained through the process. This results in a fabric without the yarn-yarn interactions imposed by the geometrical constraints resulting from fabric compression during the polymer padding treatment, and with few, if any, interfibre bonds. The fabric handle is therefore markedly less stiff than that of a padded fabric.

SEM studies reveal that the interfibre bonds formed as a result of polymer padding processes are still substantially intact after washing for 3 hours in the Cubex (see Fig. 78). As a result the crease recovery properties of the fabric are retained, and these exhibit improved levels of performance over similar treatments applied via polymer exhaustion processes. The increased values of G_0 in the padded fabrics after washing compared with those obtained after polymer exhaustion are considered to arise from the presence of the fibre-fibre bonds in the former samples.

It seems clear, therefore, that the formation of interfibre bonds through polymer padding treatments is beneficial from the point of view of improved standards of performance in terms of shrink-resist

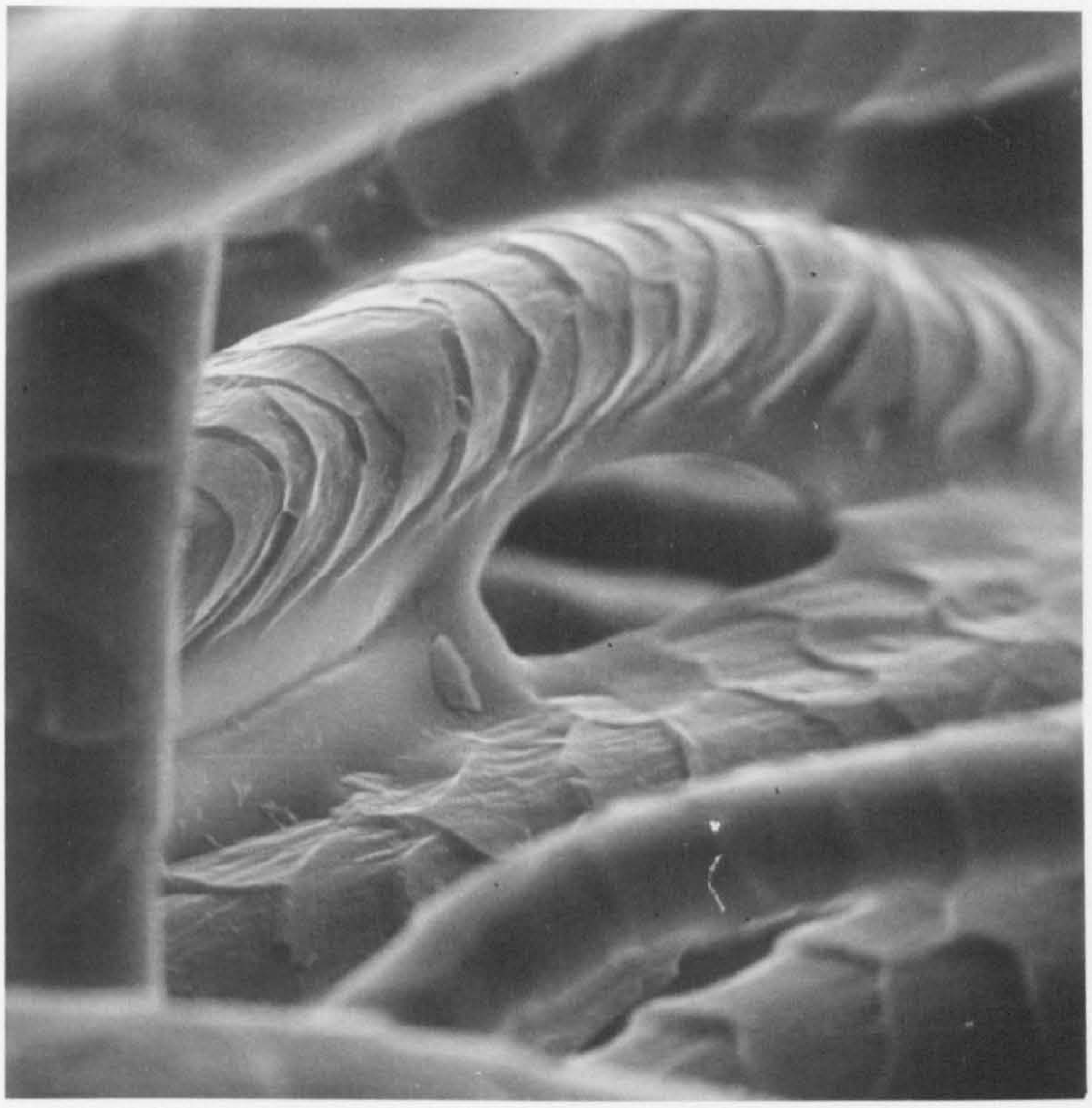


Fig. 78 - Woollen flannel - 2.5% Synthappret BAP/Impranil DLH applied by padding after 3 hours wash in the Cubex.

effectiveness, Martindale abrasion resistance and crease recovery.

Further work will be required to establish whether the presence of strong but flexible interfibre bonds will be beneficial in improving the wrinkle recovery properties of all-wool fabrics at high humidity levels. It is, however, considered that polymer padding-treatments should be more effective at the same polymer add-on level than polymer exhaustion processes for improving the easy-care performance of all-wool fabrics, where these are spun from short fibres.

As discussed previously, the improvements in Martindale abrasion resistance obtained from polymer padding treatments on all-wool worsted fabrics are of a lower order of magnitude because of the different mode of abrasion (see sections 2.4.3.1. and 2.5.3.1.). While, therefore, some improvement is to be expected in terms of resistance to creasing and wrinkling, it is probably that in all-wool worsted fabrics spun from long fibres that the fabric structure effect will be dominant and that the improvements obtained by polymer padding treatments will be much smaller, though no doubt beneficial from the performance point of view.

The effects of applied polymers on the crease recovery and wrinkle recovery of wool fabrics

Chapman (272) has conveniently summarised the various mechanisms by which elastomeric polymers may improve the wrinkle recovery of wool fabrics, viz.:

(a) the reduction of the frictional component impeding fabric recovery may be effected by the replacement of interfibre frictional contacts by elastic connections (274, 275).

(b) the rate, extent and final level of water sorption may be reduced by the presence of the surface-polymer coatings, resulting in less stress-relaxation during the wrinkling deformation (272).

(c) the deformation of the polymer during fabric bending provides an elastic restoring force that aids recovery. This latter effect may arise (i) from the deformation of the polymer coating on a single fibre (273) or (ii) from the deformation of the interfibre polymer connections (274, 275).

While experimental evidence has been presented by Denby (275) in support of mechanism (a), there does not appear to be any evidence to support mechanism (b) (276, 277). Support for mechanism (c) (i) is to be found in the work of Jones using polyether-hexamethylene diisocyanate polyurethanes and cross-linked silicones (273). However, it was thought that interfibre bonding had an adverse effect on the wrinkle recovery of fabrics because this limited fibre movement during wrinkling. This led to higher levels of strain in the wool fibres and hence to lower levels of wrinkle recovery. In other work, however, interfibre polymer connections appeared to improve the wrinkle recovery (272).

The current experimental work on the crease recovery of wool fabrics treated with Synthappret BAP/Impranil DLH is considered to be evidence which supports both mechanism (c)(i) and (c)(ii). Thus it has been proposed that at low polymer add-on levels ($<$ 0.5%) fibre encapsulation by polymer coating takes place and that this is the predominant mode of action irrespective of whether the polymer is applied via an exhaustion or a padding procedure. This clearly leads to a distinct improvement in CRA which is furthermore maintained at the same level for all the polymer add-on values applied via exhaustion. It is accordingly concluded that polymer treatments applied via exhaustion operate essentially through mechanism (c)(i) where surface-polymer coating takes place.

Previous studies (see sections 2.5.3.1. and 2.7.3.1.) have shown that with 0.5% o.w.f. Synthappret BAP/Impranil DLH applied by padding, both the shrink-resist effectiveness and Martindale abrasion resistance (MAR) are similar to that obtained at 0.5% o.w.f. by exhaustion and in the current work the improvement in CRA is also identical. This strongly supports the view that the mode of action proceeds through surface-polymer coating at low levels of polymer add-on irrespective of the method of application. In addition the Synthappret BAP/Impranil DLH film is strong but very flexible and is not removed during a 3 hour Cubex wash test (see Fig. 78). These properties are in accord with the assertion (273) that elastomeric polymers may improve the wrinkle recovery of wool provided there is good adhesion between the polymer and the wool and that little or no stress-relaxation of the polymer occurs during wrinkling.

In the specific case of application of Synthappret BAP/Impranil DLH by padding, it must be concluded that while mechanism (c)(i) is operative at low polymer add-on levels, a progressive increase in polymer add-on leads to an increase in the extent of interfibre bonding (see sections 2.5. and 2.6.). The net result is thus a further progressive improvement in CRA as mechanism (c)(ii) reinforces the improvement afforded through mechanism (c)(i).

The effects of a 3 hour Cubex test on the CRA values are minor for all polymer add-on levels applied via exhaustion or by padding (see Table 81). This supports the view previously arrived at from the maintenance of the MAR value and from SEM studies in which the interfibre bonding did not appear to be disrupted (see section 2.7.3.2. and Fig. 78). It was also noted that after a 3 hour Cubex test the values of the fabric flexural rigidity (G_o) for padded fabric were reduced to levels very close to, but consistently slightly above, those observed at the same polymer add-on applied via exhaustion (see section 2.7.3.3.). The latter were only slightly affected by the 3 hour Cubex test.

While the improvements in CRA obtained in this work by inter-fibre bonding are admittedly small, they have been previously shown to be accompanied by synergistic improvements in both shrink-resist effectiveness and MAR when Synthappret BAP/Impranil DLH is applied by padding (see section 2.6.3.6.). It is, therefore, of considerable interest to formulate improved polymer systems which lead to synergistic improvements in fabric performance. The use of more elastomeric polymer coatings and the promotion of inter-fibre bonding on both woollen and worsted fabrics through methods of application other than by exhaustion thus requires a more searching and systematic study. Apart from fabric structural parameters, the physical properties of thin polymers films and in particular the stress-relaxation behaviour of such films (272, 278) will clearly be of considerable importance in improving the easy-care properties of wool fabrics.

2.7.4. Conclusions

The addition of Impranil DLH to Synthappret BAP on a 1:1 weight basis has been shown to lead to a synergistic improvement in shrink-resist effectiveness. Application of the polymer via a padding technique leads to significantly greater improvements in both shrink-resist effectiveness and in Martindale abrasion resistance compared with those obtained by exhaustion at the same polymer add-on level.

Thus a synergistic improvement in resistance to felting of a woven woollen flannel is paralleled by a synergistic improvement in

MAR. These dramatic improvements are considered to be dependent upon the number and quality of the interfibre polymer bridges formed using this specific combination of polymers which restrict fibre movement within the fabric. Thus the formation of strong but flexible interfibre polymer bridges is promoted by padding treatments, and the synergistic improvement in MAR is maintained, and even slightly improved, after washing in a Cubex machine for 3 hours under standard conditions. This marginal improvement is considered to arise from the considerable reduction in yarn/yarn interactions and from the breakage of a small number of interfibre polymer bridges as a result of the mechanical action during the Cubex washing treatment. This subsequently leads to a better balance of work absorption within the fabric during abrasion testing.

Synthappret BAP/Impranil DLH treatments when applied via padding methods yield fabrics in which strong but flexible interfibre bonds are formed. When applied by polymer exhaustion the predominant mode of action is through encapsulation of the fibre surface. In padded fabrics, the presence of the interfibre bonds thus creates an improved level of crease recovery angle (CRA), which is greater than that observed in polymer exhaustion treatments at comparable add-on values.

The padding treatment and, to a lesser extent, the 20 s steam treatment in a blowing machine lead to appreciable compression of the woven fabric structure. The geometrical constraints imposed upon the fabric lead to increased yarn/yarn interactions which increase the resistance to fabric bending, and hence to an increase in the fabric flexural rigidity (G_o).

Washing for 3 hours in a Cubex test leads to fibre swelling and relaxation processes and to a return of the fabric towards the untreated thickness. There is thus a marked reduction in the values of G_0 which then approach the values observed in polymer exhaustion treatments. However, it is considered from the results of the SEM studies that most of the interfibre bonds are not ruptured during the 3 hour Cubex wash test and indeed these generate the improved values of CRA and the slightly higher values of G_0 in the padded fabric samples, both before and after washing.

The CRA results may be interpreted in terms of an improvement in the elastic restoring force aiding fabric recovery from bending as previously proposed for wrinkle recovery. For polymer exhaustion treatments this arises by mechanism (c)(i) the deformation of the polymer coating on a single fibre. For polymer padding treatments both mechanisms (c)(i) and (c)(ii) are operative, the latter mechanism arising from the deformation of the interfibre bonding.

It must, therefore be concluded that future research and development should be devoted to the exploitation of synergistic improvements in performance in both shrink-resist effectiveness and in abrasion resistance. In addition polymer treatments may lead to some improvement in the standard of wrinkle recovery in woven woollen fabrics, but it is considered that for worsted fabrics, the improvements will be small because of the different nature of the worsted fabric structure.

2.8. The effects of polyacrylate shrink-resist treatments

2.8.1. Introduction and Objectives

As has been shown earlier (see sections 2.4., 2.6.) and discussed in the literature survey (see section 1.8.5.) there are many types of preformed polymers that can be applied to wool fabrics for improving the physical properties and reducing the felting shrinkage. Of these types of polymers, polyacrylates have been widely used in many textile applications (155, 279-285) and several patents (286-290) have appeared which claim that the application of polyacrylates to wool fabrics reduces the felting shrinkage and increases the abrasion resistance.

Matlin and Nuessle (279) indicated that polyacrylates may be attached to wool by general adhesive forces. This concept has been extended through measurements of the surface properties of the polymers (162) and it has also been pointed out that the flow characteristics of the polymers must be correct for good results to be obtained.

Some polyacrylates impart a high degree of resistance to felting to woollen fabrics when 2-4% o.w.f. polymer is applied, but with others, 7% or more is required (279). These large differences can occur between classes of polyacrylates (155, 279) although within any one class the softer the polymer the better is the shrink-resist effect (155). The softness of the polymers is generally indicated by the value of the second-order or glass transition temperature (T_g). Most of the polyacrylates used commercially have T_g values in the range -30°C (soft) to +30°C (hard) (283, 285).

The object of this work was to study the physical properties of wool fabrics after treatment with a series of "self-cross-linking" polyacrylates or so-called "reactive acrylics". These contain reactive functional groups (carboxyl, amide, epoxy, or hydroxyl groups) which cause cross-linking when the polymers are heated in the presence of an acid catalyst (282).

2.8.2. Experimental

Materials

Fabric specifications: Fabric A (a worsted-spun fabric) and fabric C (a woollen-spun fabric) described in detail in section 2.4.2. were used.

Reagents:

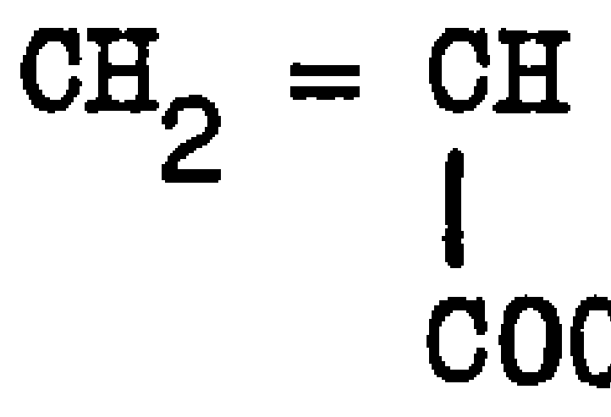
(i) Polyacrylates: The polyacrylates used were: Primal E-1070 (similar to K-3), HA-8, HA-12 and HA-16. These were aqueous dispersions containing 46% solids, supplied by Primal chemicals Pty. Ltd. The variations in T_g and polymer hardness are as follows:

Polyacrylate	T_g (°C)	Hardness
Primal E-1070	-32	Very soft
Primal HA-8	-16	Soft
Primal HA-12	+12	Medium
Primal HA-16	+30	Hard

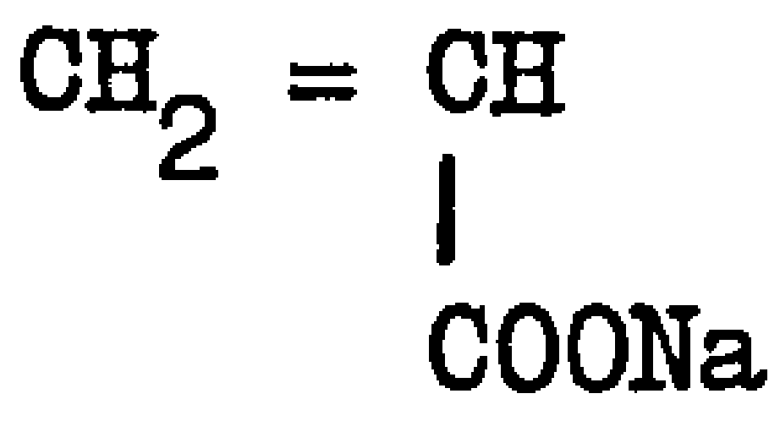
(ii) Ammonium chloride: Laboratory reagent grade (BDH).

Chemistry and Preparation of Polyacrylates

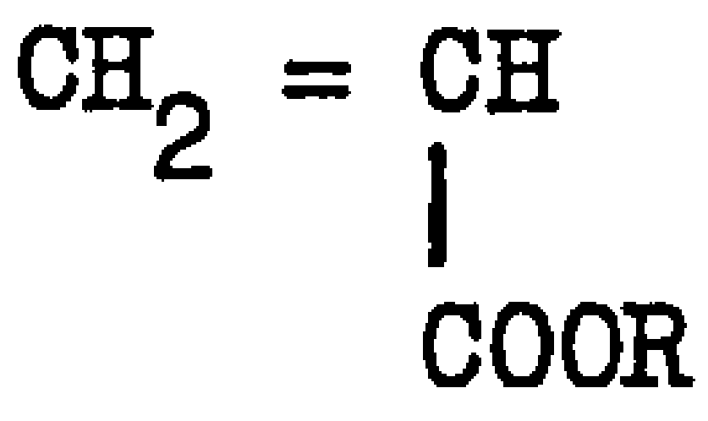
An acrylic polymer is one composed predominantly of esters or other derivatives of acrylic or methacrylic acid (280, 281, 282). Typical acrylic monomers, from which the polymers may be constructed, include: acrylic acid, methacrylic acid, and their salts, esters, amides and nitriles: (280).


$CH_2=CH-COOH$

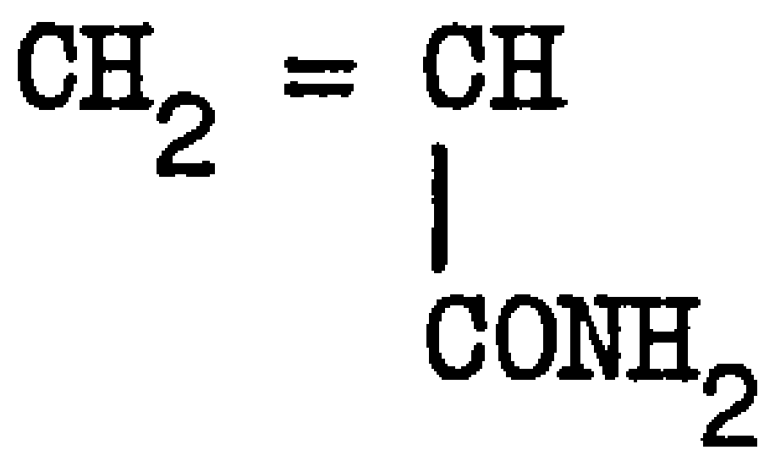
Acrylic Acid


$CH_2=CH-COONa$

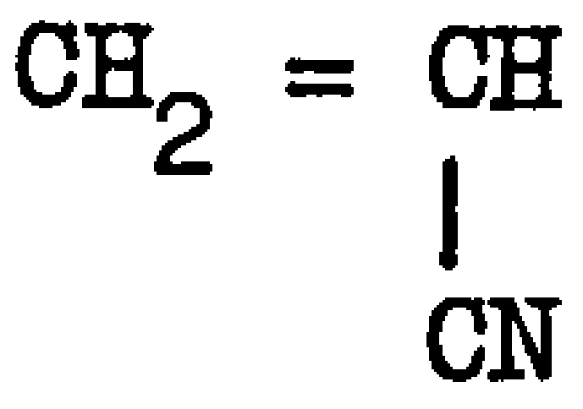
Sodium Acrylate


$CH_2=CH-COOR$

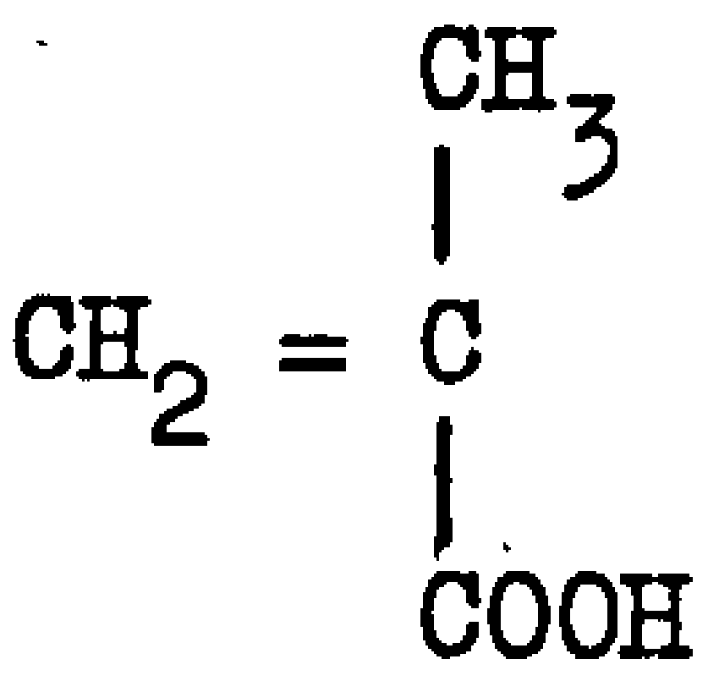
Acrylic Ester


$CH_2=CH-CONH_2$

Acrylamide


$CH_2=CH-CN$

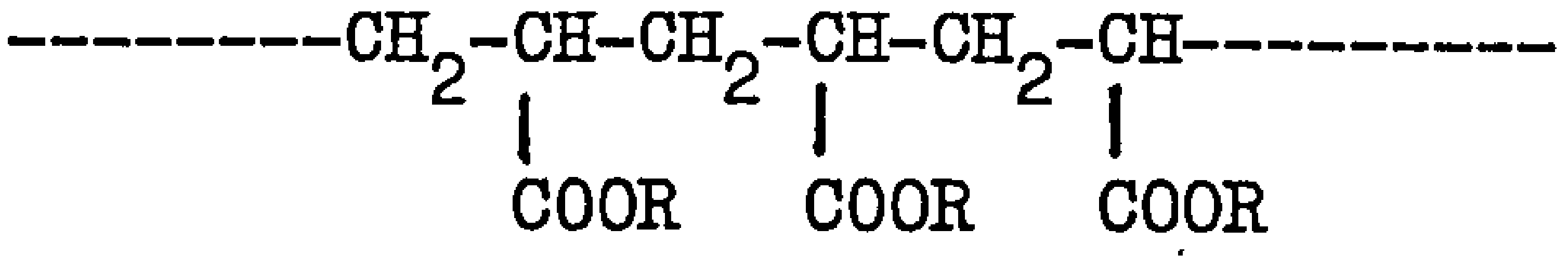
Acrylonitrile


$CH_2=C(CH_3)-COOH$

Methacrylic Acid

(etc.)

Any of these, alone or in combination, will undergo addition polymerization to form a linear polymer many thousands of units long (281).


$$-CH_2-\underset{COOR}{CH}-CH_2-\underset{COOR}{CH}-CH_2-\underset{COOR}{CH}-$$

In general an acrylic polymer may have a degree of polymerization as high as 10,000 to 50,000 monomer units (282).

By polymerization of a suitable mixture of such monomers, a polymer can be produced to suit a specific end-use. The exact choice of monomers to make up the polymer backbone is dictated by a number of considerations, one of the most important being the polymer hardness. Polymers based primarily on esters and acrylic acid will be soft, and will impart a soft handle to the fabric (280). The higher esters, such as butyl and octyl acrylate, yield even softer polymers than do methyl and ethyl acrylate. On the other hand, stiff polymers may be produced by copolymerization with methacrylate esters, particularly methyl and ethyl methacrylate, and these polymers impart a stiff handle to the fabric. This subject has been discussed in more detail elsewhere (271).

The application of the polyacrylates is normally made in one of three ways (281):

(i) From aqueous solution.
(ii) From solvent solution.
(iii) From aqueous dispersions.

The application of the polyacrylates was made from aqueous dispersions in the current work. The aqueous dispersions are made by emulsifying an appropriate mixture of monomers and then copolymerizing. The resulting product is a white, milky dispersion, containing tiny solid particles. Depending on the composition and method of preparation these usually range from 0.1 to 1 micron in diameter (281). The molecular weight of the polymer is very high, ranging from 100,000 to 5,000,000 or more.

Methods

Method of application: All the polyacrylates were applied by padding using a Konrad Peter pad mangle as described in section (2.4.2.) using 0.5% o.w.f. NH_4Cl as catalyst. All samples were dried at 100°C for 10 minutes, and cured at 140°C for 10 minutes in an air oven. Finally the samples were conditioned at 65% r.h. and 21°C for 3 days prior to testing.

Test Methods

The following test methods were employed as described previously.

(i) Cubex test for fabric area felting shrinkage (see section 2.6.2.).

(ii) Martindale abrasion test for flat abrasion resistance (see section 2.4.2.).

(iii) Tensile properties - fabric breaking load and breaking extension (see section 2.4.2.).

(iv) Flex abrasion resistance - the Stoll Flexing and Abrasion Tester (see section 2.6.2.).

(v) Fabric bending properties - the Shirley Cyclic Bending Tester (see section 2.4.2.).

2.8.3. Results and Discussion

2.8.3.1. Fabric Area Felting Shrinkage (F.A.F.S.)

The results of the F.A.F.S. tests after 1, 2 and 3 hours in a 50 l Cubex machine at 40°C for the polyacrylate-treated samples at different levels of polymer add-on are given in Table 82 and illustrated in Fig. 79 where the F.A.F.S.(%) after 3 hours in the Cubex is plotted against the polymer add-on.

It is clear that the harder the polyacrylate applied by padding the less effective the treatment is in reducing the felting shrinkage of the woollen-spun fabric C. Thus the order of decreasing effectiveness is the very soft polymer Primal E-1070 > Primal HA-8 (soft) > Primal HA-12 (medium) > Primal HA-16 (hard) > Untreated. This is in accord with previous studies (155, 156).

Comparing the results at any level of polymer add-on, the Primal E-1070 is much more effective than the other polyacrylates studied. Primal HA-16 at 1% add-on seems to be slightly more effective than Primal HA-8 and HA-12, although the results are closely spaced and the difference is probably not very significant. Experimental variations normally associated with high levels of felting shrinkage could also play a part. At higher add-on levels the order becomes Primal E-1070 > HA-8 > HA-12 > HA-16 > Untreated and this is maintained throughout (see Fig. 79). After 3 hours in the Cubex the Primal E-1070-treated sample at the 5% polymer add-on level shrank less than 2% in area, the HA-8-treated sample 13%, HA-12 24.5% and finally the HA-16-treated sample, at the same polymer add-on, about 30%. At lower levels of polymer add-on the felting shrinkage values are considerably higher.

TABLE 82. The effect of polyacrylates (by padding) on the Fabric Area Felting and Shrinkage (FAFS) (%) for Fabric C.

Polymer Add-on (% o.w.f)	Primal E-1070			Primal HA-8			Primal HA-12			Primal HA-16		
	FAFS (%) after washing for			FAFS (%) after washing for			FAFS (%) after washing for			FAFS (%) after washing for		
	1 h	2 h	3 h	1 h	2 h	3 h	1 h	2 h	3 h	1 h	2 h	3 h
Untreated*	35.3	45.0	52.2	—	—	—	—	—	—	—	—	—
1	12.1	26.3	38.6	24.2	37.99	46.8	24.2	38.0	47.4	24.2	38.0	45.0
2	9.4	17.5	30.6	13.7	27.04	38.0	16.0	30.6	41.2	21.2	34.7	43.1
3	0.8	5.7	12.9	8.2	20.5	30.6	9.8	22.0	37.3	20.5	31.9	42.5
5	0	0.8	1.7	4.9	8.17	12.9	6.6	13.7	24.4	10.5	19.7	29.9

* For untreated fabric specifications see section 2.4.2.

Fig. 79 - The Effect of polymer add-on on the F.A.F.S. (%) of fabric C (woollen) after 3 hours Cubex testing

In comparison with many of the other polymer shrink-resist treatments studied in this work, the polyacrylates do not by themselves appear to be very effective as shrink-resist treatments at low polymer add-on values. This can be seen by comparing Fig. 79 with the results of other shrink-resist treatments (see Fig. 73, 75).

The softer the polyacrylate, the more effective the shrink-resist treatment. It is considered that this must reflect the ability of the polymer film to form interfibre polymer bridges and hence to withstand repeated flexing and to resist rupture. Thus the improved molecular flexibility of the softer polyacrylate system is manifested by marked physical changes in the polymer film which improve the capability of the system to resist rupture.

Steiger (155) and Feldtman and McPhee (156) in similar studies showed that as the T_g value decreased the shrink-resist effectiveness increased and they concluded that soft elastic polymers are necessary to effect shrink-resistance. However, in another study on a variety of polyisocyanates having different back-bone structures it has been shown (292) that softness was not a necessary prerequisite for the control of felting shrinkage. Polymers based on polyester diols and polybutadiene polyols formed quite hard films but were extremely effective shrink-resist treatments. The general conclusion from these further studies was that for maximum effectiveness the polymer should form tough, rather than brittle, films. This was confirmed to a certain extent with Impranil DLH treatments where another brittle film is formed and ineffective shrink-resistance is obtained. However, no detailed quantitative measurements on film properties were made to support this conjecture conclusively.

Thus from this present work it could be concluded that polyacrylates with a T_g above -30°C either form brittle films and are not capable of resisting rupture during a 3 hour Cubex test and/or alternatively they undergo stress-relaxation too readily. The stress-relaxation properties of the polymers have been claimed by Jones (273) to be an important factor determining the wrinkle-recovery of polyacrylate-treated wool fabrics.

2.8.3.2. Martindale Abrasion Resistance (MAR)

From the results of the effects of polyacrylates on the MAR of fabric C (woollen) (see Fig. 80 and Table 83) and fabric A (worsted) (see Table 84), it is evident that the polyacrylate treatments improve the MAR of the two woven wool fabrics. Generally an increase in polymer add-on leads to an increase in MAR in agreement with previous work (154, and see sections 2.4.3.1., 2.5.3.1.).

From Fig. 80 it can be seen that for fabric C,up to 3% polymer add-on, the order of improvement in MAR is Primal E-1070 > HA-8 > HA-12 > HA-16 > Untreated, and this is the same order as that previously observed from shrink-resist effectiveness. At 5% polymer add-on Primal HA-16 is still the least effective of the polymer treatments but still better than the untreated fabric. There is, however, very little to choose between the Primal E-1070, HA-8 and HA-12. This series of experiments again suggests that a relationship between shrink-resistance and abrasion resistance exists for fabric C and that similar mechanisms are involved for improving both the abrasion resistance and reducing felting shrinkage.

From Table 84 where the increase in MAR is tabulated against the polymer add-on for the various polyacrylates on fabric A (worsted), the results obtained are clearly not as conclusive. Generally on increasing the polymer add-on the abrasion resistance is increased

Fig. 80 - The Effect of polyacrylates applied by padding on the Martindale abrasion resistance of fabric C (woollen).

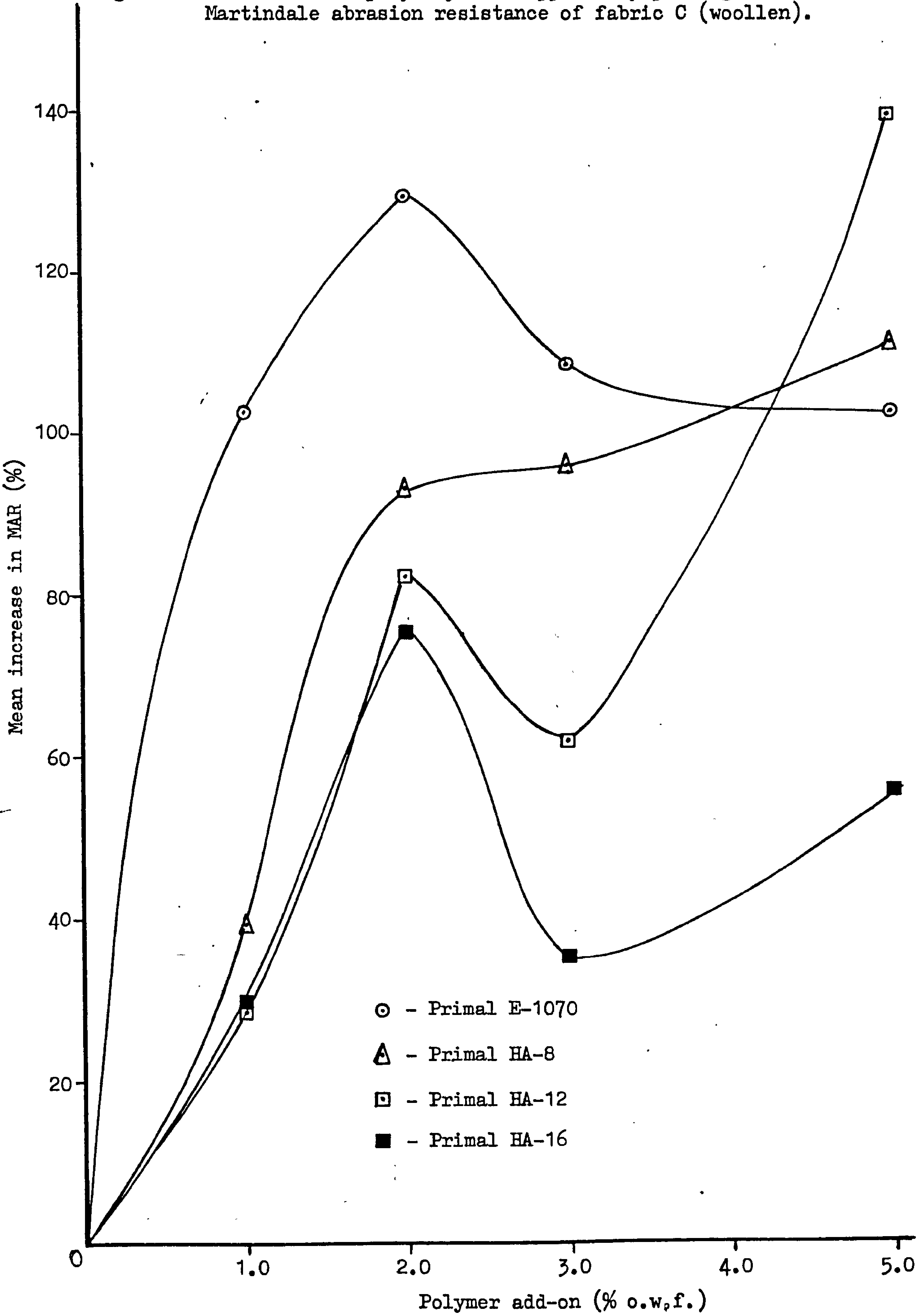


TABLE 83. Martindale Abrasion Resistance of fabric C (woollen) treated with polyacrylates (by padding).

Polymer Add-on (% o.w.f)	Primal E-1070		Primal HA-8		Primal HA-12		Primal HA-16	
	Martindale Abrasion Resistance (Rubs x 10^3)	mean	Martindale Abrasion Resistance (Rubs x 10^3)	mean	Martindale Abrasion Resistance (Rubs x 10^3)	mean	Martindale Abrasion Resistance (Rubs x 10^3)	mean
Untreated*	3.6 3.6 3.6	3.7 (0)	—	—	—	—	—	—
1	7.5 7.5 7.5	7.5 (102.7)	5.2 5.2 5.0	5.2 (39.4)	5.0 4.7 4.5	4.7 (28.4)	5.2 4.7 4.5	4.8 (30.5)
2	9.5 8.0 8.0	8.5 (129.7)	7.0 7.2 7.2	7.2 (93.5)	6.7 6.7 6.7	6.7 (82.4)	6.5 6.5 6.5	6.5 (75.7)
3	7.7 7.5 7.5	7.6 (105.4)	7.2 7.5 7.0	7.2 (96.0)	5.7 6.0 6.2	6.0 (62.2)	5.0 5.0 5.0	5.0 (35.1)
5	7.5 7.5 7.5	7.5 (102.7)	7.7 7.5 8.0	7.8 (111.6)	8.5 9.0 9.0	8.8 (139.0)	6.0 6.0 5.2	5.7 (55.4)

* For untreated fabric specificatins see section 2.4.2.

The values in the parentheses represent the mean increase (%) in MAR.

TABLE 84. Martindale Abrasion Resistance of fabric A (worsted) treated with polyacrylates (by padding).

Polymer Add-on (% o.w.f)	Primal E-1070		Primal HA-8		Primal HA-12		Primal HA-16	
	Martindale Abrasion Resistance		Martindale Abrasion Resistance		Martindale Abrasion Resistance		Martindale Abrasion Resistance	
	(Rubs x 10^3)	mean	(Rub x 10^3)	mean	(Rubs x 10^3)	mean	(Rubs x 10^3)	mean
Untreated*	13.0 12.5 10.2	11.9	—	—	—	—	—	—
1.5	12.5 15.0 12.0	13.2 (10.9)	14.0 14.0 14.0	14.0 (17.6)	15.0 15.0 15.0	15.0 (26.0)	12.0 12.0 12.0	12.0 (0.8)
3.0	13.0 15.0 12.0	13.3 (11.8)	16.0 15.0 15.0	15.3 (28.6)	15.0 16.0 15.0	15.3 (28.5)	13.5 12.5 12.5	12.8 (7.8)
4.5	13.0 15.5 12.0	13.5 (13.4)	11.0 12.0 13.0	12.0 (0.8)	15.0 17.0 16.0	16.0 (34.4)	17.0 18.5 17.0	17.5 (47.0)
6.0	15.5 12.0 14.0	13.8	16.0 16.0 16.0	16.0 (34.4)	11.0 14.0 12.0	12.3 (3.4)	15.0 17.0 15.0	15.6 (31.6)

* For untreated fabric specifications see section 2.4.2.

The values in parentheses represent the mean increase (%) in MAR.

only slightly and while the results were reproducible within a set of samples wide variations in MAR are to be noted with polymer add-on.

Primal E-1070 was the only polyacrylate to give a relatively smooth increase with increase in polymer add-on, although greater values for MAR were obtained with the other treatments, except in the case of Primal HA-8 at 4.5% add-on and HA-12 at 6% add-on, where lower levels of improvement in MAR were observed. The degree of improvement in MAR for fabric A, however, is far lower than that obtained on fabric C and as noted with other polymer treatments applied by padding (see sections 2.5.3.1. and 2.6.3.1.). The fabric structure clearly plays an important role in the improvement of MAR of wool fabrics.

Thus on woollen-spun fabric a maximum increase of about 130% was recorded for 2% add-on of Primal E-1070, and increases of up to 300% have been reported elsewhere (156). However, on fabric A (worsted-spun) an increase of not more than 28% was recorded for the same polymer add-on.

2.8.3.3. Fabric Tensile Properties

Tables 85 and 86 illustrate the results of the breaking load and breaking extension tests on the treated fabric samples of fabric C and fabric A respectively. The results indicate that all the polymers cause significant increases in breaking load but without any particular order of improvement for the different polymers studied. Generally, by increasing the polymer add-on the breaking load is increased as previously observed (in sections 2.4.3.4., 2.5.3.6., 2.6.3.4. and 142, 250-253).

The breaking extension for fabric C after treatment with polyacrylates was increased to a certain extent (maximum 13.5%) but not to the same degree as the breaking load (maximum 52.9%). For fabric A,

TABLE 85 The Effect of Polyacrylates (by padding) on the Tensile Properties of Fabric C (woollen)

Polymer Add-on (% o.w.f)	Primal E-1070				Primal HA-8				Primal HA-12				Primal HA-16			
	Breaking Load		Breaking Extension		Breaking Load		Breaking Extension		Breaking Load		Breaking Extension		Breaking Load		Breaking Extension	
	(kg)	Mean	(%)	Mean	(kg)	Mean	(%)	Mean	(kg)	Mean	(%)	Mean	(kg)	Mean	(%)	Mean
Untreated*	8.8 8.8 8.8	8.8 (0)	39.0 34.0 38.0	37.0 (0)	-	-	-	-	-	-	-	-	-	-	-	-
1	12.5 12.6	12.5 (42.1)	37.0 39.0	38.0 (2.7)	10.5 10.9	10.7 (21.1)	42.0 42.0	42.0 (13.5)	11.1 10.6	10.8 (22.8)	39.0 37.0	38.0 (2.7)	11.0 11.2	11.1 (25.7)	38.0 40.0	39.0 (5.4)
2	12.7 12.2	12.4 (41.0)	40.0 40.0	40.0 (8.1)	11.8 9.5	10.6 (20.6)	40.0 37.0	38.5 (4.0)	12.0 11.9	11.9 (35.2)	40.0 37.0	38.5 (4.0)	12.2 11.3	11.7 (33.0)	43.0 39.0	39.0 (5.4)
3	13.8 12.9	13.3 (51.2)	42.0 39.0	40.5 (9.4)	11.2 11.0	11.1 (25.7)	40.0 37.0	38.5 (4.0)	12.4 12.2	12.3 (39.3)	40.0 38.0	39.0 (5.4)	11.8 11.8	11.8 (33.6)	37.0 39.0	38.0 (2.7)
5	11.0 11.3	11.1 (26.2)	37.0 39.0	38.0 (2.7)	11.7 11.7	11.7 (32.5)	37.0 39.0	38.0 (2.7)	13.5 13.5	13.5 (59.2)	40.0 39.0	39.5 (6.7)	12.4 12.8	12.6 (42.7)	37.0 37.0	37.0 (0)

* For untreated fabric specifications see section 2.4.2.
The values in parentheses represent the mean increase (%) in Fabric Tensile Properties.

TABLE 86 The Effect of Polyacrylates (by padding) on the Tensile Properties of Fabric A (worsted)

Polymer Add-on (% o.w.f.)	Primal E-1070				Primal HA-8				Primal HA-12				Primal HA-16			
	Breaking Load		Breaking Extension		Breaking Load		Breaking Extension		Breaking Load		Breaking Extension		Breaking Load		Breaking Extension	
	(kg)	Mean	(%)	Mean	(kg)	Mean	(%)	Mean	(kg)	Mean	(%)	Mean	(kg)	Mean	(%)	Mean
Untreated*	14.3 14.2 13.9	14.2 (0)	36.0 34.0 32.5	34.2 (0)	-	-	-	-	-	-	-	-	-	-	-	-
1.5	15.6 15.6	15.6 (+9.8)	35.0 39.0	37.0 (+8.3)	15.0 15.3	15.1 (+6.6)	25.0 30.0	27.5 (-19.5)	15.9 16.7	16.3 (+14.8)	32.0 34.0	33.0 (-2.9)	17.2 15.6	16.4 (+15.3)	29.0 30.0	29.5 (-13.7)
3.0	16.1 15.8	15.9 (+12.3)	37.0 38.0	37.5 (+9.8)	15.7 15.6	15.6 (+10.2)	29.0 36.0	32.5 (-4.8)	16.4 16.2	16.3 (+14.8)	34.0 33.0	33.5 (-1.9)	16.0 15.9	15.9 (+12.3)	35.0 30.0	32.5 (-4.8)
4.5	16.9 18.2	17.5 (+23.5)	38.0 43.0	40.5 (+18.6)	15.9 16.0	15.9 (+12.3)	39.0 36.0	37.5 (+9.7)	20.5 20.5	20.5 (+44.4)	30.0 31.0	30.5 (-10.8)	16.6 16.6	16.6 (+16.9)	35.0 37.0	36.0 (+5.4)
6.0	15.9 15.6	15.7 (+10.5)	38.0 36.0	37.0 (+8.3)	16.4 15.9	16.1 (+13.7)	33.0 37.0	35.0 (+2.4)	21.2 20.7	20.9 (+47.5)	31.0 32.0	31.5 (-7.8)	17.2 17.3	17.2 (+21.4)	37.0 40.0	38.5 (+13.1)

* For untreated fabric specifications see section 2.4.2.
The values in parentheses represent the mean change (%) in Fabric Tensile Properties + = increase, - = decrease.

the breaking extension was generally relatively unaffected, the values ranging from -19.5% to +13.5% of the untreated value. In the case of Primal E-1070 an increase with all polymer add-on values was recorded.

2.8.3.4. Flex abrasion resistance

The results of the effects of the polyacrylate treatments on the flex abrasion resistance of wool fabric C (woollen-spun) are shown in Table 87. These results indicate that the flex abrasion resistance is improved by the polyacrylate treatments and with some of these to quite a considerable extent (almost to the same level as Synthappret BAP/ Impranil DLH). It is clear that the second-order or glass transition temperature (T_g) of the polyacrylates, plays an important role in the flex abrasion resistance properties and that the softer the polyacrylate (i.e. lower T_g), the greater the improvement in the flex abrasion resistance. Generally by increasing the polymer add-on the flex abrasion resistance is increased as in the case for flat abrasion resistance.

2.8.3.5. Fabric Bending Properties

The results of the effects of the polyacrylate treatments on the flexural rigidity (G_o) and coercive couple (C_o) of wool fabrics are given in Tables 88 and 89. In Fig. 81 and 82 the flexural rigidity G_o is plotted against the polymer add-on for fabric C and fabric A respectively. From these two figures it is clear (and in accordance with previous work 156, 248, 249 and sections 2.4.3.3., 2.5.3.5. and 2.6.3.5.) that G_o increases with increase in polymer add-on. The most dramatic changes are to be seen on fabric C compared with fabric A where only minor changes are observed.

The effect of the polyacrylates on the stiffness and handle of the wool fabrics is as expected from the description of the polymers.

TABLE 87. The effect of polyacrylates (by padding) on the flex abrasion resistance of fabric C (woollen).

Polymer Add-on (% o.w.f)	Primal E-1070		Primal HA-8		Primal HA-12		Primal HA-16	
	Flex Abrasion Resistance		Flex Abrasion Resistance		Flex Abrasion Resistance		Flex Abrasion Resistance	
	cycles	mean	cycles	mean	cycles	mean	cycles	mean
Untreated	160 165 175	167 (0)	—	—	—	—	—	—
1	460 390 393	410 (145.5)	205 245 205	220 (19.7)	302 287 320	305 (82.6)	315 295 298	305 (82.1)
2	508 522 520	515 (208.3)	395 315 310	340 (103.6)	350 338 310	335 (100)	305 340 275	310 (85.6)
3	460 442 500	465 (166.4)	370 412 365	380 (127.5)	345 320 323	330 (97.6)	288 260 235	260 (55.6)
5	550 530 520	530 (217.3)	400 396 376	395 (136.5)	415 425 400	415 (148.5)	354 362 350	355 (112.5)

The values in parentheses represent the mean increase (%) in fabric flex abrasion resistance.

TABLE 88. The effect of polyacrylates (by padding) on the flexural rigidty (G_o) and coercive couple (C_o) of fabric C (woollen).

Polymer Add-on (% o.w.f)	Fabric C (woollen)							
	Primal E-1070		Primal HA-8		Primal HA-12		Primal HA-16	
	G_o (mg.cm)	C_o (mg.cm)	G_o (mg.cm)	C_o (mg.cm)	G_o (mg.cm)	C_o (mg.cm)	G_o (mg.cm)	C_o (mg.cm)
1	61.2	34.7	65.2	32.6	86.6	48.4	73.3	44.8
2	71.4	45.0	77.5	37.7	96.8	58.6	76.4	53.5
3	84.1	40.8	107.0	53.5	132.5	68.8	127.4	86.6
5	86.6	43.3	122.3	63.7	193.6	122.0	163.0	112.0

TABLE 89. The effect of polyacrylates (by padding) on the flexural rigidity (G_o) and coercive couple (C_o) of fabric A (worsted).

Polymer Add-on (% o.w.f)	Fabric A (worsted)							
	Primal E-1070		Primal HA-8		Primal HA-12		Primal HA-16	
	G_o (mg.cm)	C_o (mg.cm)	G_o (mg.cm)	C_o (mg.cm)	G_o (mg.cm)	C_o (mg.cm)	G_o (mg.cm)	C_o (mg.cm)
1.5	35.7	6.1	38.7	6.6	38.7	8.0	35.6	8.6
3.0	37.2	8.2	39.8	8.7	41.0	13.2	37.7	14.0
4.5	37.7	8.7	39.8	7.6	61.1	34.6	44.8	14.2
6.0	40.8	10.2	39.8	7.6	71.3	36.7	57.0	32.0

Values for untreated Fabric C - $G_o = 53$ $C_o = 31.6$
Fabric A - $G_o = 34.7$ $C_o = 8.2$

Fig. 81 - The Effect of polyacrylates (by padding) on the flexural rigidity of fabric C (woollen).

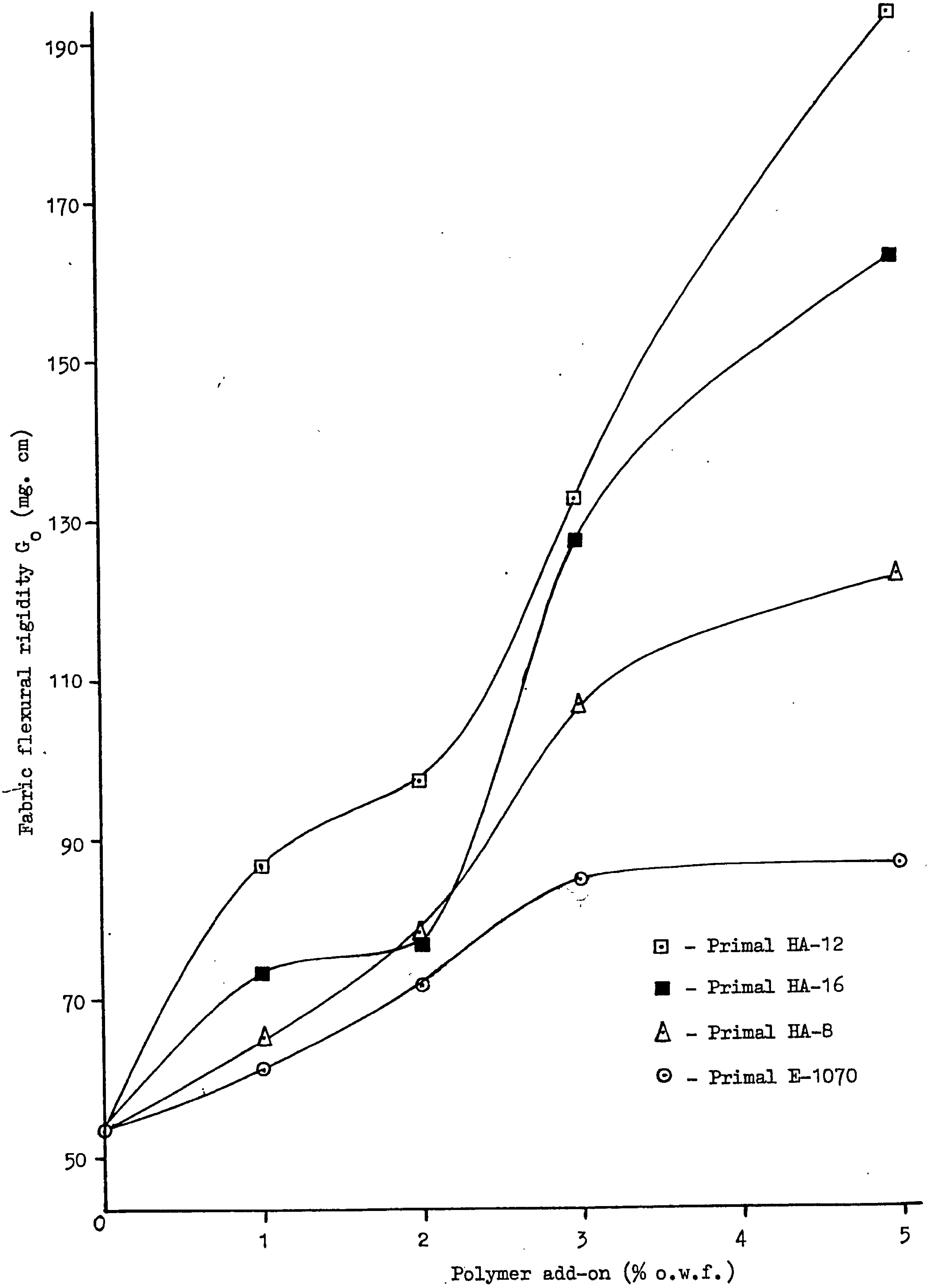
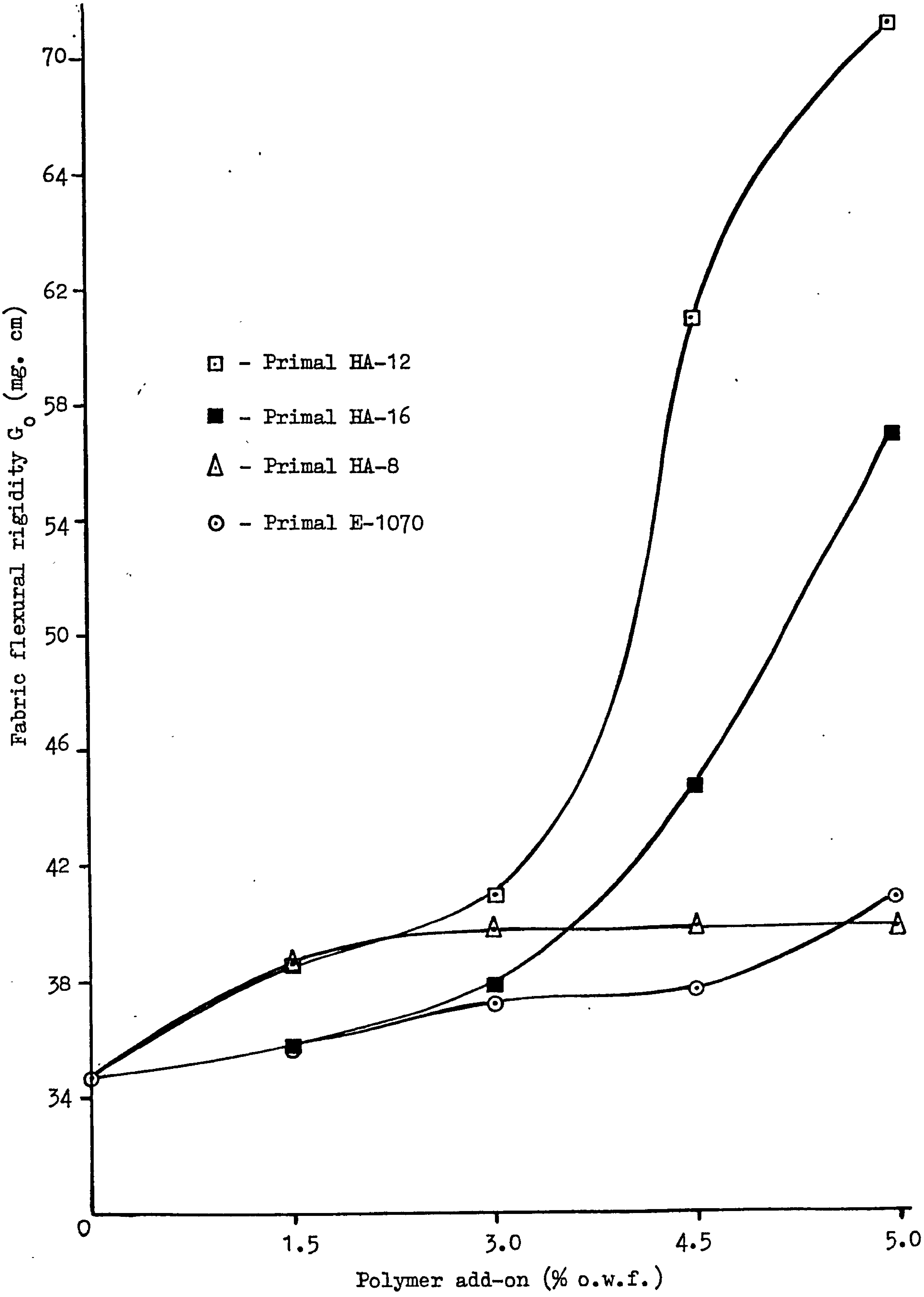


Fig. 82 - The Effect of polyacrylates (by padding) on the flexural rigidity of fabric A (worsted)



Soft polymers give a soft handle (with Primal E-1070 the handle is scarcely affected compared with untreated fabric), while harder polymers make fabrics harsher and stiffer (281, 282). The only exception was the Primal HA-12 polymer which gave a stiffer fabric than HA-16 at the same add-on levels. HA-16 theoretically was expected to give the maximum stiffness compared with the others. This phenomenon was observed with both the fabrics studied.

The results of the changes in the coercive couple C_o yield a similar pattern to that of G_o, indicating that the restraint to fibre bending and movement within the fabric is more greatly promoted by the harder (higher T_g) polymers. Primal HA-12 polyacrylate as in the case of G_o exhibited the maximum C_o value. The changes in C_o for the softer polyacrylate treatments are generally only marginal on both fabric A and C.

2.8.4. Conclusions

It is clear from the results of all this work that the polymer treatments for shrink-resist effectiveness and MAR of woven wool fabrics are dependent not only on the T_g of the polymers, but also on the type and quality of interfibre bonds as well as the fabric structure and method of polymer application.

The softer the polymer (i.e. the lower the T_g as studied in the polyacrylate system) the more effective the MAR results and the shrink-resist effectiveness. Both are increased as the polymer add-on values increase, but the results do not consistently increase with decrease in the T_g of the polymers applied.

Generally all the polyacrylate treatments, independent of the T_g, increased the breaking load and breaking extension of the wool fabrics, which appear to be of little importance in affecting the MAR results.

The flex abrasion resistance results are more consistent in that there is an increase with polymer add-on and with a decrease in the T_g of the polymers. The results of flex abrasion resistance of the polyacrylate treatments are close to those obtained with Synthappret BAP/Impranil DLH treatment (by padding), but considerably higher add-on levels were required using polyacrylates.

As with the other polymer shrink-resist treatments the flexural rigidity G_o and coercive couple C_o were increased with increase in the polymer add-on and generally the harder the polymer the higher the increases in G_o and C_o.

The fabric structure as discussed in sections 2.4.3. and 2.5.3. is very important and the results appear to be more consistent on woollen fabrics rather than worsted where the improvements are less pronounced.

It must, therefore, be concluded that the ability of the polyacrylate treatments to form interfibre bonds and the effects of the T_g of the polyacrylates studied require further investigation to elucidate in greater detail the mode of action in improving the MAR and flex abrasion resistance of woollen and worsted-spun wool fabrics. T_g is clearly not the only important factor determining the number, nature and quality of interfibre bonds formed in polyacrylate shrink-resist treatments. Polyacrylates do not appear to be very effective as shrink-resist treatments even at considerably higher add-on levels compared with other treatments such as Synthappret BAP and Synthappret BAP/Impranil DLH. This is in accord with the work of Guise and Rushforth (292) on the shrink-resist effectiveness of polyisocyanates on wool fabrics where it was shown that the T_g of the polymers is not the only necessary requirement for shrink-resist effectiveness.

The effect of the fabric structure and washing treatments also require further investigation as well as SEM studies to establish the quantity and quality of interfibre bonds formed as a result of using polymers of different T_g values.

CHAPTER 3

The Effects of Organic Solvents on the Abrasion Resistance of Woven Wool Fabrics

3.1. Introduction and Objectives

Considerable interest has been shown in the development of processing methods for textile fabrics in which an organic solvent such as perchloroethylene replaces water as the processing medium (293). Solvent processing has not yet developed sufficiently to replace aqueous methods completely but in certain applications it offers technical, environmental and economic advantages. This is true for processes such as preparation of man-made fibre fabrics for dyeing (294), the dyeing of polyester fabrics (295), the scouring and milling of wool material (296) and the application of special finishes to most types of fibres, especially wool (160, 297). A number of symposia have been devoted entirely to the subject of solvent processing (298-301).

Among the many advantages of solvent processing for wool may be included (293):

(i) Almost instantaneous wetting and solubilization of oils, greases, waxes and lubricants which lead to higher production rates in scouring.

(ii) Solvents do not normally cause swelling or shrinking of the fibres. Consequently, mechanically-produced surface effects and handle are not altered.

(iii) Solvent machines consume a minimal amount of water and there is no discharge to sewers of liquors containing dyestuffs, soaps and oils.

(iv) Rapid and less expensive removal of solvents from fabrics is possible, and

(v) the possibility exists of using reactive chemicals, which would normally otherwise react with water, to obtain special effects such as shrink-resistance.

These and other factors have combined to make solvent processing popular in the textile industry. However, despite the numerous advantages of solvent processing there are disadvantages which include:

(i) The cost of re-equipment, the retraining of operatives, and the need for more highly skilled technicians.

(ii) The still unknown attitudes of many governments to the tolerable limit of volatile solvent pollutants.

(iii) The increasing cost of solvents, the need for highly efficient solvent recovery plants, disposal of distillation residues etc.

(iv) Many processes cannot be carried out in pure perchloroethylene because ion transport is not possible. Processes involving reduction or oxidation and conventional acid or reactive dyeing cannot be carried out in pure solvent. It is possible to emulsify sufficient quantities of water to allow these processes to proceed, but for rotating drum machines the wool material must be shrink-resistant.

There is, however, little fundamental knowledge published on the effects of organic solvents on the physical properties of woven wool fabrics.

The object of this current work was therefore, to study the effects of various organic solvents on the abrasion properties of wool fabrics. In addition, other physical properties of the fabrics considered to be of importance were also studied. The results are interpreted in the light of recent studies (302, 303) on the effect of solvents on wool fibres and the accessibility of wool to organic solvents.

The experimental work carried out on the solvent treatment of wool fabrics can be conveniently discussed in three distinct but related sections.

Section 3.2. is concerned with the effects of four solvent pretreatments on the Martindale abrasion resistance, tensile properties, cyclic stress-strain and bending properties of three woven wool fabrics.

Section 3.3. is concerned with the application of a wider range of solvents and their effects mainly on the Martindale abrasion resistance. ~~Furthermore the effects of varying the treatment time~~ for certain selected solvent treatments were studied in relation to the Martindale abrasion resistance.

Section 3.4. is an account of experiments concerned with the effects of certain solvent pretreatments on the fabric flex-abrasion resistance, surface friction and the effects upon the shrink-resistance of the fabrics. Crease recovery angle and X-ray studies were also conducted in an attempt to yield a further insight into the nature of the fibre-solvent interactions and the resultant changes that occur in the fibre structure.

Section 3.2.

3.2.1. Experimental

Materials

Fabric specifications: Three woven wool fabrics were used in this study and the detailed fabric specifications have been given in section 2.4.2.

Reagents

The following reagents were used:

(i) Alcohols: (a) Methanol, (b) Ethanol. Both analar grade (Vickers laboratories Ltd.).

(ii) Azeotropic mixture (3:2 v/v) of benzene and methanol (Analar).

(iii) Perchloroethylene - Laboratory grade (Vickers laboratories Ltd.).

Methods

General method of solvent extraction

Fabric samples (30 x 30 cm) were cut from each fabric, placed in a soxhlet apparatus and extracted for 10 cycles. On completion, which generally took about 2.5 hours, the samples were removed, squeezed gently and hung vertically in a fume cupboard to dry.

Fabric samples were also pretreated with 0.1% Teepol solution or distilled water (30:1 liquor ratio) for 0.5 hour, dried in a fume cupboard, and then treated with solvents in the manner described earlier. Finally all fabric samples were conditioned at 65% r.h. and 21°C for at least 3 days before any testing was carried out.

All fabric samples shrank slightly as a result of the pretreatment and solvent extraction and the shrinkage results are illustrated in Table 90.

Methods of Testing

The general experimental methods employed were as follows:

(i) Martindale Abrasion Resistance (see section 2.4.2.).

(ii) Fabric Tensile Properties (see section 2.4.2.).

(iii) Fabric Cyclic Stress-Strain Behaviour

The Instron Tensile Tester was employed with the following machine settings:

(a) Cross-head speed - 3 $cm.min.^{-1}$

(b) Chart speed - 30 $cm.min.^{-1}$

(c) Gauge length - 20 cm.,

(d) Load cell "B" (load range up to 2 kg).

The machine was preset to extend the fabric (20 cm x 5 cm) to 10% of its original length (i.e. 2 cm). The load was then released and

TABLE 90. The effect of solvent extraction for 2.5 h on the wool fabric area shrinkage (%).

Solvent Treatment	Fabric A (worsted)	Fabric B (worsted)	Fabric C ((worsted) woollen
Benzene/Methanol	0.5	3.0	4.0
Methanol	1.0	3.5	5.0
Ethanol	0.5	2.5	4.5
Perchloroethylene	0.5	2.0	4.0
0.1% Teepol	1.0	5.4	6.0
Teepol-Benzene/Methanol	1.0	5.4	6.4
Teepol-Methanol	1.5	6.9	6.0
Teepol-Ethanol	1.0	5.4	6.0
Teepol-Perchloroethylene	1.0	6.4	6.0
Water	2.0	-	-
Water-Benzene/Methanol	2.0	-	-
Water-Methanol	2.0	-	-
Water-Ethanol	2.0	-	-
Water-Perchloroethylene	2.0	-	-

the sample allowed to revert to the unstressed condition. This cycle was repeated a total of five times. From the chart-recordings the load required for 10% fabric extension on the first and fifth cycles could be easily determined. The mean value of three samples in the weft direction was used to evaluate the results in each case.

(iv) Fabric Bending Properties (see section 2.4.2.).

3.2.2. Results and Discussion

3.2.2.1. Martindale abrasion resistance (MAR)

The results of the effects of solvent treatments on the Martindale abrasion resistance of woven wool fabrics will be considered under three headings:

(a) Commercially scoured fabrics (except fabric A which was scoured in 2% soap solution) treated with various solvents (see Table 91) and illustrated in Fig. 83.

(b) 0.1% Teepol scoured fabrics treated with the same solvents. These results are given in Table 92 and illustrated in Fig. 84.

(c) Water pretreated fabric (fabric A only) treated with the same solvents (Table 93) and illustrated in Fig. 85.

In general all the solvent treatments studied increase the abrasion resistance of the three woven wool fabrics employed in this study.

The most dramatic increases in fabric abrasion resistance are obtained after treatment for 2.5 hours in the azeotropic mixture of benzene/methanol, which on the plain weave light weight fabric (fabric A) gave a 143% increase in MAR. More moderate increases below 135% were recorded for both methanol and ethanol; the perchloroethylene treatment in this case yielding somewhat lower abrasion resistance values (see Fig. 83). It is to be noted that

TABLE 91. Martindale Abrasion Resistance of wool fabrics after solvent extraction for 2.5 h.

Solvent Treatment	Fabric A (Worsted)			Fabric B (Worsted)			Fabric C (Woollen)		
	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)
Untreated	13.0 12.5 10.2	11.9	0	11.9 11.9 11.9	11.9	0	3.6 3.8 3.6	3.7	0
Benzene/ Methanol	29.0 29.0 27.0	28.3	137.8	16.0 17.0 15.0	16.0	35.5	4.4 4.6 4.5	4.5	21.6
Methanol	28.0 28.0 28.0	28.0	135.2	14.5 14.5 14.5	14.5	22.0	4.75 4.0 4.0	4.2	14.8
Ethanol	26.0 26.0 23.0	25.0	110.0	16.0 13.0 13.0	14.0	17.6	4.25 3.75 4.25	4.1	10.8
Perchloro-ethylene	19.0 19.0 19.0	19.0	59.5	14.0 13.0 13.0	13.3	11.7	4.25 3.75 4.25	4.1	10.8

Fig. 83 - The effect of solvent extraction for 2.5 hours on the Martindale abrasion resistance of wool fabrics.

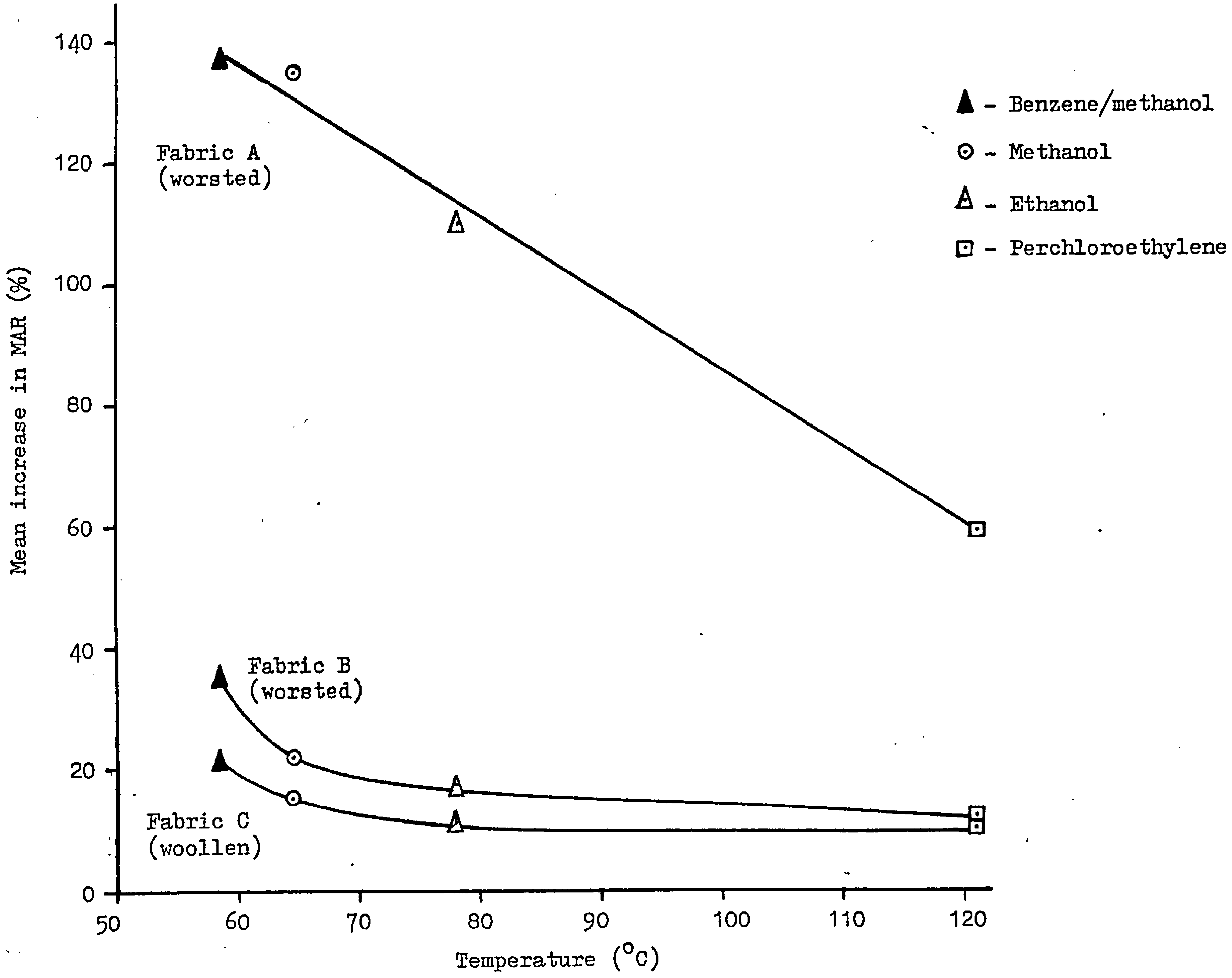


TABLE 92. Martindale Abrasion Resistance of Teepol pretreated wool fabrics after solvent extraction for 2.5 h

Solvent Treatment	Fabric A (Worsted)			Fabric B (Worsted)			Fabric C (Woollen)		
	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)
Untreated	13.0 12.5 10.2	11.9	0	11.9 11.9 11.9	11.9	0	3.6 3.8 3.6	3.7	0
0.1% Teepol	14.0 11.25 10.75	12.0	0.8	13.0 13.0 11.0	12.3	3.3	4.0 3.75 4.25	4.0	8.0
Benzene/ Methanol	30.0 28.0 29.0	29.0	143.5	17.0 16.0 16.0	16.3	37.0	4.5 4.5 5.0	4.6	25.7
Methanol	28.0 29.0 27.0	28.0	135.2	16.0 15.0 14.0	15.0	23.5	4.5 4.5 4.5	4.5	21.6
Ethanol	28.0 25.0 25.0	26.0	118.4	16.0 15.0 13.0	14.6	22.5	4.2 4.25 4.5	4.3	16.2
Perchloroethylene	20.0 19.0 19.0	19.3	62.0	16.0 13.0 13.0	14.0	17.6	4.0 4.0 4.75	4.25	14.8

Fig. 84 - The effect of solvent extraction for 2.5 hours on the Martindale abrasion resistance of 0.1% Teepol pretreated wool fabrics.

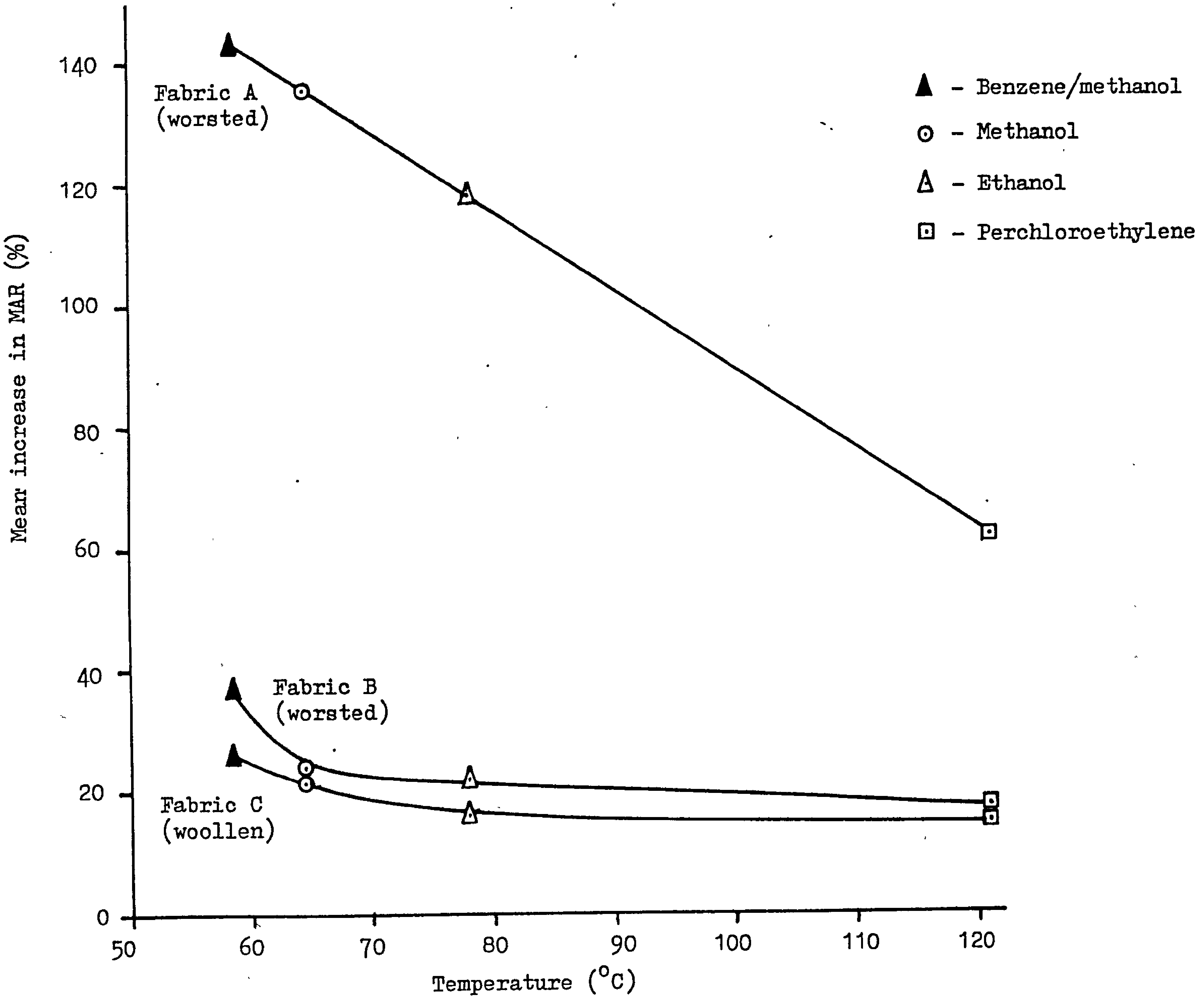
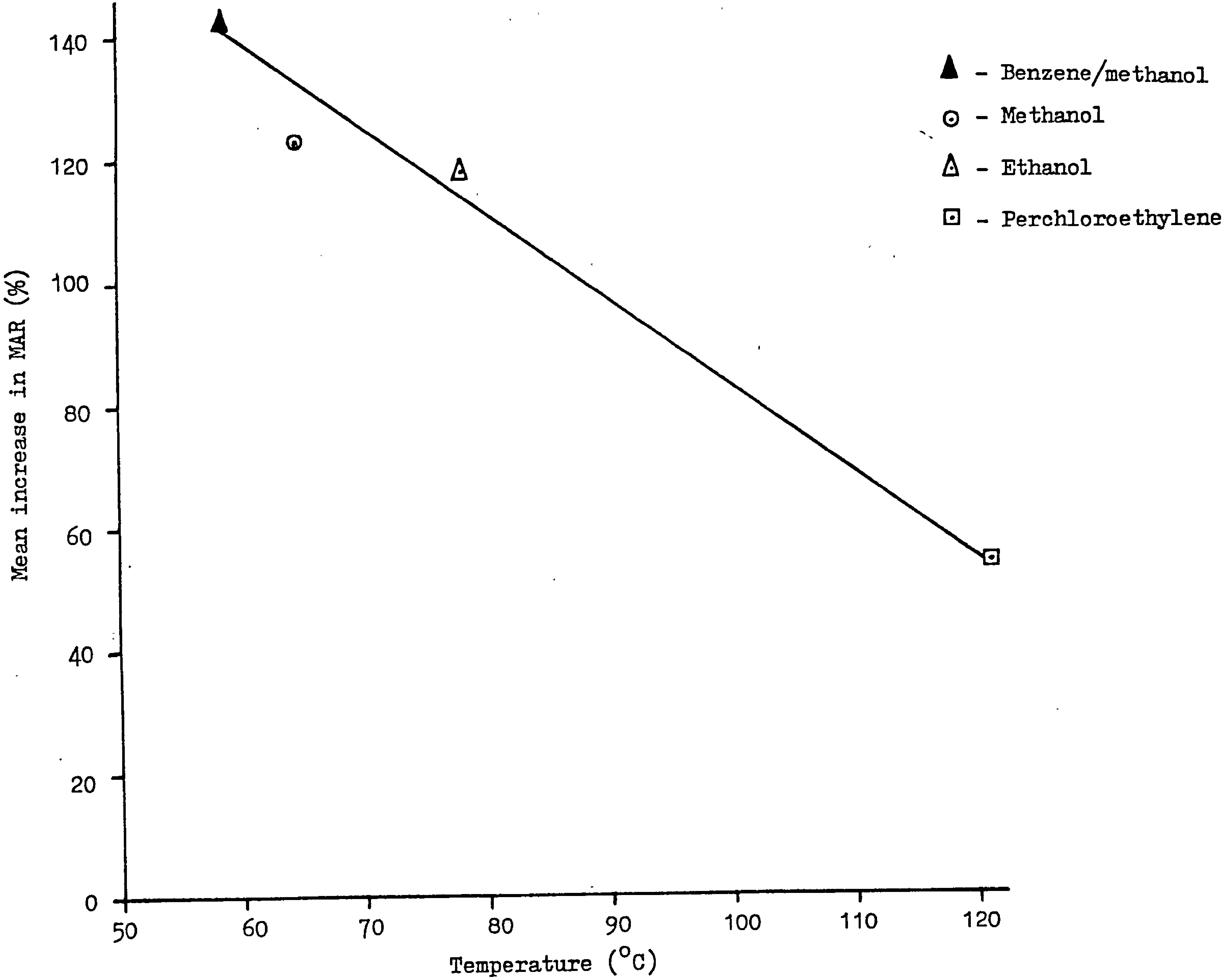


TABLE 93. Martindale Abrasion Resistance of water pretreated fabric A (worsted).

Solvent Treatment	Fabric A (worsted)		
	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)
Untreated	13.0 12.5 10.2	11.9	0
Water	12.0 12.5 13.0	12.5	5
Benzene/ Methanol	27.0 29.0 31.0	29.0	143.5
Methanol	27.5 26.5 26.0	26.6	123.5
Ethanol	28.0 26.0 24.0	26.0	118.4
Perchloro-ethylene	18.0 18.0 19.0	18.3	54.0

Fig. 85 - The effects of solvent extraction for 2.5 hours on the Martindale abrasion resistance of water pretreated fabric A (worsted).



improvement in MAR after extraction with ethanol has also been observed elsewhere (190).

In general for the solvent treatments studied the order of improvement in MAR for the various fabric samples was:

Fabric A > Fabric B > Fabric C.

The results in Fig. 83 demonstrate that the fabric structure and the nature of the solvent treatments at their respective boiling points are of importance in determining the changes in the abrasion resistance of the wool fabrics.

Fabric A appears to have a greater potential for improvement in MAR compared with the other two fabrics studied. It is important to note that this fabric has very little tendency to pill (as discussed in section 2.5.3.4.) and the twist level and cover factor are sufficient to hold the fibres together during the abrasion process. The predominant mechanism of abrasion is thus through fibre wear and general attrition. From visual examination of the way the treated fabric abrades it would appear that the abrading forces are being distributed more uniformly over the entire specimen area and this would explain the ability of the fabric to withstand these forces for longer periods, i.e. higher MAR value.

For fabric C however where the dominant mechanism of abrasion is through pilling and shedding (see section 2.5.3.4.) there appeared to be little change in these respects compared with the untreated state and therefore no marked improvements in MAR were obtained. Similar conclusions may be drawn for fabric B.

Pretreatment of the fabrics with 0.1% Teepol solution (see Table 92, Fig. 84) or water (see Table 93, Fig. 85), prior to solvent extraction gave a further slight improvement in MAR but the general trends remain the same as those observed in the solvent treatments alone. In other studies an improvement in MAR after scouring worsted fabric has also been noted (47) in accord with the results observed here using Teepol.

From the results illustrated in Fig. 83-85 it can be concluded that the boiling point as well as the nature of the solvent plays an important role in the changes obtained in MAR. As the boiling point of the solvent is increased the improvement in MAR decreased. The greatest reductions in improvement in MAR values were observed with fabric A where the effects of the solvent treatments were more pronounced. For fabrics B and C the changes in MAR as a result of the boiling point were not as marked because only marginal changes in MAR as a result of the solvent treatment were observed.

From Table (90) it is evident that all fabrics appear to relax because fabric shrinkage, although small, takes place. The amount of shrinkage that takes place is dependent upon the fabric structure as well as on the nature of the pretreatment and the solvent extraction. Generally all solvent treatments gave a similar degree of shrinkage with marginal differences where methanol was used and slightly higher fabric shrinkage occurred. The order of shrinkage for the different fabric structures was:

Fabric C > Fabric B > Fabric A.

Pretreatment with Teepol or water prior to solvent extraction enhanced the degree of fabric shrinkage and the results are not dissimilar to those of the pretreatment alone (see Table 90). The shrinkage that occurred in fabric A was very small and is not likely to contribute significantly to the improvement in MAR as a result of increased weight per unit area. Nevertheless the relaxation of the fabric and the removal of stresses and strains as a result of the solvent treatment must contribute significantly to the changed nature of the fabric abrasion process and to the more uniform distribution of the abrading forces. This in turn must lead to the marked changes in MAR values.

The changes in moisture regain as a result of the solvent treatments are minor (see Table 94) and the effects on MAR will be discussed separately in section 3.3.

TABLE 94 The effect of solvent extraction for 2.5 hours on the moisture regain of fabric A (worsted)

Untreated	12.25
Benzene/Methanol	12.35
Methanol	12.68
Ethanol	12.83
Perchloroethylene	12.76

3.2.2.2. Fabric Tensile Properties

The effects of the solvent treatments on the breaking load and breaking extension of the woven wool fabrics will be considered under three headings:

(a) Commercially scoured fabrics (except fabric A scoured in 2% soap solution) subsequently treated with the various solvents given in Table 95.

(b) 0.1% Teepol scoured fabrics treated with the various solvents given in Table 96.

(c) Water pretreated fabric (fabric A only) subsequently treated with various solvents given in Table 97.

The breaking load and breaking extension values obtained for the three wool fabrics clearly indicate that the changes produced are

TABLE 95. The effect of solvent extraction for 2.5 h on the tensile properties of wool fabrics.

Solvent Treatment	Fabric A (Worsted)				Fabric B (Worsted)				Fabric C (Woollen)			
	Breaking Load		Breaking Extension		Breaking Load		Breaking Extension		Breaking Load		Breaking Extension	
	(Kg)	mean	(%)	mean	(Kg)	mean	(%)	mean	(Kg)	mean	(%)	mean
Untreated	14.3 14.4 13.9	14.2 (0)	36.0 34.0 32.5	34.2 (0)	15.4 15.3 15.5	15.4 (0)	36.0 32.0 30.0	32.7 (0)	8.8 8.8 8.8	8.8 (0)	39.0 34.0 38.0	37.0 (0)
Benzene/ Methanol	16.2 15.4	15.8 (+11.3)	37.0 36.0	36.5 (+6.8)	16.9 16.6	16.75 (+8.8)	34.0 36.0	35.0 (7.2)	10.5 10.4	10.45 (+18.3)	37.0 37.0	37.0 (0)
Methanol	15.9 15.4	15.65 (+10.2)	39.0 32.0	35.5 (+3.9)	16.5 16.1	16.3 (+5.8)	35.0 33.0	34.0 (+4.1)	10.3 10.6	10.45 (+18.3)	37.0 37.0	37.0 (0)
Ethanol	16.0 14.5	15.25 (+7.4)	36.0 29.0	32.5 (-4.9)	16.3 15.9	16.1 (+4.5)	34.0 34.0	34.0 (+4.1)	9.3 9.1	9.2 (+4.2)	36.0 36.0	36.0 (-2.7)
Perchloro-ethylene	15.6 17.1	16.35 (+15.1)	26.0 29.0	27.5 (-19.5)	18.2 18.0	18.1 (+17.5)	32.0 31.0	31.5 (-3.5)	11.0 10.6	10.8 (+22.3)	32.5 37.0	34.2 (-7.4)

The values in parentheses represent the mean change (%) in Fabric Tensile Properties. + = increase, - = decrease.

<u>TABLE 96</u>. The effect of solvent extraction for 2.5 h on the tensile properties of Teepol pretreated wool fabrics.

Solvent treatment	Fabric A (worsted)				Fabric B (worsted)				Fabric C (woollen)			
	Breaking Load		Breaking Extension		Breaking Load		Breaking Extension		Breaking Load		Breaking Extension	
	(Kg)	mean	(%)	mean	(Kg)	mean	(%)	mean	(Kg)	mean	(%)	mean
Untreated	14.3 14.4 13.9	14.2 (0)	36.0 34.0 32.5	34.2 (0)	15.4 15.3 15.5	15.4 (0)	36.0 32.0 30.0	32.7 (0)	8.8 8.8 8.8	8.8 (0)	39.0 34.0 38.0	37.0 (0)
0.1% Teepol	14.0 14.2	14.1 (-0.7)	35.5 29.5	32.5 (-4.9)	5.5 4.9	15.2 (-1.3)	31.5 32.0	31.7 (-2.8)	9.5 9.0	9.3 (+5.3)	43.0 44.0	43.5 (+17.6)
Benzene/ Methanol	15.7 16.3	16.0 (+12.7)	41.5 4.15	41.5 (+21.5)	17.5 17.5	17.5 (+13.6)	37.0 37.0	37.0 (+13.3)	10.8 10.9	10.8 (+22.9)	40.0 39.0	39.5 (+6.7)
Methanol	16.2 15.1	15.6 (+10.2)	36.0 35.0	35.5 (+3.9)	16.6 17.2	16.9 (+ 9.7)	32.0 37.0	34.5 (+ 5.6)	10.7 10.2	10.4 (+18.3)	38.0 38.0	38.0 (+2.7)
Ethanol	15.5 14.9	15.2 (+ 7.0)	32.0 34.0	33.0 (-3.4)	16.7 16.7	16.7 (+ 8.4)	34.0 33.0	33.5 (+ 2.6)	11.1 10.1	10.6 (+20.0)	39.0 36.0	37.5 (+1.3)
Perchloro-ethylene	16.0 15.9	15.9 (+12.3)	33.0 27.0	30.0 (-12.2)	16.7 17.4	17.0 (+10.7)	32.0 32.0	32.0 (-2.0)	11.2 10.1	10.6 (+20.0)	38.0 33.5	35.7 (-3.4)

TABLE 97. The effect of solvent extraction for 2.5 h on the tensile properties of water pretreated fabric A (worsted).

Solvent Treatment	Fabric A (worsted)			
	Breaking Load		Breaking Extension	
	(Kg)	mean	(%)	mean
Untreated	14.2 14.3 13.9	14.2 (0)	36.0 34.0 32.5	34.2 (0)
Water-treated	14.7 14.4	14.5 (+ 2.5)	29.0 30.0	29.5 (-13.6)
Benzene/ Methanol	15.8 15.9	15.8 (+11.6)	39.0 33.0	36.0 (+ 5.4)
Methanol	15.5 15.7	15.6 (+ 9.9)	36.0 35.0	35.5 (+ 3.9)
Ethanol	15.5 15.7	15.6 (+ 9.9)	35.0 38.0	34.0 (- 0.5)
Perchloro-ethylene	16.2 16.6	16.4 (+15.5)	24.0 31.0	27.5 (-19.5)

The values in parentheses represent the mean change (%) in Fabric Tensile Properties. + = increase, - = decrease.

dependent mainly on the nature of the solvents as well as on the fabric structure, although the effect is not as greatly pronounced as in the abrasion resistance results.

Generally the fabric breaking load is increased in all three woven fabrics, the improvement ranging from 7 to 22%. Improvements in breaking load after solvent extraction have also been reported elsewhere (190).

It can be seen from Table 95 that the greatest improvement in breaking load within the three fabrics studied is obtained in perchloroethylene treatment but this solvent has the greatest weakening effect on the breaking extension. It has been suggested (306) that perchloroethylene treatments change the supra-molecular structure of wool by increasing the chain molecular orientation and on this basis increases in tensile strength could reasonably be expected. From Table 95 it is clear that the highest values of fabric breaking extension are obtained (i) with the azeotropic mixture benzene/methanol, and (ii) methanol. After treatment with ethanol a small increase in breaking extension was recorded for fabric B while small decreases were correspondingly recorded for fabrics A and C.

The results in Table 96 where solvent treatments were carried out after 0.1% Teepol scouring, demonstrate that the benzene/methanol treatment gives the best improvement in both breaking load and extension. Generally solvent treatments applied after 0.1% Teepol scouring give a greater improvement in breaking load and breaking extension and this could be the reason for the slightly improved performance observed in the Martindale abrasion resistance tests.

Treatment with water (see Table 97) or 2% soap scouring prior to solvent extraction on fabric A leads to similar tensile properties in that the breaking load is relatively unchanged, but the breaking extension is slightly reduced. This presumably reflects the changes in the fabric as a result of relaxation processes.

3.2.2.3. Cyclic Stress-strain Properties

The results of the effects of solvent treatments on the load required for 10% fabric extension on the first and fifth loading cycle are given in Table 98 and illustrated in Fig. 86.

The values obtained for the load required for 10% fabric extension clearly indicate for each fabric studied that these are dependent upon the nature and properties of the solvents. All the solvent treatments used in these experiments reduced the load required for 10% fabric extension and therefore increased the ease of extensibility compared with that of the untreated fabric. It has been reported (307) that if a fabric shrinks without felting this results in an increased fabric extension under a given load. The solvent which confers the greatest improvement in MAR also yields the greatest reduction in the load required for 10% fabric extension as shown in Table 98.

Plotting the values of the load required for 10% fabric extension on the first and fifth cycle against the increase in MAR (%) (Fig. 86) gave a very similar graph to that obtained when the MAR values (%) were plotted against the treatment temperature (Fig. 83). The latter of course are the boiling points of the solvent or solvent mixtures used. From Fig. 86 it can be seen that as the initial load required for 10% fabric extension is decreased the MAR was increased.

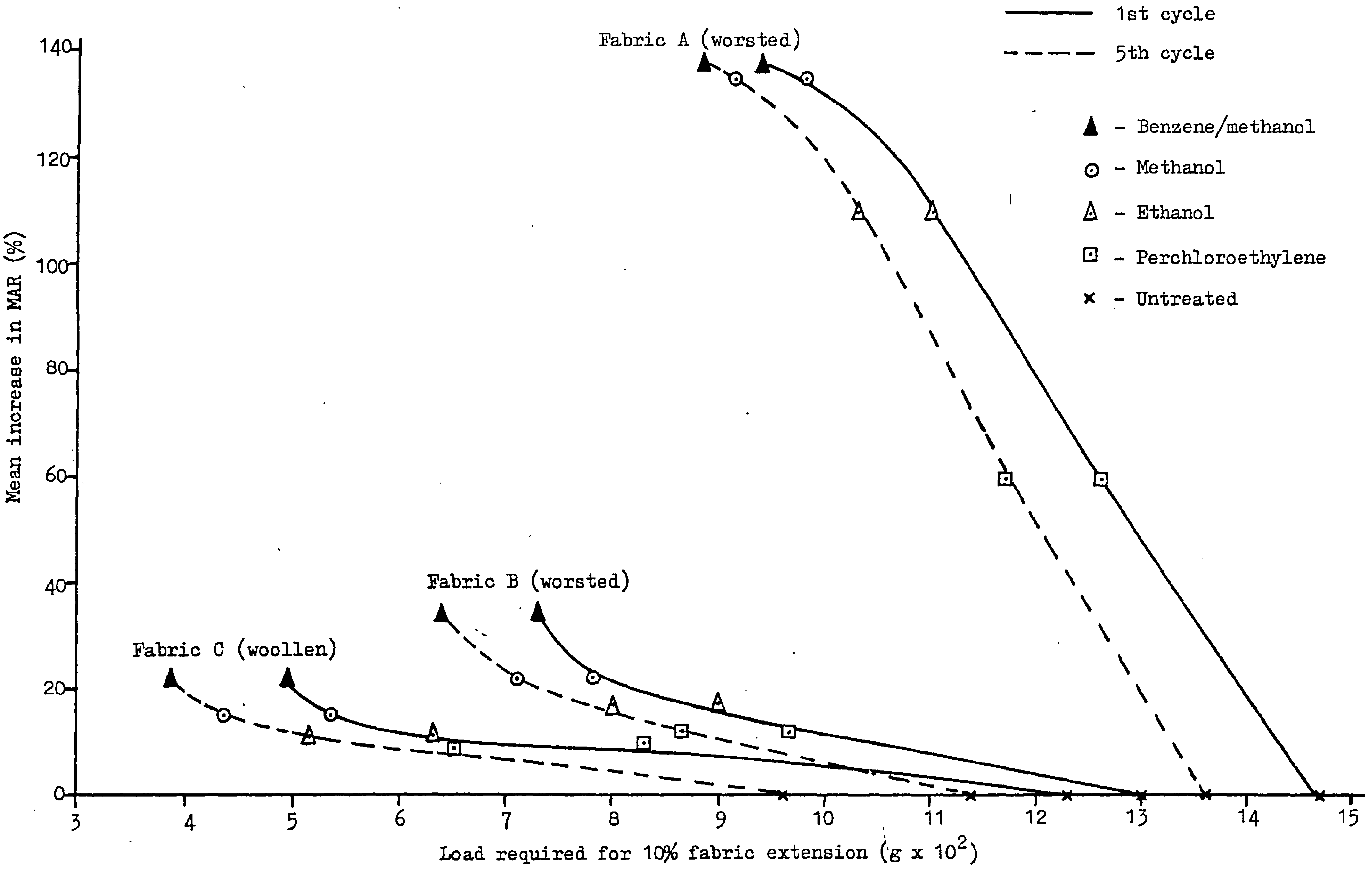
The most striking feature of Fig. 86 is the very great difference between the results of solvent treatment on the abrasion resistance of fabric A (light weight worsted) compared with fabrics B and C (worsted

TABLE 98. The effect of solvent extraction for 2.5 h on the load required for 10% extension of wool fabrics.

Solvent treatment	Load required for 10% fabric extension											
	Fabric A (worsted)				Fabric B (worsted)				Fabric C (woollen)			
	First cycle		Fifth Cycle		First cycle		Fifth cycle		First cycle		Fifth cycle	
	(g)	mean	(g)	mean	(g)	mean	(g)	mean	(g)	mean	(g)	mean
Untreated*	1470 1470	1470	1385 1335	1360	1280 1320	1300	1200 1080	1140	1200 1260	1260	940 980	960
Benzene/ Methanol	1020 860	940	960 800	885	750 710	730	650 630	640	550 440	495	395 370	385
Methanol	1050 910	980	980 850	915	760 800	780	690 730	710	620 450	535	500 370	435
Ethanol	1060 1140	1100	990 1070	1030	940 860	900	840 760	800	700 560	630	570 460	515
Perchloro-ethylene	1280 1240	1260	1200 1140	1170	920 1010	965	820 910	865	860 800	830	700 600	650

* For fabric details see section (2.4.2.)

Fig. 86 - The effects of solvent-extractions for 2.5 hours on the load required for 10% extension of wool fabrics.



twill and woollen flannel respectively). It would appear that in the case of fabric A, the tensile changes that take place subsequently give rise to more marked improvements in the MAR. This is believed to arise as a direct consequence of the fabric structure, for in this case the fabric has been observed to abrade by a process of direct wear or attrition of the wool fibres. However in fabrics B and C, pilling and fibre shedding are notable features contributing to the loss in MAR. Accordingly it is concluded that changes in the tensile properties as a result of solvent treatment will exert only minor changes in the improvement in MAR for fabrics B and C.

In Fig. 86 the load required for 10% fabric extension on the fifth cycle is also plotted against the MAR values (%) and the trend remains very similar to that observed for the first cycle, although the values are lower. A notable feature is that the solvent that gave the greater improvements in MAR also gave the least difference in load required for 10% fabric extension on the fifth cycle. As this difference in load is increased the degree of improvement in MAR is decreased. The greater the change between the first and fifth cycle for each fabric the lower the improvement in MAR, i.e. generally for every solvent the difference in load required for 10% fabric extension increases in the order: Untreated > Perchloroethylene > Ethanol > Methanol > Benzene/methanol. The order of decreasing difference in load required for 10% fabric extension between the first and the fifth cycle is: Fabric A > Fabric B > Fabric C, and indeed the order of decreasing difference in load is the order of improvement in MAR.

It must be concluded, therefore, that while the fabric structure plays an important role in determining MAR, the effect of solvent treatments and the treatment temperature modify the fabric tensile properties so that improved elasticity and reduced load required for extension lead to improved MAR values.

3.2.2.4. Fabric Bending Properties

The results of the effects of the solvent treatments on the fabric bending properties, i.e. on the values of the flexural rigidity (G_o) and the coercive couple (C_o) for worsted fabric A are illustrated in Table 99.

Extraction treatment with solvents for 2.5 hours demonstrates that solvent treatments reduce both the flexural rigidity G_o and the coercive couple C_o, and that the magnitude of the reduction appears to be dependent upon the nature of the solvent.

The values for G_o increase in the order: Untreated $>$ perchloroethylene $>$ ethanol $>$ methanol, benzene/methanol.

The values for C_o increase in the order: Untreated $>$ perchloroethylene, ethanol, methanol $>$ benzene/methanol.

From these results it must be concluded that in general the more polar the solvent used the lower the values of G_o and C_o, but the changes in all cases are small. Presumably these changes reflect fibre relaxation as a result of the solvent treatments, although the changes in tensile properties clearly will also exert some effect.

TABLE 99. The effect of solvent treatments on flexural rigidity G_o and Coercive couple C_o fabric A (worsted).

Solvent Treatment	Fabric A (worsted)	
	G_o (mg.cm)	C_o (mg.cm)
Untreated*	34.7	8.2
Benzene/ Methanol	32.6	6.1
Methanol	32.6	7.1
Ethanol	33.6	7.1
Perchloro-ethylene	34.1	7.1

The above values represent the mean value of three samples in the weft direction.

* For untreated fabric specifications see section 2.4.2.

Section 3.3.

3.3.1. Introduction

Previous studies (section 3.2.2.1.) have demonstrated that organic solvents are effective in increasing the Martindale abrasion resistance (MAR) of wool fabrics. In general an increase in MAR is observed with decrease in treatment temperature (in this case the boiling point) of the solvents and the level of improvement was greater for fabric A (worsted type) than for fabric C (woollen type).

The results of this study suggested that the level of improvement in MAR might well be dependent amongst other factors upon:

(i) nature of the solvents,

(ii) fabric structure,

(iii) treatment temperature.

The object of the experimental work carried out in this section was therefore to investigate the following parameters in more detail using a larger range of solvents viz:

(1) Nature of solvent.

(2) Treatment temperature.

(3) Time of treatment.

Fabric A was chosen for this study because of the more pronounced effects on MAR observed previously in section (3.2.2.1.).

3.3.2. Experimental

Materials

Fabric specifications: The composition of fabric A has been given in section (2.4.2.).

Reagents: In addition to the solvents previously described in section (3.2.1.) the following chemicals were used:

(i) tetrachloromethane (carbon tetrachloride), analar grade

(Vickers Laboratories Ltd.).

(ii) Trichloroethylene-laboratory reagent grade (95%) (Vickers Laboratories Ltd.).

(iii) Benzene - (Analar).

(iv) Deionised water.

(v) 2-methoxy-ethanol and 2-ethoxy-ethanol - analar grade (Vickers Laboratories Ltd.).

(vi) N, N-Dimethyl Formamide - Laboratory grade (Vickers Laboratories Ltd.).

Methods

Method of solvent treatment

Three methods of solvent treatment have been studied and the specific details of the treatments are as follows:

(i) Soxhlet extraction in boiling liquid - In this method the fabric samples were treated for 2.5 hours in boiling solvent in a soxhlet apparatus as described in section (3.2.1.). Dimethyl formamide was not soxhlet extracted because of the high boiling point (153°C) which could damage the wool fibre.

(ii) Treatment at room temperature for 2.5 hours - In this method benzene/methanol, methanol, ethanol, perchloroethylene, trichloroethylene, dimethyl formamide and 2-methoxy-ethanol were applied at room temperature and wool fabric samples were accordingly treated in a conical flask for 2.5 hours with occasional shaking.

(iii) Treatment at room temperature over a range of times - In this method methanol, ethanol, dimethyl formamide, perchloroethylene and deionised water were used for times ranging from 2.5 hours to 80 hours at room temperature.

After the treatments the wool fabric samples were removed, hung vertically in a fume cupboard and allowed to dry at room temperature. The samples treated with dimethyl formamide were rinsed for a short time (about 1 minute) with cold tap water and then similarly dried in the fume cupboard.

Finally all fabric samples were conditioned in an atmosphere of 65% r.h., and 21°C for at least 3 days before testing.

Methods of Test

Martindale Abrasion resistance (see section 2.4.2.).

3.3.3. Results and Discussion

3.3.3.1. Martindale abrasion resistance (MAR)

The results of the effects of the solvent treatments on the fabric MAR will be considered under the three headings described previously, namely:

(i) The effects of soxhlet extraction in solvent for 2.5 hours

The values of fabric MAR obtained after soxhlet extraction in boiling solvents are given in Table 100 and illustrated in Fig. 87 where these are plotted against the corresponding boiling point of each solvent used. It is clear that there is a non-linear relationship and that the increase in MAR is markedly reduced as the boiling point of the solvent increases. Above 100°C the MAR tends to level out to a more constant value and the effect of temperature is less marked than in the temperature range below 100°C.

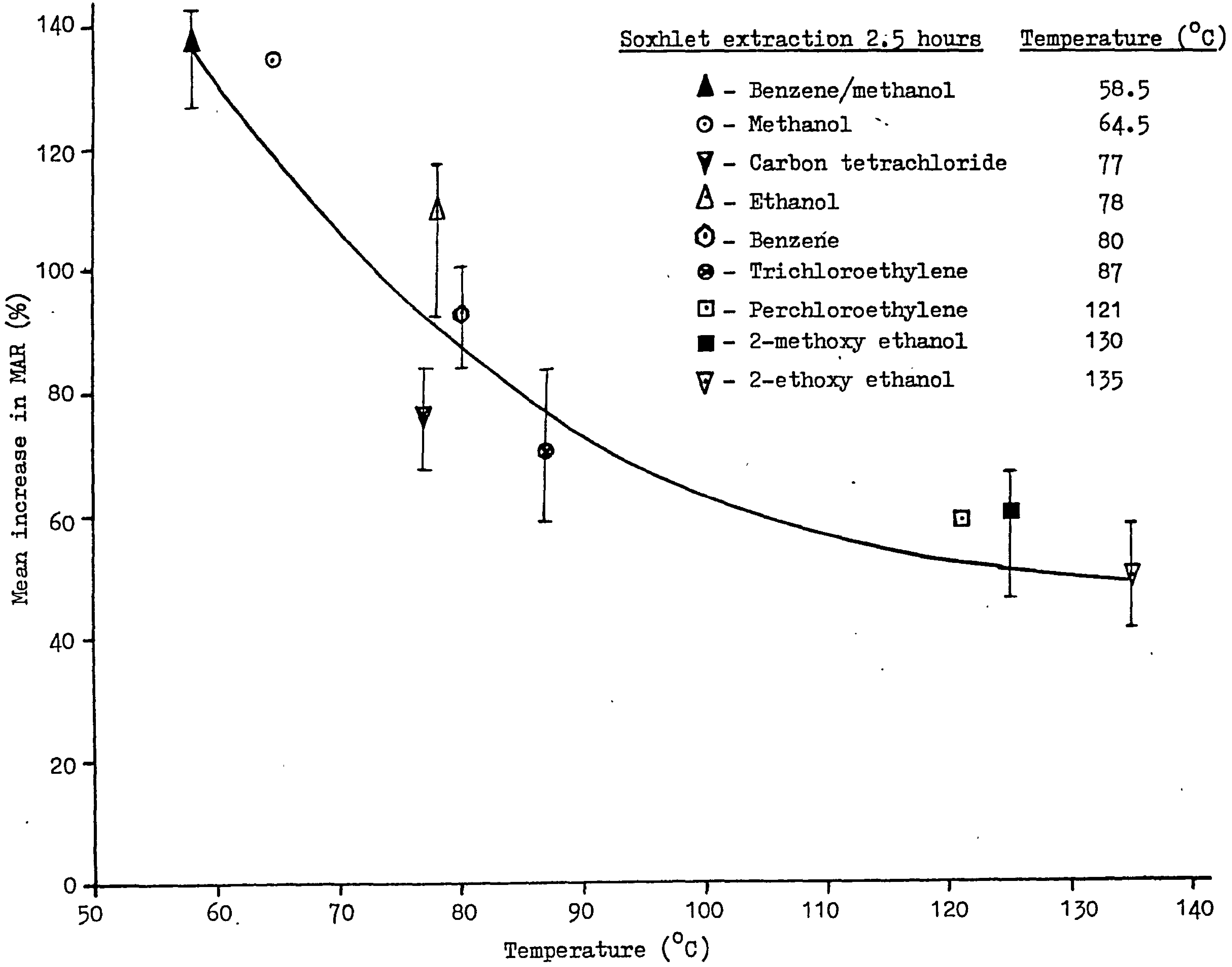
Thus benzene/methanol and methanol treatments with relatively low boiling points gave the highest level of improvement in abrasion resistance, while ethanol, benzene, carbon tetrachloride and trichloroethylene, having slightly higher boiling points, gave rise to a lower level of improvement in MAR. Finally perchloroethylene, 2-methoxy ethanol and 2-ethoxy ethanol with relatively high boiling

TABLE 100. Martindale abrasion resistance of fabric A (worsted) after solvent extraction for 2.5 h.

Solvent treatment	Fabric A (worsted)		
	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)
Untreated *	13.5 12.5 10.2	11.9	0
Benzene/ Methanol	29.0 29.0 27.0	28.33	137.8
Methanol ✓	28.0 28.0 28.0	28.0	135.2
Carbon Tetrachloride	22.0 21.0 20.0	21.0	76.5
Ethanol ✓	26.0 26.0 23.0	25.0	110.0
Benzene	22.0 24.0 23.0	23.0	93.0
Trichloroethylene	20.0 22.0 19.0	20.33	70.6
Perchloroethylene	19.0 19.0 19.0	19.0	59.5
2-Methoxy ethanol	20.0 17.5 20.0	19.15	61.0
2-Ethoxy Ethanol	19.0 19.0 17.0	18.33	50.0

* For untreated fabric specifications see section 2.4.2.

Fig. 87 - The effect of solvent extraction for 2.5 hours on the Martindale abrasion resistance of fabric A (worsted).



points gave rise to the lowest degree of improvement in MAR values.

(ii) The effects of solvent treatments at room temperature for 2.5 hours

The values of MAR obtained are shown in Table 101 and illustrated in Fig. 88, where the MAR values (%) are plotted against the solubility parameter of each solvent. The solubility parameter has previously been employed (308-313) in other studies relating to fibre-solvent interactions and it was considered of interest in the current work to establish whether any consistent trends could be detected.

However it is difficult to draw finite conclusions from the limited data illustrated in Fig. 88 because it is believed, as a result of work to be described in section (3.3.3.1.(iii)) that these results do not represent equilibrium conditions. The treatment time of 2.5 hours is relatively short and consequently further work was conducted to establish the effect of time on the fabric properties, in relation to the amount of liquid absorbed. Factors such as the molar volume of the solvent and the polarity of the diffusing molecules are also likely to be of importance in this connection.

It is considered that in the diffusion of organic solvents into wool fibres, the rate of diffusion will be dependent upon the size and shape of the diffusing molecules and will be generally controlled according to the Eyring's "hole" theory of diffusion (314) in which holes are created in the fibre as a result of thermal vibrations of a size sufficiently large to allow diffusion of penetrating molecules to occur. For this reason, an increase in molar volume of the solvent reduces the rate of diffusion within the fibre, while in addition, the amount of solvent absorbed at equilibrium decreases.

In Fig. 89 it can be seen that the MAR value for selected solvents decreases with increase in molar volume (see also Table 101)

TABLE 101. Martindale abrasion resistance of fabric A (worsted) treated with solvents for 2.5 h at room temperature (in relation to solubility parameter and molar volume).

Solvent treatment	Solubility parameter δ, $cal^{\frac{1}{2}}$ $cm^{-\frac{3}{2}}$	Molar volume (cm^3/mole)	Fabric A (worsted)		
			Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)
Untreated	-	-	13.0 12.5 10.5	11.9	0
Benzene/ Methanol	-	-	22.0 22.0 22.0	22.0	84.9
Methanol	14.5	39.5	20.0 23.0 23.0	22.0	84.9
Ethanol	12.7	58.6	19.0 21.0 20.0	20.0	68.0
Water	23.4	18.0	11.0 12.5 12.5	12.0	0
Perchloro-ethylene	9.3	103.1	19.0 20.0 19.0	19.3	62.0
Trichloro-ethylene	9.2	90.0	21.0 20.0 19.0	20.0	68.0
Dimethyl formamide	12.9	77.0	20.0 22.0 18.0	20.0	68.0
2-methoxy ethanol	11.4	79.2	16.0 18.0 18.0	17.3	45.4

Fig. 88 - The effects of solvent treatment for 2.5 hours at room temperature (in relation to solubility parameter) on the Martindale abrasion resistance of fabric A (worsted).

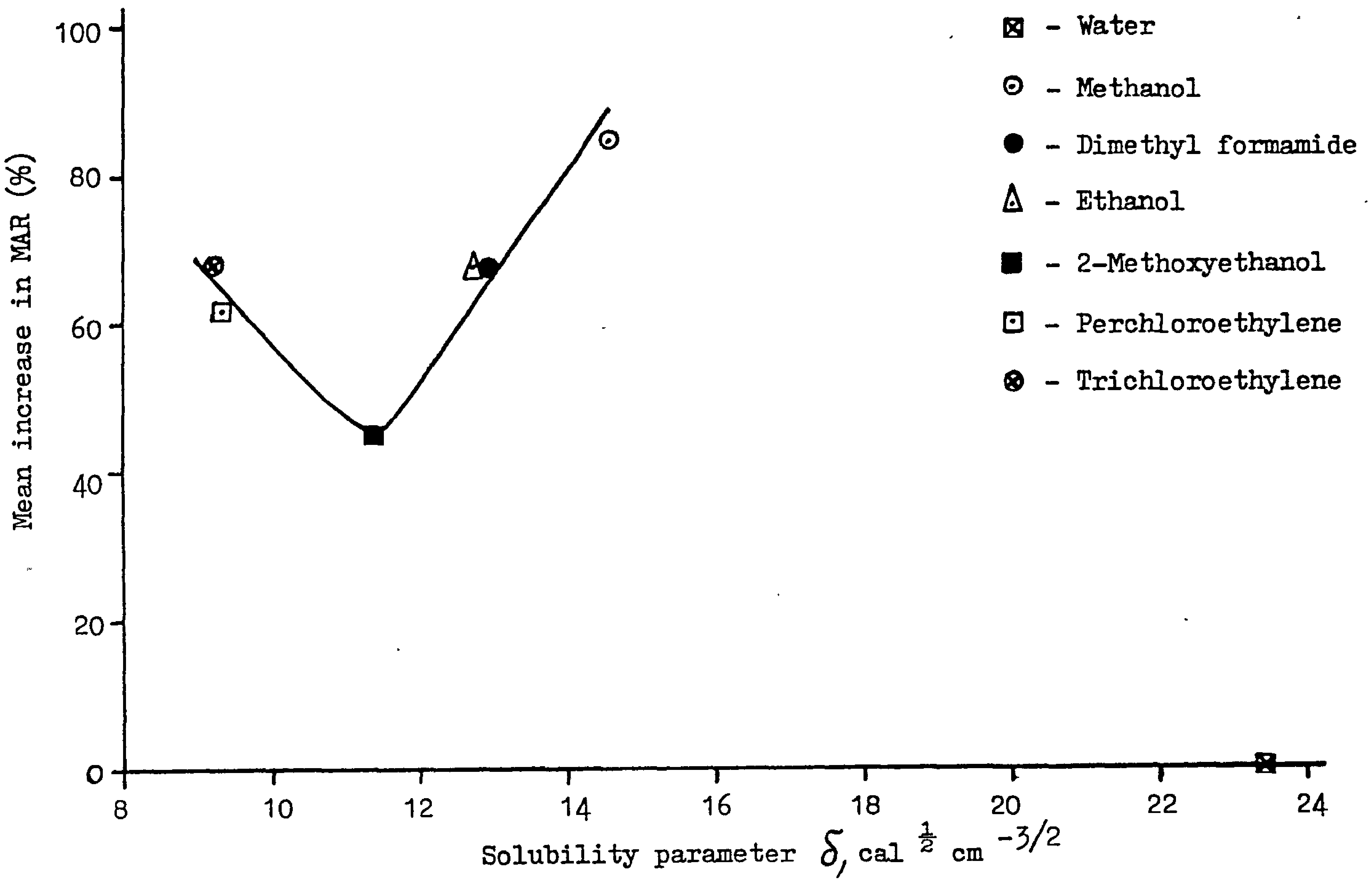
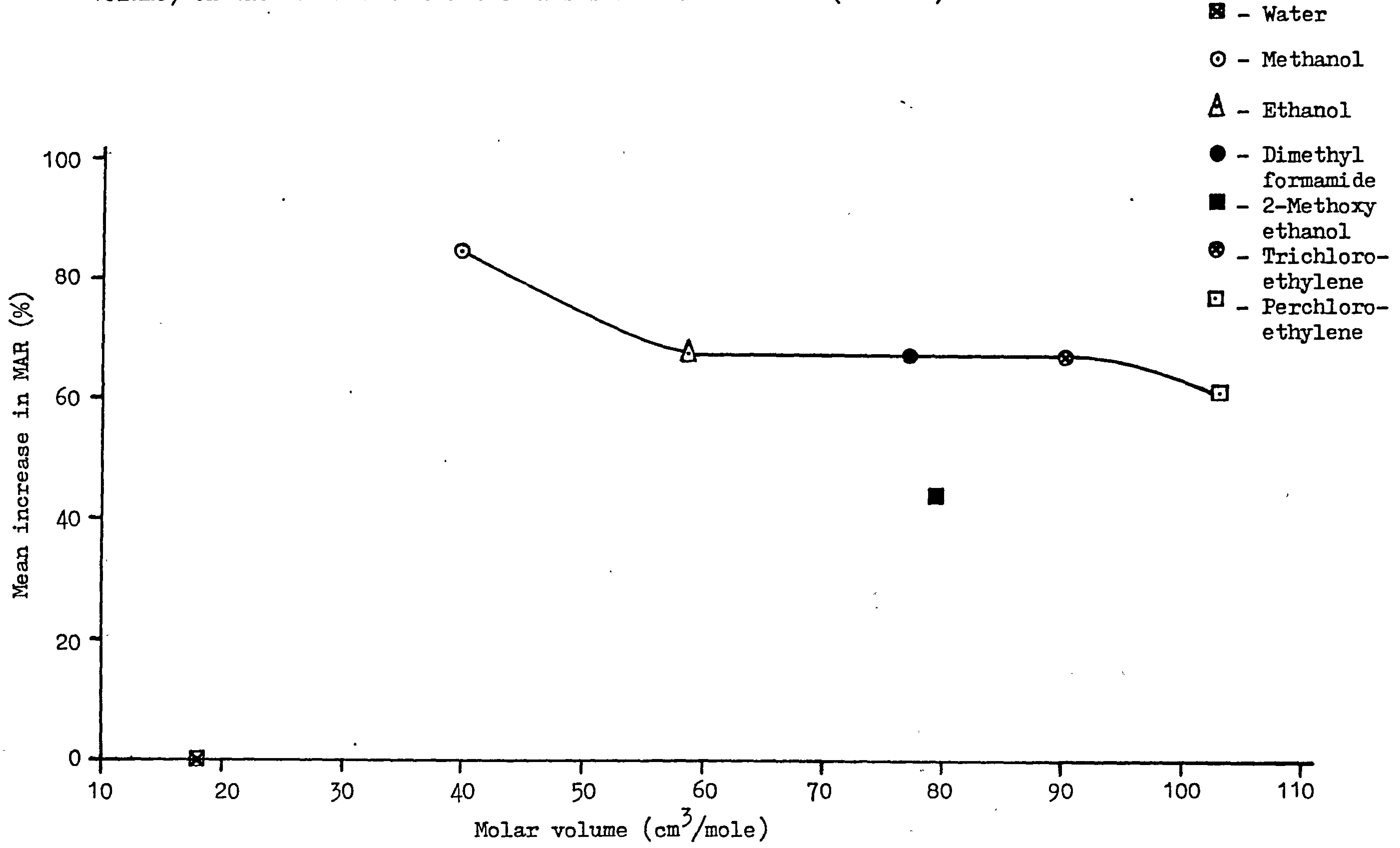


Fig. 89 - The effects of solvent treatments for 2.5 hours at room temperature (in relation to molar volume) on the Martindale abrasion resistance of fabric A (worsted).



for most of the reagents studied. However, the relationship is not simple, because the results for both water and 2-methoxy ethanol do not conform to this general trend. In addition the dielectric constant of DMF is greater than that of ethanol, whereas the MAR again, tends to decrease with decrease indielectric constant of these solvents.

Clearly solvent treatment of wool fabric after water pretreatment leads generally to an improvement in MAR for all the solvent studied at room temperature. The changes noted are not dependent upon the changes in moisture regain which are small (see Table 94) and are lower than required to affect the MAR quite considerably (24). The changes observed must reflect either changes in the fibre structure and/or in the physical properties as a result of the solvent treatment. Alternatively retention of small amounts of solvent after drying may influence the fibre and fabric properties.

(iii) The effects of immersion time for solvent treatments at room temperature

From Table 102 and Fig. 90 where the values of the increase in Martindale abrasion resistance (%) after solvent treatment are plotted against the time of the treatment it is clear that as the latter increases the degree of improvement in MAR increases.

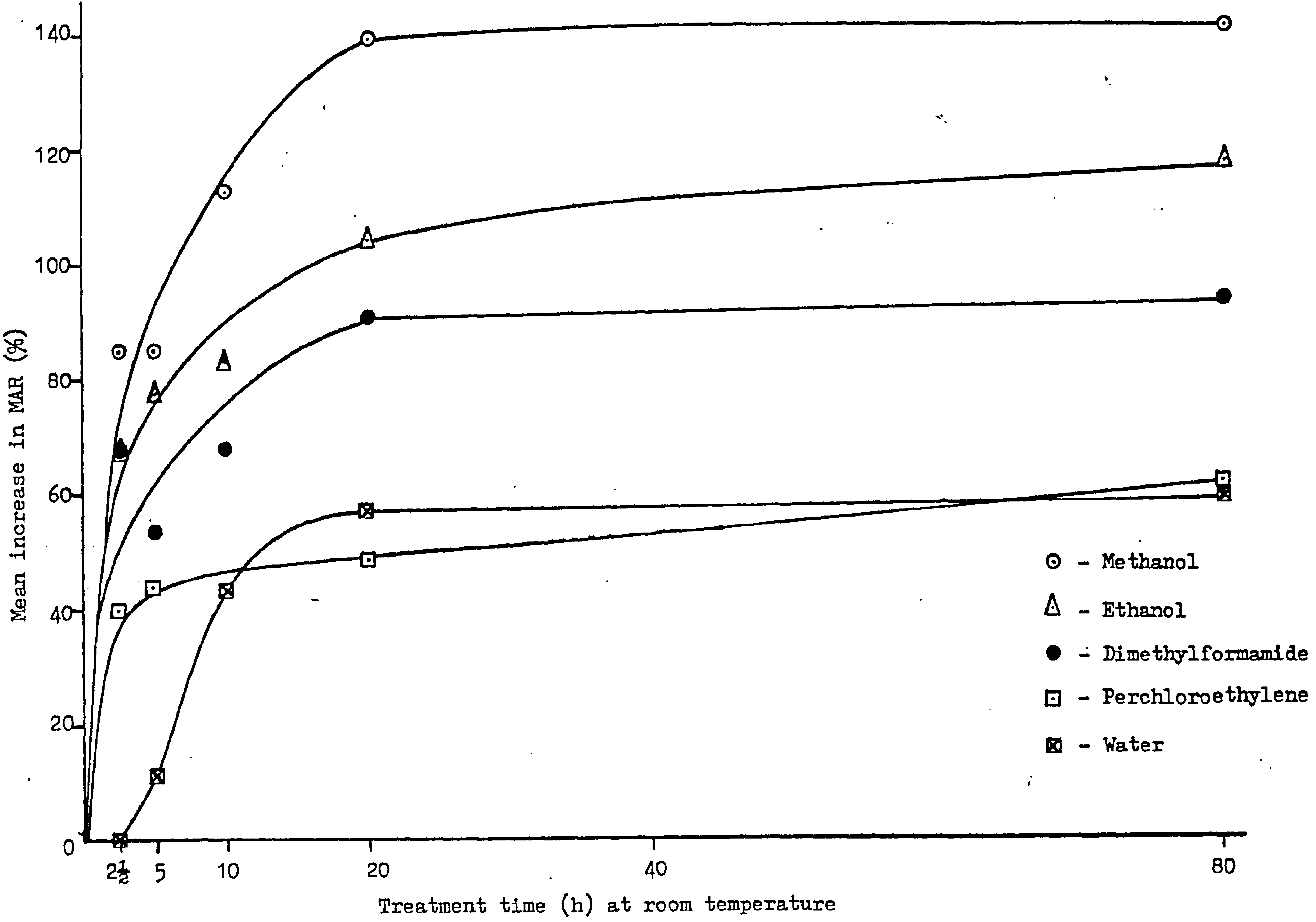
It is known that as the time of the solvent treatment increases the amount of solvent absorbed by the fibre increases until an equilibrium value is reached depending upon the treatment conditions and the nature and size of the solvent molecule (302, 303, 315-318). In the case of methanol on mohair, which is very similar in structure to wool, equilibrium is reached after about 20 hours (302). From Table 102 and Fig. 90 it is clear that the degree of improvement in

TABLE 102. The effects of immersion time for solvent treatments at room temperature on MAR of fabric A (worsted).

Time of treatment (h)	Water		Methanol		Ethanol		Dimethyl formamide		Perchloroethylene	
	Abrasion Resistance		Abrasion Resistance		Abrasion Resistance		Abrasion Resistance		Abrasion Resistance	
	(Rubs x 10^3)	mean	(Rubs x 10^3)	mean	(Rubs x 10^3)	mean	(Rubs x 10^3)	mean	(Rubs x 10^3)	mean
Untreated	13.0 12.5 10.2	11.9	-	-	-	-	-	-	-	-
2.5	11.0 12.5 12.5	12.0 (0)	20.0 23.0 23.0	22.0 (84.8)	19.0 21.0 20.0	20.0 (68.0)	20.0 22.0 18.0	20.0 (68.0)	16.0 18.0 16.0	16.7 (40.0)
5.0	12.5 14.0 13.0	13.2 (10.6)	23.0 23.0 20.0	22.0 (84.8)	20.5 22.0 20.5	21.0 (76.5)	18.0 19.0 18.0	18.3 (53.7)	16.0 18.5 17.0	17.2 (44.2)
10	17.0 19.0 15.0	17.0 (42.8)	24.0 28.0 24.0	25.3 (112.6)	22.0 21.5 22.0	21.8 (83.5)	20.5 21.0 18.5	20.0 (68.0)	18.0 17.0 16.0	17.0 (42.8)
20	18.0 20.0 18.0	18.7 (56.8)	30.0 28.0 27.5	28.5 (139.5)	24.0 25.0 24.0	24.3 (104.5)	22.0 23.0 23.0	22.7 (90.4)	18.0 18.0 17.0	17.7 (48.4)
80	18.0 21.0 18.0	19.0 (59.6)	30.0 29.0 27.5	28.8 (142.0)	26.0 26.0 26.0	26.0 (118.4)	23.0 24.0 22.5	23.1 (94.5)	18.0 20.0 20.0	19.3 (62.0)

The values in parentheses represent the mean increase in MAR (%).

Fig. 90 - The Effect of immersion time for solvent treatments at room temperature on the Martindale abrasion resistance of fabric A (worsted).



MAR has reached almost the maximum value after 20 hours and that very little change is observed if the treatment time is extended to 80 hours.

In Table 102 and Fig. 90 where the values of the increase in MAR (%) after treatment in ethanol are also plotted against the time of treatment, a very similar picture to that observed with methanol was obtained, although the degree of improvement in abrasion resistance was not as great as in the case of methanol. Furthermore equilibrium does not appear to have been reached even after 80 hours and this is in agreement with the results of studies on equilibrium imbibition values (302).

It is well-known that extraction of wool with ethanol removes wool wax and other components from the fibre (319) and this treatment has also been observed to cause pitting of the surface as observed by light microscopy (319, 320). Examination of fibre cross-sections in the transmission electron microscope indicates that ethanol extraction causes disruption of the epicuticle and exocuticle with possible removal of some protein material (320-322). In addition considerably greater quantities of a lipid or wool wax component are removed from the cuticle and cortex of the fibre (320).

It is also well known that extraction of wool fabrics with ethanol before polymer shrink-resist treatment (323) or before degradative shrink-resist treatments of various kinds (319) increases the shrink-resist effectiveness. Although a short extraction of wool fabrics with hot ethanol is an effective pretreatment for such shrink-resist processes, longer extraction times with cold ethanol are necessary to obtain similar effects (323). This is in agreement with the observations in this work where extraction with methanol or ethanol at the boil for 2.5 hours gave almost the same improvement in MAR as that obtained after 80 hours treatment at room temperature.

From Table 102 and Fig. 90 where the MAR values obtained after treatment with dimethyl formamide (DMF) are plotted against the treatment time, it is clear that the level of improvement in MAR is markedly dependent on the time of treatment. Although the imbibition values do not appear to be in the literature, DMF is a powerful solvent and the equilibrium absorption should be reached quite quickly. Indeed from the values of MAR after about 20 hours it seems that the system is almost at equilibrium. DMF is a slightly more powerful solvent than ethanol when compared on the basis of their dielectric constants ($\mathcal{E}$) (see Table 103) and therefore it might be expected that better results could be obtained with long immersion times but this was not observed.

TABLE 103 Dielectric constant of solvents (324)

Water	78.5
Methanol	32.6
Dimethyl formamide	26.6
Ethanol	24.3
Perchloroethylene	2.2

On the other hand ethanol has a smaller molar volume than DMF and thus greater amounts of ethanol might be absorbed by the fibre substrate in a given time and this would cause greater fibre modification and improved MAR values. Nevertheless, similar levels of improvement in MAR were obtained for the first 2.5 hour treatment.

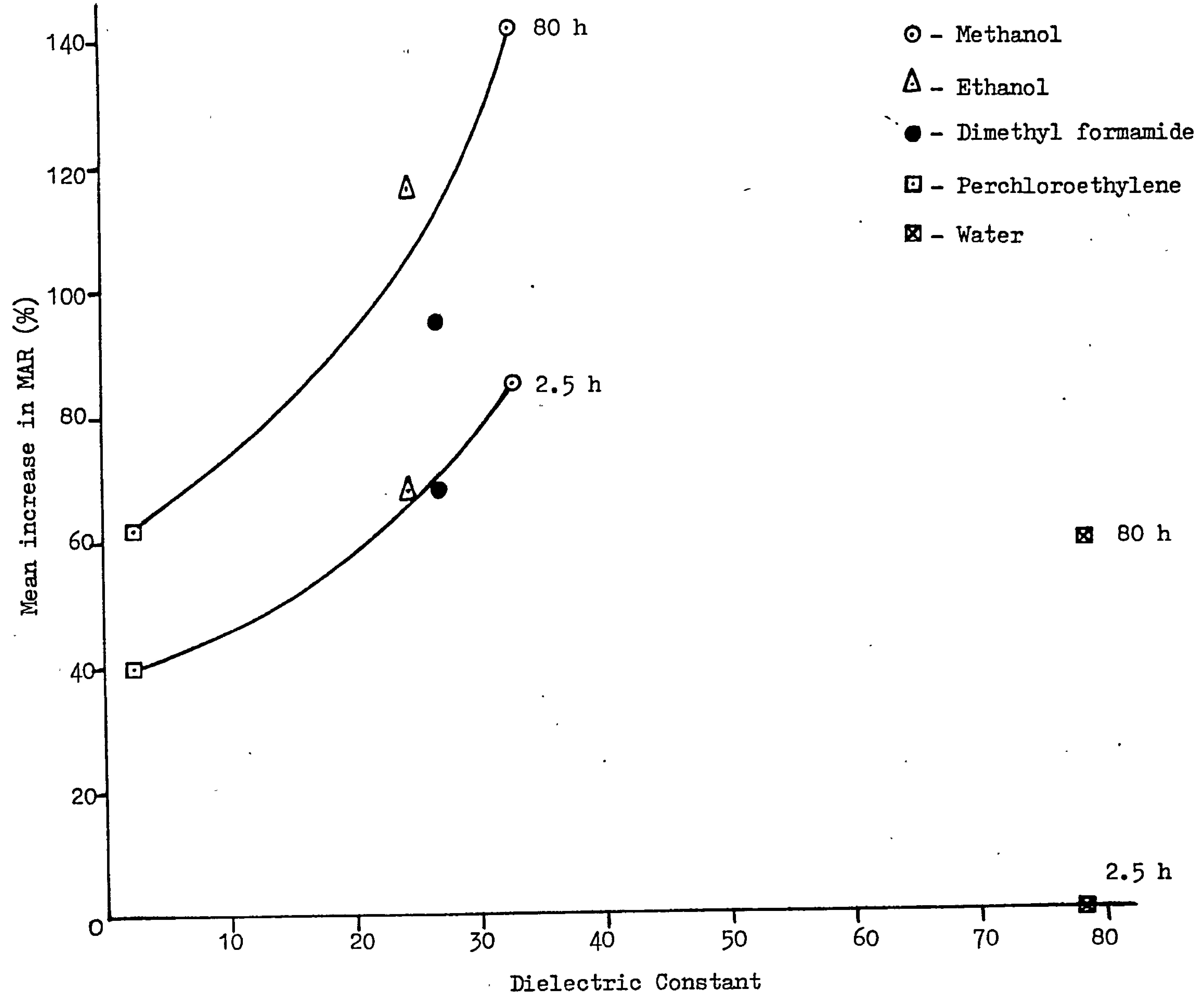
The treatment with perchloroethylene for a range of times (see Table 102 and Fig. 90) again shows the same effect, namely that the MAR values are dependent upon the time of treatment and increase towards an equilibrium value higher than the untreated fabric value. The improvement in MAR is however lower than that obtained using the more polar solvents such as methanol, ethanol and dimethyl formamide.

Water treatment over the same range of times confirms the same effect as observed with the other solvents (see Table 102 and Fig. 90), namely that the MAR values increase with the treatment time and as with the other solvent treatments approach an equilibrium value higher than the untreated fabric value. However the improvements in MAR are similar to those of the perchloroethylene treatment and lower than those obtained with methanol, ethanol or dimethyl formamide.

It might be expected on the basis of the high polarity (as demonstrated by the values of the dielectric constant in Table 103) and the low molar volume (see Table 101) of water that this should lead to the greatest changes in fibre modification and thus in MAR values, but this is not observed. However, the wool fabric has been treated in water prior to this investigation, i.e. scouring and thus the lower MAR values obtained are not surprising. An alternative explanation could be that further water treatment does not extract substances that the other organic solvents might extract, thereby modifying the fabric properties.

In Fig. 91 the values of the MAR of fabric samples treated for 2.5 hours and 80 hours at room temperature in various organic solvents are plotted against the dielectric constant ($\mathcal{E}$) of the individual solvents. It is clear for most of the reagents studied that after 2.5 hours treatment the fabric MAR is increased as the dielectric constant, and hence the polarity, of the solvents is increased. The relationship is not linear, but tends towards a

Fig. 91 The effect of dielectric constant of solvents on the Martindale abrasion resistance of fabric A (worsted)



limiting higher value for fabric MAR. The increases in MAR must, therefore, be associated in some way with the modification of the wool fibre structure as a result of the penetration by polar solvent molecules. It has previously been noted (302, 303, 315) that the amount of solvent absorbed increases as the polarity of the solvent increases. However the relationship in this study is not simple, because the results for water do not conform to this general trend, but some possible explanations for these results were given earlier.

After 80 hours treatment the overall trend remains similar to that for 2.5 hours but the MAR values are higher and even that for water which was zero at 2.5 hours is increased by about 60%. This would indicate time-dependent changes in the wool fibre structure.

In Fig. 92 the fabric MAR (%) values have been plotted against the amount of solvent absorbed by the fibre (g. mole/kg) (see also Table 104). In this instance the results of Ahmad (302) on mohair fibre have been utilized, as there appears to be little difference between mohair and wool with regard to sorption of the reagents studied and the imbibition values had not been measured directly in this work.

It is clear from Fig. 92 that an increase in the amount of solvent absorbed leads to an increase in fabric MAR. The results are of particular interest because it is apparent that while a large amount of solvent absorbed initially causes an improvement in MAR, it is equally clear that relatively small changes in the amount of solvent absorbed near the equilibrium adsorption conditions also lead to a marked increase in MAR. Indeed this latter situation is very marked with polar liquids such as methanol and ethanol. As discussed earlier on (see section 3.3.1.(iii)) the sorption of organic

Fig. 92 - The effects of imbibition values (g. moles/kg) for various solvents on the Martindale abrasion resistance of fabric A (worsted).

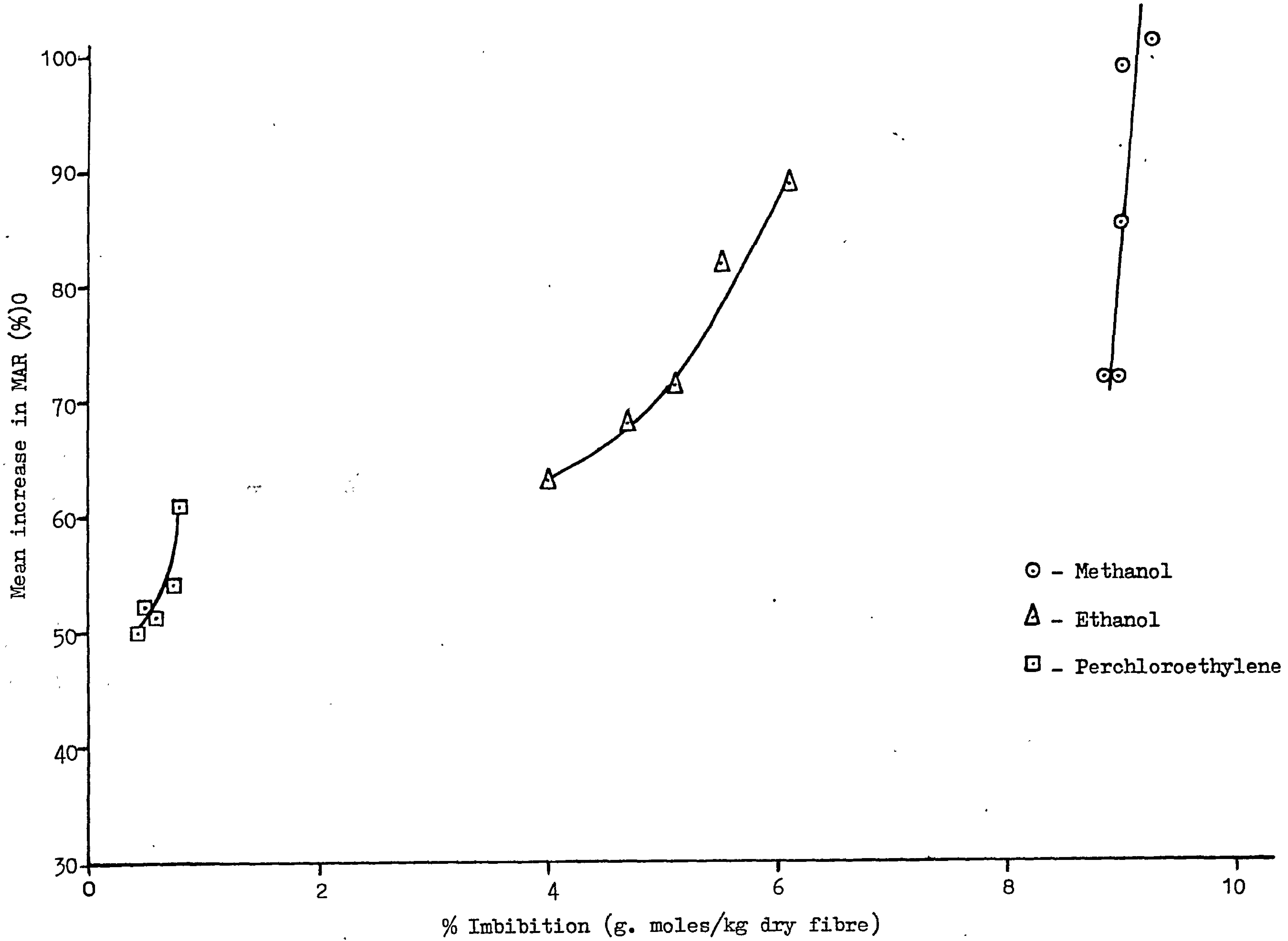


TABLE 104 Imbibition values (g. moles/kg) of mohair fibres (302) immersed in solvent for various times at 22°C

Time of immersion (h)	Reagents		
	Methanol	Ethanol	Perchloroethylene
2.5	8.85 (84.8)	4.0 (67.0)	0.45 (40.0)
5	8.93 (84.8)	4.7 (76.5)	0.50 (44.2)
10	8.98 (112.6)	5.1 (83.5)	0.58 (42.8)
20	9.0 (139.5)	5.5 (104.5)	0.73 (48.4)
80	9.25 (142.0)	6.2 (118.4)	0.80 (62.0)

The values in parentheses represent the mean increase (%) in MAR for wool fabric A determined in this work.

liquids takes place extremely rapidly and equilibrium is almost established within a few hours for methanol and more than 24 hours for ethanol (302). Hence the results may be interpreted as previously advanced in terms of a time-dependent chain molecular relaxation process in which conformational changes occur within the fibre substrate. Such changes will be more evident in highly polar solvents, whereas the changes in relatively non-polar solvents such as perchloroethylene would be of a lower order of magnitude and would proceed fairly slowly.

The chain molecular conformational changes occurring in wool immersed in highly polar solvents may in turn lead to minor increases in the equilibrium sorption values for the compounds concerned. This may reflect the results of experimental studies in which the sorption values continue to slowly rise as the immersion time is increased, although the magnitude of this effect is decreased the lower the polarity of the solvent.

Small changes in the sorption are clearly reflected by great changes in the improvement in MAR values, because the small increases in sorption values take place over a comparatively long period of time in which fibre relaxation may take place within the highly swollen fibre structure.

Thus the changes that occur in the fibre structure as a result of the solvent treatments lead to changes in fabric abrasion properties and other physical properties such as stress-strain properties (see section 3.2.2.3.) and crease recovery of wool fabrics which will be discussed separately in section (3.4.2.4.).

Section 3.4

3.4.1. Experimental

Materials

Fabric specifications: Fabric A was used throughout the experimental work described in this section while fabrics B and C were additionally used for some of the experiments. The detailed specifications of the fabrics are given in section (2.4.2.).

Reagents: In this series of experiments the following reagents were used:

(i) Alcohols: Methanol, Ethanol.

(ii) Azeotropic mixture: Benzene:Methanol (3:2 v/v).

(iii) Perchloroethylene.

(iv) N, N -dimethyl formamide.

(v) Deionised water.

The grade and supplier for the above reagents are given in sections (3.2.1. and 3.3.2.).

Methods

Method of treatment

The above reagents were used for (i) fabrics A, B and C either commercially scoured (except fabric A, 2% soap scoured), or (ii) fabrics A, B and C 0.1% Teepol-treated and soxhlet-extracted for 2.5 hours as described in section (3.2.1.).

Furthermore wool fabric samples (fabric A only) were immersed in deionised water or ethanol, dimethyl formamide or perchloroethylene for a range of treatment times at room temperature in a 2 l conical flask. The liquor ratio was 30:1 and the samples were periodically shaken during immersion. Work was also conducted on fabric A with dimethyl formamide for 2.5 hours at different temperatures. After treatment the fabric samples were removed, excess liquor removed and the samples allowed to dry at room temperature hung vertically in a fume cupboard.

For the fabric samples treated in dimethyl formamide at higher temperatures, the conical flask was immersed in a thermostatically controlled water bath. After treatment, the fabric was rinsed briefly (approximately 1 minute) in cold water and dried as previously described.

Conditioning

All the treated fabric samples were conditioned for at least 3 days at 65% r.h., and 21°C prior to testing.

Methods of Testing

(i) Flex Abrasion Resistance

The flex abrasion resistance was determined by using the Stoll flexing and abrasion tester according to A.S.T.M. method D-1175.

Details of this method are given in section (2.6.2.).

The pressure plate and folding or tensioning bar for the three wool fabrics were loaded as follows:

(i) For fabrics A and C, 3 lb was loaded on the tensioning bar and no weight on the pressure plate.

(ii) For fabric B, a ratio of 8:1, i.e. 4 lb on the folding bar and 0.5 lb on the pressure plate was used.

These were found as the result of some preliminary trials to be the optimum conditions for minimum vibration during the operation.

(ii) <u>Fabric Surface Frictional Properties</u>

For measuring the frictional properties of the fabrics the Instron Tensile Tester TM-M Metric Model was employed with slight modifications. A plate was placed on the base of the Instron and on top was placed a piece of the cross-bred wool fabric (used for flat abrasion) fixed with metal clamps. A plate with dimensions 6 x 6 cm was used to hold the fabric under test and this was pulled by the Instron against the cross-bred fabric by means of a cord passed round a frictionless pulley. With this technique a permanent record of the frictional force is obtained. The area under the trace for a given time represents the frictional force required to pull the plate with the test specimen. The area was measured by means of an integrator which was connected to the Instron.

The test specimen was cut slightly larger than the holder, folded around the plate and secured tightly with adhesive tape. The machine settings were as follows:

(i) Traverse (cross-head) speed - 5 cm min.$^{-1}$.

(ii) Chart speed - 10 cm min.$^{-1}$.

(iii) Load cell B (load range up to 2 kg).

The frictional force F (in g) was calculated as follows:

$$F = \frac{\text{integrator value x Full scale load}}{\text{5000(constant for time 60 seconds)}} = g$$

The mean value of three samples in the weft-way direction were taken to determine the frictional force.

The above technique is recommended and generally used at the I.W.S. Technical Centre (245).

Fabric Area Felting Shrinkage (F.A.F.S.)

The decrease in area of 12 x 12 cm fabric samples was measured after washing in a 50 l Cubex international machine with 12.5 l of wash liquor over a range of times. The details of the general experimental procedure are given in section (2.6.2.).

Crease Recovery Angle (CRA) - (see section 2.7.2.).

X-ray diffraction studies

X-ray photographs were taken using a copper K_α radiation from a sealed Philips tube with copper anode, operating at 40 kV and a tube current of 16 mA.

The radiation was filtered through nickel foils which removed most of the copper K_β component and some of the white radiation, and gave a transmitted beam which had a wavelength of 1.54 A^o.

A narrow beam was obtained by using in the camera a collimator made of lead glass.

3.4.2. Results and Discussion

3.4.2.1. Flex Abrasion Resistance

The results of the effects of solvent treatments on the flex abrasion resistance will be considered under two headings:

(a) Commercially scoured fabrics (except fabric A, which was scoured with 2% soap solution) treated with solvents as detailed in Table 105.

(b) 0.1% Teepol scoured fabrics treated with solvents as detailed in Table 106.

(a) In general all the solvent treatments studied reduce the flex abrasion resistance of wool fabrics with the exception of fabric C, on which no effect or slight improvement was observed. Although no simple relationship could be found between the nature of the solvent and the change in flex abrasion resistance, benzene/methanol treatment seemed to give slightly better results compared with the other solvent treatments.

(b) Treatment with 0.1% Teepol solution prior to solvent treatment gave very similar results to those of commercially scoured and solvent-treated fabrics (see Table 106), except in the case of fabric B where some improvement compared with case (a) was obtained although this was still lower than the original untreated value.

A possible explanation for the reduction in flex abrasion resistance could be that the effects of fibre relaxation could result in a reduction in the interfibre and interyarn forces. Thus lower forces would be required to pull the fibres and yarns apart, and therefore a lower number of cycles would be required to rupture the fabrics when flexing forces are applied. Alternatively the more severe nature of the flexing test and the complex mode of flexing and abrasion imparted to the fabric may well lead to different

TABLE 105. Flex abrasion resistance (FAR) of wool fabrics after solvent extraction for 2.5 h.

Type of treatment	Fabric A (worsted)			Fabric B (worsted)			Fabric C (woollen)		
	Abrasion Resistance		mean decrease in FAR (%)	Abrasion Resistance		mean decrease in FAR (%)	Abrasion Resistance		mean decrease in FAR (%)
	cycles	mean		cycles	mean		cycles	mean	
Untreated	1420 1390 1345 950	1275	0	1690 1070 1200	1300	0	160 165 175	167	0
Benzene/ Methanol	615 620 510 490	560	- 56.0	460 540	500	- 61.5	205 220 180 215	205	+ 22.7
Methanol	400 455 550 440	460	- 64.0	495 540	510	- 60.8	200 160 180 240	200	+ 19.8
Ethanol	500 480 490 527	500	- 60.8	460 415	430	- 66.9	200 230 170 190	200	+ 19.8
Perchloro-ethylene	600 415 400 500	480	- 62.3	535 480 495	500	- 61.5	190 140 195	175	+ 4.8

TABLE 106. Flex abrasion resistance (FAR) of Teepol pretreated wool fabrics after solvent extraction for 2.5 h.

Type of treatment	Fabric A (worsted)			Fabric B (worsted)			Fabric C (woollen)		
	Abrasion Resistance		mean decrease in FAR (%)	Abrasion Resistance		mean decrease in FAR (%)	Abrasion Resistance		mean decrease in FAR (%)
	cycles	mean		cycles	mean		cycles	mean	
Untreated	1420 1390 1345 950	1275	0	1640 1070 1200	1300	0	160 165 175	167	0
Benzene/ Methanol	610 585 600	600	- 53.0	720 610	665	- 48.8	210 240	225	+ 34.7
Methanol	525 495 505	510	- 60.0	490 530	515	- 60.4	160 200	180	+ 7.8
Ethanol	430 440	435	- 65.9	520 475	500	- 61.5	215 185	200	+ 19.8
Perchloro-ethylene	475 450	465	- 63.5	685 765	725	- 44.2	215 160	185	+ 10.8

results compared with the Martindale abrasion test.

3.4.2.2. Fabric Surface Frictional Properties

The effects of solvent treatments on the fabric surface frictional properties are considered under two headings:

(a) commercially scoured fabrics (except fabric A which was scoured with 2% soap solution) treated with solvents, detailed in Table 107 and illustrated in Fig. 93.

(b) 0.1% Teepol scoured fabrics treated with solvents detailed in Table 108 and illustrated in Fig. 94.

(a) In general all solvent treatments studied appear to reduce the surface friction of the fabrics. Although the level of reduction in surface friction is not very pronounced because of experimental scatter the general trend appears to be similar for the three fabrics studied (see Fig. 93).

The fabric surface friction was decreased in the order: Benzene/methanol > methanol > ethanol > perchloroethylene > Untreated. Indeed this was the order observed in section 3.2.2.1. for improving the MAR and therefore a meaningful relationship may well exist. Plotting the surface friction results against the increase in MAR (%) yields a similar picture (see Fig. 93) to that of the increase in MAR (%) against the treatment temperature of the solvents. It is clear from Fig. 93 that as the surface friction decreases the MAR increases.

Fabrics treated with 0.1% Teepol solution prior to solvent treatments gave very similar results with an even higher reduction in fabric friction. The general trends for the three fabrics are similar to those obtained under condition (a) (see Fig. 94).

TABLE 107. Surface frictional properties of wool fabrics after solvent extraction for 2.5 h.

Solvent treatment	Fabric A (worsted)		Fabric B (worsted)		Fabric C (woollen)	
	Frictional Force (g)	mean	Frictional Force (g)	mean	Frictional Force (g)	mean
Untreated	234.3 233.9	234.1	169.3 163.6	166.4	172.3 162.4 159.7	164.8
Benzene/ Methanol	231.9 226.7	229.3	159.4 156.8 154.5	156.9	160.9 160.9	160.9
Methanol	236.7 224.1	230.4	165.9 156.2 152.6	158.2	162.5 158.2	160.3
Ethanol	233.8 227.6	230.7	166.8 158.3 156.0	160.3	160.8 161.6	161.2
Perchloro-ethylene	233.5 229.5	231.5	169.4 157.9 155.5	160.9	165.9 158.1	162.0

Fig. 93 - The effects of solvent extraction for 2.5 hours on the surface frictional properties of wool fabrics.

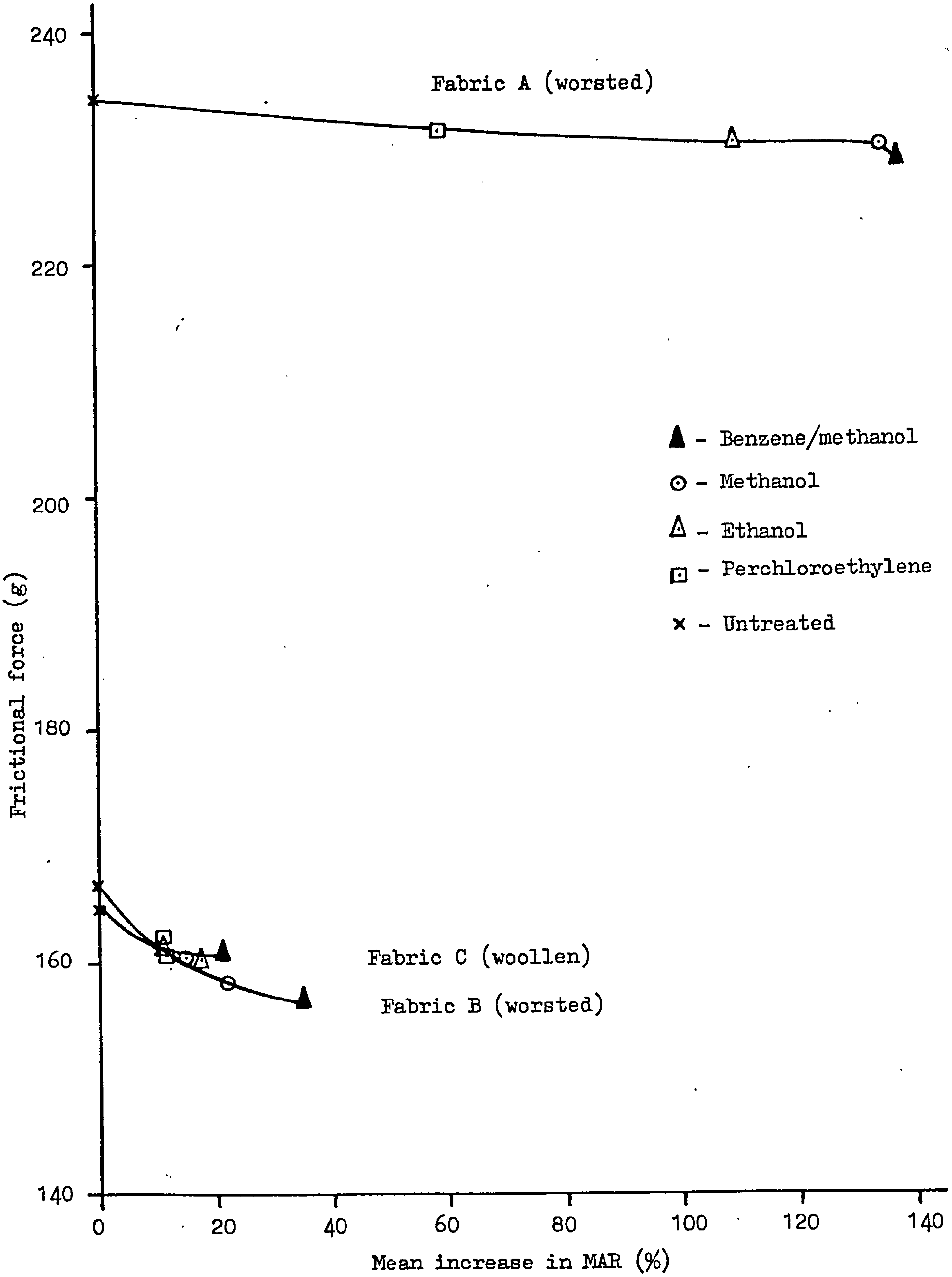
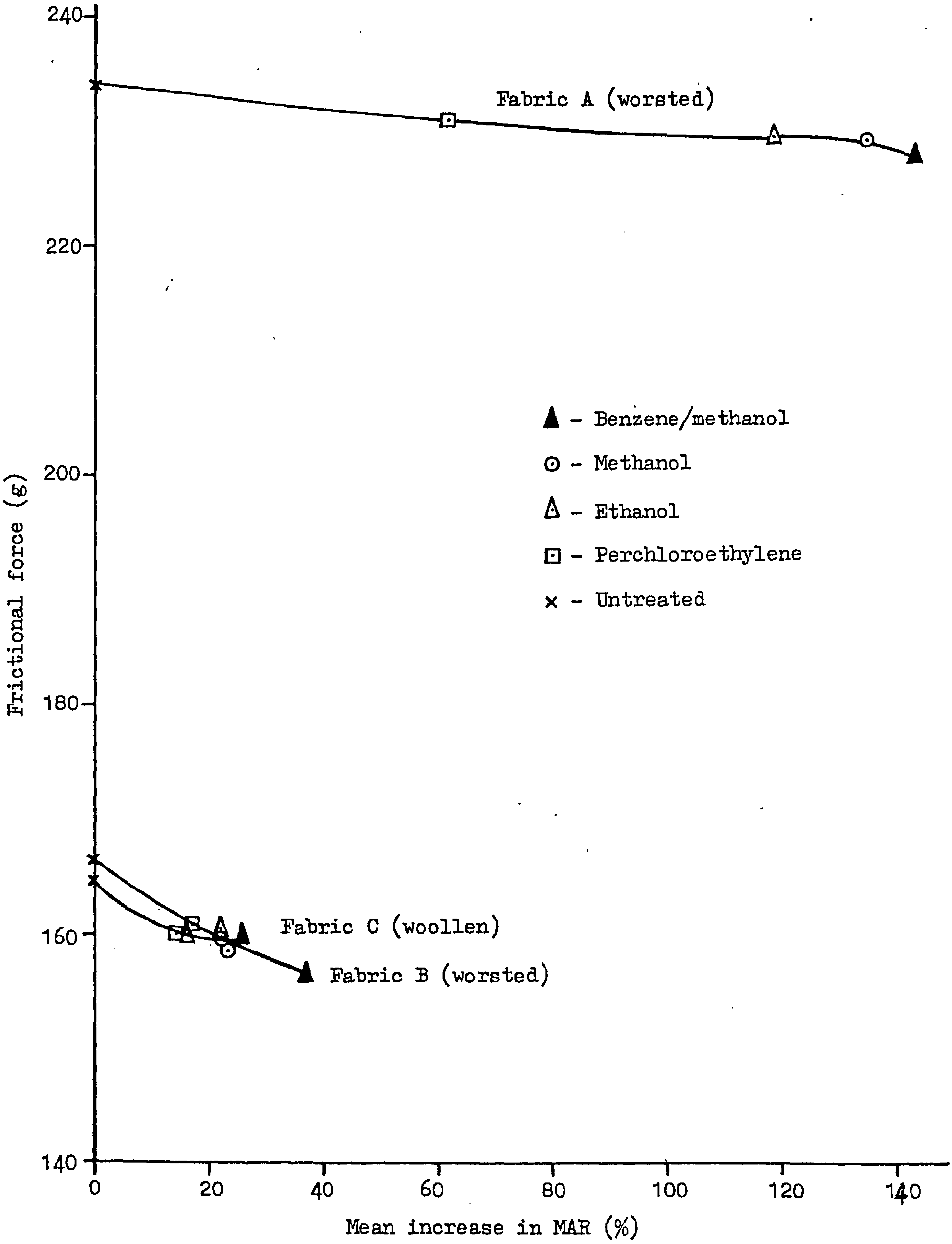


TABLE 108. Surface frictional properties of Teepol treated wool fabrics after solvent extraction for 2.5 h.

Solvent treatment	Fabric A (worsted)		Fabric B (worsted)		Fabric C (woollen)	
	Frictional Force		Frictional Force		Frictional Force	
	(g)	mean	(g)	mean	(g)	mean
Untreated	234.3 233.9	234.1	169.3 163.6	166.4	172.3 162.4 159.7	164.8
Benzene/ Methanol	231.6 224.8	228.2	163.8 154.7 151.2	156.5	166.9 156.8 156.0	159.9
Methanol	229.7 228.9	229.3	161.8 159.2 154.2	158.4	163.0 159.6 157.1	159.9
Ethanol	228.3 231.4	229.8	163.2 161.8 155.7	160.2	161.1 159.0	160.1
Perchloro-ethylene	231.3 230.9	231.1	164.1 159.2 157.9	160.4	160.9 160.9 159.5	160.1

Fig. 94 - The effects of solvent extraction for 2.5 hours on the surface frictional properties of 0.1% Teepol pretreated wool fabrics.



3.4.2.3. Fabric Area Felting Shrinkage (F.A.F.S.)

The values for the felting shrinkage of the solvent-extracted fabrics after washing in a 50 l Cubex International machine for various times are given in Table 109 and illustrated in Fig. 95 and 96 for fabric A and fabric C respectively.

It is clear that with both fabrics used (A and C) the general shape of the fabric area felting shrinkage (F.A.F.S.) (%) against the time of washing curve is very similar and the order of felting is the same, namely: Untreated > Perchloroethylene > ethanol > benzene/methanol.

The reason for this phenomenon is believed to arise at least partially from the changes in the Directional Frictional Effect (D.F.E.). It has been established that benzene/methanol, ether/ethanol, and perchloroethylene treatments reduce the D.F.E. in the order Benzene/methanol > ether/ethanol > perchloroethylene (325). Reduction in the D.F.E. after extraction with ethanol has also been reported elsewhere (326).

It is well known that reducing the D.F.E. leads to a reduction in the felting shrinkage in wool fabrics and indeed this is observed in this experimental work.

It has also been shown (see section 2.6.3.6.) that if a degree of shrink resistance is observed, then an accompanying improvement in MAR is also obtained. A similar picture clearly emerges here in the solvent treatments and the same order of improvement in MAR as in the order of reduction in fabric area felting shrinkage is obtained.

The degree of shrink resistance obtained on fabric A is better than that of fabric C and this may explain the better results in MAR

TABLE 109. The effect of solvent extraction for 2.5 h on the fabric area felting shrinkage (FAFS) of wool fabrics.

Solvent treatment	Fabric A (worsted)					Fabric C (woollen)				
	FAFS (%) after washing for					FAFS (%) after washing for				
	20 min	40 min	60 min	120 min	180 min	20 min	40 min	60 min	120 min	180 min
Untreated	2.5	9.81	17.6	36.25	48.89	12.92	21.25	29.19	42.52	48.67
Benzene/ Methanol	0	2.5	8.17	21.32	33.48	6.56	12.11	20.5	34.0	41.88
Ethanol	0.8	4.17	9.81	25.0	38.89	6.56	13.67	21.98	36.06	43.17
Perchloro-ethylene	1.67	6.58	12.15	30.62	45.69	7.36	15.21	23.44	38.0	45.02

Fig. 95 - The effect of solvent extraction for 2.5 hours on the area felting shrinkage of fabric A (worsted)

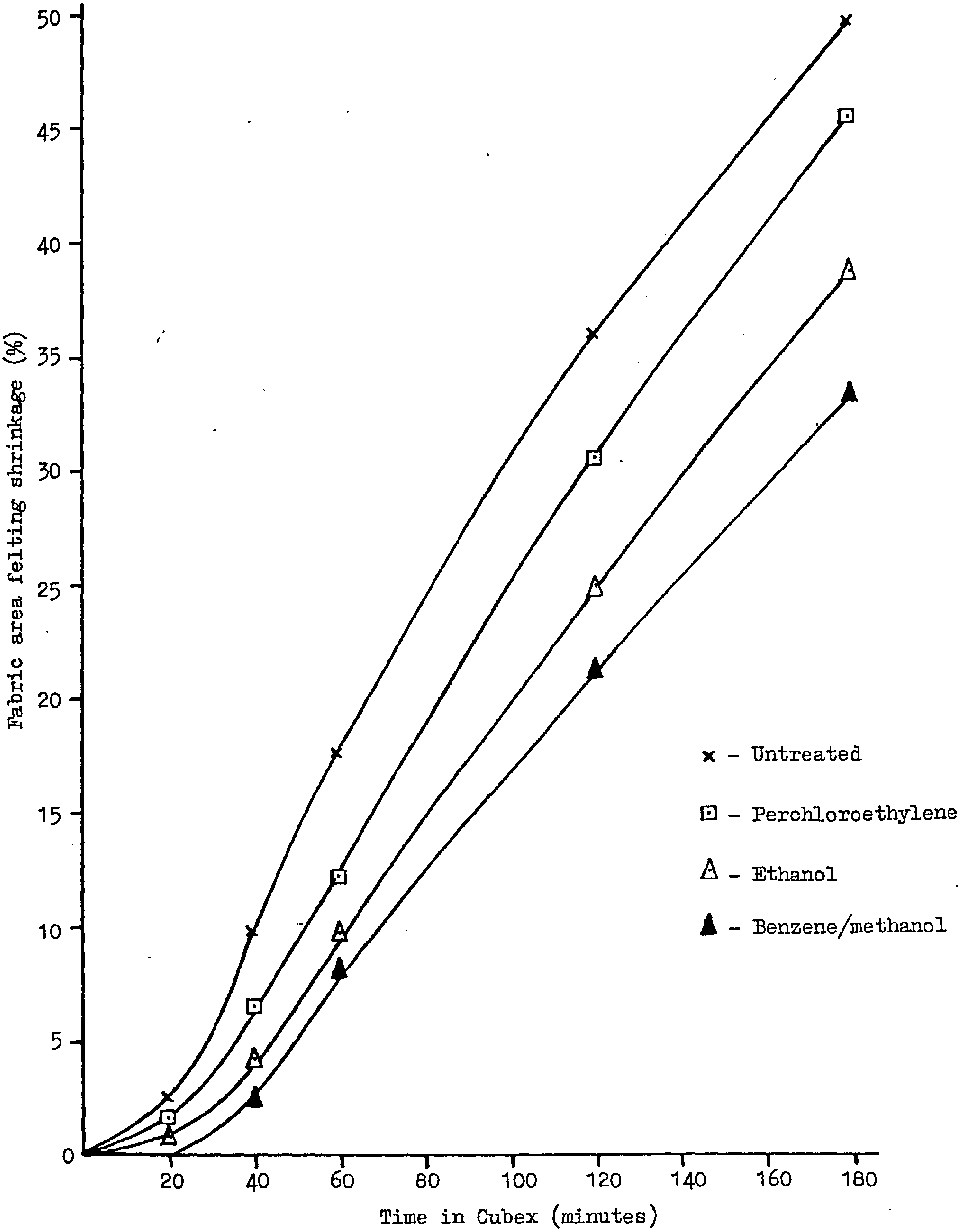
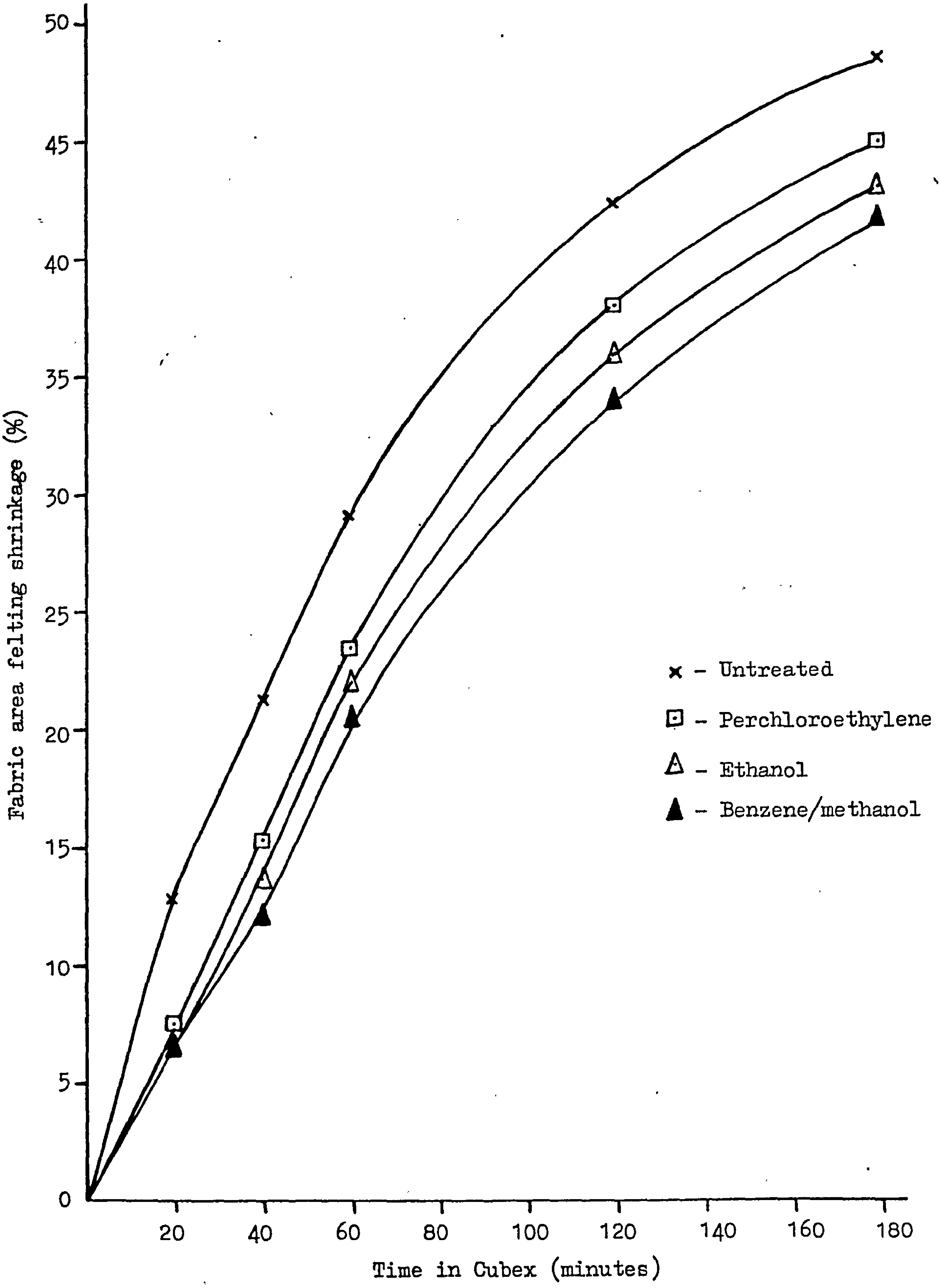


Fig. 96 - The effect of solvent extraction for 2.5 hours on the fabric area shrinkage of fabric C (woollen).



obtained on fabric A. Another supporting factor for the better results on the MAR of fabric A is that it does not form pills, which have been previously shown in section (2.5.3.4.) to reduce the MAR.

3.4.2.4. Crease Recovery Angle (CRA)

The effects of the treatment time at 21°C on the CRA of wool fabric pre-conditioned at 65% r.h. at 21°C are illustrated in Table 110. It is clear that deionised water, even in a brief rinsing treatment, exerts a marked reduction in the CRA. However, as with all the solvent treatments studied, the CRA tends towards a limiting or equilibrium value which is significantly lower than that for the original fabric. In addition, the rate of change in the CRA progressively decreases with increase in treatment time.

Both dimethyl formamide (DMF) and ethanol are more effective than perchloroethylene in reducing the CRA of wool fabric. The results for the latter solvent appear to reach equilibrium fairly rapidly, whereas DMF and ethanol exhibit a greater time-dependent response under similar immersion conditions.

It must be concluded, therefore, that the CRA of wool fabric is reduced to a greater extent by immersion in polar solvents. Indeed the greater the polarity of the solvent, as indicated by the value of the dielectric constant ($\mathcal{E}$) at 25°C (see Table 103), the greater the reduction in the CRA. Thus the order of decreasing CRA is in the series water ($\mathcal{E} = 78.5$), $>$ DMF ($\mathcal{E} = 26.6$) $>$ Ethanol ($\mathcal{E} = 24.3$) $>$ Perchloroethylene ($\mathcal{E} = 2.2$).

These observations are interesting, for it has been observed from a number of studies (302, 303, 315) on the imbibition of water and organic solvents by dry textile fibres, that in numerous instances there is a linear relation between the imbibition and the dielectric

TABLE 110. The effect of immersion time in various liquids upon the crease recovery angle of scoured wool fabric.

Treatment:	Fabric Crease Recovery Angle (degrees) after immersion time (h).	2.5	5	10	20	80
Untreated	169.3 (1.7)	-	-	-	-	-
Water Rinsing	159.6 (2.0)	-	-	-	-	-
Water	-	155.5 (3)	151.0 (2.1)	149.3 (1.8)	148.3 (2)	145.3 (2.3)
Dimethyl formamide	-	151.5 (0.4)	151.0 (0.5)	150.0 (0.3)	149.3 (1.6)	148.3 (1.6)
Ethanol	-	164.0 (1.2)	159.5 (5.2)	158.8 (3.1)	156.0 (3.7)	152.0 (2.5)
Perchloroethylene	-	164.0 (1.7)	160.0 (0.5)	159.0 (1.3)	159.0 (1.2)	159.0 (0.8)

Values in parentheses are the coefficients of variation (%).

TABLE 110 a. Fabric Crease Recovery angle (degrees) after 2.5 h treatment in Dimethyl formamide.

Treatment Temperature (°C)	Crease Recovery Angle (degrees)	C.V.
20	151.5	0.4
50	149.0	1.7
80	144.0	4.1

constant of the immersion medium. This relationship is observed under conditions of equilibrium sorption where the imbibition is expressed in terms of g. mole. solvent adsorbed per kg dry fibre.

Typical results for water and aliphatic n-alcohols on dry nylon 66 fibres are presented in Fig. 97, while similar results have also been obtained using a homologous series of n-monocarboxylic acids on dry nylon 66 fibres (315). The results of Ahmad (302) and of Sengupta (303) who studied the absorption of water and n-aliphatic alcohols on mohair and wool fibres respectively are in accord with the proposed linear relationship between equilibrium sorption and the polarity of the solvent.

From these results, it must be concluded, therefore, provided the molecular size and shape of the solvent molecules are such that diffusion and sorption within wool take place, that such processes and their associated effects upon the fibre structure will be markedly influenced by the nature of the polarity of the solvent.

It is well-established (303, 316, 327) that polar hydroxylic solvents such as ethanol penetrate wool fibres readily and that appreciable amounts of ethanol are adsorbed under equilibrium conditions. This process normally takes longer than 24 hours at room temperature. However, in the case of relatively non-polar solvents such as perchloroethylene, the molecular size and shape is such that the rate of diffusion is low compared with linear chain compounds. In a similar manner benzene is known to be absorbed at a very slow rate by wool, the equilibrium sorption remaining at a low value (316, 327).

In Fig. 98 the conditioned values of the CRA for untreated wool fabric and for fabric samples treated for 80 hours at 21°C in the

Fig. 97 - Amount of liquid adsorbed per kg dry nylon 66 fibre as a function of the dielectric constant of the liquid

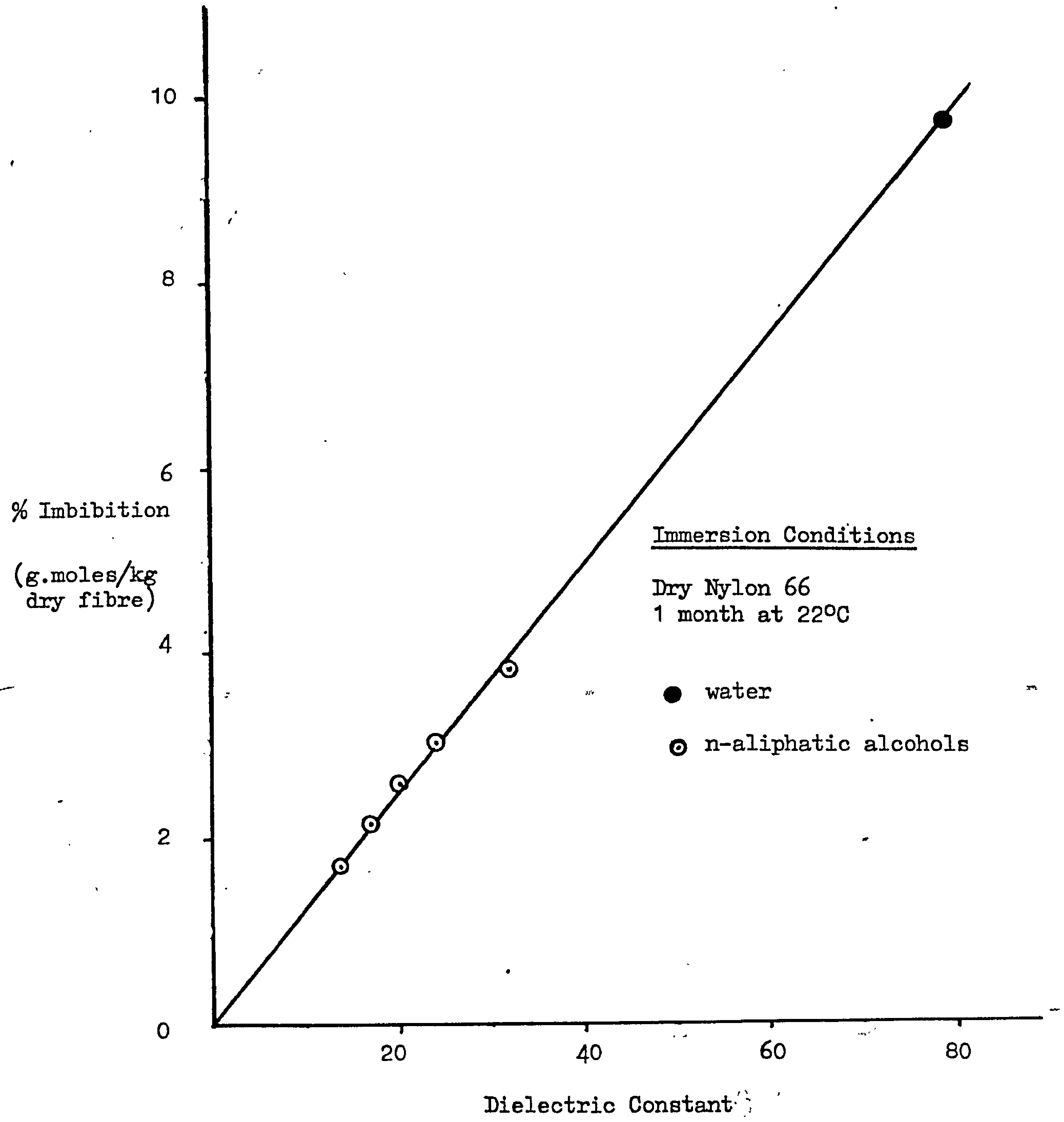
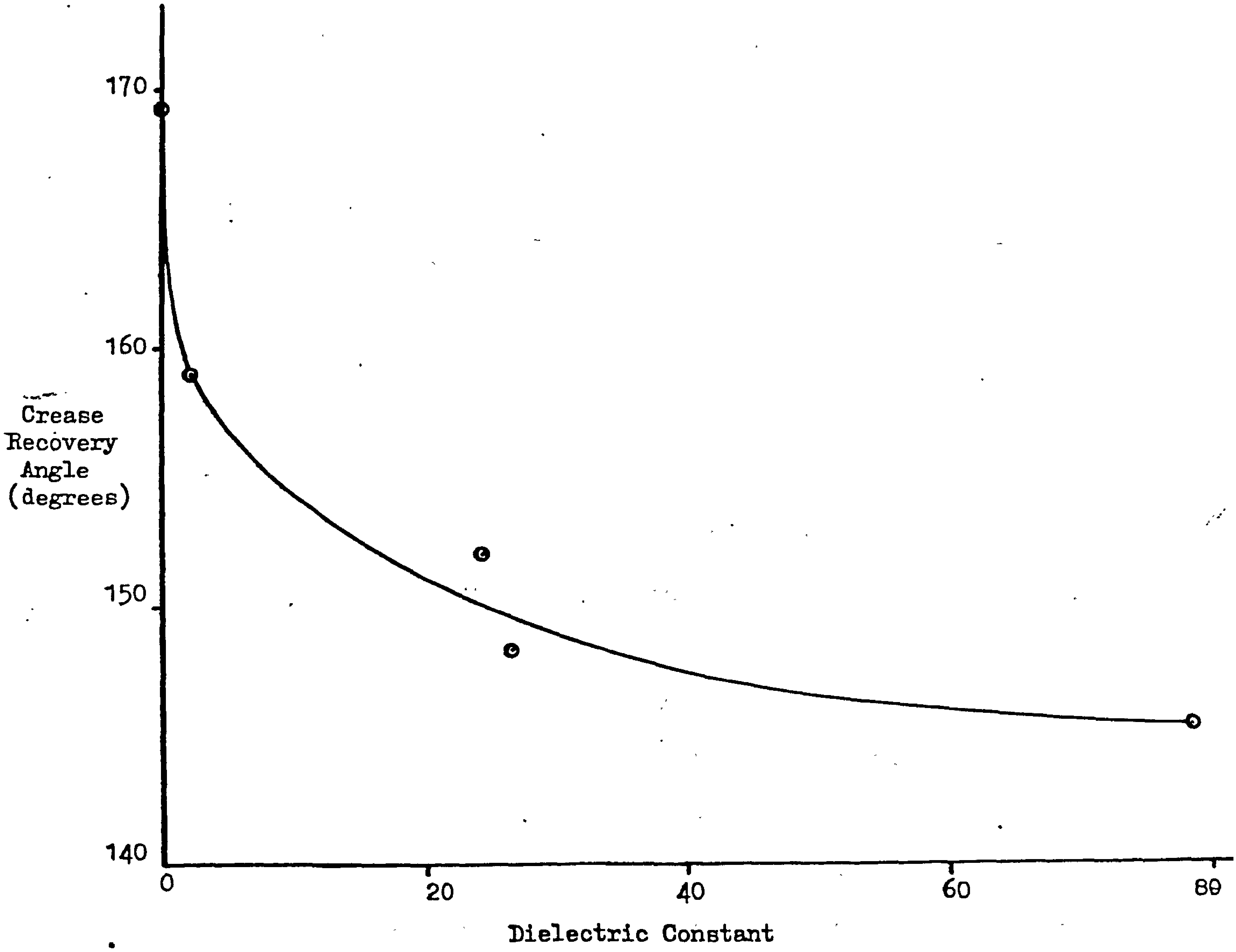


Fig. 98 - The relation between the crease recovery angle of wool fabric and the dielectric constants of the immersion media



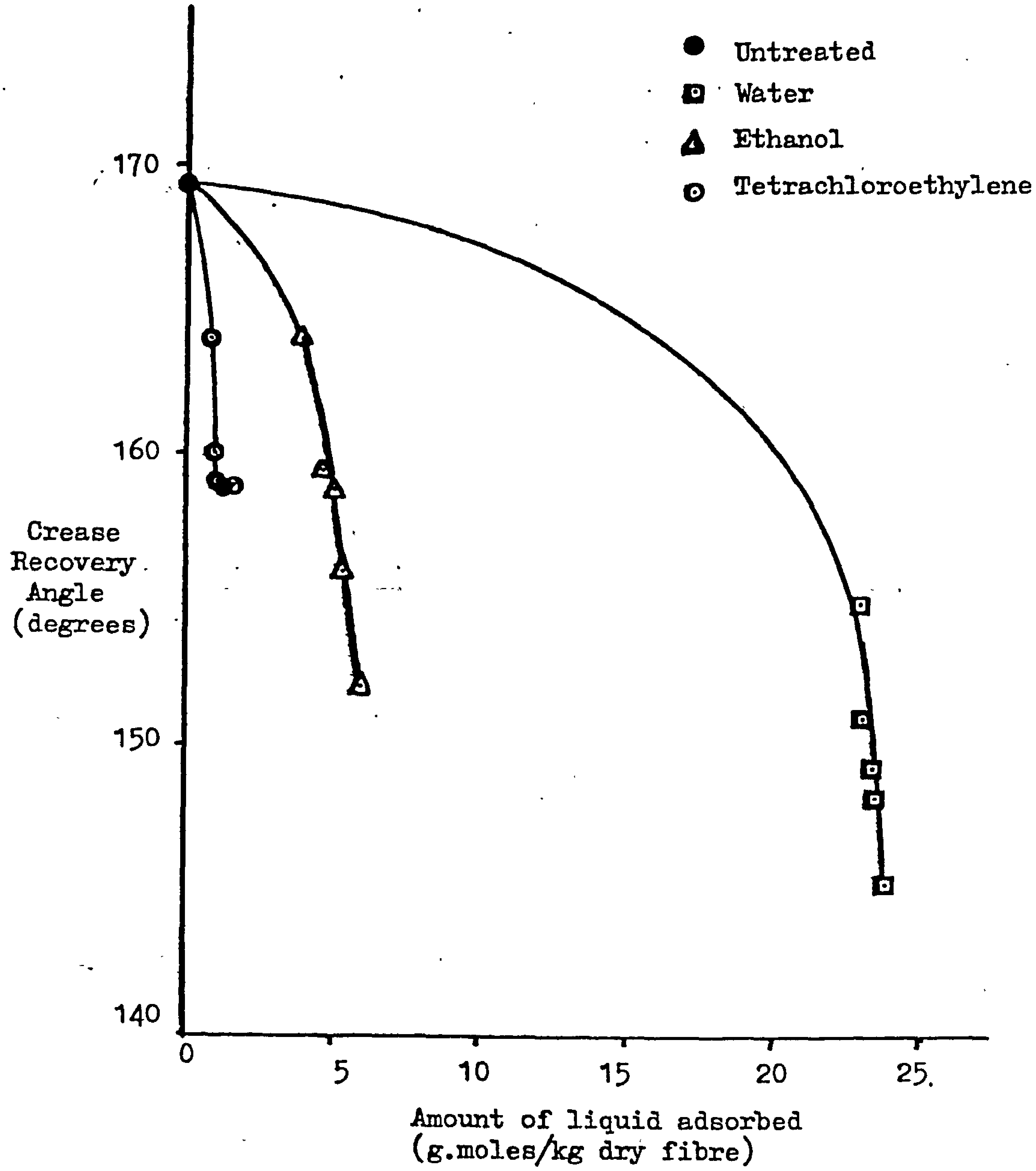
various immersion media are plotted against the dielectric constant of the individual solvents. The CRA-dielectric constant plot is non-linear, tending towards a lower CRA limit as the dielectric constant is increased. The reduction in CRA with increase in the dielectric constant is thus considered to arise as a result of the greater weakening of the fibre structure caused by the diffusion and adsorption of the more polar liquids.

The sorption of polar solvents such as water, DMF and ethanol must lead to the disruption of weaker bonds within the wool fibre such as hydrogen bonds and dispersion (Van der Waal's) forces. The disruption of these bonds which help to stabilise the fibre structure, it has been postulated, gives rise to limited fibre swelling which in turn facilitates the diffusion of further penetrant molecules into the fibre. Both processes thus operate continuously and concurrently until the solvent-fibre system reaches an equilibrium condition.

This process has been studied in more detail in Fig. 99 in which the CRA has been plotted against the amount of solvent absorbed by the fibres, by utilising the data of Ahmad (302) on mohair fibres. These were considered to be relevant and comparable to similar studies on wool and the imbibition values for the range of immersion times utilised in this study were, therefore, employed.

It is clear from Fig. 99 that an increase in the amount of solvent adsorbed generally leads to a reduction in fabric CRA. It is pertinent to point out that whereas equilibrium may be established within a matter of hours with water, this process takes 1 to 3 days in ethanol at room temperature. The results expressed in Fig. 99 thus cover a range of immersion times from 2.5 hours to 80 hours.

Fig. 99 - The relation between the crease recovery angle of wool fabric and the amount of liquid adsorbed



During the entry of the solvent molecules the fission of some of the weaker stabilising bonds must take place and the molecular chains must rearrange their positions within the fibre. The rate of fission of the bonds, the rearrangement of the chain molecules and the establishment of the equilibrium sorption condition will depend upon the bond-breaking ability of the penetrant molecules (303). This in turn will be dependent upon the polarity (i.e. the value of the dielectric constant) (302, 303, 315).

Hence the results in Fig. 99 may be interpreted in terms of a time-dependent chain molecular relaxation process in which conformational changes occur within the swollen fibre. Such changes will naturally proceed at a faster rate in the highly polar solvents, whereas in relatively non-polar solvents such as perchloroethylene, the changes appear to be of a lower order of magnitude, involving different stabilising bonds and proceeding at a slow rate. It is presumed, therefore, that the bonds mobilised in this case are more likely to be hydrophobic bonds and weak dispersion forces, which are normally considered to be of lesser importance than disulphide bonds and hydrogen bonds in stabilising wool fibres.

The greater decrease in CRA within the narrow sorption range near equilibrium sorption compared with the more gradual changes taking place below an immersion time of 2.5 hours is evidence in favour of such a time-dependent chain molecular relaxation process in the case of water and ethanol. Perchloroethylene treated fabrics appear to reach an equilibrium value, because of the relatively non-polar nature of this solvent and hence an inability to break polar bonds of the type involved with water and ethanol. Conformational relaxation effects may, in certain cases, promote a slightly greater uptake in the case of highly polar solvents during studies in which long periods of immersion are involved. Thus a shift to a slightly higher sorption value results with the attainment of a more highly swollen fibre environment.

Upon the removal of the solvent, new stabilising bonds are formed which stabilise the wool fibre in the new equilibrium position. The net result of this relaxation process is thus manifested in a reduction in the fabric CRA.

It can be seen that an increase in the immersion temperature should facilitate the diffusion and hence the sorption of polar solvents and in turn the rate of molecular relaxation will increase appropriately. This is reflected in the CRA values in Table 110a for DMF which after 2.5 hours at 80°C gives a lower CRA than for water after 80 hours at 21°C, not withstanding the lower dielectric constant of DMF compared with water, and the greater molecular size of DMF which would limit the rate of diffusion into wool.

A general decrease in CRA has been reported by Koenig (328, 329) and by Moore and O'Connell (330) in an attempt to increase the crease recovery of wool fabrics by the application of mono-or difunctional isocyanates from polar organic solvents such as pyridine or dimethyl formamide. In general it was concluded that the CRA was reduced as a result of the treatment in the polar media employed.

A reduction in the CRA has also been noted during the course of recent work (331) directed towards the reaction of isocyanates with wool. In this study, wool was treated with DMF for 0.5 hour at 105°C and the free isocyanate subsequently removed by soxhlet extraction for 12 hours in ethanol, prior to conditioning at 65% r.h., 21°C and measurement of the CRA.

3.4.2.5. X-ray diffraction studies

The α-helical meridional reflections of the wool fibre structure appear to be only slightly affected as a result of the solvent treatments. These very slight changes do not represent any real disruption of the oriented α-helical structure and are due presumably to slight changes in the position of the structure, i.e. a different chain molecular arrangement (as a result of the relaxation process) but the basic structure remains the same. These observations are in contrast to the changes brought about by ethylene glycol treatment at 150 °C for 60 s, which will be discussed in section 4.3.7.

3.5. Conclusions

It has been demonstrated that all the solvent treatments studied improve the MAR of the range of wool fabrics studied compared with the untreated MAR values.

The greatest improvements in MAR were noted for fabric A (light weight worsted) compared with the lower level of improvement reported for fabrics B (worsted twill) and C (woollen flannel) respectively. Thus, the nature of the fabric structure (as previously noted in section 2.4.4.) is of great importance.

Low molar volume solvents, which are usually associated with low boiling points exert more pronounced changes in wool fibres at lower temperatures and hence greater improvements in MAR are observed.

Solvent treatments over a range of times at room temperature bring about changes in the MAR of the wool fabric studied. As the treatment time increases the MAR increases towards an equilibrium value considerably higher than the untreated fabric value for the highly polar solvents.

The improvements in MAR, are considered to be associated with the modification of the wool fibre structure as a result of the penetration of solvent molecules. The more polar the solvent the greater the improvement in MAR. It is considered that large amounts of the highly polar solvents are initially absorbed causing a marked improvement in MAR thereafter relatively small changes in the amount of solvent absorbed near the equilibrium adsorption conditions also lead to smaller increases in MAR.

Treatment of wool fabrics with organic solvents reduces the flex abrasion resistance. This might be due to the more severe nature of the flexing test and the complex mode of flexing and abrasion imparted to the fabric during testing. However, the effect, as in the case of MAR, is fabric structure-dependent.

Minor reductions in fabric surface frictional properties and larger reductions in fabric area felting shrinkage have also been observed as a result of treatment of wool fabrics with organic solvents. The more polar the solvent the greater the reduction in these properties. These changes are considered to arise from a reduction in the D.F.E., which is known to affect the felting propensity.

The effects of organic solvents on wool fabrics lead to a decrease in the crease recovery angle (CRA). The greater the polarity of the liquid as measured by the value of the dielectric constant, and the greater the amount of liquid adsorbed, then the greater is the accompanying reduction in CRA.

The results have been interpreted in terms of a time-dependent molecular chain relaxation process in which conformational changes take place within the swollen wool fibre. Such changes are promoted by longer immersion times and accelerated by increasing the temperature of the treatment.

X-ray diffraction studies showed that even highly polar organic solvent treatments cause only minor changes in the α-helical meridional reflections of the wool fibre structure. These are presumably due to slight changes in the position of the structure i.e. a different chain molecular arrangement, but the basic structure remains the same.

Further work is required to establish more clearly the nature of the fibre-solvent interactions and the changes in fabric abrasion for a wider range of organic solvents and treatment conditions. In particular the direct measurement of the absorbed solvent in relation to the improvement in MAR should be studied.

CHAPTER 4

The Effects of Ethylene Glycol at 150°C on the Abrasion Resistance of Woven Wool Fabrics

4.1. Introduction and Objectives

Stretch fabrics are defined (332) as fabrics that possess a higher extensibility than normal fabrics under small loads. This property when achieved can be utilized to obtain increased comfort or freedom of action in various types of garment.

Although stretch woven wool fabrics have been available for a number of years the stretch is generally only in one direction. Usually this is achieved by multi-step procedures which do not always lead to a condition of stretch that is durable to aqueous laundering (322). In addition a reduction in abrasion resistance and alteration in fabric handle can result from such treatment (332-334).

In recent years a simple procedure has been reported where it has been shown (335-337) that woven wool and wool blend fabrics develop two-way stretch when treated in a slack condition. Alternatively, setting occurs if the fabric is held taut during the treatment (338, 339). The procedure involves a brief treatment of the fabric with ethylene glycol at an elevated temperature, followed by water rinsing and drying. This treatment develops stretch in wool and wool blend fabrics without detracting from the desirable qualities of the wool. Besides imparting stretch, the treatment is claimed to increase both the settability of wool and the rate of dye uptake (337, 338, 340).

This treatment has been utilized in this experimental work in order to evaluate the effects of ethylene glycol at 150°C for a range of treatment times up to 60 s on the flat and flex abrasion resistance of wool fabrics. Additional studies have been conducted on the changes in the fabric cyclic bending properties, cyclic stress-strain behaviour and tensile properties etc., using two woven wool fabrics with different characteristics (fabrics A and C).

4.2. Experimental

Materials

Fabric specifications: Two woven wool fabrics have been used throughout this experimental work. Fabric A, a worsted-spun, light weight fabric and fabric C, a woollen-spun flannel. The detailed specifications for fabric A and fabric C are given in section 2.4.2..

Reagents: Ethylene glycol (Laboratory reagent grade) (BDH) was used without further purification.

Methods

Method of treatment

The treatment procedure involved complete immersion of the preconditioned fabric (30 x 30 cm) in the heated ethylene glycol (150°C) for the designated time in a suitable container in a fume cupboard. This was followed by rapid removal of the sample and rinsing in cold tap water (15-20°C) for about 30 minutes. The fabrics, after rinsing, were hung vertically in a fume cupboard and allowed to dry at room temperature. Finally the fabrics were conditioned at 65% r.h. and 21°C for at least 3 days before testing.

Test Methods

(i) Fabric cyclic stress-strain behaviour - the Instron Tensile Tester was used for this test and the machine settings and procedural details have been described fully in section 3.2.1.

(ii) Martindale Abrasion Resistance - (see section 2.4.2.).

(iii) Rate of Fabric Weight Loss - (see section 2.4.2.).

(iv) Flex Abrasion Resistance - (see section 2.6.2.).

(v) Fabric Tensile Properties - (see section 2.4.2.).

(vi) Fabric Bending Properties - (see section 2.4.2.).

(vii) X-ray Diffraction Studies - (see section 3.4.1.).

4.3. Results and Discussion

4.3.1. Cyclic Stress-strain properties

The results of the effects of ethylene glycol treatment on the load required for 10% fabric extension on the first and fifth stress-strain cycles for wool fabrics A and C are given in Table 111. From these results it is clear that generally ethylene glycol treatment increases the ease of fabric extension and of recovery (i.e. stretch) as reported elsewhere (336-338). Although the mechanism by which the fabric stretch is obtained is not clear, it was originally suggested that during the treatment partial melting of the α-helix portion of wool occurred along with stabilization of the new structure through cross-linkage by esterification (336-338). However, more recent evidence suggests that cross-linkage by esterification does not, in fact, take place, although reaction of ethylene glycol with single hydroxyl groups in the wool may lead to some esterification which is catalysed by the presence of acid (341).

Some of the stretch which is obtained is due to the increased elasticity (see Fig. 100a, b and 101a, b). In addition perhaps the greatest contribution to the improved fabric stretch properties occurs as a result of the fabric shrinkage and crimp interchange. Fibre supercontraction could probably account for a minor proportion of the shrinkage.

In SEM studies (see Fig. 102) the fibre is shown to develop a rib-like structure. Buckling of the cuticular layer is characteristic of supercontracted wool fibres (342-345). However the buckling of the scale surface in this work is in the longitudinal direction, i.e. parallel

<u>TABLE 111.</u> The effect of treatment time in ethylene glycol at 150°C on the load required for 10% extension of wool fabrics.

Time of treatment (s)	Fabric A (worsted)				Fabric C (woollen)			
	Load required for 10% fabric extension (g).		Reduction in load for 10% extension (%)	Fabric shrinkage (%)	Load required for 10% fabric extension (g).		Reduction in load for 10% extension (%)	Fabric shrinkage (%)
	First cycle	Fifth cycle			First cycle	Fifth cycle		
Untreated *	1470	1360	7.5	-	1260	960	23.8	-
15	520	480	7.7	4	360	320	11.1	29.4
30	380	360	5.3	18.2	400	360	10.0	39.4
45	-	-	-	26.9	-	-	-	46.7
60	520	500	3.9	52.0	1600	1560	2.5	57.7

* For untreated fabric specifications see section 2.4.2.

Fig. 100 - Load required for 10% extension of fabric A (worsted) treated in ethylene glycol at 150°C.

Fig. 101 - Load required for 10% extension of fabric C (woollen) treated in ethylene glycol at 150°C.

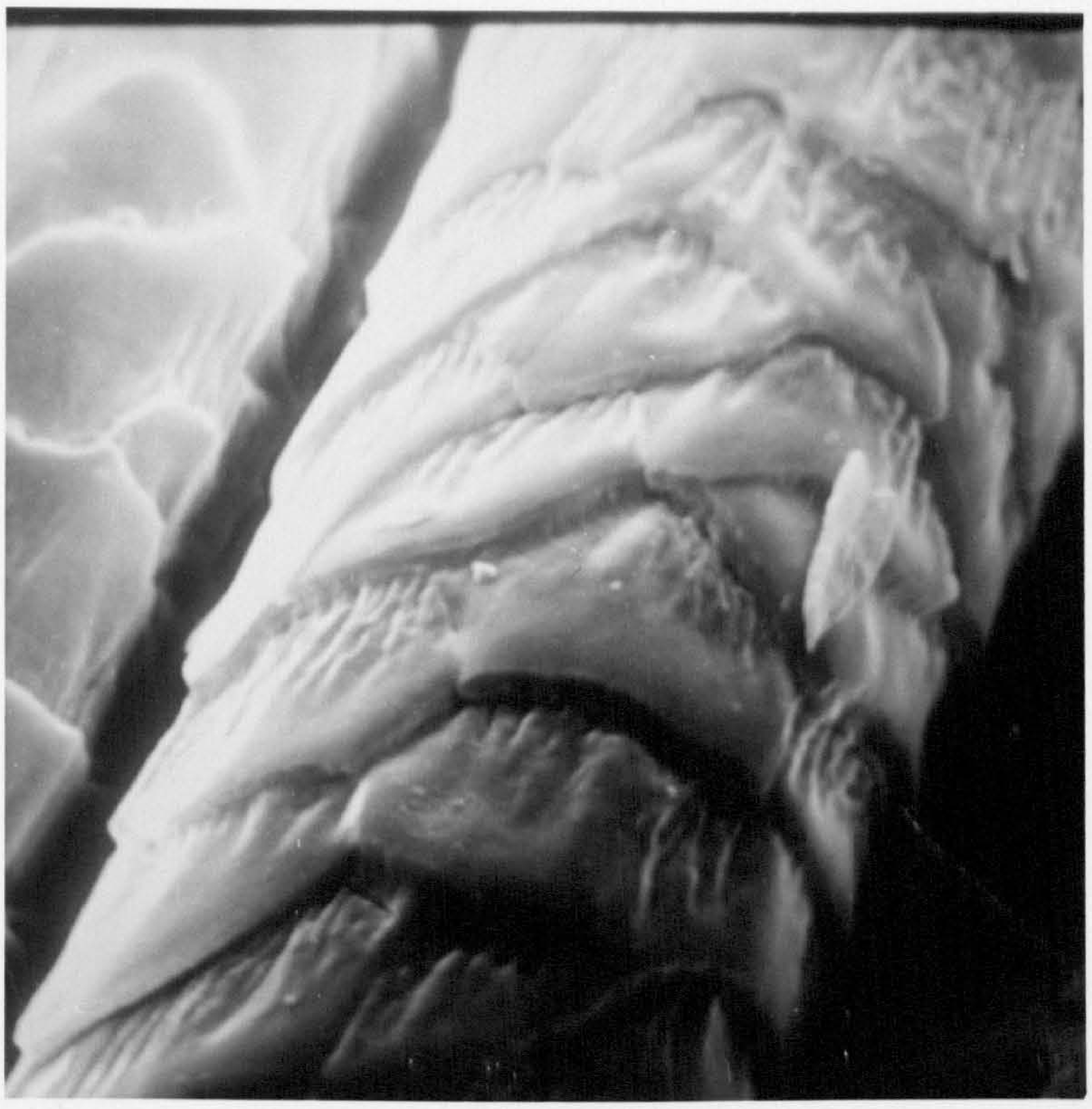


Fig. 102 - Wool fibre treated with ethylene glycol at 150°C for 60 s (2300X).

to the main fibre axis, whereas in other treatments lateral buckling was observed (342-345). The longitudinal buckling is believed to arise through swelling and rapid contraction of the fibre during the treatment (346). This phenomenon is worthy of further study as it does not appear to be a common occurrence.

From Table 111 it can be seen that the load required for 10% fabric extension in the fifth stress-strain cycle is always slightly less than that required for the first cycle. The greater the reduction in load required for 10% extension the more easily will the fabric be deformed under the action of an applied load. From the results in Table 111 fabric A generally appears to be less affected in this respect than fabric C. The percentage reduction in load required for 10% fabric extension between the first and the fifth cycle for fabric A is relatively small when comparing the untreated and treated fabric states. The percentage reduction decreases generally as the treatment time in ethylene glycol increases. The residual stretch in fabric A (i.e. the extension after the applied load has been removed) does not appear to be altered markedly as a result of the ethylene glycol treatment but the untreated fabric has only a very small residual stretch (see Fig. 100) so that significant changes would not be expected to be observed with this fabric. However, for fabric C the reduction (%) in load required for 10% fabric extension between the first and fifth cycle is decreased as the treatment time is increased (23.8% for the untreated sample and 2.5% for the 60 s treatment.). This is a significant reduction and is accompanied by an improvement in elastic properties as seen from the progressive reduction in residual stretch. From Fig. 101 it is clear that the residual stretch of the untreated fabric (3.2%) is reduced to (2-0.8%)

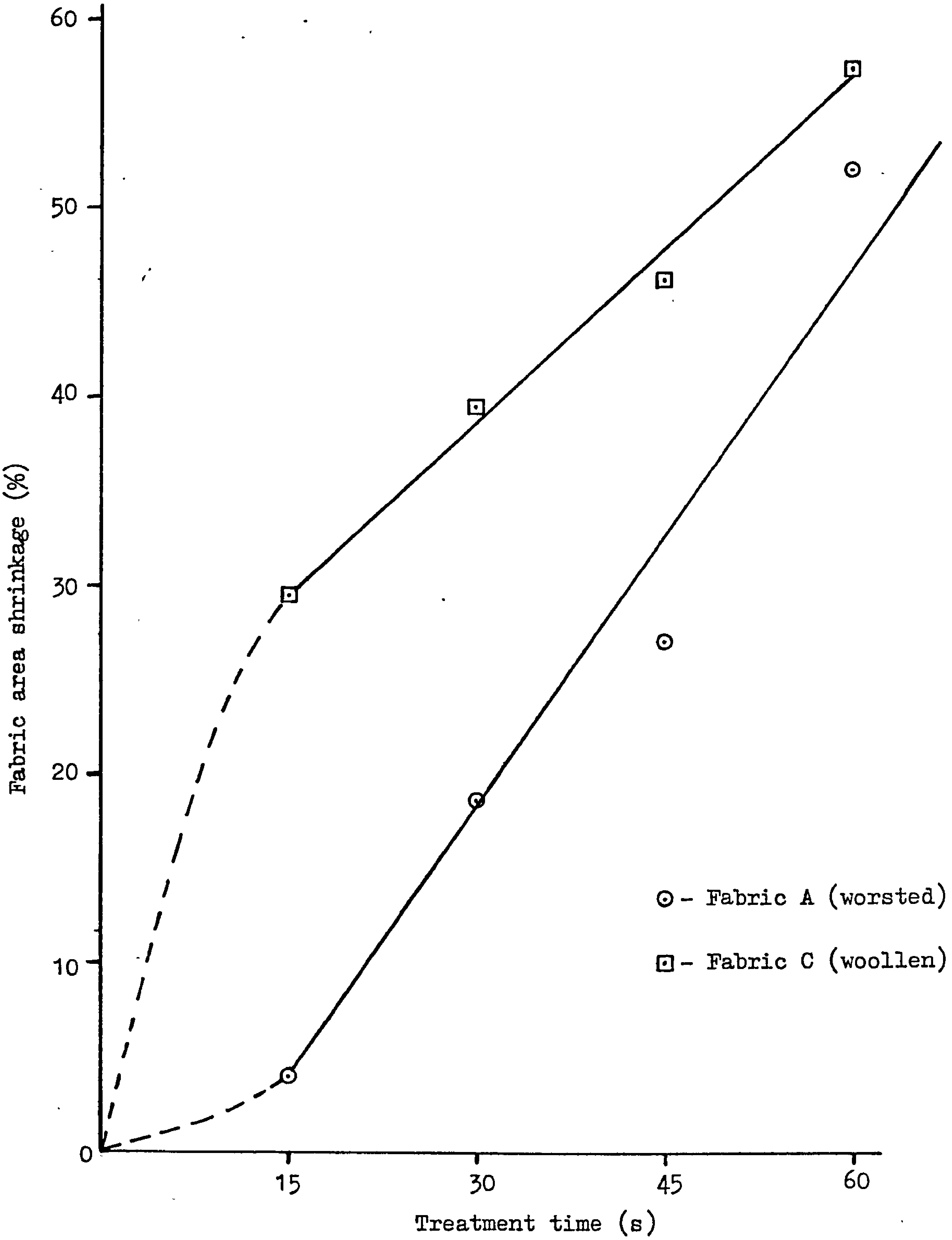
after ethylene glycol treatment. Generally the residual stretch is decreased as the time of the treatment is increased.

The fabric shrinkage that occurs during the treatment with ethylene glycol at 150°C on the two woven wool fabrics studied is given in Table 111 and illustrated in Fig. 103. From the values obtained it is clear that the amount of fabric shrinkage depends greatly not only upon the time of treatment, but also upon the fabric construction and composition, as previously demonstrated elsewhere (336-338).

The rate of fabric shrinkage after an initial period would appear to be sensibly linear with respect to treatment time for the fabrics and conditions studied (see Fig. 103). Clearly however with treatment times longer than 60 s this linear relationship will not persist because of the very high levels of fabric shrinkage attained ($>50\%$). As expected on the basis of the two woven fabric structures examined in this work, the woven woollen flannel (fabric C which is more open in structure) shrinks at a greater rate and to a larger extent than the more tightly woven worsted fabric A.

In Fig. 103 where the fabric shrinkage (%) is plotted against the time of treatment (s), it is apparent that there is no linear relationship from zero time to 15 s of treatment with respect to fabric shrinkage, as compared with 15 to 60 s treatment. This might well be explained taking into account the induction time required for diffusion of the compound into the fibre. For fabric C with the more open structure the penetration and diffusion should be much faster than for fabric A, and hence the ethylene glycol treatment may lead to more marked changes in this fabric.

Fig. 103 - The effect of ethylene glycol treatment at 150°C on the fabric area shrinkage (%) of wool fabrics.



The handle of the fabrics is changed considerably after the 60 s treatment. Fabric A becomes stiffer because of the fabric shrinkage, but appears to be in a more rubber-like state. Fabric C becomes markedly stiffer (due to fabric shrinkage) and a higher load is then required for 10% fabric extension (see Table 111) but the residual stretch is still much lower than for the untreated fabric (see Fig. 101).

4.3.2. Martindale Abrasion Resistance (MAR)

(i) Treatment under slack conditions

The MAR values of wool fabrics treated in a slack condition with ethylene glycol are given in Table 112 and illustrated in Fig. 104.

It is clear that treatment of woven wool fabrics with ethylene glycol at 150°C for periods of time up to at least 30 s can be beneficial for the MAR. Beyond 30 s treatment the abrasion resistance properties are progressively decreased. Thus treatment of wool fabrics for 15 s to 30 s can increase the MAR by 70-90% and 40-60% respectively. Treatment for 45 s can still be beneficial for fabric A where an increase similar to that attained after 30 s treatment was again obtained. However, for fabric C a decrease in MAR of about 23% compared with the untreated fabric was recorded. Treatment with ethylene glycol for 60 s is detrimental for both fabrics A and C and a considerable reduction in MAR is obtained. Values of 55% and 65% reduction for fabric A and fabric C respectively were recorded after 60 s treatment.

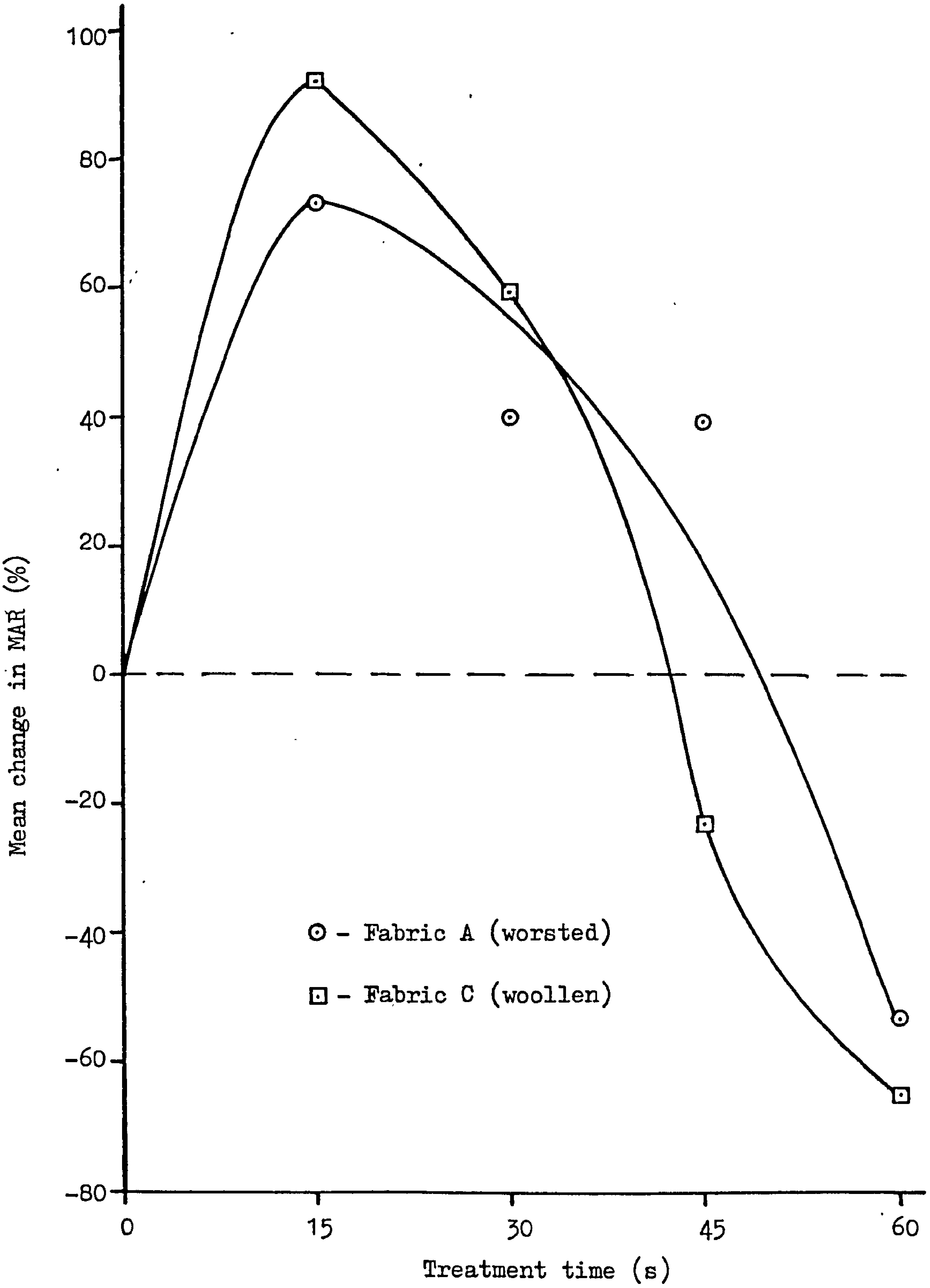
It is considered that the increase in MAR is due partly to the fabric shrinkage, which, increases the effective fabric weight per unit area generating more fibres per unit area of the fabric surface in the abrasion test. The improvement is also derived from

TABLE 112. Martindale Abrasion Resistance of Wool Fabrics treated with ethylene glycol at 150°C (under slack conditions).

Time of Treatment (s)	Fabric A (Worsted)			Fabric C (Woollen)		
	Abrasion Resistance (Rubs x 10^3)	mean	mean change in MAR (%)	Abrasion Resistance (Rubs x 10^3)	mean	mean change in MAR (%)
Untreated *	13.0 12.5 10.2	11.9	0	3.6 3.8 3.6	3.7	0
15	22.0 20.0 20.0	20.6	+73.1	7.5 6.6 7.25	7.1	+92.0
30	17.5 17.5 15.0	16.6	+40.0	6.5 5.75 5.5	5.9	+59.5
45	16.0 16.0 16.0	16.0	+39.5	2.75 2.75 2.9	2.8	-23.0
60	5.5 5.5 5.5	5.5	-53.7	1.3 1.3 1.3	1.3	-64.8

* For untreated fabric specifications see section 2.4.2.

Fig. 104 - The effect of ethylene glycol treatment at 150°C on the Martindale abrasion resistance of wool fabrics.



the improved elastic properties of the fabric.

From Fig. 105 where the fabric shrinkage (%) is plotted against the mean change in MAR (%), it is apparent that the increase in MAR is greater after small increases in fabric shrinkage. As the fabric shrinkage increases further the mean increase in MAR decreases. For fabrics C and A treatment times longer than 30 s and 45 s respectively increase the fabric shrinkage to a great extent and reduce the MAR considerably.

The decrease in MAR is considered to be due to the marked fabric shrinkage which in this instance (treatment time beyond 30 s) renders the crowns of the weave structure more pronounced. In addition to this phenomenon, the attrition process is probably accelerated due to the greater stiffness and brittleness of the fibres after long treatment times at high temperature (150°C). Brittleness has previously been observed with wool fibres exhibiting a disoriented β-type structure (346).

In section (5.3.2.) it will be shown that prior felting of fabric C increases the MAR and on this basis similar increases should be expected if the fabric is allowed to shrink. However, in the case of the ethylene glycol treatment this is not observed for treatment times in excess of 30 s at 150°C. The shrinkage of fabric C during washing enables the protruding surface fibres to felt and hence cover the yarns in the surface of the fabric. The fabric surface is thereby protected to a greater extent fron direct attrition while, in addition, the mass per unit area of the fabric under abrasion is increased. In the case of the ethylene glycol treatment, visual examination and SEM studies (see Fig. 106 and 107) confirm that this does not appear to happen for although the mass per unit area is increased, the protruding surface

Fig. 105 The relationship between the fabric area shrinkage and Martindale abrasion resistance of wool fabrics treated with ethylene glycol at 150°C.

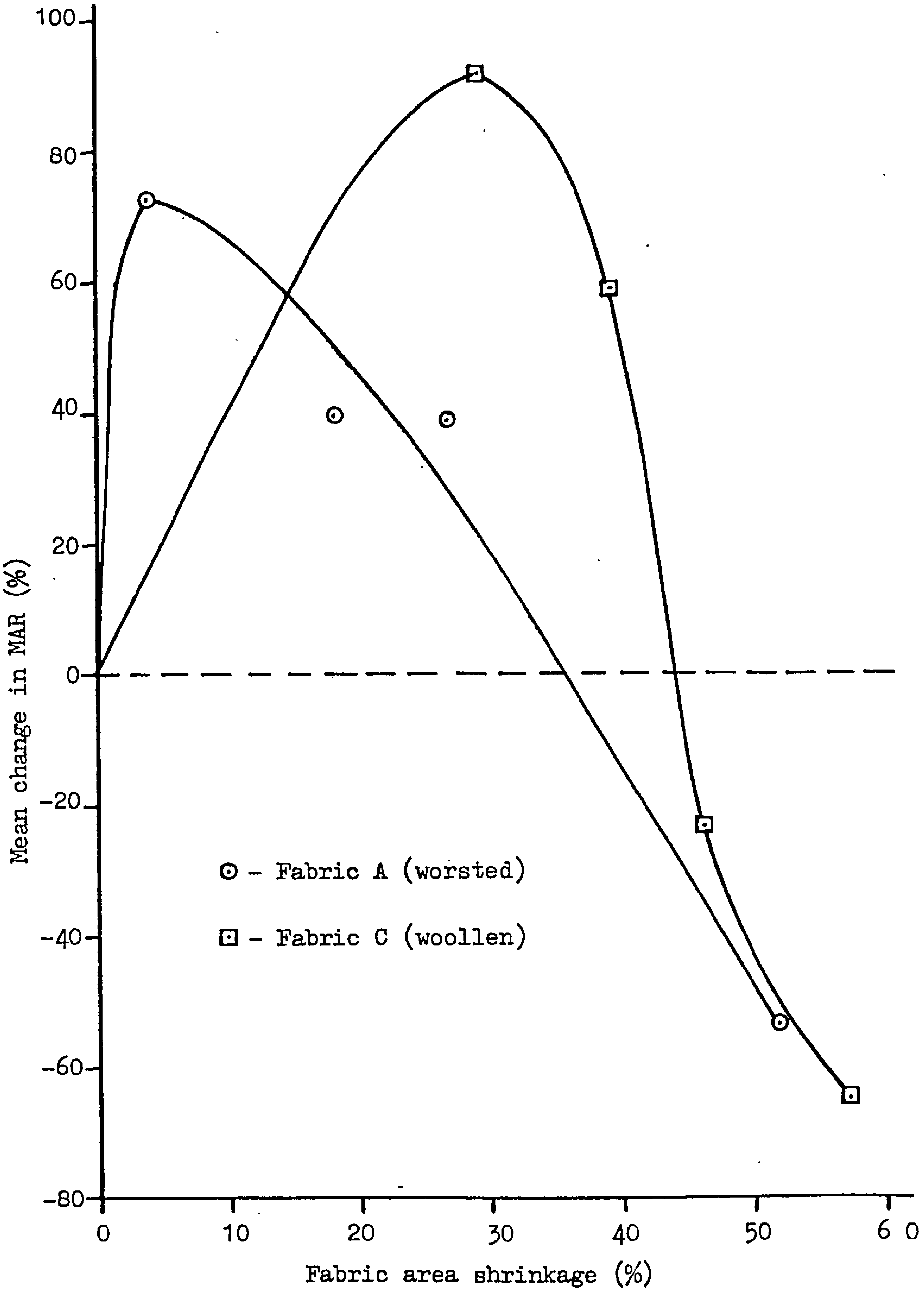


Fig. 106 - S.E.M. photograph of untreated fabric A (56X).

Fig. 107 - S.E.M. photograph of ethylene glycol treated fabric A for 60 s (56X).

fibres do not cover the yarns in the same way as in the felted fabric and therefore do not protect the fabric structure. The main mechanism of abrasion in this case is thus fibre attrition and wear and this is accelerated with increased treatment times beyond 30 s for fabric C.

Thus ethylene glycol treatment causes not only fabric property changes such as shrinkage but also changes in fibre properties which become more important in determining the MAR where long treatment times at 150°C are involved.

(ii) Treatment under taut conditions

The results of the MAR obtained after treatment in ethylene glycol at 150°C in a taut state for the two woven wool fabrics are given in Table 113. It is clear that for fabric A, as the time of treatment increases the level of improvement in MAR is increased. For 30 s treatment in this state the level of improvement in MAR is better than that obtained after 15 s in the slack state, which was in fact the maximum value recorded for fabric A. For fabric C, as the time of treatment increases the level of improvement in MAR is decreased. The best level of improvement in MAR was obtained after 15 s treatment, which is similar to the improvement obtained in fabric A after 30 s treatment.

The increase in MAR is considered to be due to the modification of the elastic properties of the fibres and not due to increase in fabric weight per unit area, because the fabric is held in a taut state and therefore no shrinkage took place.

4.3.3. Rate of Fabric Weight Loss

The results of the weight loss of flannel fabric (fabric C) during flat abrasion, after treatment in ethylene glycol at 150°C,

TABLE 113. Martindale Abrasion Resistance of wool fabrics treated with ethylene glycol at 150°C (under taut conditions).

Time of treatment (s)	Fabric A (worsted)			Fabric C (woollen)		
	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)
Untreated	13.0 12.5 10.2	11.9	0	3.8 3.6	3.6 3.7	0
15	18.0 18.0 19.0	18.3	54.0	6.5 6.0 6.5	6.3	71.0
30	22.0 22.0 20.0	21.3	79.3	5.0 4.5 5.0	4.8	30.6

are given in Table 114.

It is clear that the weight loss after treatment for 15 s is lower than that of the untreated fabric after the first 1000 rubs. This continues until the end-point is reached where the weight loss was only 50% of the untreated value. After 1000 rubs the order of increasing weight loss is: 60 s > 45 s > 30 s > untreated > 15 s, but after 2000 rubs the order becomes: untreated > 45 s > 30 s > 15 s, the 60 s treatment reaching the end-point at 1250 rubs.

The initial higher weight loss for treatment times > 30 s is probably due to the majority of the loose surface fibres and fuzz being removed rapidly without pill formation. After this, fibre attrition and wear are the dominant mechanisms of abrasion so that the rate of weight loss is almost at a constant value until the end-point is achieved.

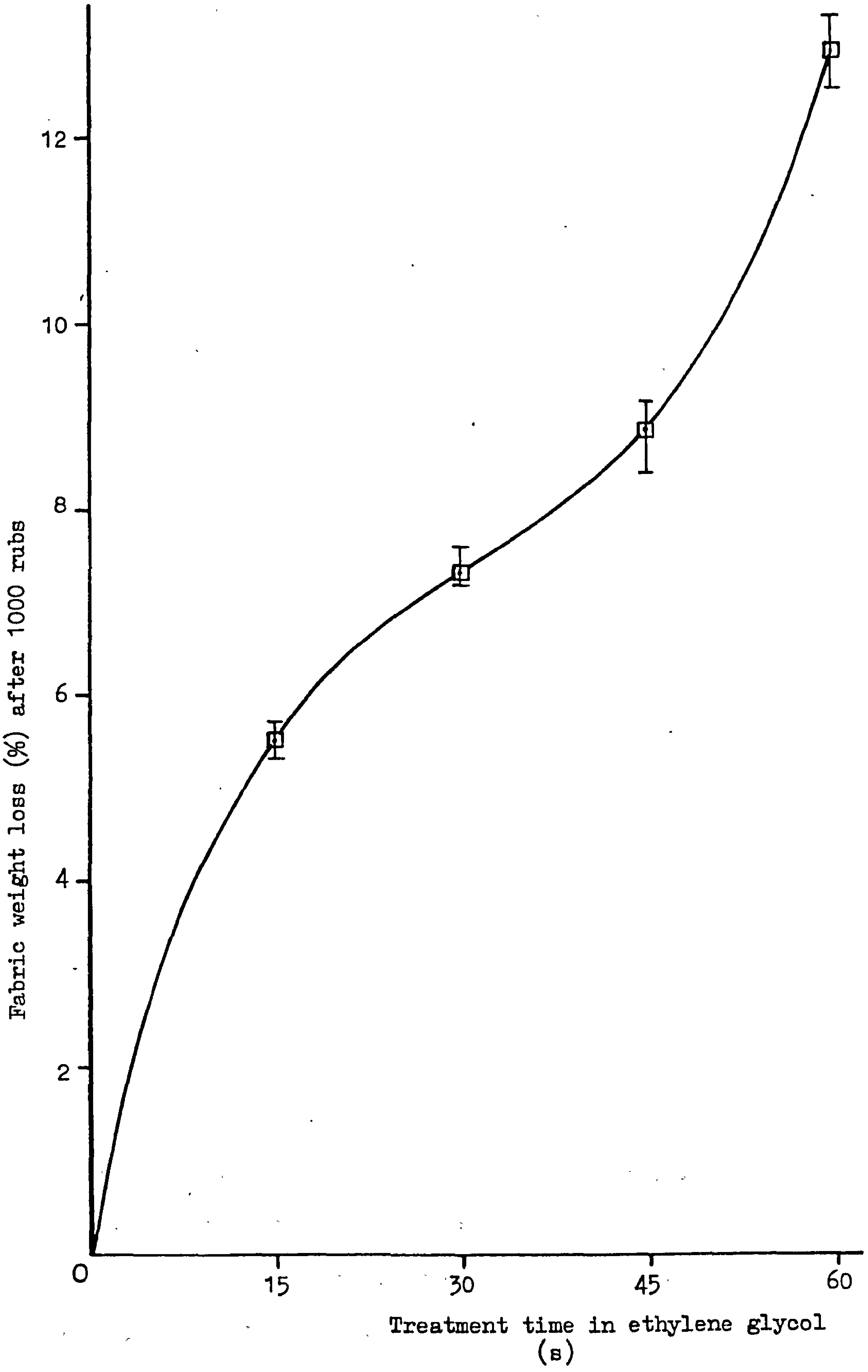
The samples treated for 45 and 60 s have a higher weight loss (%) compared with the untreated fabric and the end-point is reached much more quickly especially after 60 s treatment. In the latter case the crowns of the fabric (after 57% area shrinkage) are very pronounced and fibre attrition on the crowns is considered to start in the initial stages of abrasion as soon as the surface fibre is removed from the sample.

The increase in weight loss (%) after 1000 rubs of the treated samples with increasing time of treatment is shown in Fig. 108. The shape of the curve obtained is the mirror image of the plot of change in MAR (%) against the time of treatment in ethylene glycol. The quantitative results of abrasion resistance testing support the initial findings on this fabric that ethylene glycol treatment improves the MAR up to 30 s treatment, beyond which the abrasion

TABLE 114. The effect of ethylene glycol treatment at 150° C on the weight loss (%) of fabric C (woollen).

No. of Rubs	Weight loss of fabric C treated with ethylene glycol at 150° C for									
	Untreated Fabric		15 s		30 s		45 s		60 s	
	(%)	mean	(%)	mean	(%)	mean	(%)	mean	(%)	mean
250	-	-	-	-	-	-	-	-	7.29 7.52 7.75	7.5
500	-	-	-	-	-	-	7.04 6.92 6.67	6.9	9.51 9.51 9.81	9.6
750	-	-	-	-	-	-	-	-	11.2 11.38 11.74	11.4
1000	6.41 6.88 5.97	6.4	5.38 5.58 5.76	5.6	7.63 7.10 7.27	7.3	9.14 8.79 8.47	8.8	12.54 12.99 13.36	13.0
1250	-	-	-	-	-	-	-	-	14.25 14.96 15.43	14.9
1500	-	-	-	-	-	-	10.81 10.32 10.21	10.5	-	-
2000	12.65 13.41 12.47	12.8	7.7 8.08 8.03	7.9	9.95 9.49 9.77	9.7	12.11 11.72 11.53	11.8	-	-
2500	-	-	-	-	-	-	13.57 13.21 12.90	13.2	-	-
3000	18.49 21.94 21.37	20.6	9.29 9.62 9.54	9.5	11.68 11.54 11.72	11.6	14.89 14.65 14.29	14.6	-	-
4000	24.73 29.95 27.35	27.3	10.48 10.90 10.74	10.7	13.45 13.66 13.58	13.6	-	-	-	-
5000	-	-	11.66 12.57 12.13	12.1	15.44 15.77 15.57	15.6	-	-	-	-
6000	-	-	12.82 13.98 13.23	13.3	17.31 17.96 17.29	17.5	-	-	-	-
7000	-	-	15.28	14.4	-	-	-	-	-	-

Fig. 108 - The effect of ethylene glycol treatment at 150°C on the weight loss (%) of fabric C (woollen).



resistance is impaired. For fabric C the effect of fabric shrinkage on the rate of weight loss is plotted in Fig. (109). It would appear that up to about 40% area shrinkage the weight loss after 1000 rubs increases in a linear fashion. This corresponds to a treatment time of 30 s in ethylene glycol at 150°C. The upward trend in the weight loss results above 40% fabric area shrinkage suggests that in this particular fabric the greater brittleness or stiffness of the treated fibres leads to a greater rate of loss in weight. This will naturally be associated with lower values of MAR.

4.3.4. Flex Abrasion Resistance

The results for the effects of ethylene glycol treatment at 150°C on the flex abrasion resistance of woven wool fabrics are given in Table 115 and illustrated in Fig. 110.

From these results it is clear that the ethylene glycol treatment increases the flex abrasion resistance for treatment times up to 45 s for fabric A, and up to 30 s for fabric C. Although increases in flex abrasion resistance in both fabrics are obtained initially after 15 s, the flex abrasion resistance decreases with increase in treatment time. This is similar to the results obtained in flat abrasion resistance. Fabric A has a much greater flex abrasion resistance than fabric C and the loss in this property is more severe for this fabric after treatment for 60 s in ethylene glycol at 150°C.

An increase in flex abrasion resistance after 30 s treatment in ethylene glycol at 150°C has also been reported elsewhere (336). The same factors responsible for the changes in flat abrasion resistance are considered to be responsible for the changes in flex abrasion resistance, namely the changes in the fabric structure and the physical properties of the fibres.

Fig. 109 - The relationship between the fabric shrinkage area shrinkage and the weight loss for fabric C (woollen).

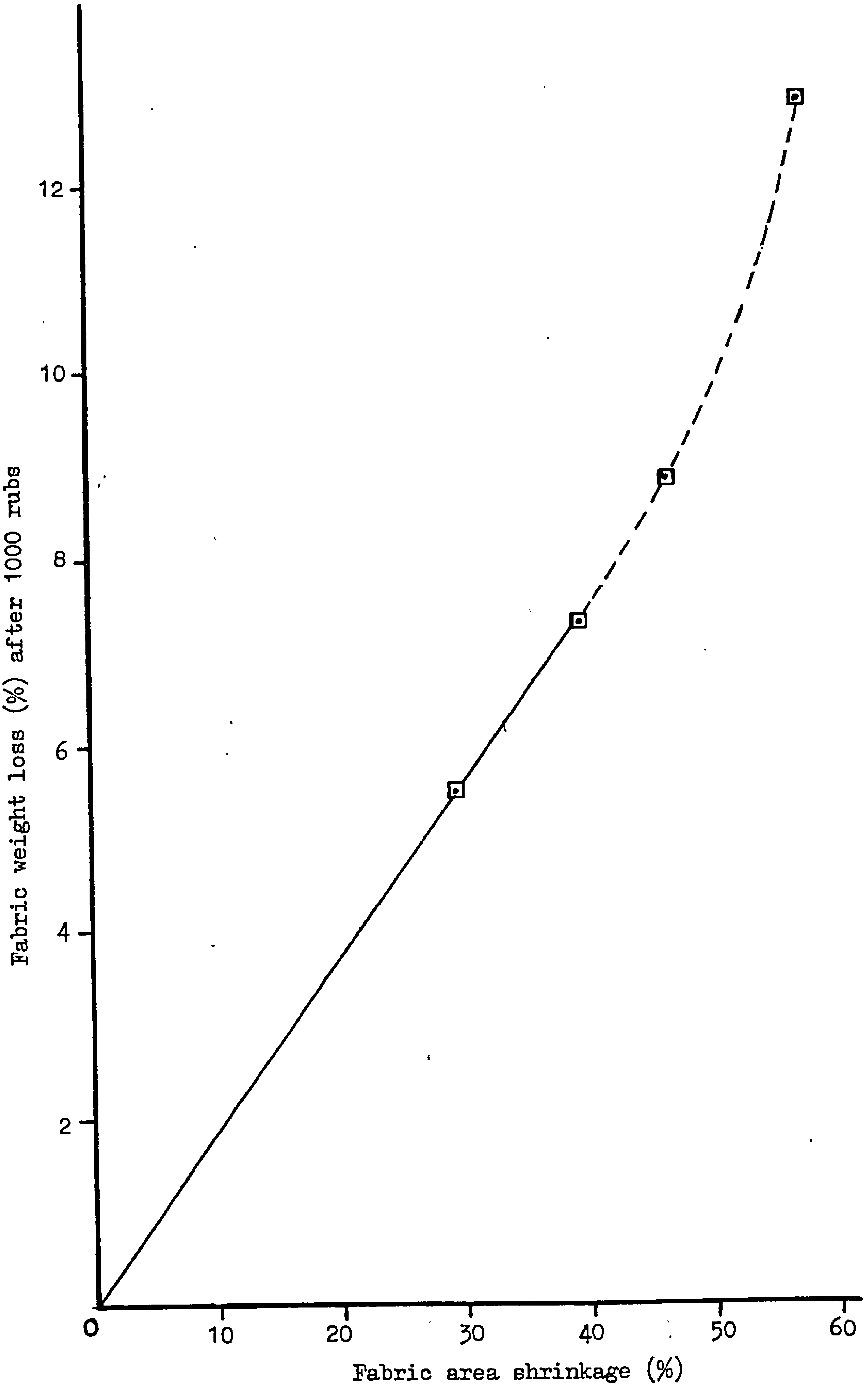
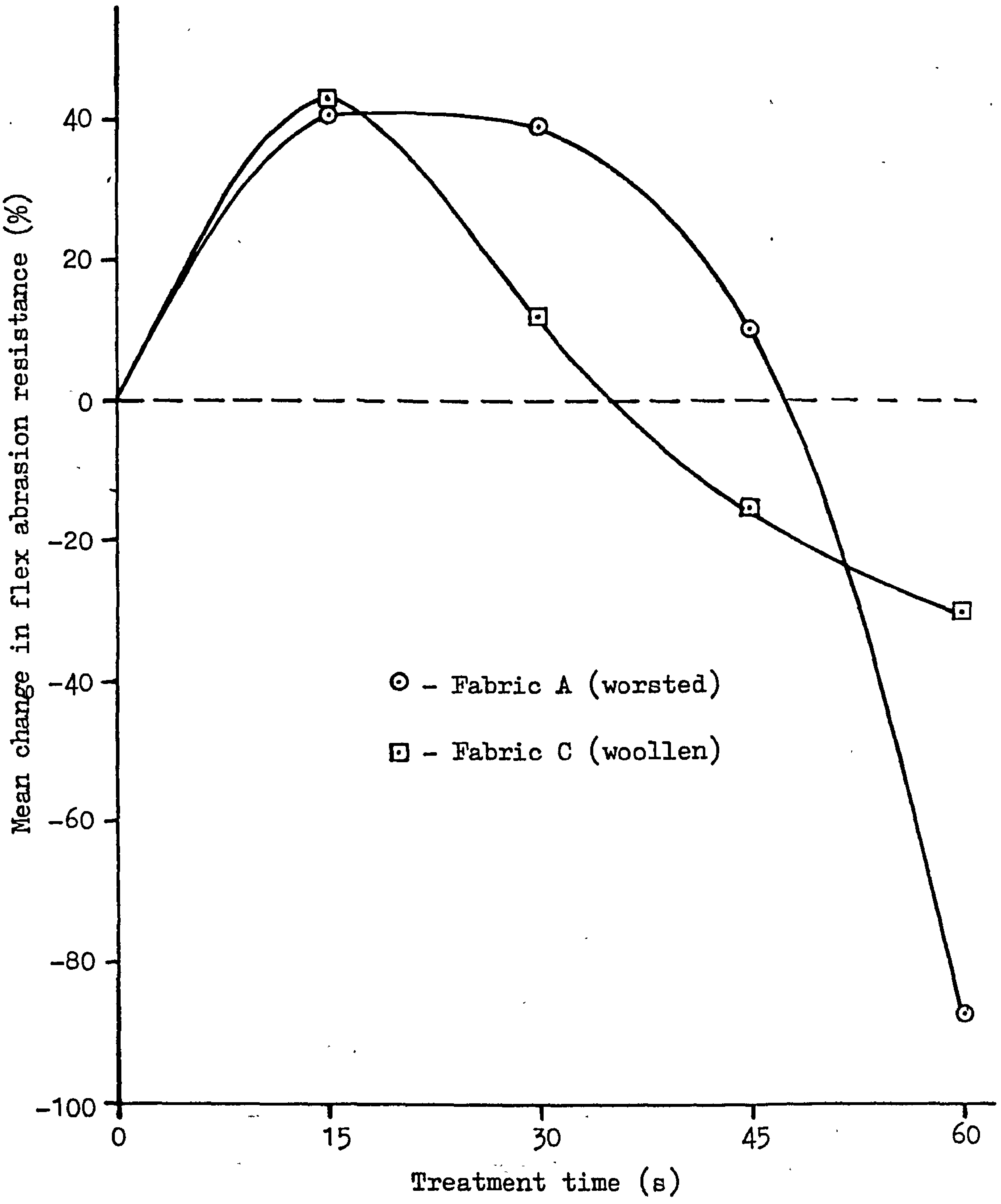


TABLE 115. The effect of ethylene glycol treatment at 150°C on flex abrasion resistance (FAR) of wool fabrics.

Time of treatment (s)	Fabric A (worsted)			Fabric C (woollen)		
	Flex Abrasion Resistance cycles	Flex Abrasion Resistance mean	mean change in FAR (%)	Flex Abrasion Resistance cycles	Flex Abrasion Resistance mean	mean change in FAR (%)
Untreated	1420 1390 1345 950	1276	0	160 165 175	167	0
15	1680 1910	1795	+ 40.7	238 239 240	239	+ 43.1
30	1895 1650	1772	+ 38.9	165 210	187	+ 12.0
45	1600 1225	1412	+ 10.7	138 135 150	141	- 15.6
60	160 150	155	- 87.8	125 110	117	- 30.0

+ = increase, - = decrease in flex abrasion resistance.

Fig. 110 - The effect of ethylene glycol treatment at 150°C on the flex abrasion resistance of wool fabrics.



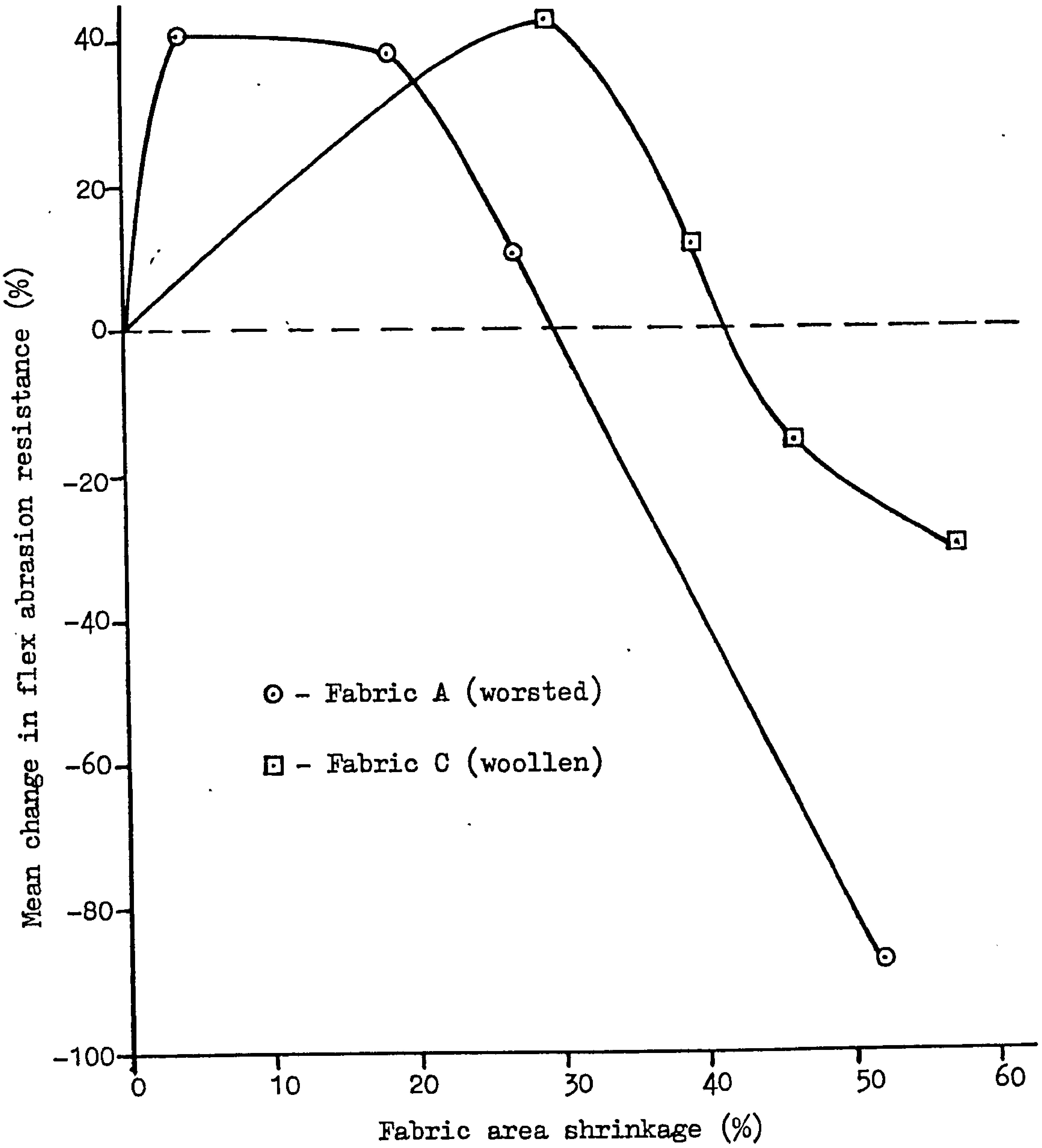
From Fig. 111 where the fabric shrinkage (%) is plotted against the mean change in flex abrasion resistance, it is apparent that the flex abrasion is greatest at small fabric shrinkages. As the fabric shrinkage increases (as a result of treatment time) the flex abrasion resistance decreases. This is similar to the results obtained in flat abrasion resistance (see Fig. 105). Therefore, ethylene glycol treatments, as discussed earlier in section (4.3.2.), cause changes in the fabric structure as a result of shrinkage which are considered to exert subtle effects upon the flex and flat abrasion resistance. In addition changes in fibre properties occur which become crucial in determining the flex and flat abrasion resistance for long treatment times at 150°C (viz. $>$ 45 s).

4.3.5. Fabric Tensile Properties

The results of the effects of ethylene glycol at 150°C on the breaking load and breaking extension of woven wool fabrics A and C in a slack state are illustrated in Table 116.

Wool keratin is believed (347) to consist of ordered and disordered regions that contribute to the interesting mechanical properties. The crystalline (or ordered) portion which accounts for about 40% of an unstretched fibre, has the α-helix conformation. On stretching in water beyond about 22% extension the α-helices in the micro-fibrils start to unfold to an extended zig-zag structure which is referred to as β-keratin. Provided the fibre is not stretched beyond about 30% (in water), the fibre will return to its original length and the β-structure reverts to the α-helix. The α-helices have been shown to undergo melting at different temperatures, depending on the reaction medium. For example in a vacuum melting begins at about 215°C (121).

Fig. 111 - The relationship between the fabric area shrinkage and thee flex abrasion resistance of wool fabrics treated with ethylene glycol at 150°C.



<u>TABLE 116</u>. The effect of ethylene glycol treatment at 150°C on the tensile properties of wool fabrics.

Time of Treatment (s)	Fabric A (Worsted)				Fabric C (Woollen)			
	Breaking Load		Breaking Extension		Breaking Load		Breaking Extension	
	(Kg)	mean	(%)	mean	(Kg)	mean	(%)	mean
Untreated	14.3 14.2 13.9	14.2	36.0 34.0 32.5	34.0 (0)	8.8 8.8 8.8	8.8 (0)	39.0 34.0 38.0	37.0 (0)
15	14.9 15.1	15.0 (+ 5.6)	32.0 30.0	31.0 (+11.2)	10.0 10.3	10.1 (+21.7)	38.0 39.0	38.5
30	15.9 15.2	15.5 (+ 9.5)	42.0 34.0	38.0 (+11.2)	10.3 11.2	10.7 (+21.7)	39.0 51.0	45.0 (+21.6)
45	13.9 14.6	14.2 (0)	37.0 43.0	40.0 (+17.1)	11.8 9.6	10.7 (+21.2)	49.0 32.0	40.5 (+ 9.5)
60	15.0 15.0	15.0 (+ 5.6)	49.0 46.0	47.5 (+39.0)	13.4 13.3	13.3 (+51.2)	33.5 29.0	31.2 (-15.5)

The values in parentheses represent the mean change (%) in Fabric Tensile Properties.
+ = increase, - = decrease.

In water melting occurs at about 130°C (348). α-helix melting is an irreversible phenomenon that brings about profound changes in the mechanical properties of wool.

As discussed earlier, partial melting (or disruption) of α-helices is believed to take place during treatment of wool with ethylene glycol at 150°C and therefore changes in the mechanical properties should be expected. From Table 116 it is clear that the breaking load of fabric A is not significantly changed, for only minor increases are recorded even after 60 s treatment. However the large fabric shrinkage that takes place during the treatment should have led to proportionately larger values of breaking load, so that on balance it would appear that the physical properties of wool are reduced by the treatment. The breaking extension of fabric A generally increases as the time of treatment increases, the maximum value (39%) being obtained after 60 s but the accompanying fabric shrinkage is 52%, so that the net effect is a reduction in the fabric breaking extension compared with the untreated value when the shrinkage factor is taken into account.

From Table 116 where the results of breaking load and breaking extension of fabric C are also given, it is obvious that the breaking load is generally increased as the time of the treatment increases. Indeed an increase of 51% in breaking load was recorded for the fabric treated for 60 s. The fabric shrinkage in this case was 57%, i.e. again a net decrease compared with untreated fabric. The breaking extension as in the case of fabric A is increased but in a non-linear fashion with respect to the time of treatment. In the case of fabric treated for 60 s in ethylene glycol a decrease in breaking extension was recorded. In this case the fabric shrinkage noted previously was 57%, but the fabric becomes quite stiff and brittle in texture and breaks easily, in contrast to that of fabric A which became rubber-like under the same treatment conditions.

For individual wool fibres increases in breaking extension and both increases or decreases in breaking load have been reported elsewhere (336) after treatment in ethylene glycol at 150°C for up to 30 s treatment time. However, the increase in breaking extension is decreased as the time of treatment is increased from 5 to 30 s.

4.3.6. Fabric Bending Properties

The results of the effects of ethylene glycol treatment on the flexural rigidity G_o and coercive couple C_o of fabrics A and C are illustrated in Table 117.

From Fig. 112, where G_o is plotted against the time of treatment in ethylene glycol, it is clear that for both fabrics this increases as the time of treatment increases. The increase in flexural rigidity G_o is considered to be mainly due to fabric shrinkage but changes in the physical properties of the fibres are probably also reflected. The degree of fabric stiffness introduced by the ethylene glycol treatment is higher for fabric C, where an increase of about 600% compared with the untreated fabric is obtained. For fabric A the comparable increase is only 70%.

Although both fabrics A and C have relatively similar degrees of shrinkage after 60 s treatment, the increase in flexural rigidity is only marked for fabric C, which consists of short and coarser fibres.

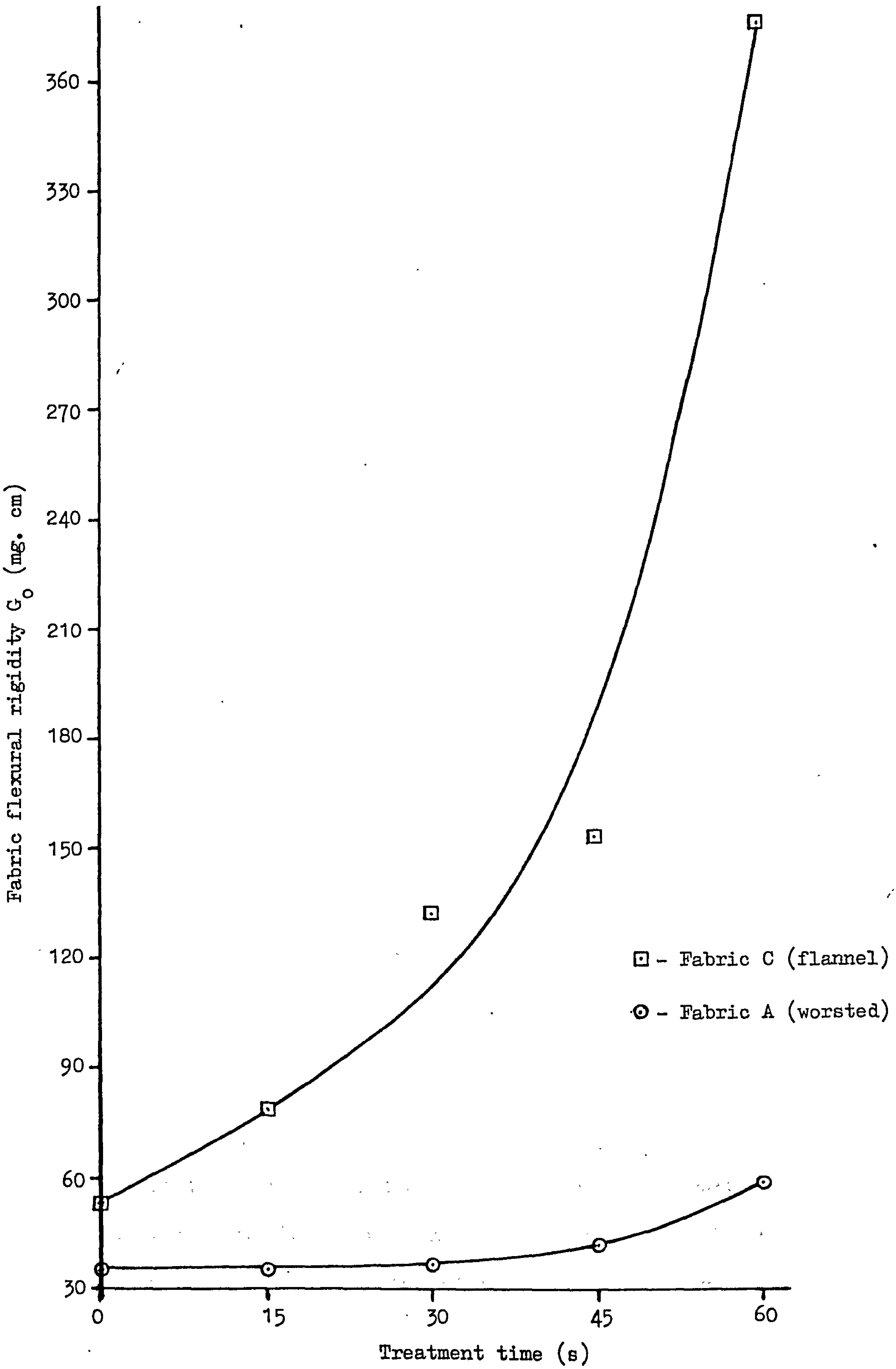
The results of the bending tests also demonstrate that the values of the coercive couple (C_o) for fabric A reflect the results obtained earlier relating MAR with treatment time in ethylene glycol. Thus the values for 45 s and less, are lower than untreated while the 60 s

TABLE 117. The effect of ethylene glycol treatment at 150°C on flexural rigidity G_o and Coercive couple C_o of wool fabrics.

Time of treatment (s)	Fabric A (worsted)		Fabric C (woollen)	
	G_o (mg.cm)	C_o (mg.cm)	G_o (mg.cm)	C_o (mg.cm)
Untreated	34.7	8.2	53.0	31.6
15	35.0	5	79.0	35.7
30	37.0	7	132.5	51.0
45	42.0	7	152.9	68.8
60	59.0	16	377.0	137.6

The above values represent the mean values of three samples in weft-way.

Fig. 112 - The effect of ethylene glycol treatment at 150°C on the flexural rigidity of wool fabrics.



value is greatly increased (see Fig. 113). This indicates an inverse relationship to that observed in Fig. (104) where the MAR is greater than untreated for treatment times up to 45 s, but lower after 60 s. This may reflect the marked changes in fabric shrinkage that take place as a result of ethylene glycol treatment at 150°C. A similar inverse relationship is demonstrated for fabric C (compare Fig. 113 with Fig. 104) but in this case all the values for C_o are greater than the untreated value. However as before the greatest increase in C_o is recorded after 60 s treatment.

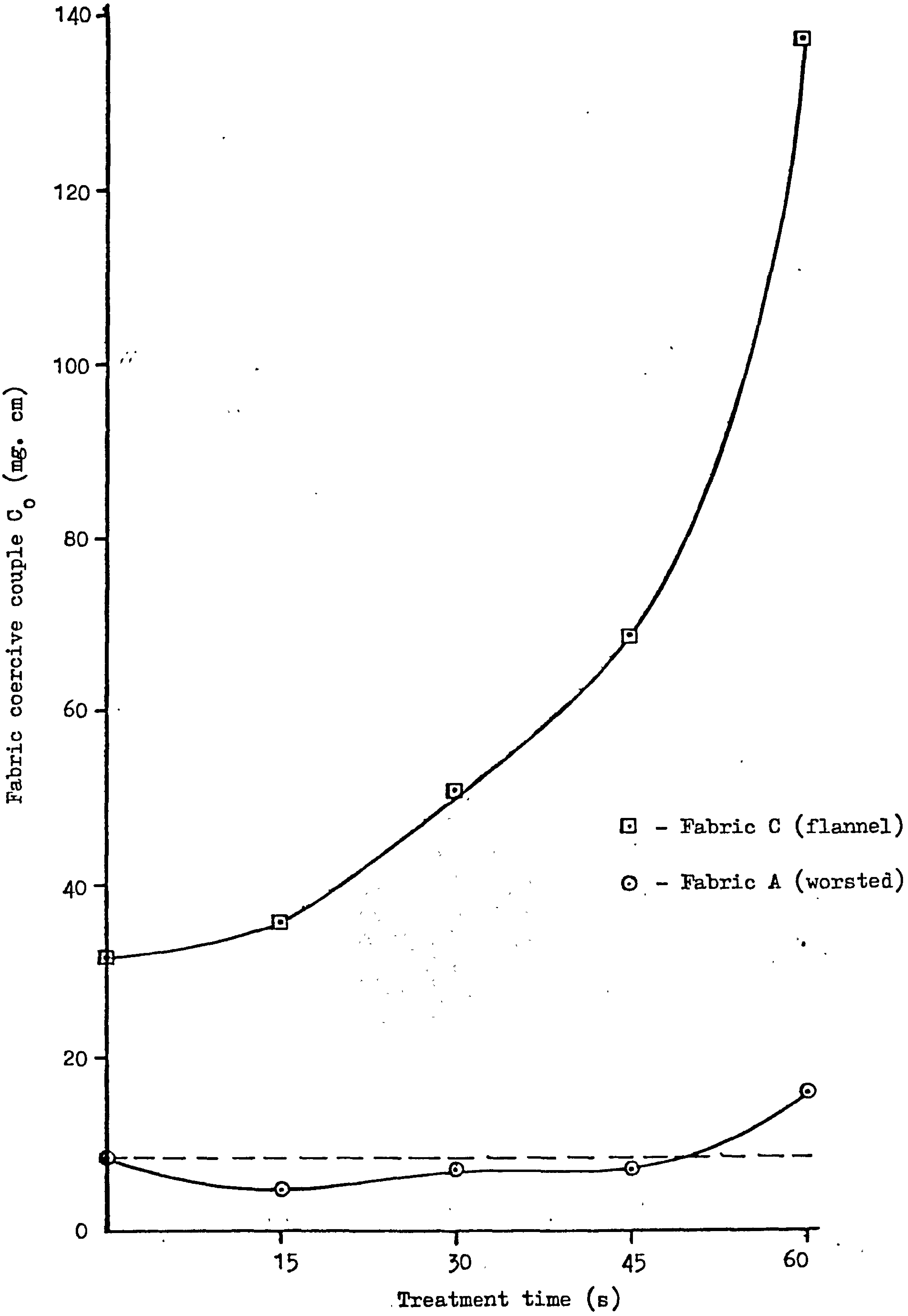
It is important to note that the increases in G_o and C_o for fabric C are of a greater magnitude than those observed with fabric A.

4.3.7. X-ray Diffraction Studies

The numerous reflections on the meridian of the X-ray diffraction pattern of untreated wool fibre (α-keratin) (see Fig. 114), are all indicative of long-range axial periodicities. The values of these axial periodicities, or repeats, calculated as Bragg spacings, range from 0.15 nm (the reflection furthest from the origin) to 6.6 nm (the innermost reflection normally observable) (349). In the case of treated wool fibre in ethylene glycol at 150°C for 60 s, these axial repeats (indicative of the initial α-helical structure) have been disrupted and a disoriented β type structure is observed (see Fig. 115).

These X-ray diffraction studies confirm the initial suggestion that disruption (or partial melting) of the α-helical structure of wool takes place (336-338). In addition it provides supporting evidence for the suggestion advanced in this work (see sections 4.3.2. and 4.3.4.) that conformational changes in fibre structure occur which become crucial in determining the flat (Martindale) and flex abrasion resistance as a result of long treatment times in

Fig. 113 - The effect of ethylene glycol treatment at 150°C on the coercive couple of wool fabrics.



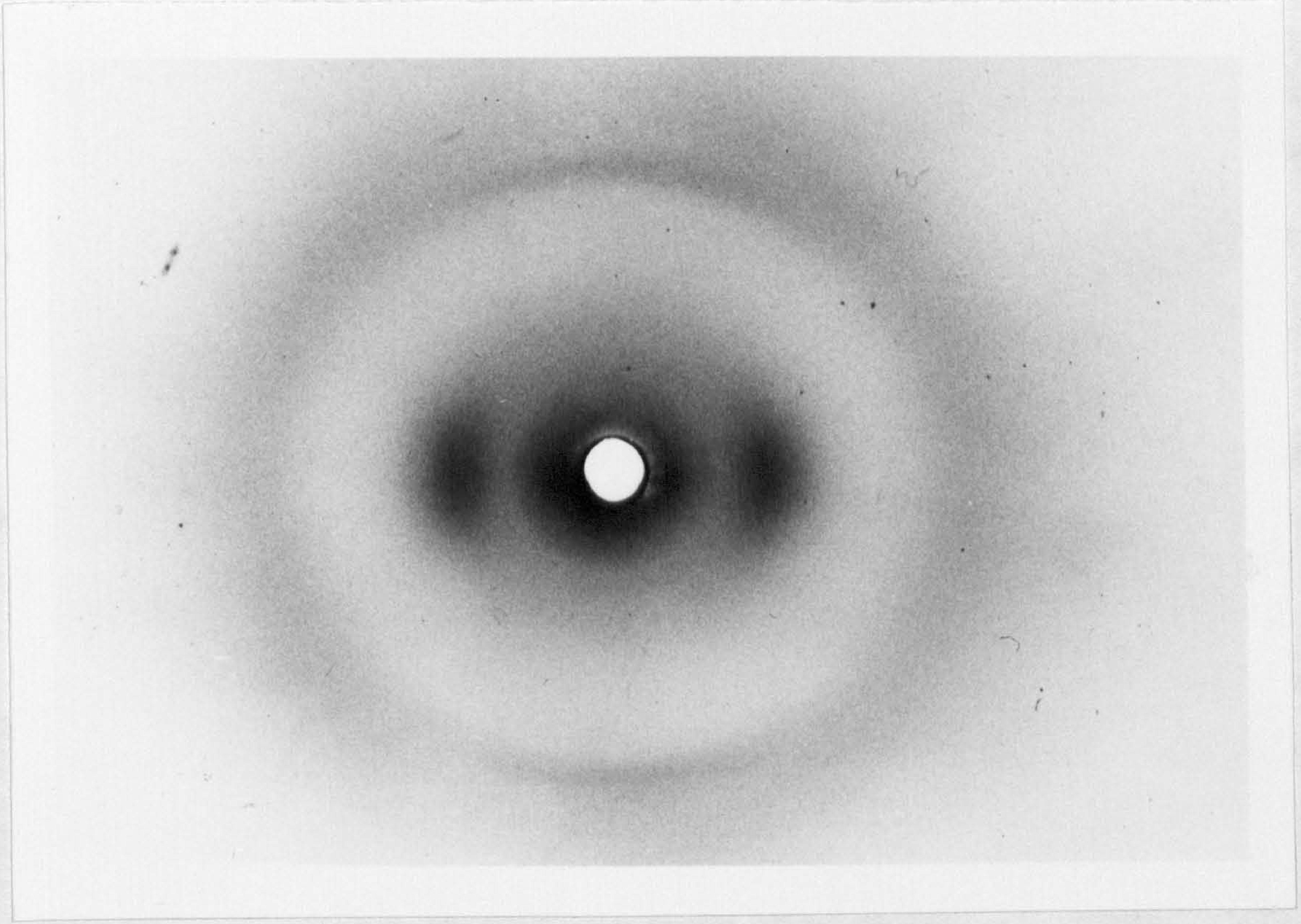


Fig. 114 - X-ray diffraction pattern of untreated wool fibre.

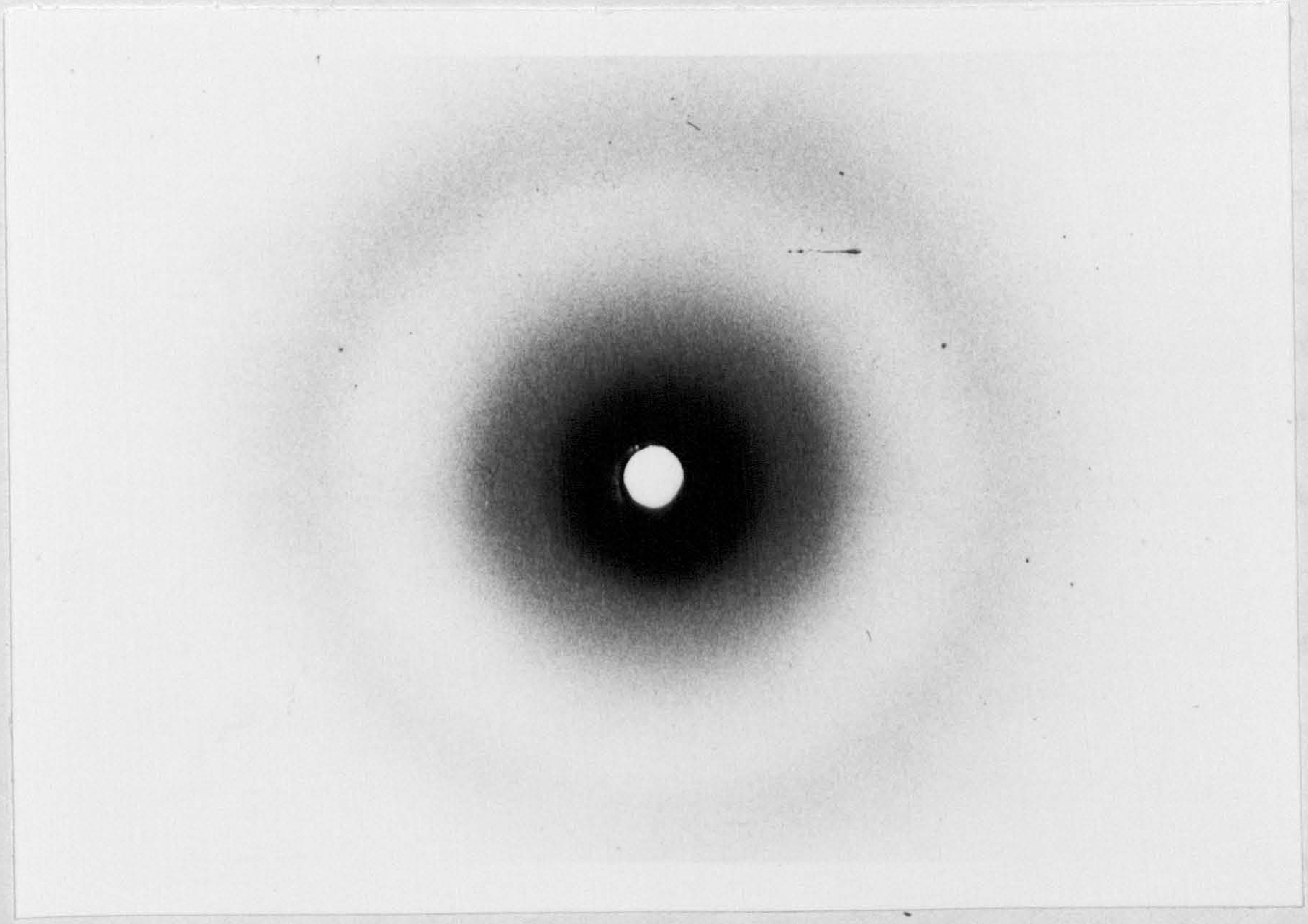


Fig. 115 - X-ray diffraction pattern of ethylene glycol treated wool fibre at 150°C for 60 s.

ethylene glycol at 150°C (viz. > 45 s). However, there is hardly any change in the wool fibre structure after treatment for only 15 s in ethylene glycol from the appearance of the untreated wool fibre.

4.4. Conclusions

From the results of this experimental study it can be concluded that the elastic properties of wool fabrics are improved as a result of the treatment in ethylene glycol at 150°C.

Fabric shrinkage takes place during the treatment which increases with increase in treatment time and it is fabric structure-dependent. Supercontraction, i.e. lateral buckling of the wool scale surface is not shown to occur, although longitudinal buckling of the wool scale surface (an unusual phenomenon) was observed in S.E.M. studies.

The MAR is improved for treatment times up to 30 s. This is considered to be due to fabric shrinkage and improvement in elastic properties. Treatment times longer than 30 s reduce the MAR and this is thought to arise as a result of the fibre conformational changes that take place at this high temperature (150°C). X-ray diffraction studies confirm that conformational changes take place and disruption of the α-helical structure of wool has been shown to occur. However, changes in fibre structure are only minor for the treatment in ethylene glycol at 150°C for 15 s.

The flex abrasion resistance results are similar to the MAR results, but the decreases in flex abrasion resistance (%) after longer treatment times at 150°C are much more severe compared with the comparable MAR values. This is presumably due to greater severity and complex mode of flexing and abrasion in the former test. The changes in MAR and flex abrasion resistance are again fabric structure-dependent.

CHAPTER 5

The effect of deamination and esterification on the abrasion resistance of woven wool fabrics

5.1. Introduction and Objectives

In sections (2.4.6., 3.5. and 4.4.) it has been established that treatments which affect the rate of fibre felting or the physical properties of the fibres can exert a significant influence upon the abrasion resistance of wool fabrics.

The object of the work to be described in this section is concerned with the extension of these observations by a study of the effects of selected chemical treatments upon the flat abrasion resistance of wool fabrics. The treatments selected in this instance were deamination and esterification because such treatments have previously been shown to modify the felting and physical properties of wool fibres presumably through modification of the salt linkages in the wool fibre (350, 351).

5.2. Experimental

Materials

Fabric specifications: fabric A and fabric C have been used throughout this experimental work. Their detailed specifications are given in section (2.4.2.).

Reagents: the following reagents have been used for the treatments in this experimental work:

(i) sodium nitrite - analar grade (B.D.H.);
(ii) acetic acid glacial, A.R. (Vickers);
(iii) methanol - analar grade (Vickers);
(iv) hydrochloric acid - 35% W/W A.R. (Vickers).

Methods

Methods of treatment

(a) Deamination: In the deamination process wool fabric samples of about 30 x 30 cm were treated in a solution prepared by dissolving 43.1 g sodium nitrite in a mixture of 35.5 g of acetic acid and 64.5 g of water (350, 351).

The reaction time was 48 hours and the liquor to wool ratio was 20:1. After reaction the samples were removed and washed with cold running tap water for 30 minutes, rinsed with deionised water and dried at room temperature by hanging vertically in a fume cupboard. Finally the samples were conditioned in an atmosphere of 65% r.h. and 21°C for at least 3 days before testing.

(b) Esterification: Esterification of wool (352, 353) with alcohols and a catalytic amount of hydrogen chloride has been advanced for three decades or more and was originally regarded as specific for carboxyl groups. However, later evidence showed that in addition to the esterification of carboxyl groups significant conversion of primary amide groups into esters occurs, especially with alcohols such as ethanol, propanol, butanol (354).

The esterification of wool in the present study was carried out in a conical flask using methanol in the presence of 0.1N HCl as catalyst. The fabric samples (30 x 30 cm) were treated in this media for 96 hours at room temperature (20-25°C). These conditions have previously been shown (354) to be the best for selective modification of the carboxyl groups in wool without affecting significantly the primary amide groups. The liquor to wool ratio used was 40:1. The flask was sealed and a drying tube with anhydrous calcium chloride was placed to prevent ingress of moisture.

After 96 hours the fabric samples were removed and washed several times with distilled water, then soaked for 20 hours and then washed again with distilled water. Finally the samples were hydroextracted and dried at room temperature in a fume cupboard, followed by conditioning at 65% r.h. and 21°C for 3 days prior to testing.

Test Methods

The general experimental methods employed were as follows:

(i) Martindale Abrasion Resistance (see section 2.4.2.).

(ii) Fabric Tensile Properties (see section 2.4.2.).

(iii) Fabric Area Felting Shrinkage (see section 2.6.2.).

5.3. Results and Discussion

5.3.1. Felting Shrinkage

The results of the effects of deamination and esterification on the fabric area felting shrinkage (F.A.F.S.) after washing in a Cubex machine are given in Table 118 and illustrated in Fig. 116 and 117.

The F.A.F.S. (%) values obtained on the two wool fabrics suggest that both deamination and esterification reduce the felting shrinkage slightly for treatment times in the Cubex less than about 30 minutes. For longer Cubex treatment times deaminated samples shrink to a greater extent for both fabrics studied, while even after 90 minutes both the esterified fabric samples shrink at a lower rate than the untreated fabric. In the case of fabric A the reduction in area compared with the untreated sample is some 25% while for fabric C it is approximately 23% less than the untreated, giving essentially the same results.

It has been shown that wool fabrics milled in acid solution shrink at a faster rate than those milled in water (206). This has

TABLE 118. The effect of Deamination and Esterification on the fabric area felting shrinkage (%) of wool fabrics during cubex testing.

Time in Cubex	Fabric A (worsted)			Fabric C (woollen)		
	Fabric area felting shrinkage (%)			Fabric area felting shrinkage (%)		
(min)	Untreated *	Deaminated	Esterified	Untreated *	Deaminated	Esterified
10	0	0	0	8.5	6.9	5
20	4.2	3	1	13.6	12.6	7.9
30	6.7	6	3.9	20.0	18.1	11.6
60	15.4	18.3	10.0	29.3	29.5	21.7
90	25.1	30.4	18.8	37.2	38.6	28.6

* For untreated fabric specifications see section 2.4.2.

Fig. 116 - The effects of deamination and esterification treatments on the fabric area felting shrinkage (%) of fabric A (worsted) during Cubex testing.

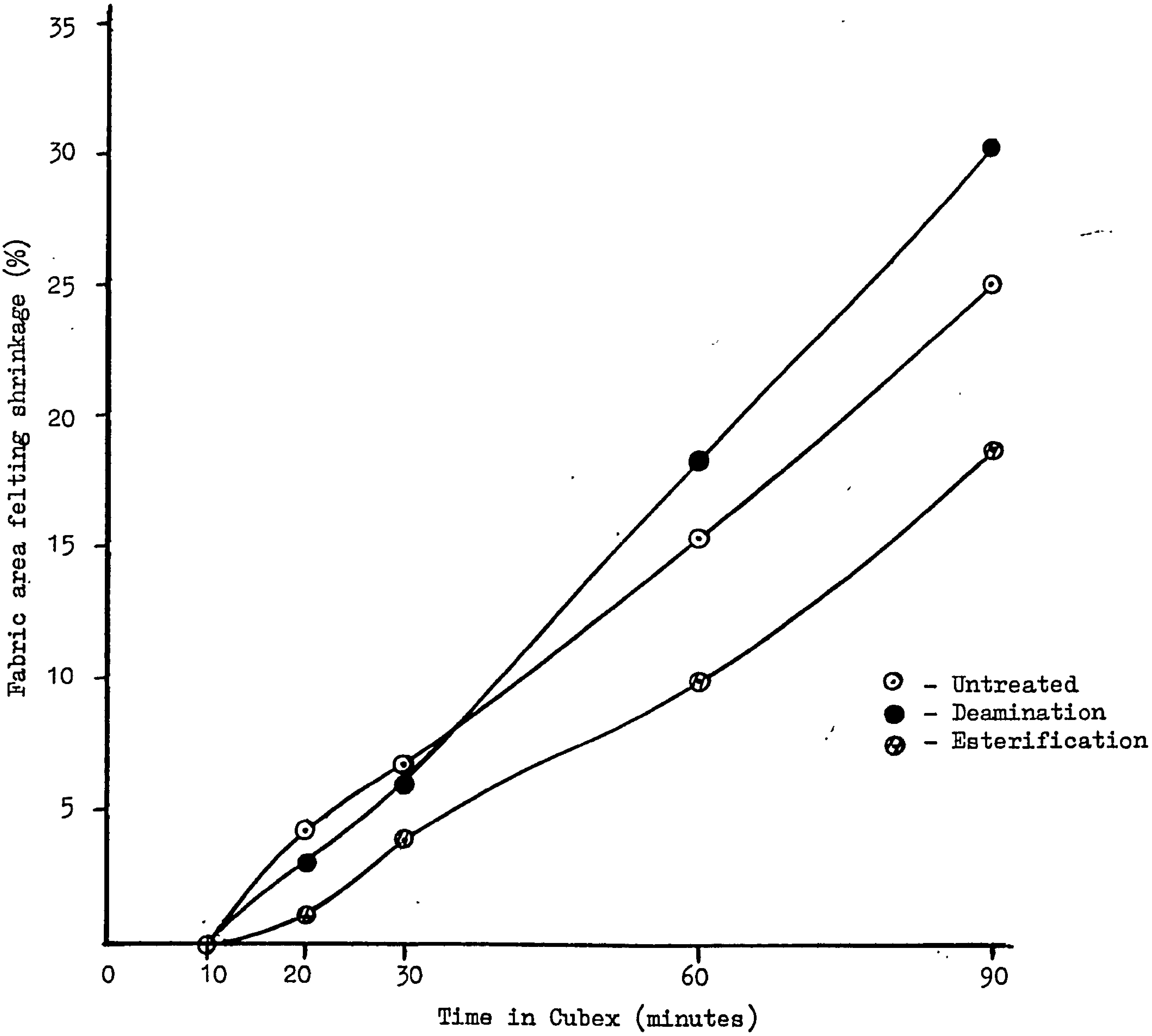
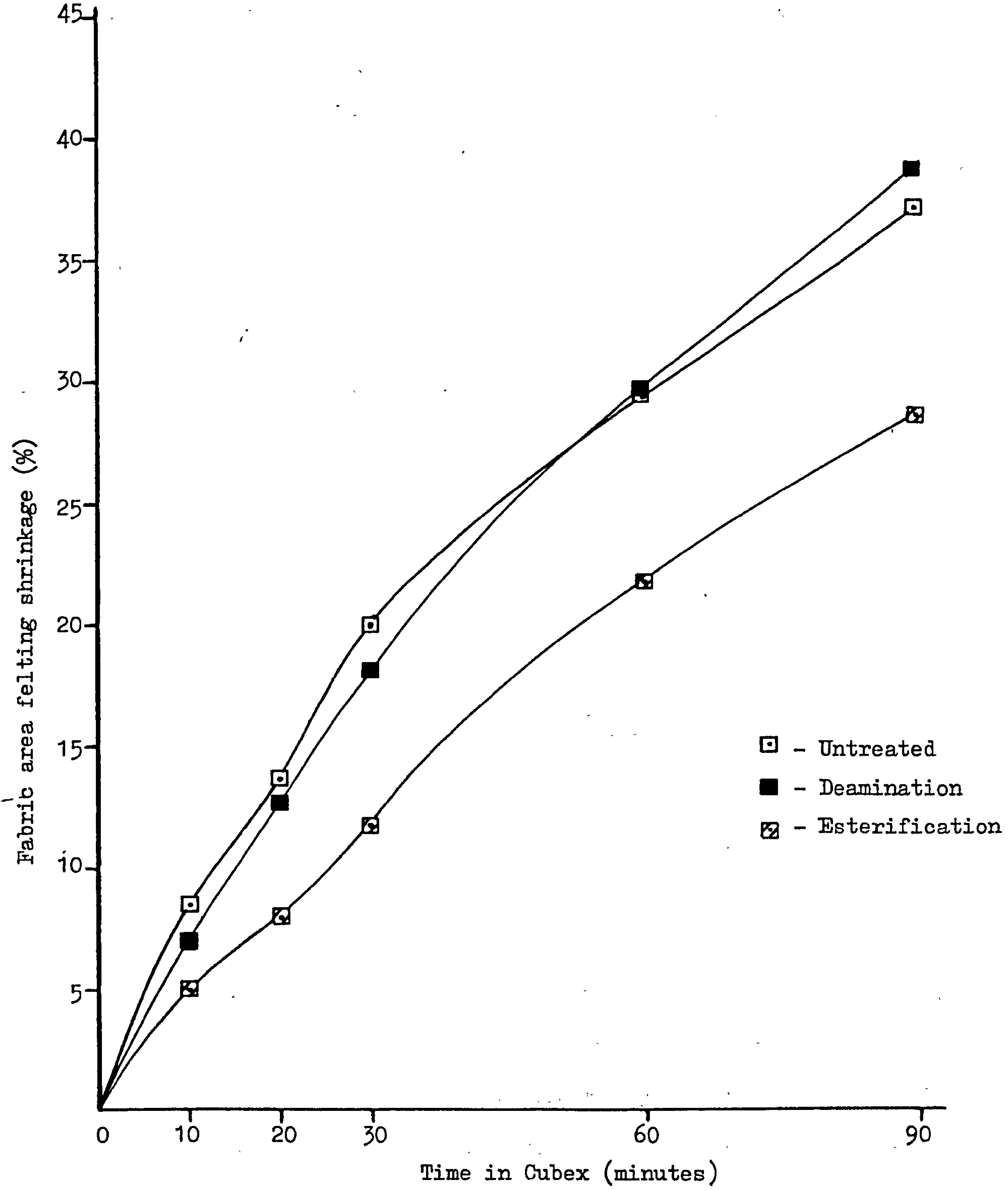


Fig. 117 - The effects of deamination and esterification treatments on the fabric area felting shrinkage (%) of fabric C (woollen) during Cubex testing.



been claimed to be due to the greater ease of extension of the fibres in the acid medium through fission of the salt linkages. Deamination (as achieved via the nitrous acid treatment) is considered to function in a similar fashion. It has also been demonstrated that such deaminated wool samples shrink at the same rate in the presence of 1% sulphuric acid (pH 1.1) or water at pH 5.5 (350, 351). Comparison of the deaminated with the untreated wool samples showed that the deaminated fabric felted at a greater rate than the untreated in water but at a slower rate when acid was present as the felting medium. These results are consistent with the hypothesis that salt linkages are of importance in felting phenomena and that the fission or elimination of salt linkages leads to an increased rate of felting under the conditions cited.

Comparing the above findings with the results obtained in this study, in which the felting takes place at approximately pH 7.0, it is clear that in the deaminated samples treated for less than 30 minutes the rate of felting is lower than the untreated, after which the rate of felting is greater than untreated for both fabrics A and C.

From Fig. 116 and 117 it becomes clear that the initial rate of felting of the untreated wool samples is almost constant with felting time after the usual induction period. By contrast, the deaminated samples exhibit a slower rate of felting. The much faster rate of felting after about 30 minutes, for the deaminated samples is in accord with the results of other workers (350, 351).

The faster rate of felting after about 30 minutes for the deaminated samples is in accord with the suggestion of other workers (350, 351). This may be explained in terms of the breakage of salt linkages as a result of the deamination process thus yielding greater ease of fibre extension which in turn may lead to higher rates of felting (206). This initial slower rate of felting is somewhat difficult to interpret in the same terms. However it has been suggested that the proposed reaction scheme for the action of nitrous acid on the N-terminal amino groups is not specific and that side reactions such as oxidation of the disulphide bonds (355), removal of tyrosine (356) etc., in addition to the reaction shown below (357) may take place.

$$\text{Wool-CH}_2\text{-NH}_2 + \text{HNO}_2 \longrightarrow \text{Wool-CH}_2\text{-OH} + \text{N}_2 + \text{H}_2\text{O}$$

Clearly these side reactions may exert an additional influence upon the changes in the physical properties of the wool fibre and indeed as it is well known the fibres are coloured brown by the nature of the treatment.

The rate of felting of the esterified samples (see Fig. 116 and 117) is slower than that of the untreated fabric and initially appears to be almost constant with treatment time in a similar manner to untreated fabric.

From examination of the felting shrinkage results of the individual treatments with acetic acid, 0.1N Hydrochloric acid and methanol given in Table 119 it is clear that the samples treated with acetic acid and 0.1N hydrochloric acid have an initial rate of felting slightly lower than that of the untreated fabric but overall there is little difference observed between the treated and the untreated samples. In the case of the methanol-treated samples the initial rate of felting and the rate of felting throughout the Cubex test is much lower that those of the acetic acid-treated, 0.1N hydrochloric

TABLE 119. The effects of Acetic acid, Hydrochloric acid and Methanol on the fabric area felting shrinkage of wool fabrics during cubex testing.

Time in cubex (min)	Fabric A (worsted)				Fabric C (woollen)			
	FAFS (%)				FAFS (%)			
	Untreated*	Acetic acid	0.1 N Hydrochloric acid	Methanol	Untreated*	Acetic acid	0.1 N Hydrochloric acid	Methanol
10	0	0	0	0	8.5	4.1	5.9	4
20	4.2	3.4	2.5	1	13.6	9.0	9.8	6.6
30	6.7	7.5	5.8	3	20.0	16.0	15.4	11.7
60	15.4	14.1	16.8	9.8	29.3	25.6	26.9	21.7
90	25.1	23.1	27.1	16.4	37.2	36.0	35.2	28.6

* For untreated fabric specifications see section 2.4.2.

acid-treated or untreated samples.

It has been previously shown (325) that solvents such as benzene /methanol, ethanol and perchloroethylene reduce the D.F.E. of wool fibres and the rate of felting is also correspondingly reduced (see section 3.4.2.3.). Indeed, the felting results of methanol-treated samples are very similar to those obtained with benzene/methanol and ethanol for both fabrics. Comparing the degree of felting obtained on the esterified samples for both fabrics and the degree of felting of the methanol-treated samples it can be seen that the results are almost identical. It is therefore considered that the reduced felting of the esterified wool samples is primarily due to the presence of methanol during the treatment which modifies the D.F.E. of the wool fibres and therefore reduces the degree of felting.

5.3.2. Martindale abrasion resistance (MAR)

From the abrasion resistance results given in Table 120 it is clear that both the deamination and the esterification treatments described earlier improve the level of abrasion resistance of the worsted-and woollen-type fabrics (fabric A and C).

The level of improvement in MAR was 59.5% in worsted-type spun fabric (fabric A) and 19% in woollen-type spun fabric (fabric C) after deamination. The corresponding values were 70% in fabric A and 24% in fabric C after the esterification treatment.

Investigations to establish the effects of the individual chemicals used in the above two treatments were also carried out. Thus treatment with acetic acid for 48 hours omitting the sodium nitrite from the deamination treatment and treatment with 0.1N hydrochloric acid and methanol for 4 days in separate flasks as well as the esterification treatment were carried out.

TABLE 120. Martindale Abrasion Resistance of wool fabrics after deamination and esterification, acetic acid, hydrochloric acid and methanol treatments.

Type of treatment	Fabric C (woollen)			Fabric A (worsted)		
	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)
Untreated	3.6 3.8 3.6	3.7	0	13.0 12.5 10.2	11.9	0
Deaminated	4.2 4.2 4.7	4.4	19.0	17.0 20.0 20.0	19.0	59.5
Esterified	4.6 4.6 4.6	4.6	24.3	20.0 22.0 19.0	20.3	70.6
Acetic acid	5.1 5.1 5.1	5.1	37.8	20.0 21.0 20.0	20.3	70.6
HCl 0.1N Four days	4.7 4.7 4.7	4.7	28.4	13.5 15.0 14.0	14.2	19.0
Methanol Four days	5.5 5.0 6.0	5.5	48.6	25.0 28.0 25.0	26.0	118.5

The results from these individual treatments are illustrated in Table 120. From the values obtained it becomes apparent that with the exception of 0.1N hydrochloric acid, the treatments with the individual reagents give rise to a greater level of improvement in MAR compared with deamination and esterification treatments.

Deamination using acetic acid and sodium nitrite reduces slightly the improvement in abrasion resistance obtained using acetic acid alone; and esterification (hydrochloric acid and methanol) reduces the level of abrasion resistance obtained with methanol alone. It is of interest to record that the abrasion resistance of fabric A after esterification is the same value as the mean abrasion resistance of the separate methanol and hydrochloric acid treatments.

The individual values of abrasion resistance obtained after treatment of both fabrics in methanol are higher than those obtained with acetic acid. This could be one reason why higher values of abrasion resistance were obtained in the esterification treatment.

It is known (206) that treatment of wool with acid breaks salt linkages and hydrogen bonds, which modify the physical properties of wool and therefore these changes in abrasion resistance might well arise as a result of this modification. In addition, no doubt, conformational changes within the fibres may lead to a more favourable response to abrasional forces.

It has also been shown (see section 3.2.2.3.) that treatment of wool fabric with methanol increases the ease of deformation but retains or improves the power of recovery of the fabric from deformation while experiments on wool fibres have shown (325) that the directional frictional effect (D.F.E.) is reduced, and hence the rate of felting is decreased. For these reasons, at least, it is considered that methanol treatments give rise to an improvement in the MAR. It has been indicated (see sections 3.2.2.3. and 4.3.1.) that the changes in the fabric deformation and recovery properties are of more importance for improving the MAR of fabric A (worsted) compared with fabric C (woollen), so that the higher improvement after methanol treatment may be explained in these terms. For fabric C (woollen-spun) the binding of the short fibres to prevent fibre migration is considered to be a more important factor and therefore the level of improvement in MAR will not be as great with fabric C when treatments that modify the deformation-recovery properties are employed.

Abrasion tests were also carried out on the felted fabric samples after 90 minutes washing in the Cubex international machine. The results obtained are given in Table 121 and show that the abrasion resistance of the untreated-felted flannel fabric (fabric C) is similar to that in the deaminated-felted and esterified-felted condition, which in these three cases is increased by about 200% over the untreated fabric value (unfelted). In the case of fabric A the felted samples in each case have lower values of abrasion resistance than the equivalent sample prior to felting. The greatest decrease in the felted samples was in the case of the deaminated fabric where a drop in MAR from 160% to 117.5% of the untreated value (100%) was recorded.

In the case of fabric C, more felting during washing takes place, so that the fabric density increases and the felted fibres that cover the fabric weave structure protrude from the surface thereby protecting the underlying yarns for a longer period during abrasion testing. Because the fibres are entangled (felted) and

TABLE 121. Martindale abrasion resistance of deaminated and esterified wool fabrics after cubex testing.

Type of treatment	Fabric C (woollen)			Fabric A (worsted)		
	Abrasion Resistance (Rubs x 10^3)	mean	mean increase in MAR (%)	Abrasion Resistance. (Rubs x 10^3)	mean	mean change in MAR (%)
Felted Untreated	10.0 11.0 11.0	10.7	189	12.0 11.0 11.0	11.3	- 5.0
Felted Deaminated	12.0 11.0 10.0	11.0	197	14.0 14.0 14.0	14.0	+ 17.5
Felted Esterified	11.0 11.0 11.0	11.0	197	16.0 21.0 21.0	19.3	+ 61.6

+ = increase, - = decrease in Martindale Abrasion Resistance (%).

less capable of migrating to the fabric surface the fibre loss through shedding during abrasion testing is decreased, there is less pilling and hence a higher abrasion resistance. It has been shown (see section 2.5.3.4.) that polymer treatments on fabric C reduce fibre migration, pilling and shedding and lead to high levels of abrasion resistance. Thus any mechanism which reduces fibre migration (felting), pilling, and shedding should improve the abrasion resistance of woollen-type fabrics such as fabric C.

In the case of fabric A, where the main abrasion mechanism is through fibre attrition and wear, the degree of felting that occurs increases the fabric density but the number of free protruding surface fibres covering the worsted fabric weave structure and protecting the underlying yarns is significantly lower. Felting renders the crowns of the weave structure more pronounced and therefore more susceptible to the abrasion forces. The effects of deamination and esterification on the abrasion resistance in the fabric are thus still pronounced in the felted stage, compared with those of fabric C where there is not much difference, and the values are still higher than those of the untreated felted fabric.

5.3.3. Fabric Tensile Properties

The results of the effect of deamination and esterification treatments on the breaking load and breaking extension of fabric A and fabric C conditioned at 65% r.h. and 21°C are given in Table 122.

From the values obtained it is clear that deamination treatment slightly reduces the breaking load in both fabrics. A reduction of 2% in fabric A and 5.6% in fabric C was recorded. Slight changes in breaking extension were also observed. In fabric C an increase of 2.7% and in fabric A a decrease of 1.9% was recorded. These

TABLE 122. The effect of deamination and esterification treatments on the Tensile Properties of wool fabrics.

Type of treatment	Fabric A (worsted)				Fabric C (woollen)			
	Breaking Load		Breaking Extension		Breaking Load		Breaking Extension	
	(Kg)	mean	(%)	mean	(Kg)	mean	(%)	mean
Untreated	14.3 14.4 13.9	14.2 (0)	36.0 34.0 32.5	34.2 (0)	8.8 8.8 8.8	8.8 (0)	39.0 34.0 38.0	37.0 (0)
Deamination	13.9 13.9	13.9 (-2.1)	33.0 34.0	33.5 (-1.9)	8.6 8.1	8.3 (-5.4)	38.0 38.0	38.0 (+2.7)
Esterification	16.0 14.9	15.4 (+8.8)	44.0 44.0	44.0 (+28.8)	9.6 9.5	9.5 (+8.1)	43.0 45.0	44.0 (+18.9)

The values in parentheses represent the mean change (%) in Fabric Tensile Properties.
+ = increase, - = decrease.

differences are very small and it is not possible to draw definite conclusions from the small number of samples tested.

The esterification treatment improves both the extension at break by 19% on fabric C and by 29% on fabric A, and the breaking load by 8-9% in both fabrics. These values are considerably larger than those observed in the deamination treatment.

5.4. Conclusions

It is clear from the results of this work that deamination and esterification treatments reduce the rate of fabric area felting shrinkage for treatment times up to 30 minutes. Longer Cubex treatment times increase the rate of F.A.F.S. for the deaminated wool samples but for the esterified wool samples the rate of F.A.F.S. is still lower. The trends for both fabrics A and C are similar but the extent of F.A.F.S. (%) for fabric A (worsted) is somewhat lower than that of fabric C (woollen).

The MAR is improved in both instances for the two woven wool fabrics and the level of improvement in MAR is better for fabric A compared with fabric C. This fabric in contrast to fabric C has little or no propensity for pilling and this favours improved MAR values.

The MAR values after Cubex testing are higher for fabric C in both deaminated and esterified felted samples, but these are very similar to the MAR value of the untreated felted sample. This improvement in MAR is believed to be due to felting and hindrance of fibre migration in addition to protection of the weave structure by the felted fibres covering the fabric. This is in contrast to the results obtained with ethylene glycol treatment at 150°C for 60 s (see section 4.3.2.) where a high degree of shrinkage occurred but did not improve the MAR. In that case the fabric did not felt and thus the structure was not covered and protected.

In the case of fabric A, where there are few free fibre ends to felt and cover the structure, the felting produces more pronounced fabric crowns which are more susceptible to abrasive forces and this lowers the MAR values.

However, it must be concluded that the results of this study provide only limited information about the effects of deamination and esterification on the abrasion resistance of woven wool fabrics and therefore further work would be required in order to establish the effects of these treatments more clearly.

CHAPTER 6

The Effects of High Temperature Decatising on the Abrasion Resistance of Woven Wool Fabrics

6.1. Introduction and Objectives

The use of steam in fabric processing is an essential part of wool finishing treatments such as blowing, decatising, polymer curing, etc. Generally steam is employed at or near atmospheric pressure in order to prevent damage to the wool which may possibly occur at high temperatures. However, in some cases the use of steam at elevated temperatures can lead to considerable reductions in time of treatment which are essential in certain processes such as flat setting, dye fixation in melange printing (178) etc.

The object of the work to be described in this section is concerned with the use of an autoclave to study the effects of steaming at a relatively high temperature (130°C) for a range of times on the flat (Martindale) and flex abrasion resistance of woven wool fabrics. In addition studies on the tensile properties, cyclic bending behaviour and cyclic stress-strain behaviour of the treated fabrics were also carried out.

6.2. Experimental

Materials

Fabric specifications: The three woven wool fabrics A, B and C have been utilized in this study. Their detailed specifications have been described in section (2.4.2.).

Methods

Method of Treatment

The fabric samples (30 x 30 cm) were introduced into the autoclave by means of a tray and vacuum was applied to remove any air present and to achieve thorough fabric penetration.

The pressure was increased to 25 p.s.i.g. and the temperature elevated to 130°C. The fabric samples were treated in this state for the designated time and vacuum was applied again to remove the steam and cool the fabrics. The fabric samples were conditioned at 65% r.h., and 21°C for at least 3 days before testing was carried out.

Methods of Testing

The general experimental methods employed were as follows:

(i) Martindale Abrasion Resistance (see section 2.4.2.).
(ii) Flex Abrasion Resistance (see section 2.6.2.).
(iii) Fabric Tensile Properties (see section 2.4.2.).
(iv) Fabric Bending Properties (see section 2.4.2.).
(v) Fabric Cyclic Stress-Strain Behaviour (see section 3.2.1.).

6.3. Results and Discussion

6.3.1. Martindale Abrasion Resistance (MAR)

Table 123 shows the results of the effects of steaming in an autoclave at 130°C, on the MAR (%), calculated on the basis of the untreated fabric values.

In Fig. 118 the change (%) in MAR is plotted against the time of treatment at 130°C for the three fabrics studied. It is clear that the effects of steaming at this high temperature are quite pronounced. For fabrics A and C, steaming for 5 minutes at 130°C gives rise to an improvement in MAR but longer treatment times reduce the MAR considerably. For fabric B a decrease in MAR is observed with all treatment times studied, but a lower reduction in MAR was observed after the 5 minute treatment.

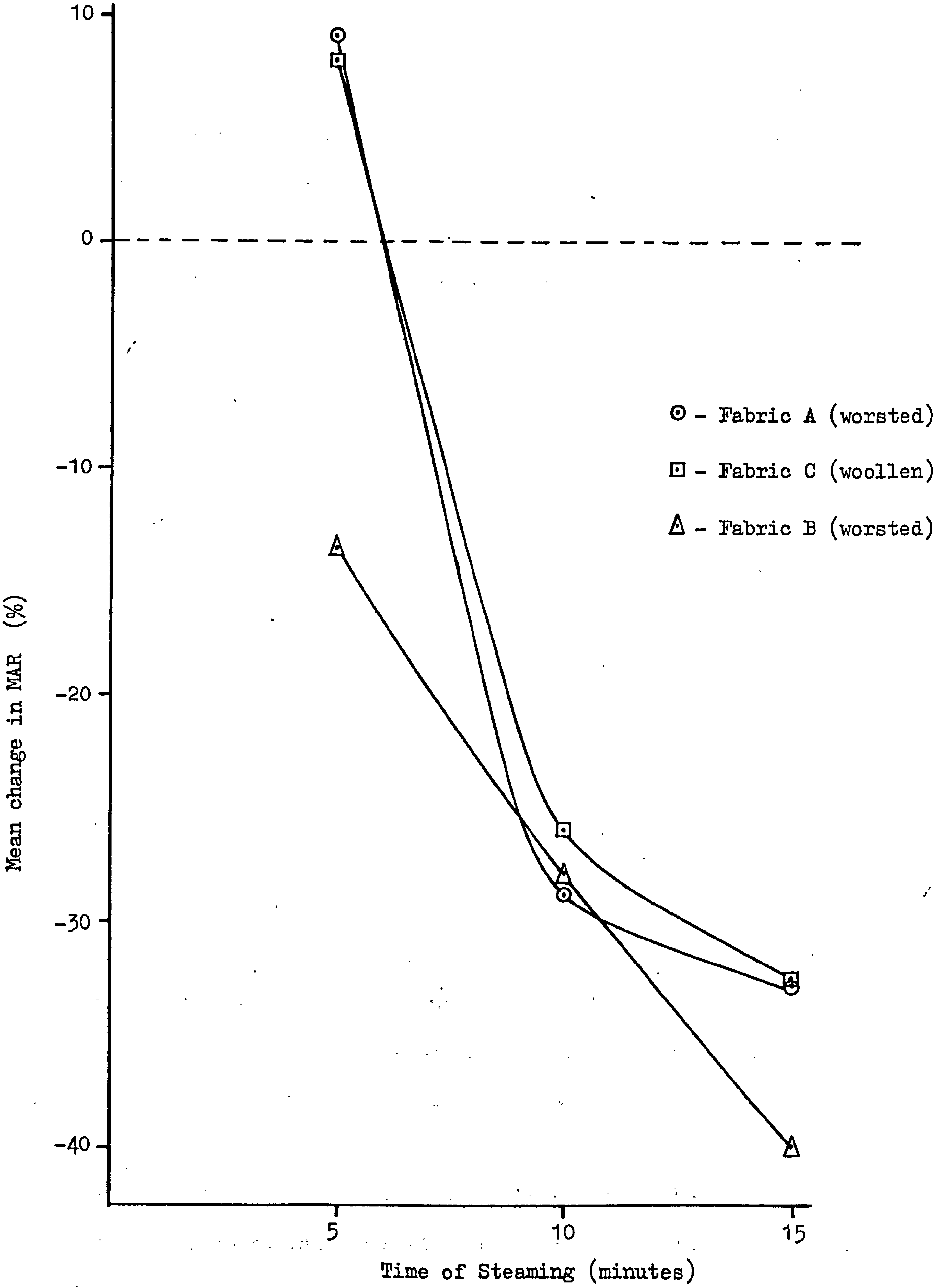
The change (%) in abrasion resistance for both fabrics A and C is very similar and almost all values under the same conditions

TABLE 123. Martindale Abrasion Resistance of wool fabrics treated in an autoclave at 130°C.

Time of treatment (min)	Fabric A (worsted)			Fabric B (worsted)			Fabric C (woollen)		
	Abrasion Resistance (Rubs x 10^3)	mean	mean change in MAR (%)	Abrasion Resistance (Rubs x 10^3)	mean	mean decrease in MAR (%)	Abrasion Resistance (Rubs x 10^3)	mean	mean change in MAR (%)
Untreated	13.0 12.5 10.2	11.9	0	11.9 11.9 11.9	11.9	0	3.6 3.8 3.6	3.7	0
5	13.0 13.0 13.0	13.0	+ 9.2	11.0 8.5 11.5	10.3	13.4	4.0 4.0 4.2	4.0	+ 8.1
10	8.5 8.5 8.5	8.5	-28.6	9.5 9.0 7.5	8.6	27.7	2.75 2.75 2.75	2.75	-25.7
15	8.0 9.0 7.0	8.0	-32.8	7.0 7.5 7.0	7.2	39.9	2.5 2.5 2.5	2.5	-32.4

+ = increase, - = decrease in Martindale Abrasion Resistance.

Fig. 118 - The Effect of autoclave steaming at 130°C on the Martindale abrasion resistance (MAR) of wool fabrics.



coincide. A similar level of MAR (%) is observed with fabric B after steaming for 10 minutes.

The wearing process during Martindale abrasion testing of the treated wool samples appears to be more uniform (i.e. rather than wearing at specific points) compared with the untreated fabric samples. This might be due to the fibre relaxation that takes place during steaming, thus allowing the abrasive forces to be spread more uniformly over the test sample area leading to a slight improvement in MAR after 5 minutes treatment. There must accordingly be little fibre damage taking place within this short period of steaming.

It was observed that the pilling of fabric C (woollen flannel) is reduced considerably after steaming at 130°C and therefore fibre wear and attrition presumably take place during the abrasion process. This is in contrast to the general fibre migration and pilling previously observed with untreated fabric as the main mechanism of abrasion.

Treatment times longer than 5 minutes decrease the abrasion resistance even though more uniform wearing and less pilling for fabric C appears to occur during the abrasion process. The MAR value decreases with increased steaming times at 130°C.

Walde, Barr and Edgar (173) showed that the degradation of plain woven-wool fabric, which had previously been boiled for 1 hour in water and then extracted with anhydrous diethyl ether for 18 hours, increased with increasing steam pressure and with the time of steam treatment.

Haas (175) has reported fibre damage by steaming above atmospheric pressure and suggested that excessive damage could be minimized by the use of a vacuum treatment prior to steaming. In the present work this suggestion was taken into consideration and the fabric samples were vacuum treated prior to steaming at 130°C.

It has also been reported (178) that the presence of alkali or acid in the fibre may influence the rate and extent of degradation when wool is treated with steam at elevated temperatures. It was shown that wool in a mildly acid state can be treated with steam at 12 p.s.i.g. for periods up to 60 minutes without undue damage to the fibres. If however residual alkali is present, steam treatment even at atmospheric pressure causes considerable damage. In the present experimental study the pH state of the fabrics was in the neutral region (see section 2.4.2.) and therefore excessive damage from this cause is unlikely.

The changes in fabric dimensions were negligible after steaming at 130°C and therefore this factor is not considered to affect the MAR values of the treated fabrics.

6.3.2. Flex Abrasion Resistance

The effects of autoclave steaming at 130°C on the flex abrasion resistance (calculated as a percentage on the untreated value) are shown in Table 124 and illustrated in Fig. 119. From these results it is clear that similar changes are observed to those obtained in the MAR studies (see section 6.3.1.). Only on fabric A (light weight worsted) was some improvement in flex abrasion resistance observed after the 5 minute steam treatment. Treatment times longer than 5 minutes decrease the flex abrasion resistance for both fabrics A and C.

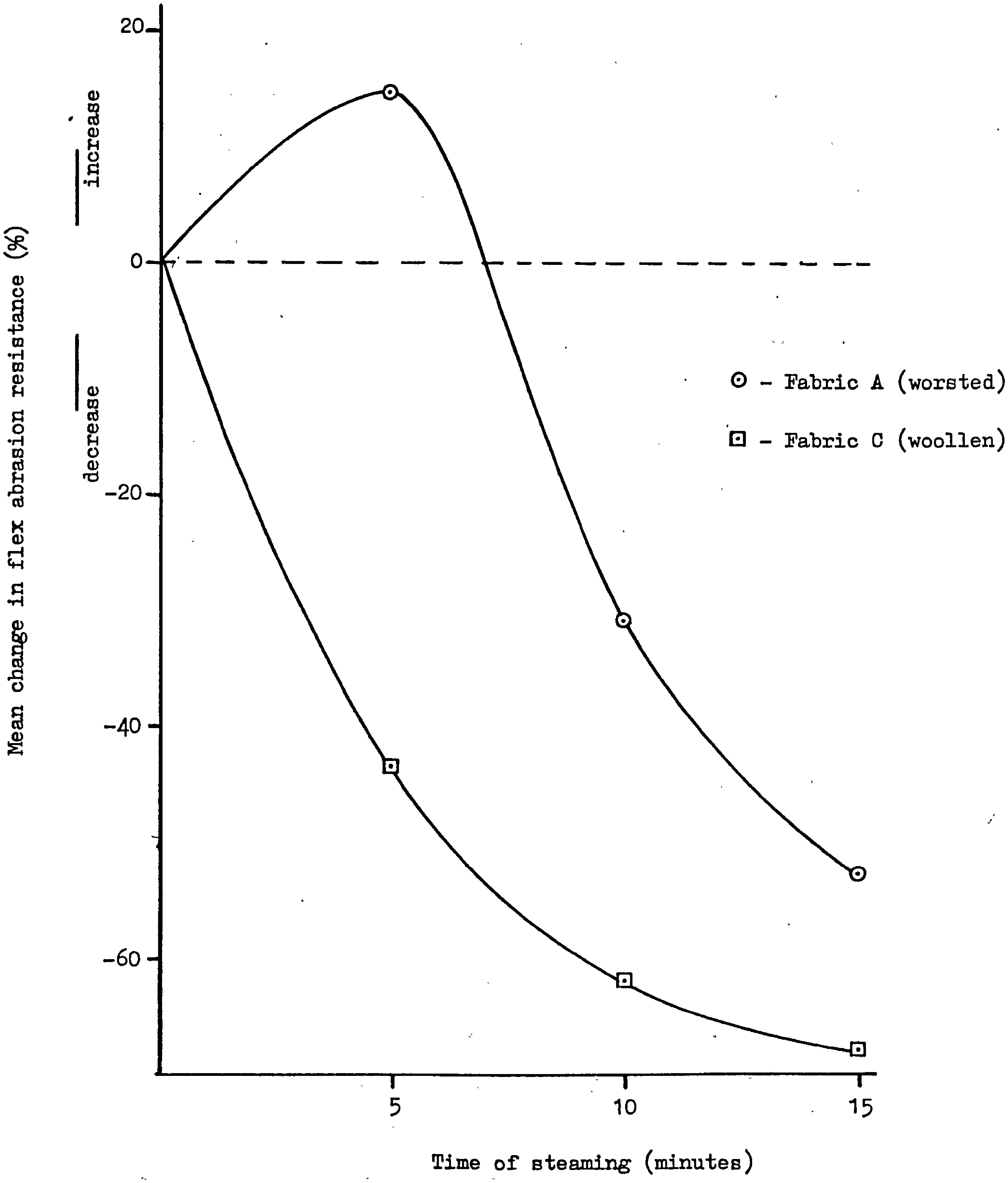
The flex abrasion resistance of fabric C is affected to a greater extent than fabric A. After 15 minutes steaming at 130°C, the flex abrasion resistance of fabric A is reduced to about half (606 cycles),

TABLE 124. The effect of autoclave steaming at 130°C on flex abrasion resistance (FAR) of wool fabrics.

Time of treatment (min)	Fabric A (worsted)			Fabric C (woollen)		
	Flex Abrasion Resistance cycles	Flex Abrasion Resistance mean	mean change in FAR (%)	Flex Abrasion Resistance cycles	Flex Abrasion Resistance mean	mean change in FAR (%)
Untreated	1420 1390 1345 950	1276	0	160 165 175	167	0
5	1460 1295 1638	1465	+ 14.8	95 95 95	95	- 43.1
10	780 820 1050	883	- 30.8	70 60 62	64	- 61.6
15	660 560 600	606	- 52.5	53 56 53	54	- 67.6

+ = increase, - = decrease in flex abrasion resistance.

Fig. 119 - The Effect of autoclave steaming at 130°C on the flex abrasion resistance of wool fabrics.



and that of fabric C to about one third (54 cycles) of the untreated values (1276 cycles for fabric A and 167 cycles for fabric C respectively).

The reduction in flex abrasion resistance for both fabrics is much greater compared with the reduction in MAR for the same treatment time. This is in accord with the more complex mode of abrasion and severity of action obtained in the flex abrasion test.

6.3.3. Fabric Tensile Properties

The results of the effects of autoclave steaming at 130°C on the breaking load and breaking extension of the wool fabrics studied are presented in Table 125. From these results it is evident that steaming does affect the breaking load and breaking extension of the woven wool fabrics. For fabrics A and C the maximum reduction in breaking load is observed after 10 minutes steaming, while for fabric B after only 5 minutes steaming. After 5 minutes and 15 minutes steaming on fabric A the changes in breaking load are hardly noticeable.

The greatest decrease in breaking load for fabrics A, B and C were: 6.3%, 27% and 41% respectively. Thus, it is clear that the least damage occurred on fabric A.

The fabric breaking extension is reduced in all the fabrics studied after steaming at 130°C. The decrease does not follow any particular trend with an increase in treatment time but is generally similar to that observed for the breaking load values.

Decreases in breaking load and breaking extension after treatment in an autoclave at 132°C have previously been reported (176).

Humfeld, Elmquist and Kettering (174) reported that after steaming bleached all-wool serge in a moist condition for 30 minutes

TABLE 125. The effect of autoclave steaming at 130°C on the tensile properties of wool fabrics.

Time of treatment (min)	Fabric A (worsted)				Fabric B (worsted)				Fabric C (woollen)			
	Breaking load		Breaking Extension		Breaking load		Breaking Extension		Breaking load		Breaking Extension	
	(Kg)	mean	(%)	mean	(Kg)	mean	(%)	mean	(Kg)	mean	(%)	mean
Untreated	14.3 14.4 13.9	14.2 (0)	36.0 34.0 32.5	34.2 (0)	15.4 15.3 15.5	15.4 (0)	36.0 32.0 30.0	32.7 (0)	8.8 8.8 8.8	8.8 (0)	39.0 34.0 38.0	37.0 (0)
5	12.3 14.6 15.2	14.0 (1.2)	23.0 28.0 22.0	24.3 (28.8)	10.4 11.4 11.9	11.2 (27.1)	23.5 24.0 24.5	24.0 (26.5)	7.5 6.2 6.4	6.7 (23.8)	32.5 27.0 30.0	29.8 (19.5)
10	13.6 13.6 12.7	13.3 (6.3)	22.0 19.5 18.5	20.0 (41.4)	14.0 14.0 14.0	14.0 (9.1)	27.0 27.0 26.5	27.0 (17.3	5.2 5.2 5.1	5.2 (41.1)	23.0 23.0 23.0	23.0 (37.8)
15	14.1	14.3 (0)	21.0	23.8 (30.2)	12.8	13.5 (12.3)	29.5	28.0 (14.3)	5.5	5.8 (33.7)	23.0	25.3 (31.5)

The values in parentheses represent the mean decrease (%) in fabric tensile properties.

at 15 p.s.i.g., a strength loss of 31% was observed. In another report (358) on the steaming of wool fabric at 120°C for 10 minutes the strength of the treated fabric was 96% of the original and the yellowing of white fabric was only just noticeable. In the present experimental study the yellowness of the steamed fabrics after 5 minutes is hardly noticeable but thereafter it increases with increase in treatment time, although quantitative measurements were not carried out.

Elliot, Stevens and Whewell (177) have studied the effects of steam pressure and temperature on the breaking extension and percentage reduction in work (R.W.) to stretch wool fibres to 30%. From their results it was clear that as the steam pressure increased the breaking extension decreased. The change in % R.W. brought about by steaming wool fibres for various times is little affected by the time of steaming if the temperature does not exceed 110°C. At 120°C however, the changes produced were very time-dependent.

6.3.4. Fabric Bending Properties

The effects of steaming at 130°C on the fabric flexural rigidity G_o and coercive couple C_o for fabric A and fabric C are shown in Table 126.

In Fig. 120 the G_o values (mg. cm) are plotted against the steaming time (minutes) for both fabric A and fabric C. It is clear that G_o is initially increased for both fabrics A and C by 5.5% and 15% respectively, and thereafter G_o remains unchanged with increase in steaming time.

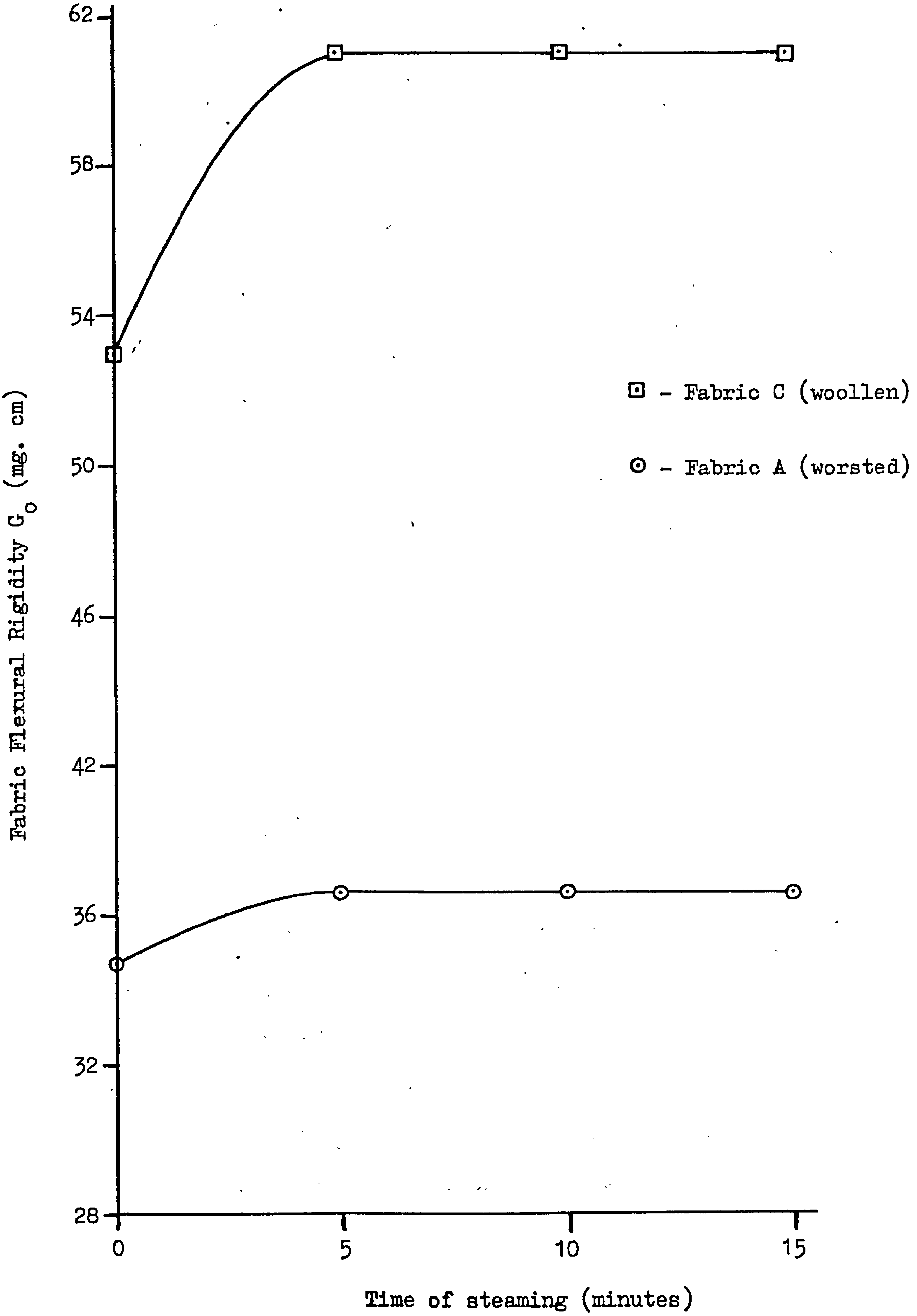
The increase in flexural rigidity G_o might be explained in terms of the fibre setting that takes place during high temperature steaming and as a result of this a more stable fabric configuration is produced. Thus, heavier stresses would need to be applied to the fabric

TABLE 126. The effect of autoclave steaming at 130°C on the flexural rigidity G_o and Coercive couple C_o of wool fabrics.

Time of treatment (min)	Fabric A (worsted)		Fabric C (woollen)	
	G_o (mg.cm)	C_o (mg.cm)	G_o (mg.cm)	C_o (mg.cm)
Untreated	34.7	8.2	53.0	31.6
5	36.6	5.1	61.1	24.2
10	36.6	6.1	61.1	26.5
15	36.6	6.1	61.1	26.5

The above values represent the mean values of three samples in weft-way.

Fig. 120 - The Effect of autoclave steaming at 130°C on flexural rigidity G_o of wool fabrics.



in order to deform this more stable fabric form to the same extent as that of the untreated fabric.

In Fig. 121 the coercive couple (frictional) C_o values (mg. cm) are plotted against the time of steaming (minutes). It is apparent that C_o is reduced by 38% and 23% for fabric A and fabric C respectively, after 5 minutes steaming. After this initial period of time the decrease in C_o is brought to 25% for fabric A and 16% for fabric C for both the 10 minutes and 15 minutes treatment time. Reduction in the frictional restraint couple after steaming has previously been observed elsewhere (359).

The reduction in C_o, i.e. reduction in inter-fibre friction may be explained in terms of the fibre relaxation that takes place during the steaming treatment and by the reduction in frictional restraint at crossover points in the weave structure.

6.3.5. Cyclic Stress-strain Properties

The results of the effects of high temperature steaming (130°C) on the load required for 10% fabric extension on the first stress-strain cycle are shown in Table 127 and illustrated in Fig. 122.

From these results it is clear that the load required for 10% fabric extension is decreased after steam treatment. It is also clear that as the steaming time is increased the load required for 10% fabric extension is decreased.

These results are in accord with other studies (177) in which steaming at high temperature was shown to bring about time-dependent changes in the percentage reduction in work to stretch wool fibres by 30%.

Fig. 121 - The Effect of autoclave steaming at 130°C on the coercive couple C_o of wool fabrics.

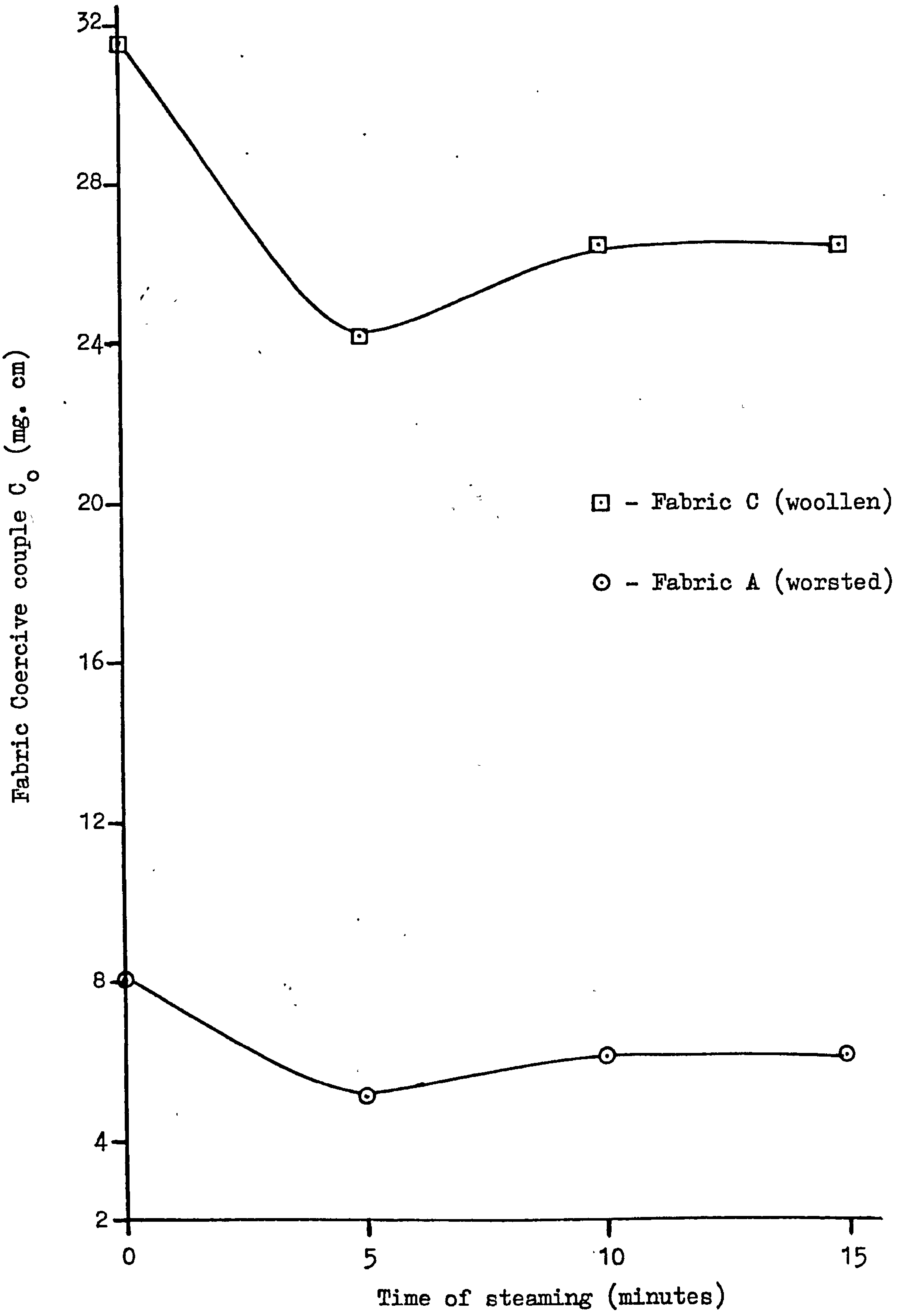
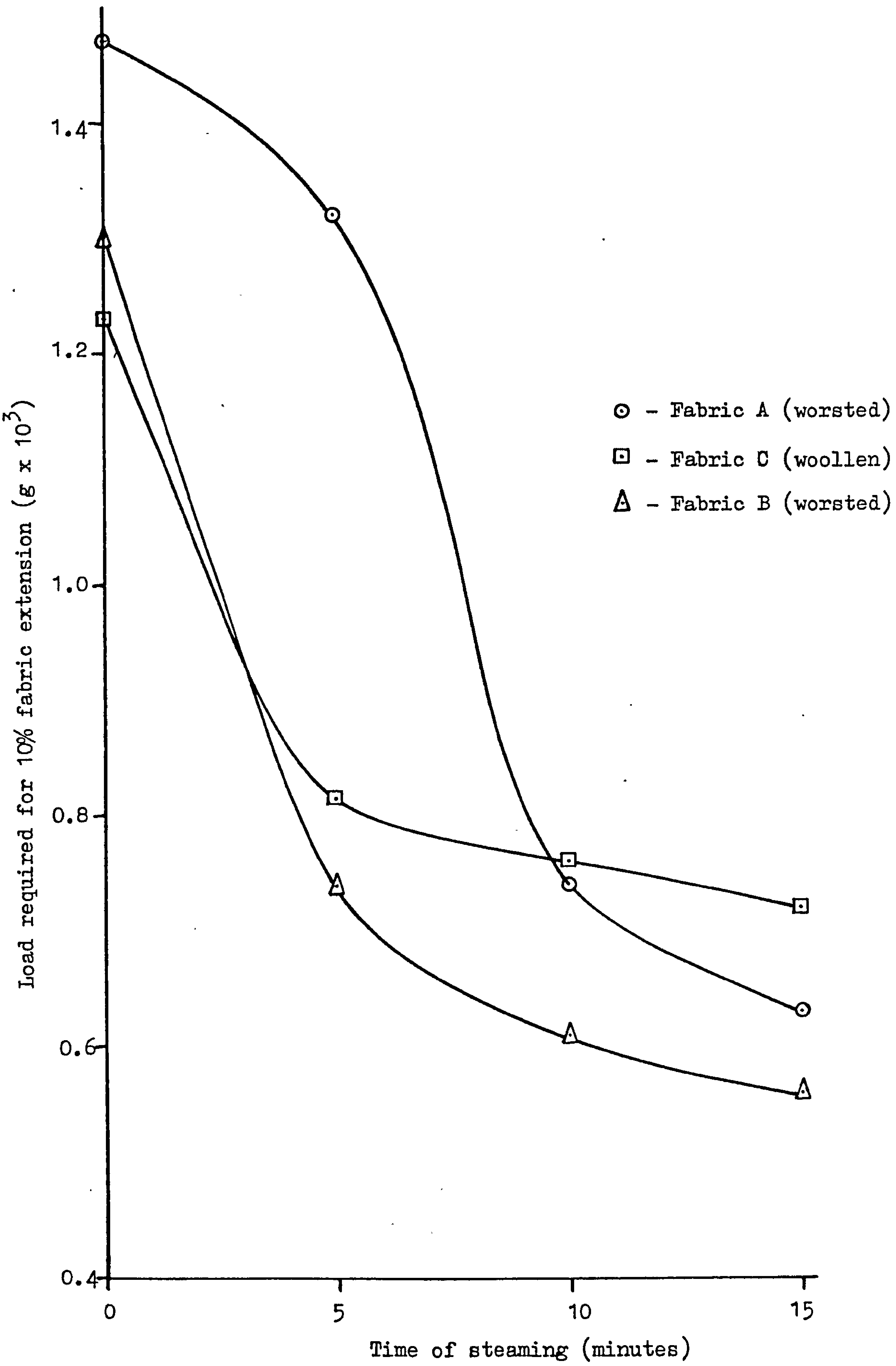


TABLE 127. The effect of autoclave steaming at 130°C on the load required for 10% extension of wool fabrics.

Time of treatment (min)	Load required for 10% extension (g)		
	Fabric A (worsted)	Fabric B (worsted)	Fabric C (woollen)
Untreated*	1470	1300	1230
5	1320 (10.2)	740 (43.1)	815 (33.7)
10	740 (49.7)	610 (53.1)	760 (38.2)
15	640 (56.5)	560 (57.0)	720 (41.5)

* For untreated fabric specifications see section 2.4.2. The values in parentheses represent the decrease (%) in load required for 10% fabric extension.

Fig. 122 - The effect of autoclave steaming at 130°C on the load required for 10% extension of wool fabrics.



6.4. Conclusions

The results reported in this section are generally in accord with previous studies in that the effects of steaming treatments at high temperature are very time-dependent.

The MAR is generally slightly improved when a very short time (5 minutes) is employed presumably as a result of the relaxation processes taking place during steaming and thus allowing the abrasional forces to be applied more uniformly over the whole specimen area. In addition the fabric pilling is reduced which favours improved MAR and the fibre damage is considered to be minimal within this short time. Treatment times longer than 5 minutes decrease the MAR of the wool fabrics. This may be due to fibre damage taking place at this high temperature. This effect is time-dependent i.e. as the treatment time increases the reduction in MAR increases.

The flex abrasion resistance of wool fabrics is affected in a similar manner but to a greater extent that occurring in the MAR test. This is in accord with the more complex mode of abrasion and severity of action obtained in the flex abrasion test.

The steaming treatments at this high temperature (130°C) also affect the tensile properties of the wool fabrics and are time-dependent but in a complex manner.

Changes in G_o and C_o due to steaming at 130°C have also been observed. The increase in G_o is thought to be due to the fibre setting that takes place and to the production of a more stable fabric structure. The decrease in C_o is considered to be due to fibre relaxation that takes place during steaming treatment and a decrease in the fibre interfriction is as a result obtained.

The load required for 10% fabric extension is decreased with increased steaming time.

It must therefore be concluded that steaming at this very high temperature (130°C) should be carried out over relatively short times, because with long treatment times considerable reductions in the abrasion and other properties take place and these may affect the fabric performance.

CHAPTER 7

The Effects of Dyes on the Abrasion Resistance of Woven Wool Fabrics

7.1. Introduction and Objectives

Previous studies relating to the effects of dyes upon the abrasion resistance of woven wool fabrics have been discussed earlier (see section 1.9.). In this section it is intended to report on some limited experimental work conducted on the three woven wool fabrics A, B and C using two dyes, an equalising acid dye Azo Rhodine 2G (Sandoz - C.I Acid Red I) and an acid milling dye Carbolan Red B (I.C.I. - C.I Acid Red 138) utilising the general testing methods used in the rest of the experimental work. Thus the amount of dye (o.w.f.) and the pH conditions have been varied in each case and the Martindale abrasion resistance and other relevant fabric properties measured.

7.2. Experimental

Materials

Fabric specifications: The three woven wool fabrics A, B and C have been utilized and their detailed specifications have been given in section 2.4.2.

Dyes and Chemicals:

Azo Rhodine 2G (Sandoz) C.I Acid Red I.

Carbolan Red B (I.C.I.) C.I Acid Red 138.

Sulphuric acid A.R. (Vickers Laboratory Ltd.).

Anhydrous sodium sulphate (Glauber's salt) (Laboratory reagent grade - B.D.H.).

Glacial acetic acid A.R. (Vickers Laboratory Ltd.).

Ammonium sulphate (Laboratory reagent grade - B.D.H.).

Methods

Dyeing Methods

(i) Azo Rhodine 2G

Fabric samples (35 x 10 cm) were dyed in a John Jeffreys Mark I Rotadyer in 1 litre stainless steel pots.

The dyebath was set at a liquor ratio of 35:1 with:

Sulphuric acid (3% o.w.f.)
Sodium sulphate (10% o.w.f.)
and Azo Rhodine 2G (1-8% o.w.f.).

The pH of the blank dyebath was found to be 2.2. The dyebath constituents were transferred to the stainless steel pots and the prewetted fabric samples were added. The sealed pots were transferred to the ethylene glycol bath of the Rotadyer, which was at a temperature of 100°C. The time required for the dyebath to reach this temperature had previously been determined to be about 25 minutes. The materials in the dyebath were thus raised to the boil in 25 minutes and treated at this temperature for 1 hour. The pots containing the dye solutions and materials were rotated by mechanical means in the John Jeffreys Mark I Rotadyer. After the completion of dyeing, the dyed samples were washed with cold running tap water, dried in a fume cupboard at room temperature and finally conditioned at 65% r.h. and 21°C for at least 3 days prior to testing.

(ii) Carbolan Red B

In this case the dyebath was set with:

acetic acid (1% o.w.f.)
ammonium sulphate (3% o.w.f.)
and Carbolan Red B (1-8% o.w.f.).

The dyebath containing the acetic acid and ammonium sulphate was prepared at room temperature at a liquor ratio of 35:1. The pH was found to be 3.7. The above solution together with the pre-wetted samples (35 x 10 cm) were added to the pots of the Rotadyer. The pots were transferred to the ethylene glycol bath set at 60°C and the materials treated at this temperature for 10 minutes, in addition to 15 minutes time required to reach this temperature. The dyestuff was added and the temperature raised to 80°C over 15 minutes. The treatment was continued at this temperature for 20 minutes and then the temperature was raised to 100°C over 15 minutes and dyed at this temperature for 1 hour. At the completion of dyeing the dyed samples were washed with cold tap water and dried in a fume cupboard at room temperature. Finally the samples were allowed to condition in an atmosphere at 65% r.h. and 21°C for 3 days before any testing was carried out.

Test Methods

The general experimental methods employed were as follows:

(i) Martindale Abrasion Resistance (see section 2.4.2.).

(ii) Flex Abrasion Resistance (see section 2.6.2.).

(iii) Fabric Tensile Properties (see section 2.4.2.).

(iv) Fabric Surface Frictional Properties (see section 3.4.1.).

(v) Fabric Cyclic Stress-Strain Behaviour (see section 3.2.1.).

7.3. Results and Discussion

7.3.1. Martindale Abrasion Resistance (MAR)

The results of the MAR of dyed wool fabric samples are illustrated in Tables 128 and 129 for Azo Rhodine 2G (equalising acid dye) and Carbolan Red B (acid milling dye) respectively. From these results it is clear that the mean change in MAR is dependent upon the amount of

TABLE 128. Martindale Abrasion Resistance of wool fabrics dyed with Azo Rhodine 2G.

Amount of Dye (% o.w.f.)	Fabric A (Worsted)			Fabric B (Worsted)			Fabric C (Woollen)		
	Abrasion Resistance (Rubs x 10^3)	mean	mean change in MAR (%)	Abrasion Resistance (Rubs x 10^3)	mean	mean change in MAR (%)	Abrasion Resistance (Rubs x 10^3)	mean	mean change in MAR (%)
Untreated*	13.0 12.5 10.2	11.9	0	11.9 11.9 11.9	11.9	0	3.6 3.8 3.6	3.7	0
Control	8.0 6.5 6.5	7.0	- 41.2	10.3 12.0 10.7	11.0	- 7.5	3.3 3.5 3.6	3.5	- 5.0
1	8.2 9.3 7.0	8.1	- 31.9	11.0 13.0 11.0	11.7	- 1.6	3.9 3.8 3.5	3.8	+ 2.7
2	7.2 9.5 8.2	8.3	- 30.2	12.0 14.0 11.5	12.5	+ 5.0	4.1 4.2 4.0	4.1	+10.8
4	6.7 5.7 4.6	5.7	- 52.1	11.7 11.0 10.0	10.9	- 8.4	3.6 4.2 4.3	4.0	+ 8.1
8	8.0 8.75 8.0	8.3	- 30.2	10.5 11.0 9.5	10.3	-13.4	3.5 3.6 3.7	3.6	- 2.7

* For untreated fabric specifications see section 2.4.2. + = increase, - = decrease in MAR.

TABLE 129. Martindale Abrasion Resistance of wool fabrics dyed with Carbolan Red B.

Amount of dye (% o.w.f.)	Fabric A (Worsted)			Fabric B (Worsted)			Fabric C (Woollen)		
	Abrasion Resistance (Rubs x 10^3)	mean	mean change in MAR (%)	Abrasion Resistance (Rubs x 10^3)	mean	mean change in MAR (%)	Abrasion Resistance (Rubs x 10^3)	mean	mean change in MAR (%)
Untreated	13.0 12.5 10.2	11.9	0	11.9 11.9 11.9	11.9	0	3.6 3.8 3.6	3.7	0
Control (Blank dyebath)	12.7 16.0 16.0	14.9	25.2	10.5 10.5 10.5	10.5	-11.7	4.7 4.5 5.7	5.0	35.1
1	18.0 18.0 12.5	16.1	35.3	14.5 12.0 12.5	13.0	+ 9.2	5.5 5.0 5.1	5.2	40.5
2	13.0 18.0 20.5	17.1	43.7	16.0 12.0 15.5	14.5	+21.8	6.0 5.0 5.5	5.5	48.6
4	15.0 18.0 14.7	15.9	33.6	15.0 14.0 13.5	14.2	+13.3	4.6 4.2 5.2	4.7	27.0
8	11.5 13.0 11.0	11.8	0	12.0 11.5 11.0	11.5	- 3.3	5.1 4.6 3.5	4.4	18.9

+ = increase, − = decrease in Martindale abrasion resistance (MAR) dye (o.w.f.), the type of dye and the dyeing conditions as well as on the fabric structure. It can be seen in these experiments that the optimum amount of dye for obtaining the best results in MAR for both types of dye is around 2% o.w.f. The magnitude of the change in MAR differs according to the dye used, the exhaustion in both cases being approximately 95%.

Azo Rhodine 2G, applied at pH 2.2 appeared to adversely affect the MAR with the exceptions of fabric C at 1, 2 and 4% and fabric B at 2% o.w.f. where slight increases in MAR were recorded. Treatment in a blank dyebath (i.e. omitting the dye) reduced the MAR of all the woven wool fabrics studied.

Treatment with Carbolan Red B appeared to be beneficial for all three fabrics and increases of up to 48% in MAR were recorded with 2% o.w.f. The pH in this dyeing process was 3.7. Thus the pH appeared to be of great importance in these two dyeing operations.

The above findings are generally in accord with previous work, where it was shown that the pH conditions can affect the wearing properties of wool fibres (125). Peryman (125) showed that no change in abrasion resistance of wool yarn occurred after boiling at pH values around 3, but between pH 3-7 increases of up to 20% were obtained. Below the region of pH 3 and close to pH 2, great losses in abrasion resistance were observed. Peryman (125) suggested that the increase in abrasion resistance was associated with the conditions of treatment. These could result in supercontraction of the fibres, and so produce a more compact yarn, more able to withstand abrasion. In the current study the increases in abrasion resistance are considered to arise more probably from the fact that fabric shrinkage takes place during the dyeing treatments (see Table 130). From Table 130 it can be seen that dyeing with Carbolan Red B introduces more fabric shrinkage and

TABLE 130 The effects of blank dyeing treatments on the fabric area felting shrinkage (F.A.F.S.) of wool fabrics

Type of Fabric*	F.A.F.S. (%)	
	Blank Azo Rhodine 2G treatment	Blank Carbolan Red B treatment
A (worsted)	3.0	3.5
B (worsted)	8.8	9.8
C (woollen)	9.8	11.2

* For untreated fabric specifications see section 2.4.2.

this treatment gives improved MAR values (see Table 129).

In another report Lui, Speakman and King (181) showed that the wearing properties of wool fabrics are little affected when small amounts of acid dyes are used and sometimes can even be beneficial for the wearing properties of wool fabrics.

Extensive work on the effects of dyeing with acid and chrome dyes by determining the changes in the reduction in work to stretch single fibres to 30% extension, bursting strength and wet abrasion have been reported by Carter (183). The results suggested that dyeing in the presence of large amounts of sulphuric acid produced significant adverse modification, as did the afterchrome method of dyeing, although with both methods only slight reductions in fabric bursting strength were recorded. In the case of wet abrasion the acid dyeing showed a decrease in abrasion resistance, while dyeing in sulphuric acid led to the greatest reduction in abrasion resistance. All the other dyeings showed an increased wet abrasion resistance, the greatest increase being in the afterchrome method using acetic acid. These findings are in accord with the results of this work in which greater reductions in MAR were observed when dyeing from sulphuric acid (pH 2.2).

Recent studies (47) on dyeing have confirmed the findings of this work that the MAR of plain weave worsted fabrics is reduced quite markedly at pH 2.2, although different dyes were used. In the same study it was shown that the abrasion resistance depends greatly on the pH and temperature of the dyeing treatment. Dyeing at room temperature at pH 5 in the presence of n-propanol resulted in marked improved MAR. Other workers (122, 187, 188) have also reported that solvent-assisted dyeing produces less adverse changes in physical properties than conventional dyeing, and the effects on MAR are therefore worthy of study.

In respect of the woollen flannel (fabric C) the fabric shrinkage values were higher than those of fabrics A and B and moreover it was observed visually that the dyeing treatments reduced the pilling of fabric C although no quantitative studies were carried out. As pilling appears to play an important role in the abrasion properties of fabric C, it would be expected on this basis that the rate of pilling and weight loss would be reduced, leading to higher MAR values.

7.3.2. Flex Abrasion Resistance

The effects of dyeing on the flex abrasion resistance are shown in Tables 131 and 132 for Azo Rhodine 2G and Carbolan Red B respectively. From Table 131 it is clear that the dyeing with Azo Rhodine 2G had very little effect on the flex abrasion resistance of the wool fabrics studied. Slight improvement in flex abrasion resistance may also be

TABLE 131. Flex abrasion resistance of wool fabrics dyed with Azo Rhodine 2G.

Amount of Dye (% o.w.f.)	Fabric A (Worsted)			Fabric B (Worsted)			Fabric C (Woollen)		
	Flex Abrasion Resistance		mean change in FAR (%)	Flex Abrasion Resistance		mean change in FAR (%)	Flex Abrasion Resistance		mean change in FAR (%)
	cycles	mean		cycles	mean		cycles	mean	
Untreated	1420 1390 1345 950	1275	0	1690 1070 1200	1300	0	160 165 175	167	0
Control (Blank dyebath	1240 1210 1150	1200	- 5.9	1200 1300	1250	- 3.4	135 160	145	- 13.2
1	1470 1290 1100	1300	+ 2.0	1280 1250 1450	1330	+ 2.3	175 170	172	+ 3.0
2	1355 1765	1550	+21.6	1270 1435 1625	1440	+ 10.8	180 140	160	- 4.2
4	1335 905	1120	-12.6	1250 1350 1400	1330	+ 2.3	150 150	150	- 10.2
8	1000 1020	1010	-20.8	1550 1600 1290	1480	+ 13.8	195 155	175	+ 4.8

+ = increase, - = decrease in flex abrasion resistance (FAR)

TABLE 132. Flex abrasion resistance (FAR) of wool fabrics dyed with Azo Rhodine 2G.

Amount of dye (% o.w.f.)	Fabric A (worsted)			Fabric B (worsted)			Fabric C (woollen)		
	Flex Abrasion Resistance		mean decrease in FAR (%)	Flex Abrasion Resistance		mean increase in FAR (%)	Flex Abrasion Resistance		mean decrease in FAR (%)
	cycles	mean		cycles	mean		cycles	mean	
Untreated	1420 1390 1345 950	1275	0	1690 1070 1200	1300	0	160 165 175	167	0
Control (blank dyebath)	1000 1020	1010	20.8	1710 1250 1660	1540	18.5	95 105	100	40.1
1	930 970	950	25.5	1750 1600 1750	1700	30.8	130 110	120	28.1
2	660 780	720	43.5	1265 1430 1995	1560	20.0	105 115	110	34.1
4	600 750	675	47.0	1530 1660 1400	1530	17.7	95 105	100	40.1
8	1200 1000	1100	13.7	1880 1360 1360	1530	17.7	120 150	135	19.2

obtained at certain dye levels. Generally the dyed samples have a better abrasion resistance than the controls (blank treatment samples), which in all three cases are lower than the values of the untreated fabrics.

From Table 132 it is apparent that dyeing with Carbolan Red B reduces the resistance to flex abrasion with the exception of fabric B (twill) where increases in flex abrasion resistance were obtained. Generally the values of flex abrasion resistance with Carbolan Red B lie within the same range of values obtained for the control sample.

7.3.3. Fabric Tensile Properties

The effects of dyeing with Azo Rhodine 2G and Carbolan Red B on the breaking load and breaking extension of the wool fabrics are given in Tables 133 and 134.

From these results it is suggested that the breaking load for all three woven wool fabrics is increased by both dyeing methods. Increasing the amount of Azo Rhodine 2G leads to an increase in fabric breaking load. The blank treatment (control) had no effect on the breaking load. The greatest increase in breaking load (12.7%) with Azo Rhodine 2G was obtained on fabric C at 2% o.w.f.

Dyeing with Carbolan Red B increases the breaking load of the wool fabrics more than Azo Rhodine 2G. Increasing the amount of dye in the dyebath leads to a higher fabric breaking load with woollen flannel fabric (fabric C). This is not observed for fabric A (light weight worsted) or fabric B (twill), where the level of improvement in breaking load is very similar to that of the blank treatment.

The breaking extensions of the Azo Rhodine 2G dyed fabric samples are reduced for fabrics A and B compared with the untreated fabric values. For fabric C decreases in breaking extension were observed

TABLE 133. The effect of dyeing with Azo Rhodine 2G on the Tensile Properties of wool fabrics.

Amount of Dye (% o.w.f.)	Fabric A (Worsted)				Fabric B (Worsted)				Fabric C (Woollen)			
	Breaking Load		Breaking Extension		Breaking Load		Breaking Extension		Breaking Load		Breaking Extension	
	(Kg)	mean	(%)	mean	(Kg)	mean	(%)	mean	(Kg)	mean	(%)	mean
Untreated	14.3 14.2 13.9	14.2 (0)	36.0 34.0 32.5	34.2 (0)	15.4 15.3 15.5	15.4 (0)	36.0 32.0 30.0	32.7 (0)	8.8 8.8 8.8	8.8 (0)	39.0 34.0 38.0	37.0 (0)
Control (Blank dyebath)	14.3 13.9	14.2 (0)	31.0 30.0	30.5 (-10.7)	16.1 15.5	15.8 (+2.6)	31.0 32.0	31.5 (-3.5)	8.3 9.3	8.8 (0)	31.0 35.0	33.0 (-10.8)
1	14.2 14.5	14.3 (+1.1)	30.0 33.0	31.5 (-7.7)	16.2 16.8	16.5 (+7.1)	32.0 27.0	29.5 (-9.6)	9.7 8.8	9.3 (+4.9)	36.0 36.0	36.0 (-2.7)
2	15.4 15.4	15.4 (+8.4)	34.0 34.0	34.0 (-0.4)	16.8 16.2	16.5 (+7.1)	32.0 31.0	31.5 - 3.5	10.2 9.7	9.9 (+12.7)	39.0 41.0	40.0 (+8.1)
4	15.6 15.4	15.5 (+9.1)	32.0 31.0	31.5 (-7.7)	16.6 16.2	16.4 (+6.5)	30.0 33.0	31.5 (-3.5)	9.5 9.1	9.3 (+5.3)	36.0 39.0	37.5 (+1.3)
8	15.4 15.2	15.3 (+7.7)	22.0 31.0	26.5 (-22.4)	16.8 16.0	16.4 (+6.5)	30.0 31.0	30.5 (-6.6)	9.1 8.3	8.7 (+1.2)	36.0 37.0	36.5 (-1.3)

The values in parentheses represent the mean change (%) in Fabric Tensile Properties. + = increase, - = decrease.

TABLE 134. The effect of dyeing with Carbolan Red B on the Tensile Properties of wool fabrics.

Amount of Dye (% o.w.f.)	Fabric A (Worsted)				Fabric B (Worsted)				Fabric C (Woollen)			
	Breaking Load		Breaking Extension		Breaking Load		Breaking Extension		Breaking Load		Breaking Extensio	
	(Kg)	mean	(%)	mean	(Kg)	mean	(%)	mean	(Kg)	mean	(%)	mean
Untreated	14.3 14.4 13.9	14.2 (0)	36.0 34.0 32.5	34.2 (0)	15.4 15.3 15.5	15.4 (0)	36.0 32.0 30.0	32.7 (0)	8.8 8.8 8.8	8.8 (0)	39.0 34.0 38.0	37.0 (0)
Control (Blank dyebath)	15.6 15.8	15.7 (+10.7)	31.0 29.0	30.0 (-12.2)	16.7 16.7	16.7 (+8.4)	36.0 32.0	34.0 (+4.1)	8.5 8.5	8.5 (-3.7)	38.0 42.0	40.0 (+8.1)
1	15.1 16.4	15.7 (+10.9)	32.0 31.0	31.5 (-7.8)	16.1 16.5	16.3 (+5.8)	32.0 31.0	31.5 (-3.5)	9.2 9.2	9.2 (+4.2)	40.0 42.0	41.0 (10.8)
2	15.5 15.7	15.6 (+9.8)	35.0 30.0	32.5 (-4.8)	16.3 16.7	16.5 (+7.1)	32.0 32.0	32.0 (-2.0)	9.5 9.1	9.3 (+5.3)	42.0 43.5	42.7 (+15.5
4	15.2 15.5	15.3 (+8.1)	28.0 34.0	31.0 (-9.2)	16.7 16.3	16.5 (+7.1)	35.0 35.0	35.0 (+7.2)	10.5 10.1	10.3 (+16.6)	39.0 37.0	38.0 (+2.7)
8	14.8 15.7	15.2 (+7.4)	27.0 31.0	29.0 (-15.1)	16.9 16.7	16.8 (+9.1)	37.0 36.0	36.5 (+11.7)	10.1 10.5	10.3 (+16.6)	36.0 39.0	37.5 (+1.3)

The values in parentheses represent the mean change (%) in Fabric Tensile Properties. + = increase, - + decrease.

but increases at 2 and 4% o.w.f. were also obtained. Fabric C was the main fabric where increases in MAR were generally obtained. The greatest decrease in breaking extension was observed on fabric A (light weight worsted) and the most severe losses in MAR were recorded on this fabric.

In the case of the Carbolan Red B dyeings, decreases in breaking extension were also recorded for fabric A but to a less severe extent. With fabrics B and C increases in breaking extension were mainly recorded.

It has been shown (125) that the loss in conditioned fibre strength after treatment under conditions used in dyeing practice does not exceed 15% and generally less than 10% (i.e. when wool was treated at the boil for 3 hours within the pH range 1.5 - 9.0). It was also established that within the narrower pH range of 3-3.5 the losses in fibre strength were quite small and probably not significant. Under more acidic or more alkaline conditions the losses were progressively greater. In this experimental work no losses in strength of the fabrics were observed but between fabric and fibre there is not really direct comparison. In the case of breaking extension the losses were less when dyeing was carried out at near pH range 3-3.5 but greater when dyeing was carried out at pH values below 3-3.5.

Therefore, the results from this limited experimental study confirm the suggestion (125) that dyeing at pH values near 3-3.5 has no significant effect on the tensile properties and that below or above that pH range greater losses may take place.

7.3.4. Fabric Surface Frictional Properties

The effects of dyeing on the surface friction of the fabrics studied are illustrated in Table (135).

TABLE 135. Surface frictional properties of wool fabrics after dyeing with Azo Rhodine 2G and Carbolan Red B.

Amount of Dye (% o.w.f.)	Azo Rhodine 2G						Carbolan Red B					
	Fabric A		Fabric B		Fabric C		Fabric A		Fabric B		Fabric C	
	Frictional Force (g)	mean	Frictional Force (g)	mean	Frictional Force (g)	mean	Frictional Force (g)	mean	Frictional Force (g)	mean	Frictional Force (g)	mean
Untreated	234.3 233.9	234.1	169.3 163.6	166.4	172.3 162.4 159.7	164.8	234.3 233.9	234.1	169.3 163.6	166.4	172.3 162.4 159.7	164.8
Control (Blank dyebath)	241.5 238.1	239.8	177.9 169.4 166.6	171.3	169.7 163.6	166.6	235.0 228.2	231.6	-	-	166.7 162.3 157.5	162.1
1	242.4 235.1	238.7	175.3 168.1 164.0	169.1	169.1 162.4	165.7	233.5 228.4	230.9	-	-	164.6 159.9 158.2	160.9
2	241.4 236.5	238.9	176.7 168.6 161.1	168.8	167.5 163.6	165.5	234.2 227.8	231.0	-	-	164.4 161.6 158.1	161.3
4	249.5 237.1 231.4	239.3	176.6 164.7 164.4	168.5	171.2 161.3	166.2	232.8 229.7	231.2	-	-	164.7 161.7 157.0	161.1
8	241.5 235.9	238.7	172.2 172.6	172.4	167.5 163.6	165.5	239.5 229.4	234.4	-	-	166.8 160.3 157.3	161.4

When dyeing with an equalising acid dye (Azo Rhodine 2G) at pH 2.2, the surface frictional properties are increased for the three wool fabrics. Although the results are somewhat scattered, the mean values of the dyed samples are not significantly different from the values of the blank-treated samples.

When dyeing with an acid milling dye (Carbolan Red B) at pH 3.7 the surface frictional properties are reduced for the fabrics studied and again as in the case of Azo Rhodine 2G, the mean values of the surface frictional properties of the dyed samples lie within the band of the untreated and the blank dyebath sample values.

Thus from these results it must be concluded that the conditions of dyeing, such as pH, are of importance in affecting the surface frictional properties of wool fabrics. These observations are generally in accord with previous studies (360) that the kinetic friction of dyed wool yarn is reduced when dyeing is carried out at pH 4 compared with increased yarn friction at pH 7.

From the changes in fabric area shrinkage (%) during the blank treatment illustrated in Table 130 it can be seen that the F.A.F.S. decreases in the order: fabric C > fabric B > fabric C for both dyeing treatments studied. The fabric surface frictional difference generally decreases in the order: fabric A > fabric B > fabric C which is in the reverse order. While the degree of F.A.F.S. will have some effect on the MAR, the changes in fabric surface frictional properties observed in the present study are only marginal and are unlikely to affect significantly the abrasional properties of the fabric studied.

7.3.5. Fabric Cyclic Stress-strain Behaviour

The effects of dyeing with Azo Rhodine 2G and Carbolan Red B on the load required for 10% fabric extension are given in Table 136 and illustrated in Fig. 123 and 124 respectively. From these results it is clear that both dyeing treatments studied reduce the load required for 10% fabric extension, i.e. the ease of extension is increased. The greater changes in load required for 10% fabric extension are observed with fabric B and C and also when dyed with Carbolan Red B.

For all three fabrics studied the greater ease of fabric extension was observed with 2% o.w.f. dye in the two dyeing procedures and this level gave the best MAR results with both dyes studied.

The recovery from 10% extension was also recorded and calculated for fabric A in the Carbolan Red B treatment (see Table 137). From these results it is obvious that the % hysteresis is slightly reduced on the dyed samples and in the same order as the MAR is increased.

TABLE 137 The effects of dyeing with Carbolan Red B on the hysteresis (%) of fabric A

Amount of dye (% o.w.f.)	% hysteresis
Untreated	28
1	26
2	22
4	24
8	26

In similar experiments but at 30% extension Lui, Speakman and King (181) showed that the % hysteresis of dyed fabrics with large amounts of dye is increased but with small amounts (up to 5%) the % hysteresis is decreased. The smaller the % hysteresis the greater the power of recovery of the fibres from deformation and therefore the greater the elasticity.

TABLE 136. Load required for 10% fabric extension after dyeing with Azo Rhodine 2G and Carbolan Red B.

Amount of Dye	Azo Rhodine 2G						Carbolan Red B					
	Load required for 10% extension						Load required for 10% extension					
	Fabric A (worsted)		Fabric B (worsted)		Fabric C (woollen)		Fabric A (worsted)		Fabric B (worsted)		Fabric C (woollen)	
(% o.w.f.)	(g)	mean	(g)	mean	(g)	mean	(g)	mean	(g)	mean	(g)	mean
Untreated *	1470	1470	1280	1300	1200	1230	1470	1470	1280	1300	1200	1230
	1470		1320		1260		1470		1320		1260	
Control (Blank dyebath)	1000	1070	410	385	210	230	1000	1080	270	270	250	267.5
	1140		360		250		1160		270		285	
1	550	595	365	360	220	225	880	965	270	265	210	210
	640		355		230		1050		260		210	
2	530	545	360	335	190	195	610	685	270	255	180	185
	560		310		200		760		240		190	
4	920	940	400	370	295	280	1020	1050	360	330	220	217.5
	960		340		265		1080		300		215	
8	1340	1390	650	575	285	295	1020	1080	450	415	280	270
	1440		500		305		1140		380		260	

* For untreated fabric specifications see section 2.4.2.

Fig. 123 - The effect of dyeing with Azo Rhodine 2G on the load required for 10% extension of wool fabrics.

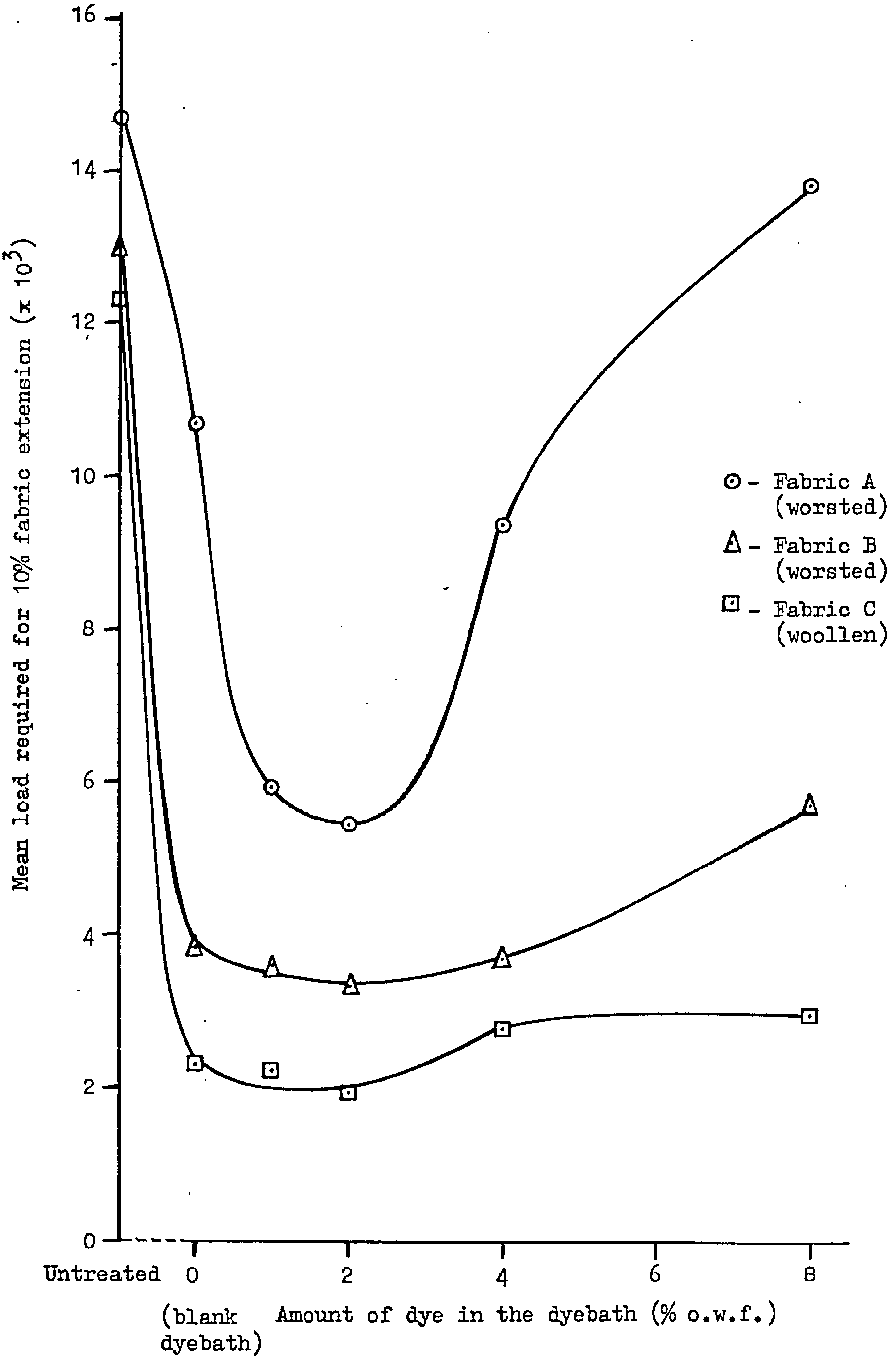
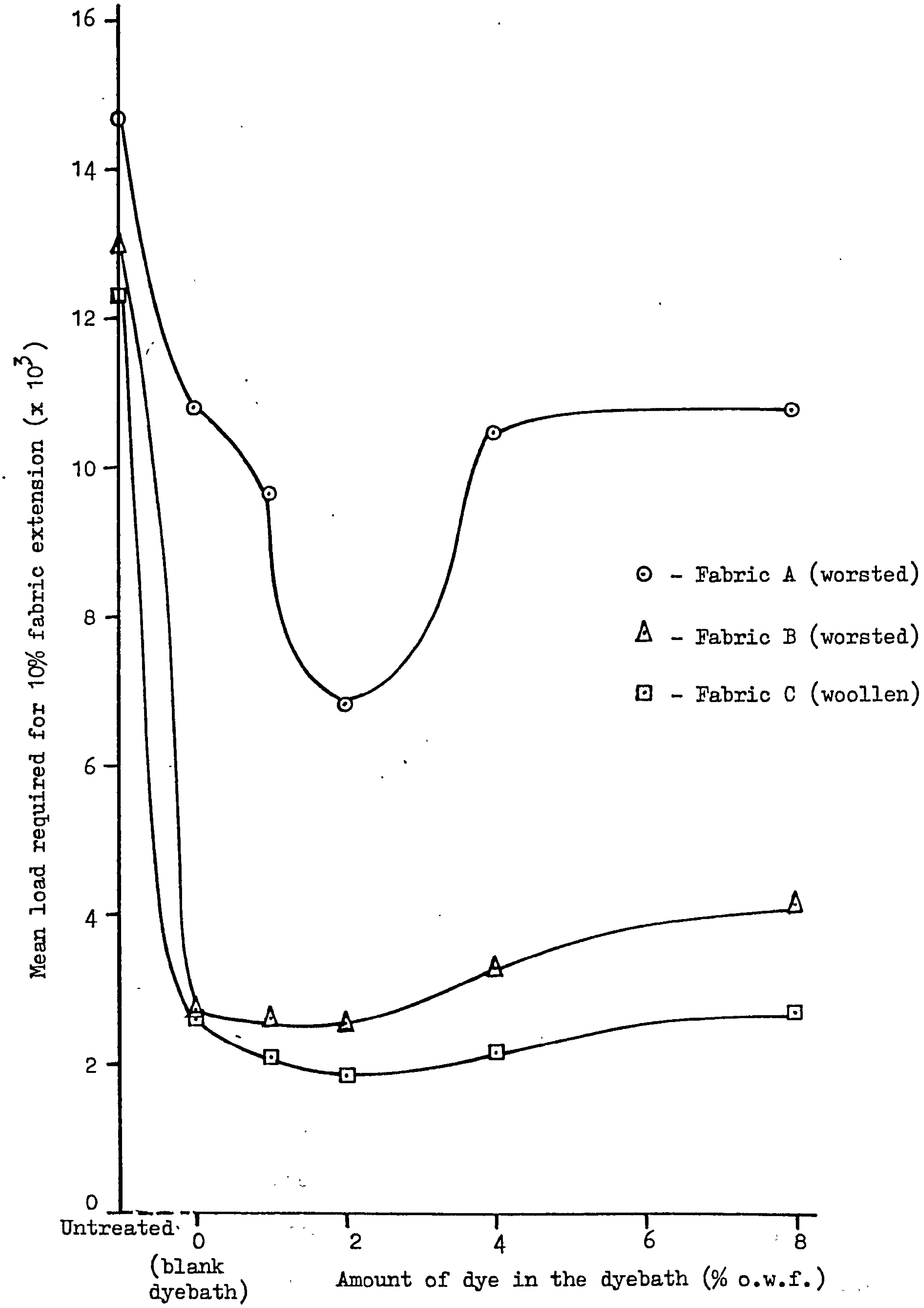


Fig. 124 - The effect of dyeing with Carbolan Red B on the load required for 10% extension of wool fabrics.



7.4. Conclusions

From the results of this study it can be concluded that the nature of the dye is intimately interrelated with the conditions of application e.g. pH, and this appears to be the most important factor in affecting the MAR of wool fabrics.

Under the conditions studied the optimum MAR was obtained at 2% o.w.f. dye level for both dyes employed. Clearly this cannot be regarded as being universally applicable as the optimum dyeing conditions for all dyes for wool fabrics, but it might well be taken into consideration.

The changes in surface frictional properties are only marginal but the shrinkage that occurs as a result of the dyeing treatments may well affect the results.

The flex abrasion resistance results are not similar to the MAR results. The treatment that gave the lowest MAR value gave the highest flex abrasion resistance. Improvement in flex abrasion resistance was mainly observed on fabric B, which was of twill structure compared with fabrics A and C which are plain weave structures. Thus the fabric structure is likely to be of importance, when MAR and flex abrasion resistance are compared.

It must be concluded, therefore, that from this limited study, it is difficult to draw detailed conclusions, except that the pH and the amount of dye (% o.w.f.) may be important factors. However, further work would be required to elucidate the effect of a wider range of dyes and of dyeing conditions on a particular fabric structure in order to ascertain the effects of dyeing treatments on the abrasional properties of wool fabric. The choice of a particular fabric structure is very important in view of the results obtained in this section and other preceding experimental sections of this thesis.

Dyeing conditions should also be selected in order to minimise felting shrinkage which may affect the results. Furthermore, solvent-assisted dyeing should also be investigated in order to ascertain the effects on the MAR in view of the results obtained in section 3.5., where the MAR of wool fabrics, especially worsted, was increased considerably as a result of the solvent treatments.

CHAPTER 8

The Wet Abrasion of Woven Wool Fabrics

8.1 Introduction and Objectives

Recent work by Nhan and Denby has clearly demonstrated that the Martindale abrasion resistance (MAR) of wool fabrics is very dependent upon the relative humidity during abrasion testing (24). The MAR increased markedly as the relative humidity was increased from 8 to 83%, although the most pronounced changes occurred in the high relative humidity range (> 65% r.h.). An interesting observation was that at 100% r.h. where the specimen was rubbed against the abradant fabric in the presence of liquid water, the Martindale abrasion tester value was 6,500 rubs compared with 10,750 rubs to hole at 8% r.h. Indeed the value for wet fabric (100% r.h.) was markedly lower than the value of 58,000 rubs obtained at 83% r.h. It was further pointed out that shrink-proofing the fabric exerted little influence upon the value obtained under wet abrasion conditions.

From the results discussed earlier (see sections 2.4.4., 2.5.4., 2.6.4.) it was shown that the MAR of woven wool fabrics is improved by applying polymer shrink-resist finishes and conditioning and testing under normal testing conditions (65% r.h., 21°C). In view of the low wet MAR of shrink-proofed wool fabric reported by Nhan and Denby, a range of shrink-resist treated woven wool fabrics have been subjected to abrasion under a variety of wet conditions on the Martindale abrasion tester, and the results form the basis of this study.

8.2. Experimental

Fabrics: The two woven wool fabrics A and C were used in this study, and the constructional details were given in section 2.4.2.

Chemicals:

(i) Synthappret BAP (Bayer).

(ii) Impranil DLH (Bayer).

(iii) Lankrolan SHR3 (Diamond Shamrock).

(iv) DC 109 (Dow Corning).

(v) Hercosett 125 (Hercules inc.).

(vi) Sodium Hypochlorite (11.35% available chlorine) Laporte Chemicals, Sulphuric acid (laboratory reagent - BDH).

The shrink resist treatments were applied by typical commercial techniques utilising either padding or exhaustion treatments which have been described in detail in sections 2.4.2. and 2.5.2.

Conditioning

All fabric samples were conditioned for at least one week at 65% r.h. and 21°C prior to abrasion testing.

Martindale Abrasion Resistance (see section 2.4.2.).

Methods for Conducting the Abrasion Tests

Fabric samples were abraded under four separate testing conditions:

(1) Both the samples and abradant were conditioned and abraded at 65% r.h. and 21°C.

(2) The samples were wetted out initially with distilled water to 100% pick-up with the abradant in the normal conditioned state (65% r.h.). No liquor replenishment was given during abrasion testing.

(3) Both the samples and the abradant were wetted out initially to 100% pick-up with distilled water, and no liquor replenishment made during testing.

(4) Both the samples and the abradant were wetted out to an initial pick-up of > 200% (saturated conditions) and no further addition of water made during testing. Under this set of experimental conditions, liquid water was still present in both the samples and the abradant at the end-point of the test.

In all the above tests the surrounding atmosphere was controlled at 65% r.h. and 21°C.

8.3. Results and Discussion

Preliminary tests were conducted on the various fabric samples to ensure that the shrink-resist treatments did not change the level of the normal moisture regain at 65% r.h. and 21°C. The results of Table 138 confirm that there are no substantial changes in the moisture regain of the samples studied. Indeed the majority of the samples had slightly lower moisture regain values.

TABLE 138

Treatment	Moisture Regain (%) Wool Flannel	Moisture Regain (%) Lightweight Worsted
Untreated	12.46	12.25
0.5% Chlorination	11.95	11.65
4% DC 109 (padded)	11.02	-
2.5% Synthappret BAP/Impranil DLH (padded)	12.22	-

The results are given in Table 139 and 140 for the wool flannel (fabric C) and lightweight worsted fabric (fabric A) respectively. It is clear that the polymer shrink-resist treatments significantly increase the MAR of the woollen flannel when the tests are conducted under test condition (1), namely at 65% r.h. and 21°C. In general, polymer shrink-resist treatments applied via the padding technique exhibit a greater improvement in MAR than those obtained by exhaustion

TABLE 139. Wet Martindale abrasion resistance of fabric C (woollen).

Type of treatment	Fabric C (flannel)								Water left after condition (4)
	Condition 1		Condition 2		Condition 3		Condition 4		
	Rubs x 10^3	mean	Rubs x 10^3	mean	Rubs x 10^3	mean	Rubs x 10^3	mean	(%)
Untreated *	3.6 3.8 3.6	3.7	8.0 8.0 8.0	8	11.0 11.0 11.0	11.0	4.2 4.7 4.5	4.5	230
0.5% o.w.f. chlorination	5.0 5.0 5.5	5.2	6.5 6.0 6.5	6.3	11.0 11.0 11.0	11.0	5.5 5.5 5.5	5.5	345
1% Lankrolan SHR3 (exhausted)	6.5 6.0 6.5	6.3	9.0 9.0 9.5	9.2	10.0 12.0 11.0	11.0	3.6 3.6 3.6	3.6	350
4% DC109 (padded)	7.5 7.5 8.5	7.8	9.0 9.0 8.5	8.8	12.0 11.5 13.0	12.1	5.0 4.1 4.2	4.4	290
2.5% BAP/DLH (padded)	16.0 17.0 16.0	16.3	-	-	-	-	4.5 5.0 4.0	4.5	260
2.5% BAP/DLH (exhausted)	9.0 8.5 8.5	8.6	10.0 11.0 11.5	10.8	-	-	4.0 4.9 4.2	4.4	240
2% Hercosett 125 (padded)	9.0 9.0 9.0	9.0	16.0 17.0 16.0	16.3	-	-	5.5 5.5 5.5	5.5	370

* For untreated fabric specificatons see section 2.4.2.

TABLE 140 Wet Abrasion Resistance of fabric A (worsted)

Type of Treatment	Fabric A (worsted)			
	Condition 1		Condition 2	
	Rubs x 10^3	Mean	Rubs x 10^3	Mean
Untreated*	13.0 12.5 10.2	11.9	16.0 16.0 16.0	16.0
0.5% Chlorination	12.0 12.0 12.0	12.0	13.5 13.0 13.5	13.3

* For untreated fabric specifications see section 2.4.2.

and the reasons for this phenomenon have been discussed in section 2.5.3.1.. 0.5% Chlorination improves the MAR under normal testing conditions but the improvement is greater for fabric C (woollen) than for fabric A (worsted).

The abrasion resistance of the wetted fabric samples varies markedly according to the nature of the abrasion conditions. In general the results under condition 3 (wet sample/wet abradant at 100% pick-up) are greater than those for condition 2 (wet sample/conditioned abradant 65% r.h.). Both of these sets of results are greater than those obtained under condition 4 (wet sample/wet abradant > 200% pick-up) which in turn is greater than the results measured on (conditioned sample/conditioned abradant). Thus in this series of experiments, the conditions of testing where large amounts of liquid water are present lead to an improvement in abrasion resistance, whereas Nhan and Denby have previously noted a slight reduction in abrasion resistance on testing fabric under wet conditions.

Clearly, however, the amount of water initially applied and its distribution during wet abrasion testing is of crucial importance, for as Nhan and Denby have succinctly pointed out, testing under conditions of high r.h. ($>$ 65%) leads to a dramatic increase in the abrasion resistance. In the current series of experiments it is considered that the results may be interpreted in terms of the gradual changes in the moisture distribution in the sample and the abradant with time throughout the test conditions.

In a controlled experiment, untreated fabric samples (preconditioned at 65% r.h. 21°C) were padded with distilled water to 100% pick-up (based on conditioned fabric weight) and then abraded against an abradant fabric preconditioned at 65% r.h. and 21°C. After 100 rubs on the Martindale Abrasion Tester, the samples and foam backing were removed and weighed. The original 100% pick-up in the sample was reduced to 65.9%, while the foam backing retained 8% of the water lost from the sample. Clearly neglecting evaporation losses, the abradant fabric would absorb the remaining 26.1% of the water lost in the system, and this would be distributed primarily over the area of contact of the abraded area.

Thus under condition (2) capillary water from the wet sample will be transferred to the abradant fabric so that the moisture level in the sample is reduced while that of the abradant is increased. As time passes during the abrasion test, the rubbing action and exposure to the surrounding conditioned atmosphere (65% r.h.) leads to a reduction in the moisture regain of both the sample and the abradant. In this manner the moisture regain falls into the highly effective region for increasing fabric abrasion resistance, i.e. $>$ 65% and $<$ 100% r.h. It is for these reasons that the abrasion resistance measured under condition (2) is increased. The greater improvement obtained under condition (3) reflects the effectively lower rate of drying in the system compared with test condition (2) because in condition (3) the abradant is also initially wetted out. The fabric sample and abradant will thus progress more slowly through the high r.h. region thereby yielding improved abrasion resistance. The abrasive action of the wet abradant cloth should be lower than that of a similar conditioned fabric (65% r.h.) so that an improvement in MAR would be expected on this basis apart from any other contributory factors.

In subsidiary experiments in which the amount of liquor left in the fabric was measured, little change in the result of abrasion testing was observed, provided the water left in the fabric at the end-point was in the range 120-250% on the dry fabric weight. Under these conditions both the sample and the abradant must contain liquid as capillary water for the duration of the abrasion test so that the abrasion results are sensibly independent of the initial pick-up if this is at a high level.

The differences between the untreated and the shrink-resisted fabric C results are relatively small under test condition (4), but again all samples are improved if the final regain in the fabric samples lies in the range > 65 and < 100% r.h. Polymer shrink-resist treatments affect the mode of fabric abrasion, although under wet saturated conditions there is little improvement in abrasion resistance. It was particularly noted that polymer treatments applied by padding tended to simulate the wearing conditions observed when untreated fabric was abraded in the conditioned state. Thus samples abraded under conditions (2) and (3) behaved similarly to condition (1). However, the polymer treatments applied by exhaustion were considerably disrupted at the end-point and in general lower MAR under condition (4) was obtained compared with the polymer treatments applied by padding.

It must be concluded, therefore, that the results of this study are in accord with those of Nhan and Denby for the high relative humidity range, but care must clearly be exercised when liquid water is present in the sample of the abradant. The amount and distribution of the water are important factors while the rate of drying of the sample and abradant during the test could lead to variability in the results if this is not carefully controlled. In contrast to Nhan and Denby's results, polymer shrink-resist treatments measured under condition (1) led to an increase in MAR compared with an untreated fabric tested under identical conditions.

In a similar manner the results for polymer treated samples under conditions (2) and (3) are still greater than those of the untreated fabric sample measured under condition (1). With the exception of 1% Lankrolan SHR 3, all results of condition (4) samples are also marginally greater than for untreated fabric measured under condition (1). The results obtained under the various wet treatments studied will clearly depend upon the mode of abrasion in each case. It was particularly noticeable under condition (4) that the appearance of the samples at the end-point differed markedly from those measured under conditions (1-3). In condition (4) the whole area of the sample under test is abraded more or less uniformly, while the yarns become thinner and significant lengths of fibres are lost during the test.

8.4. Conclusions

The abrasion resistance of untreated and shrink-resist treated wool fabrics has been shown to be markedly dependent upon the moisture regain of the samples under test. The results of Nhan and Denby (24) are confirmed in that the gradual drying out of the sample during the abrasion test in conditions (2) and (3) may lead to the sample being abraded in the 65-100% r.h. region, which leads to significantly higher abrasion resistance.

The presence of large amounts of liquid water in the sample and the abradant (> 120% pick-up for the fabrics studied on this work) during abrasion testing is believed to significantly alter the mode of fabric abrasion, and the results for shrink-resist treated fabrics are consequently much closer to the untreated fabric value under the same conditions.

Under condition (1) (both sample and abradant at 65% r.h.) both the chlorination and the polymer shrink-resist treatments give rise to an improvement in MAR. The reason for this is unlikely to depend upon the changes in the moisture regain of the specimen, but is believed to be associated with the operative mode of fabric abrasion under these conditions. In addition, polymer shrink-resist treatments applied by padding yield higher abrasion resistance values than those applied via exhaustion.

Summary and Conclusions

A literature survey is presented which summarises current views on the general mechanisms and factors involved in the abrasion of textile fabrics and the effects of selective finishing treatments on the abrasion resistance of wool fabrics. In addition details of the abrasion testing conditions used in this work for determining the fabric abrasion resistance have been described.

The experimental work is concerned with the changes in the Martindale abrasion resistance (MAR) of three woven wool fabrics, namely fabric A (plain weave light weight worsted), fabric B (twill worsted) and fabric C (woollen flannel) produced by the following treatments.

(1) The application of polymer shrink-resist finishes, by padding and by exhaustion treatments.

(2) Treatment with organic solvents.

(3) Treatment with ethylene glycol at 150°C.

(4) Deamination and esterification.

(5) High temperature steaming (130°C).

(6) Dyeing.

(7) The presence of water during abrasion testing.

The results obtained in this thesis demonstrate conclusively that the above-described treatments alter the abrasion behaviour of the woven wool fabrics studied.

In general all the polymer shrink-resist treatments studied improved the MAR of woven wool fabrics. The level of improvement in MAR of the woven wool fabrics depends on:

(i) the nature of the applied polymer shrink-resist treatment;

(ii) the polymer add-on;

(iii) the nature of the fabric structure, and

(iv) the method of polymer application. i.e. by padding or by exhaustion.

Padding treatments lead to a significantly higher level of MAR, especially on short fibre fabrics (woollen-spun), compared with applications by exhaustion for the same polymer and same polymer add-on level. These results are consistent with the view that in padding processes the formation of a greater number of inter-fibre polymer bridges is promoted as well as fibre encapsulation. The latter is the predominant mode of action in exhaustion processes.

This has been confirmed in S.E.M. studies of polymer-treated fabrics. Thus the preferential formation of inter-fibre polymer bridges in padded polymer-treated fabrics leads to the prevention of short fibres from migrating and felting in woven wool fabrics thereby reducing fabric pilling and loss of fibres during abrasion testing. It is for this reason that padding treatments give rise to a greater improvement in MAR and reduction in fabric area felting shrinkage (F.A.F.S.) compared with those obtained by exhaustion techniques in which fibre encapsulation would appear to be the main operative mechanism by which shrink-resistance is obtained. The ability of the polymer to form tough but elastic films leads to a greater improvement in MAR for wool fabrics. In this way synergistic improvement in both MAR and shrink resistance are obtained on fabric C using Synthappret BAP/Impranil DLH.

The presence of inter-fibre polymer bridges creates an improved level of crease recovery angle (CRA) in padded fabrics, which is greater than that observed in polymer exhaustion treatments at comparable add-on values. The CRA results have been interpreted in terms of an improvement in the elastic restoring force aiding fabric recovery from bending as previously proposed for wrinkle recovery.

The relation of the improvements in MAR to results on the Stoll flexing and abrasion tester and to changes in other physical properties of the fabric have been determined.

The effects of solvent treatments on the abrasion resistance of the same range of woven wool fabrics were studied using the Martindale technique. All the solvent treatments studied improved the MAR. The greatest improvements in MAR were noted for fabric A (light weight plain weave worsted which had little or no propensity for pilling) compared with the lower levels of improvement reported for fabric B (worsted twill) and fabric C (woollen flannel) respectively.

It would appear that low molar volume, highly polar solvents are more effective than high molar volume, relatively non-polar solvents for improving fabric MAR. The effects are time-dependent and are considered to arise from conformational changes within the wool fibres as a result of the adsorption of polar solvent molecules. These results were not accompanied by similar improvements in the Stoll test.

Reductions in F.A.F.S. have also been observed as a result of the treatment of wool fabrics with organic solvents. The more polar the solvent the greater the reduction in the rate of felting. In the light of other published work these reductions are considered to arise from a reduction in the directional frictional effect (D.F.E.) of solvent-treated wool fibres.

The effects of organic solvents on wool fabrics lead to a decrease in the CRA. The greater the polarity of the liquid, as measured by the value of the dielectric constant, then the greater is the accompanying reduction in CRA. Other relevant physical properties have also been discussed and suggestions for further work have been given.

Treatment of wool fabrics with ethylene glycol at 150°C for times up to 30 s improved the MAR. High levels of fabric shrinkage and improvements in elastic properties have been noted. Treatment times longer than 30 s reduce the MAR and this is considered to arise as a result of the fibre conformational changes that take place at this high temperature. X-ray diffraction photographs demonstrated that disruption of the α-helical structure of wool takes place after treatment for 60 s in ethylene glycol at 150°C. Buckling of the scale structure parallel to the main fibre axis (a rather unusual phenomenon) was also observed in S.E.M. studies.

Treatment at this relatively high temperature (150°C) leads to yellowness and finally embrittlement of the fabric, possibly due to the setting processes taking place. Changes in other physical properties have been observed and related to the MAR results.

Deamination and esterification treatments of wool fabrics appear to improve the MAR. The level of improvement in MAR is greater for fabric A compared with fabric C. Esterification treatment yields better MAR results than deamination treatment. The rate of F.A.F.S. is reduced after esterification. The changes in MAR and F.A.F.S. of the esterified wool samples are considered to arise as a result of the solvent (methanol) present during the treatment.

The MAR of wool fabrics is slightly improved when a short time of steaming (5 minutes) at 130°C was employed. Treatment times longer than 5 minutes decrease the MAR of the wool fabrics. This is presumably due to fibre damage taking place at this high temperature.

This effect is time-dependent, i.e. as the treatment time increases the reduction in MAR increases. This is in accord with the results from the ethylene glycol treatment at 150°C. Other physical properties have also been discussed and optimum steaming conditions have been suggested.

From the results of the dyeing of wool fabrics it was concluded that the nature of the dye is intimately interrelated with the conditions of application, e.g. pH, and this latter appeared to be the most important factor affecting the MAR of wool fabrics.

Under the conditions studied the optimum MAR was obtained at 2% dye o.w.f. for both dyes employed. Clearly this cannot be regarded as being universally applicable as the optimum dyeing conditions for all dyes for wool fabrics, but it might well be taken into consideration in future work. Changes in other physical properties were also discussed and suggestions for further work have been given.

The MAR of untreated and shrink-resisted wool fabrics has been shown to be markedly dependent upon the moisture regain of the samples under test. This is in agreement with previous work published which suggested that samples being abraded in the 65-100% r.h. region lead to significantly higher MAR. The reasons for the marked improvements in MAR of the polymer-treated fabrics studied are not dependent upon the changes in the moisture regain of the fabric, but upon the nature of the polymer, polymer add-on level and method of application. Under wet abrasion conditions the mode of fabric abrasion is altered and this has been discussed.

It must be concluded therefore, that the nature of the fabric structure is of considerable importance from the point of view of the method that can be used to improve the MAR. Thus processes that minimise fibre migration, felting and reduce fabric pilling and loss of fibres during abrasion testing, increase the MAR of woollen-spun (short fibre) fabrics. It should thus be possible to design polymer shrink-resist treatments that lead to a synergistic improvement in both MAR and shrink-resistance, thereby improving the fabric easy-care performance and/or reducing process costs. However, with worsted (long fibre) fabrics the mechanism of fabric abrasion is different and a more fruitful method may be the application of methods that improve the fibre elasticity.

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