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FUNDAMENTAL ASPECTS OF THE MERCERISING PROCESS [1]

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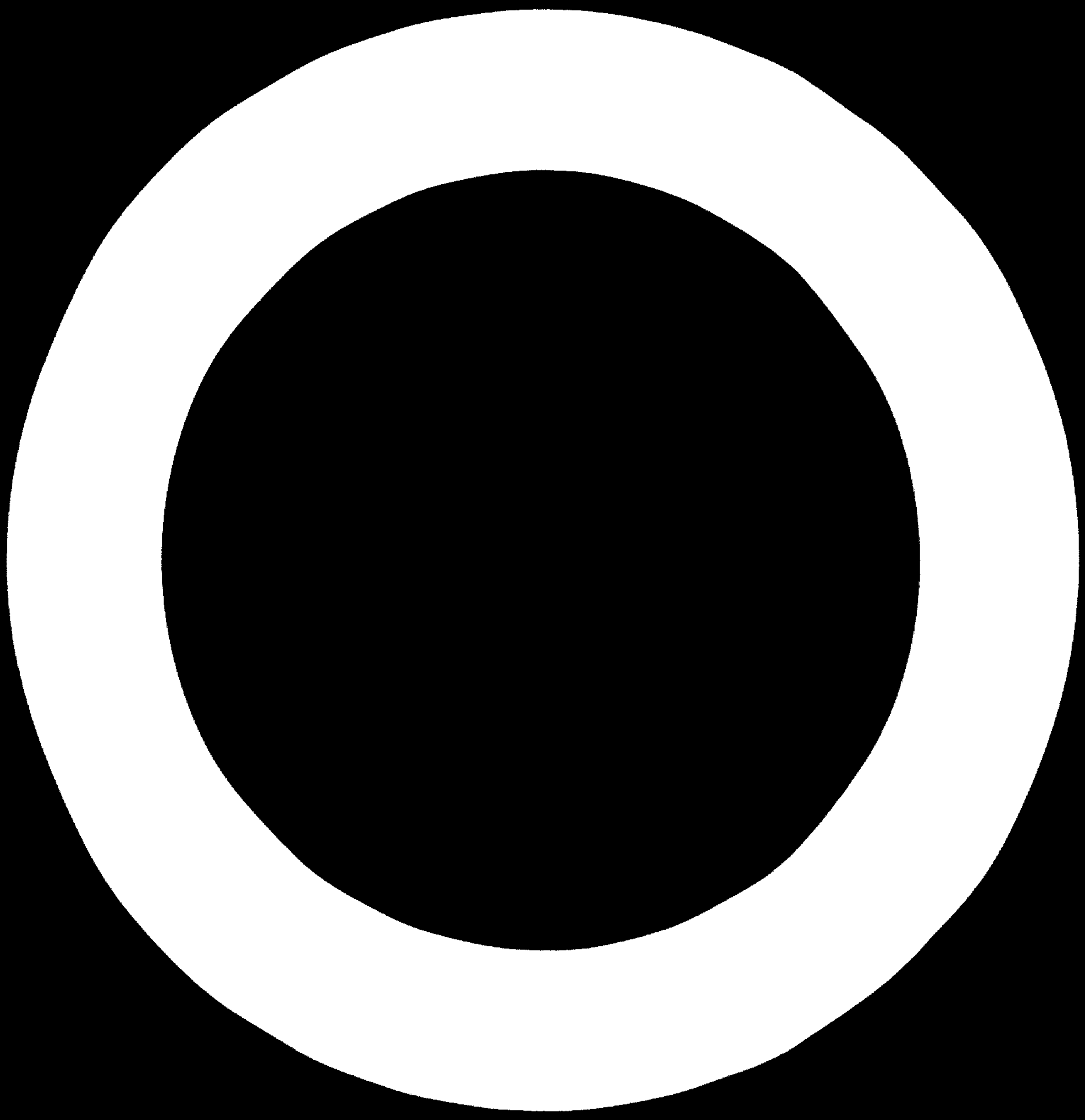


FUNDAMENTAL ASPECTS OF THE MERCERISING PROCESS.

INTRODUCTION

The commercial objectives of the mercerising process for cotton fabrics can be quite simply stated as follows (SLIDE 1).

Dyestuff cost savings
Uniformity of dyeing
Lustre
Dimensional stability
Flat setting
Retention of tensile strength
after easy-care finishing

The possibilities and limitations in achieving these objectives, in terms of the currently available machinery, will be dealt with by the following speaker. In the present paper, we will have a look at the fundamental background of the mercerising phenomenon to try to get some insight into what is happening to the cotton fibre to bring about such changes, and to try to estimate what is perhaps the maximum theoretical potential benefit of the mercerising process.

I. MECHANISMS

Let us start with a brief description of the cotton fibre and the way it is changed by mercerising-strength caustic soda solutions.

A cotton fibre is constructed from so-called elementary fibrils which are, in effect, long, thin crystals of cellulose which are apparently very strong as it is very difficult to disintegrate them mechanically. In the cross-section of a mature fibre there will be several millions of such crystalline fibrils which aggregate together into bundles of a few hundreds. These fibrillar bundles are packed together in concentric layers to form the fibre. The fibrillar bundles do not lie straight along the fibre axis, but spiral around at an angle which varies from about 55° near the fibre surface to about 20° at the inside. Periodically along the length, the direction of the spiral changes at a so-called fibrillar reversal zone (SLIDE 2).

From this brief description it is easy to see that most of the physical and mechanical properties of cotton fibres are strongly dependent upon the uniformity and density of packing of the fibrillar bundles.

In the original fibre, as it grows in the cotton field, the uniformity of fibrillar packing seems to be rather good, but the fibre is completely swollen with water and possibly the fibrillar bundles have not yet formed. When the boll bursts and the fibres are exposed to the atmosphere, the water dries out and the fibre collapses into the familiar convoluted flattened tube (SLIDE [illegible]).

This enforced collapse causes disruptions in the orderly packing of the fibrils, and the presence of the fibrillar reversal zones means that collapse does not proceed in a uniform and consistent way. Different varieties of cotton, and fibres of different maturities may undergo a more-or-less severe collapse, according to their basic geometrical differences.

These imposed non-uniformities in fibrillar packing lead to a reduced tensile strength and the complicated shape leads to a drastic change in the way the fibre reflects light. The change is towards a much more diffused reflection, which reduces the lustre and the apparent intensity of colour after dyeing with a given strength of dye. Moreover, the great variability in shape from fibre to fibre, especially as between immature and mature fibres, gives an apparently large <u>variability</u> in the perceived colour after dyeing with a given strength of dyestuff. As a matter of fact, an immature cotton fibre will absorb more dyestuff per unit of fibre weight, than a mature one from a given dyebath, because of the greater proportional influence of the more accessible primary wall and outer layers. Nevertheless, after dyeing, immature fibres have a paler perceived shade because of the unfavourable fibre shape.

Mercerising solutions are able to swell the fibre up to about the same diameter that it had when growing in the boll. In addition, swelling also proceeds inwardly, to fill up the lumen, since under a free swelling situation, the fibre will also contract in length. This large degree of swelling is possible because strong caustic soda solutions are able to penetrate not only inbetween the fibrillar bundles, but also between and even inside the elementary fibrils.

The degree to which the commercial objectives of mercerising can be achieved depends upon the extent to which this swelling is allowed to proceed and upon the tensions to which the fibre is subjected during swelling, rinsing and drying.

The diagram, (SLIDES 4 & 5) gives an idea of the kind of changes which a cotton fibre can undergo during the transition from the never dried state, through collapse and then mercerising. These diagrams are, of course, approximations, because they refer to a mature fibre with an undamaged primary wall. Less mature fibres assume a more flattened ribbon shape on first collapsing, and they do not develop the almost circular cross-section after mercerising, although wall-thickening does occur. If the primary wall is damaged, then the fibre may be able to swell to a higher degree. Swelling in the diameter is accompanied by shrinkage in length (SLIDE 6).

Besides the maturity and the integrity of the primary wall, probably the most important influences upon the degree of swelling are the tension on the fibres and the temperature of the swelling liquor (SLIDE 7).

In practice, tensions in the fibres are caused by the restraints imposed by yarn and fabric structure, and the degree of swelling is also influenced by the ability of the liquor to penetrate into the yarn or fabric. This penetration will be obstructed if the fibres on the surface of the yarns or fabric are able to swell very rapidly, so as to quickly seal off the interior.

A detailed study was made in Holland some time ago of the yarn mercerising process, in which a range of yarns was treated with a range of concentrations at various temperatures for different times. The degree of mercerising was assessed by an iodine staining technique. It was found that the most important factors were the viscosity (n) of the liquor, the degree of swelling (z) of the fibres, the time (t) and the tension (s).

From the results, the following empirical relationship was derived (SLIDE 8).

$$p \sim 20 \, \frac{nz^2}{t-1} \, (\log S - 1.15)$$

Where p is the percentage of fibres which remained unmercerised.

According to these results, the viscosity of the liquor and especially the degree of swelling of the fibres must be kept to a minimum, in order to ensure adequate penetration into the interior of the yarn. Also, very short times and very high tensions must be avoided.

The viscosity of the liquor and the swelling of the fibres are minimised by raising the temperature; tensions are minimised by allowing unrestricted shrinkage of the yarn and by avoiding very tight constructions. Presumably, the same considerations apply to fabric treatments.

Slide 9 shows the changes in total swelling, i.e. the change in volume as indicated by the water retention values after rinsing out the swelling liquor. The higher the temperature, the lower is the degree of swelling for a given concentration of caustic soda, when the concentration is above about 8% w/w.

The influence of temperature on penetration is illustrated by slides 10 & 11, which are cross-sections of yarns taken from fabrics which had previously been mercerised at different temperatures and then dyed. The low temperature treatment shows a clearly non-uniform treatment, whereas the high temperature process has given a much more uniform dyeing.

II. CHANGES IN FIBRE PROPERTIES

The most interesting properties of mercerised fabrics are the improved colour-yield on dyeing, which allows large savings in dyestuffs, and the better uniformity of dyeing, which allows an improved product to be made with the same dye recipe.

These improvements have sometimes been attributed to the increased absorptivity and rate of dyeing of mercerised fibres. Certainly, it is true that rates of dyeing can be increased by up to ten fold, as illustrated in tables I & II, and the equilibrium uptake can also be improved significantly. These two tables also illustrate the effect of fibre fineness upon dyeing rate - the finer the fibre, the faster the rate of dyeing. This is to be expected, of course, and is explained on the grounds of the greater specific surface area of finer fibres. The tables also indicate that the type of dyestuff has a large influence. Generally speaking, dyestuffs with a small molecular size are less influenced by fibre fineness/maturity and by mercerising than dyestuffs with a large molecular size.

However, the important point about mercerised fabrics is that they have an apparently deeper shade than corresponding unmercerised materials, even when the percentage add-on of dyestuff is the same. This phenomenon has to do with the amount and the quality of the light which is reflected from the fibre surfaces, and this has a purely geometrical cause (SLIDE 12).

There are at least two major geometrical changes, namely the elimination, or substantial decrease, of the fibre convolutions to yield a more smooth and almost circular cross-section, and the thickening of the fibre wall. The effect of the removal of convolutions and the approach towards a circular cross-section can be judged from slide 13, which actually refers to data obtained mostly on unmercerised fibres, but will serve our purpose well since it shows the influence of the ratio of the major and minor axes of the fibre cross-section upon the intensity of the reflected light. The effect of mercerising is to reduce this ratio and thereby to considerably increase the intensity of the light reflected, i.e. the lustre. But as well as the amount of light directly reflected, the quality of the light is changed. Because of the thicker fibre wall after mercerising, the path length of the light through the fibres is increased and therefore the unmercerised fibre appears paler, just as a solution of dye of a certain concentration appears lighter in a fine capillary glass tube compared to the same solution in a larger tube.

III. FIBRE STRENGTH

Mercerisation is capable of causing quite large increases in the tensile strength of cotton fibres. To understand this, we have to realise that the strength of raw fibres is strongly influenced by the degree of structural disorder which has been caused during the collapse which the fibre underwent during its first drying out in the cotton field.

The extent to which a mercerisation process can eliminate these structural weak places and potential weak places is a measure of the increases in tensile strength which can be realised. This depends upon the cotton variety and the conditions of the mercerising treatment.

Slide 14 shows data from the literature, and IIC has also carried out extensive experiments on the mercerising of different cotton varieties in fibre bundle form. The general conclusion seems to be that cottons which are initially strong obtain only a rather moderate increase (up to say 50%), whereas in weaker cottons, the strength can be substantially increased - sometimes by more than 100%.

More important than the variety, however, are the conditions of treatment, in particular, the extent to which the fibres are allowed to shrink in the mercerising liquor, and the extent to which they are restretched before or during rinsing.

If the fibres are held under tension and not allowed to shrink, the maximum tensile strength cannot be developed and there is usually a drastic loss in the extensibility.

When the fibres are allowed to shrink, there is an optimum degree of re-stretching for the development of maximum tensile strength, as illustrated in Slide 15. The position of this optimum varies a bit according to variety, but generally is in the region of about 95% of the original length.

The elongation at break is also affected by the degree of re-stretching (Slide 16), but in general, we have found that the extensibility of the original, unmercerised fibres, is regained when the re-stretching level is again to about 95% of the original fibre length.

It is interesting to note that the 95% re-stretching level also seems to give the maximum changes in fibre density and fibrillar orientation, and further more, it marks approximately the end of the re-stretching which can be achieved by exerting a very small force upon the fibre bundle. In other words, increasing the degree of re-stretching beyond 95% requires increasingly higher forces, gives little or no further benefit in tensile strength and orientation, but reduces the extensibility to well below that of the starting material.

IV. RETENTION OF STRENGTH AFTER CROSSLINKING

Many of the cotton fabrics which are mercerised are later given some form of easy-care treatment by crosslinking and it was a basic objective of our detailed research into the mercerising of cotton fibres to find out if and by how much the tensile strength of cotton could be retained after crosslinking (SLIDE 17).

Now, in many conventional cotton fabrics this loss in tensile strength is not very important, since it is not necessarily a good indication of the durability of the fabric in a given end-use. However, for some end-uses and for lightweight fabrics it would be very useful to be able to eliminate this tensile strength loss. In fact, we found that cotton fibres which had been given the optimal mercerising treatment, would lose little or no strength even after a rather high degree of crosslinking.

To see whether this behaviour would carry through into fabric performance, a special roving mercerising equipment was constructed which was capable of producing a few tens of kilograms of more-or-less optimally mercerised fibres within a reasonable time. These rovings, together with control material which had been processed only through water, were spun into yarns and woven into fabrics.

The fabrics were given a standard easy-care treatment at two different levels to give either good or excellent easy-care performance.

The results (SLIDE 18) show that for an easy-care level which is more than adequate for most purposes, a 95% strength retention can be expected. Even for the super "durable press" type of high performance finish, a retention of 81% was possible.

Present piece mercerising processes are not capable of producing this level of improvement, partly because of the interference of yarn and fabric structure in preventing effective penetration and full swelling, and partly because not enough energy and effort has been put into the development of more efficient and effective piece mercerising processes.

V. LIQUID AMMONIA

In recent years, a fairly large amount of work has been carried out on an alternative swelling process for cotton yarns and fabrics which involves the use of liquified ammonia. Two entirely different systems of ammonia processing have been developed; one for the treatment of yarns, the other for fabrics.

A detailed examination of these two new processes is outside the scope of this paper, but it is worth noting that, although there are some superficial similarities between mercerising and ammonia treatment, we are, in fact, dealing with entirely different systems and they should not be confused under the common heading of mercerising processes. A few slides will serve to illustrate this point.

Slide 19 shows the results of a yarn untwisting test in liquid ammonia, compared to caustic soda. Note that ammonia has a faster rate of swelling, but a lower oquilibrium value. Fabrics were held to constant length during swelling and the tension developed was measured (SLIDE 20). Note that ammonia causes much higher forces to be generated than caustic soda. Not only is the shrinking force higher in ammonia, but it is not significantly reduced by applying a pretension to the fabric before swelling begins. (SLIDE 21).

From these two sets of data, and many others, we have concluded that the cotton fibre when swollen with ammonia behaves in an entirely different manner from the caustic swollen material.

The major benefits from caustic soda mercerising are brought about by the ability to re-stretch and re-shape the fibre whilst it is fully swollen. Such manipulation of an ammonia swollen fibre seems to be hardly possible.

The effect seems to be strongly influenced by the concentration of ammonia in the fibre. At levels of below about 60% the fabric once more is capable of easy deformation (SLIDE 22).

Results of experiments on fibre bundles have also suggested that the basic fibre strength of cotton is only slightly increased by swelling in ammonia and re-stretching, and that furthermore,the retention of strength after crosslinking is less than that of mercerised fibres.

Crosslinking experiments on ammonia treated fabrics have suggested that the most important factor is the method of easy-care finishing. When the classical methods are used, it is difficult to find an advantage for ammonia treated fabrics. However, when the newer finishing methods are used - methods which attempt to obtain a more uniform distribution of crosslinking - then the ammonia treated fabric seems to respond significantly better than either mercerised or unmercerised fabrics, at least so far as tensile strength retention is concerned.

TABLE I

RATE OF DYEING OF COTTON FIBRES

	$t_{\frac{1}{2}}$ min*
SEA ISLAND	0.7
SAKEL	1.1
SAKEL, MERCERISED	0.25
EGYPTIAN UPPERS	1.5
AMERICAN	1.4
AMERICAN,MERCERISED	0.35
INDIAN	3.7

* time to reach half the equilibrium uptake.

RECIPE: 0.12% Sky Blue FF, 5% NaCl 40 volumes at 90°C

TABLE II

RELATIVE RATES OF DYEING AND EQUILIBRIUM UPTAKES OF DELTAPINE COTTON AS A FUNCTION OF MATURITY

MICRONAIRE	RELATIVE RATE			RELATIVE EQUILIBRIUM UPTAKE		
	UNMERCERISED	MERCERISED	M/U	UNMERCERISED	MERCERISED	M/U
RECIPE A						
3.69*	1.0	7.78	7.78	1.0	1.26	1.26
3.34	0.96	8.51	8.87	1.03	1.24	1.20
2.56	2.60	9.96	3.83	1.01	1.25	1.24
RECIPE B						
3.69*	1.0	2.44	2.44	1.0	1.50	1.50
3.34	1.22	2.56	2.10	1.02	1.56	1.53
2.56	1.67	3.22	1.93	1.10	1.62	1.47

* Normal mature fibres used as reference point

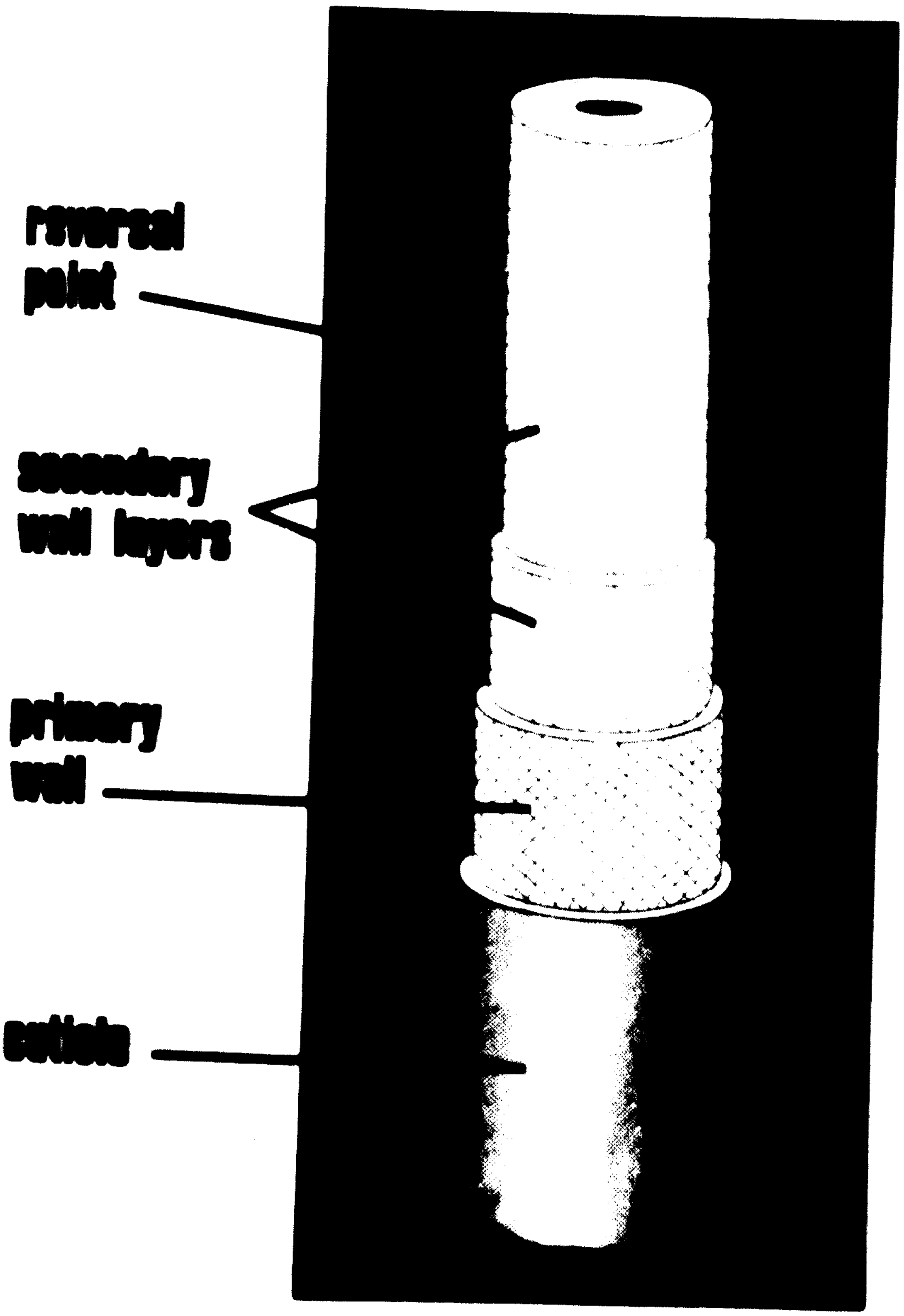
SLIDE 1

OBJECTIVES OF MERCERISING

- ★ DYESTUFF COST SAVING
- ★ UNIFORMITY OF DYEING
- ★ LUSTRE
- ★ DIMENSIONAL STABILITY
- ★ FLAT SETTING
- ★ RETENTION OF TENSILE STRENGTH AFTER EASY-CARE FINISHING

SLIDE 2

COTTON FIBRE STRUCTURE

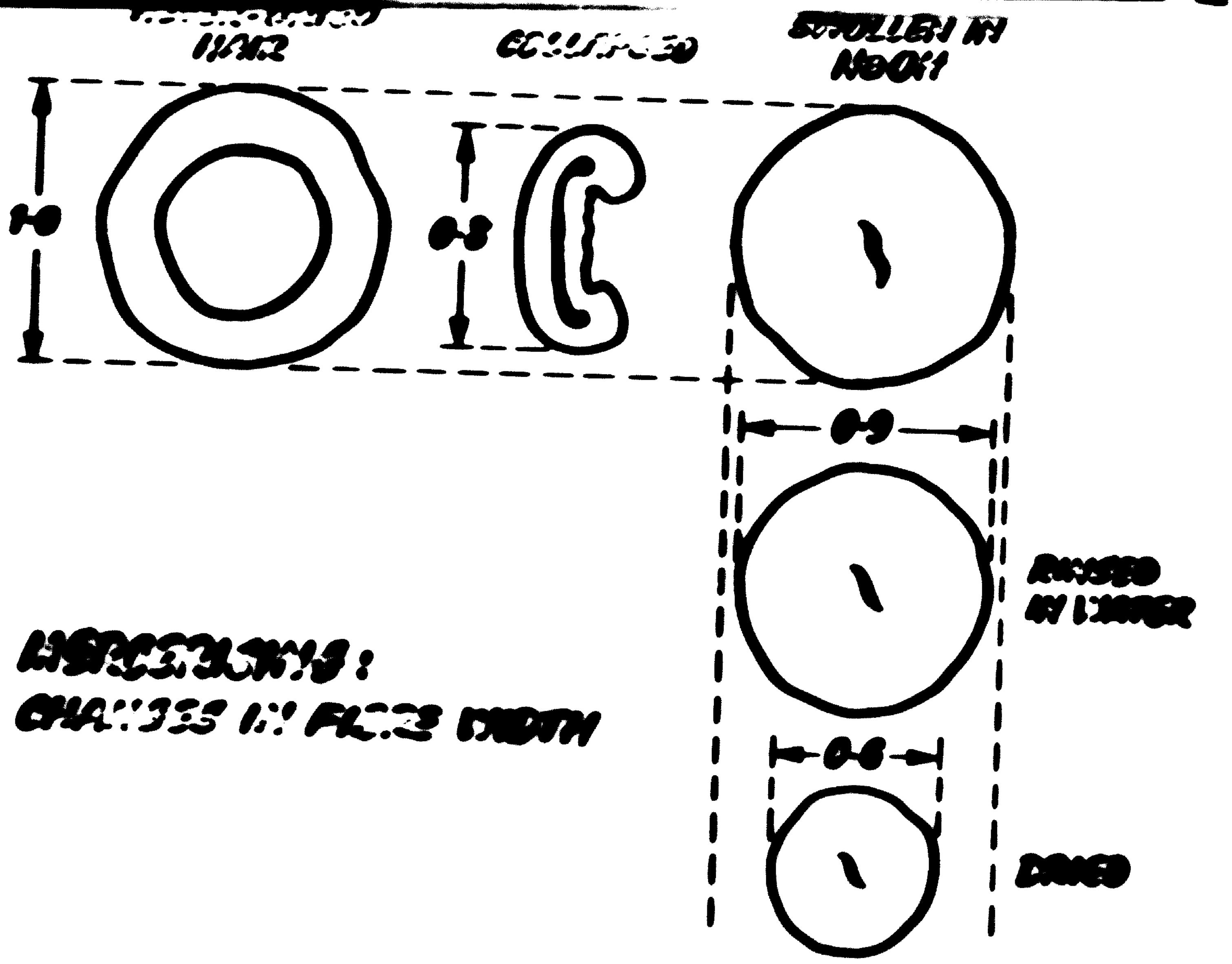


COTTON FIBRE STRUCTURE

secondary wall only

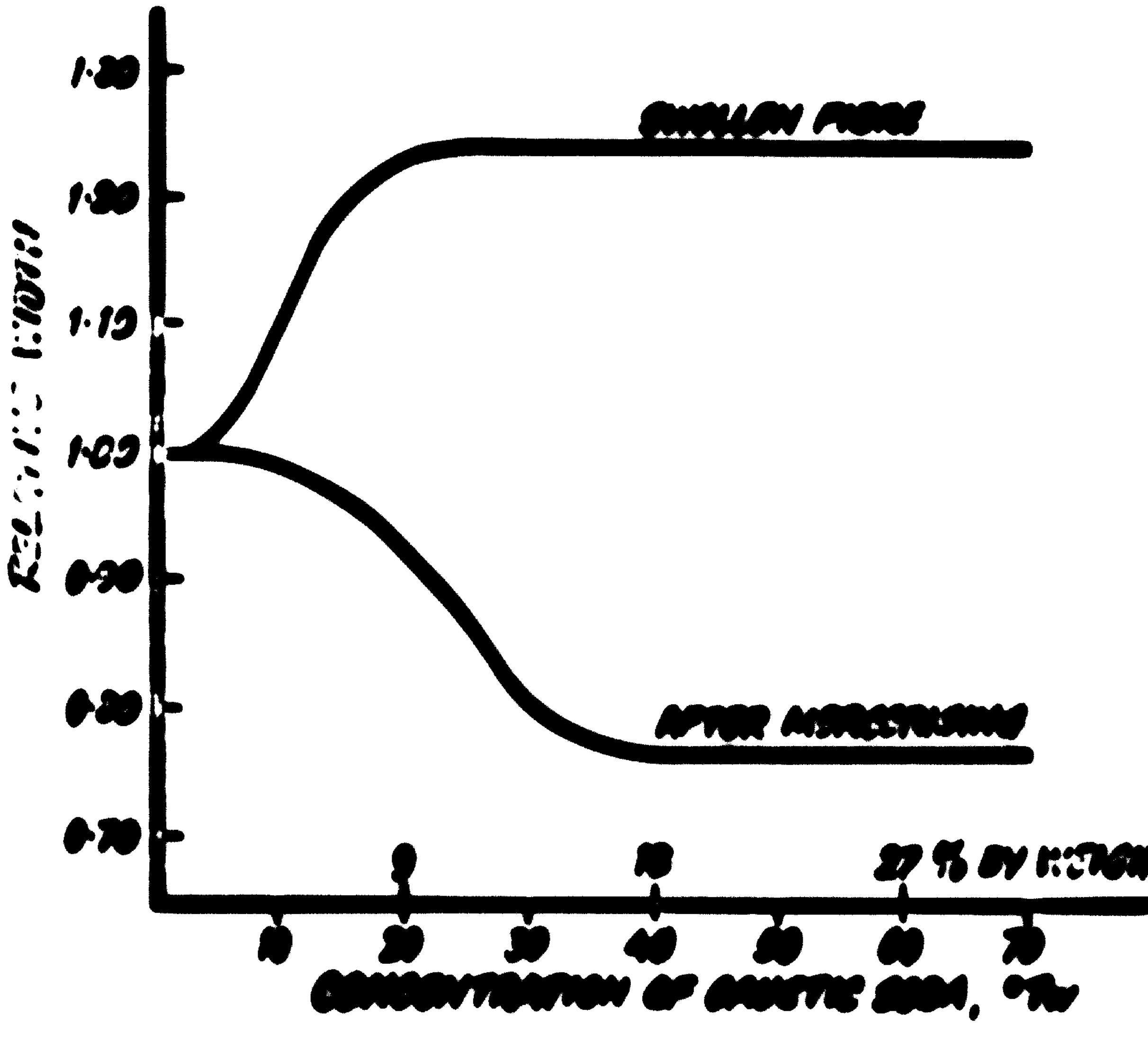
SLIDE 4

MERCERIZING:
CHANGES IN FIBRE WIDTH



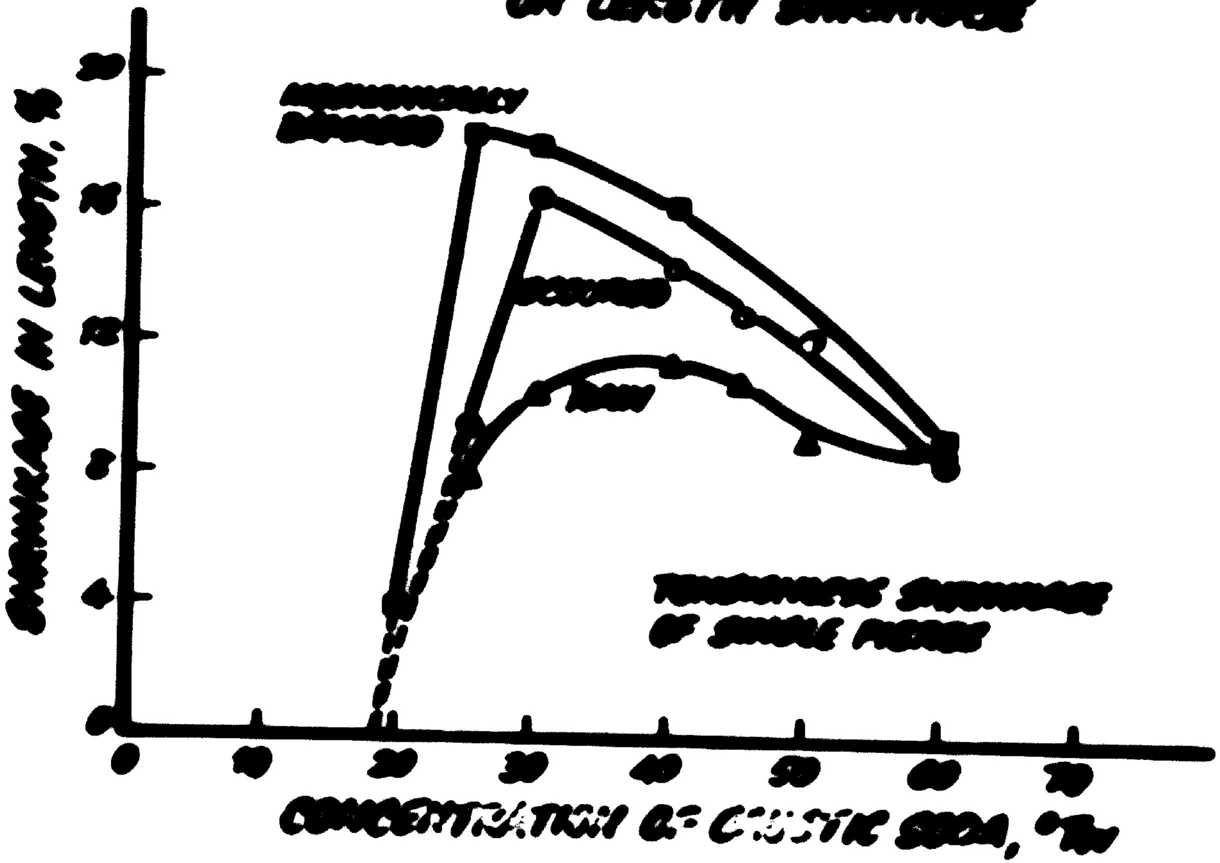
SLIDE 5

CHANGE OF FIBRE WIDTH (MAJOR AXIS) IN CAUSTIC S



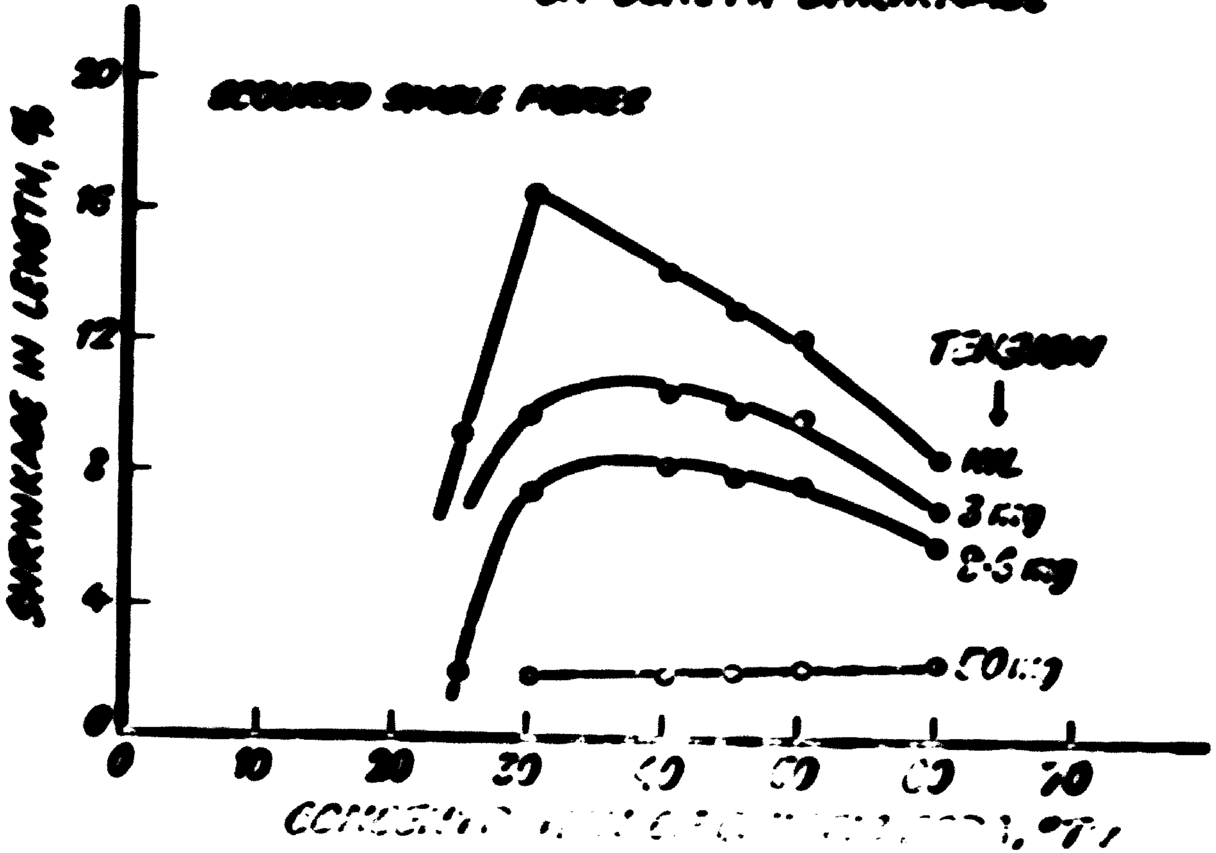
SLIDE 6

MERCERISING: INFLUENCE OF PRIMARY WALL ON LENGTH SHRINKAGE

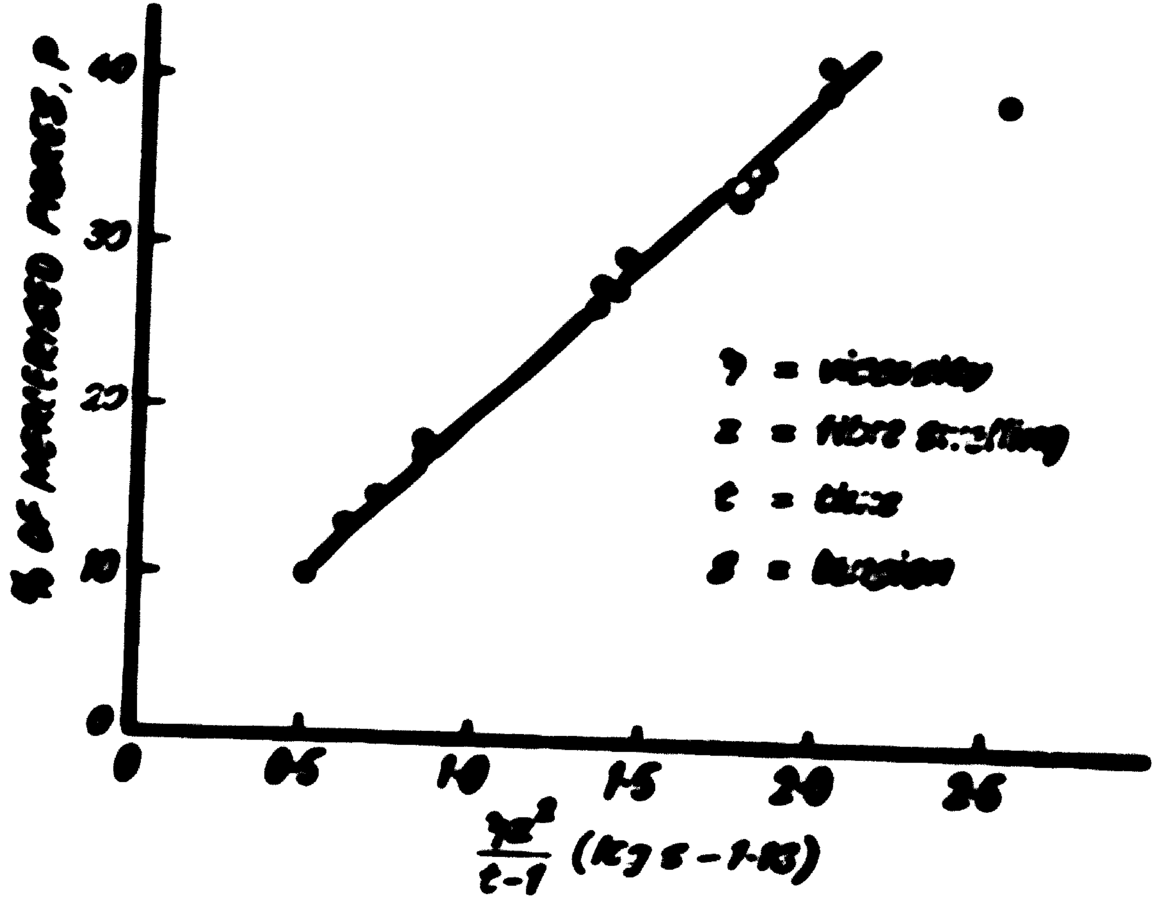


SLIDE 7

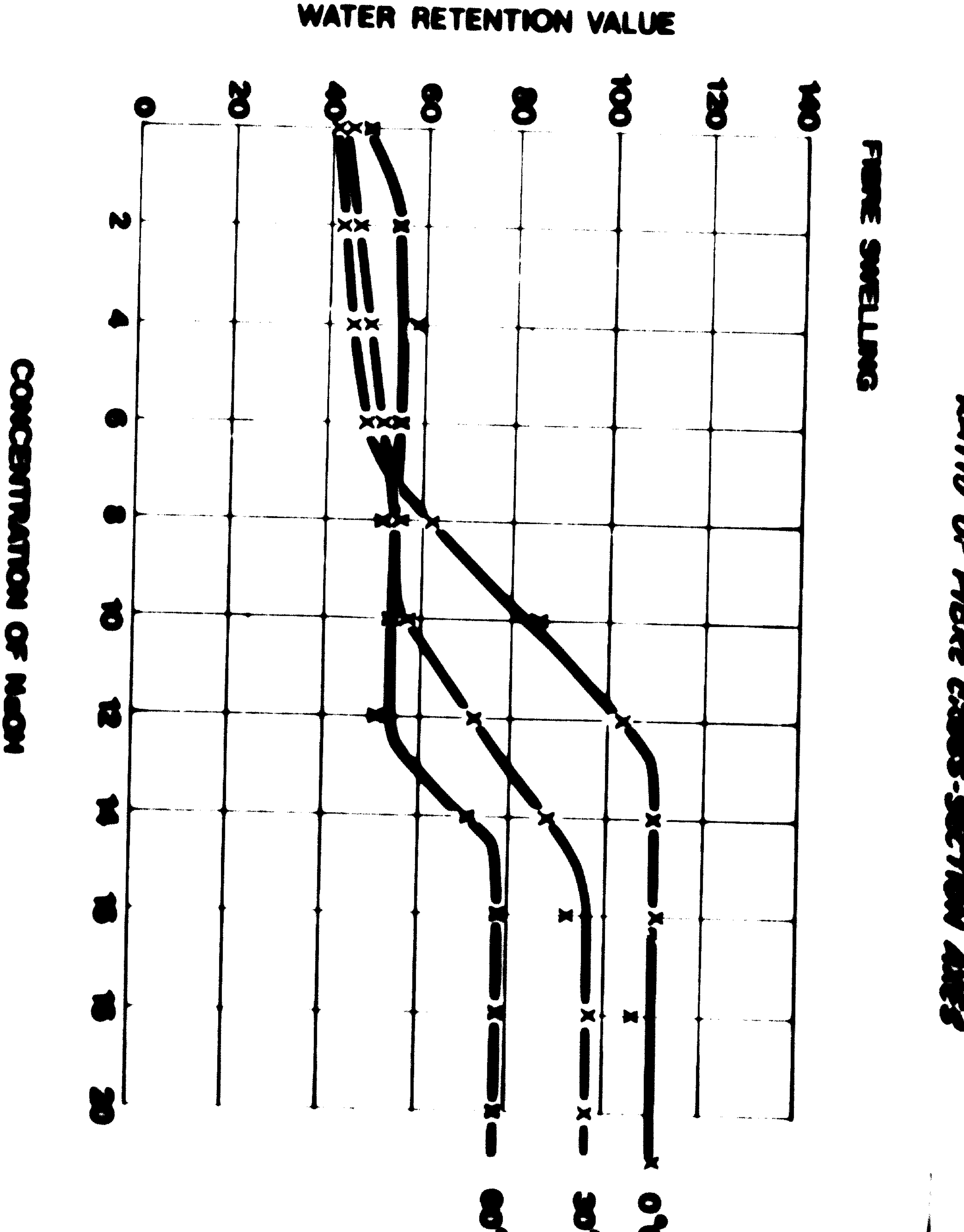
MERCERISING: INFLUENCE OF TENSION ON LENGTH SHRINKAGE



YARN MERCERISATION: EFFECT OF PROCESS VARIABLES

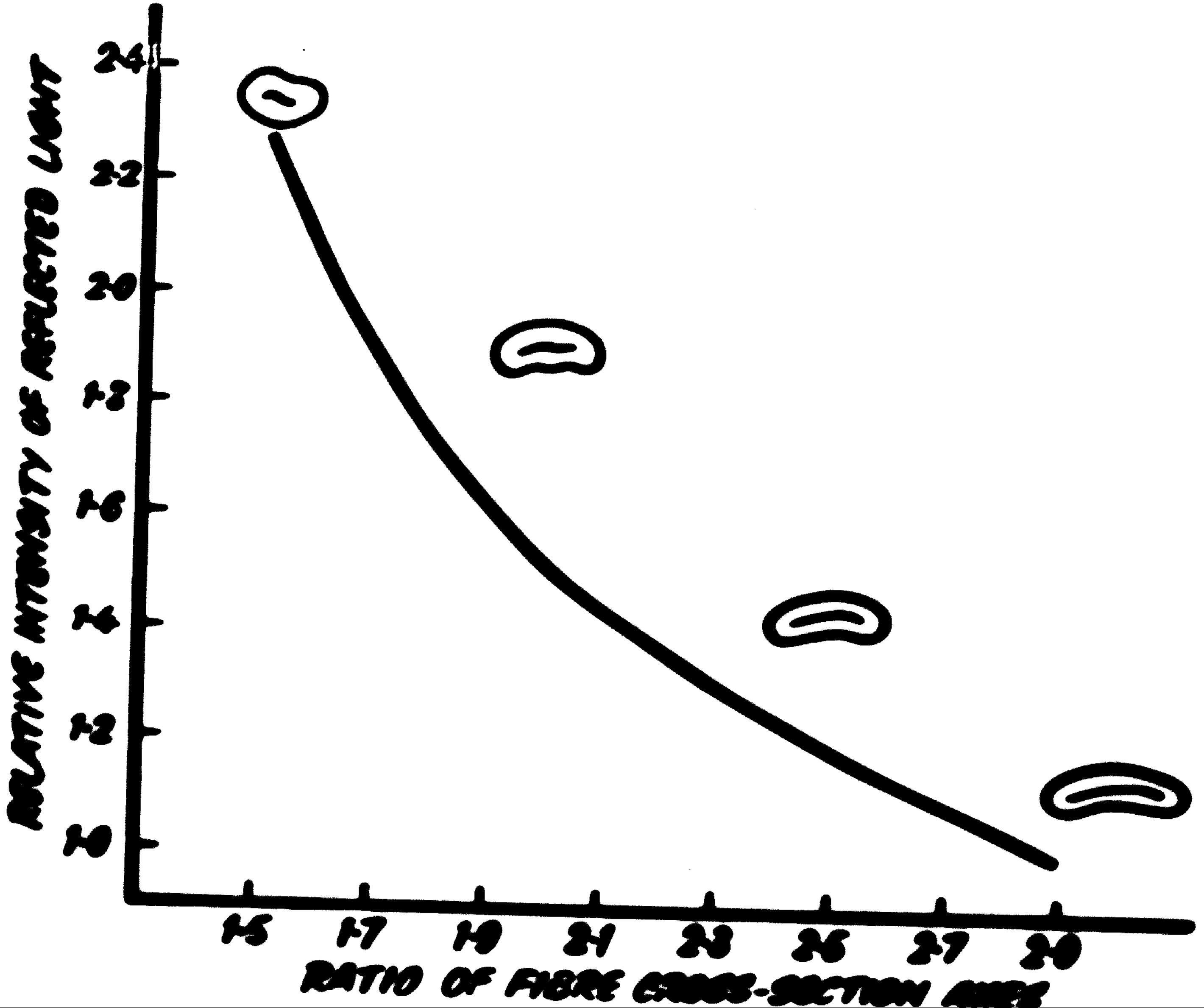


SLIDE 9


WATER RETENTION VALUE
0
20
40
60
80
100
120
140
FIBRE SWELLING
RATIO OF FIBRE CROSS-SECTION AREA
2
4
6
8
10
12
14
16
18
20
CONCENTRATION OF NaOH
0°C
30°C
60°C

SLIDE 11

LUSTRE: INFLUENCE OF FIBRE AXES RATIO



SLIDE 11

MERCERISING AT CONSTANT TENSION

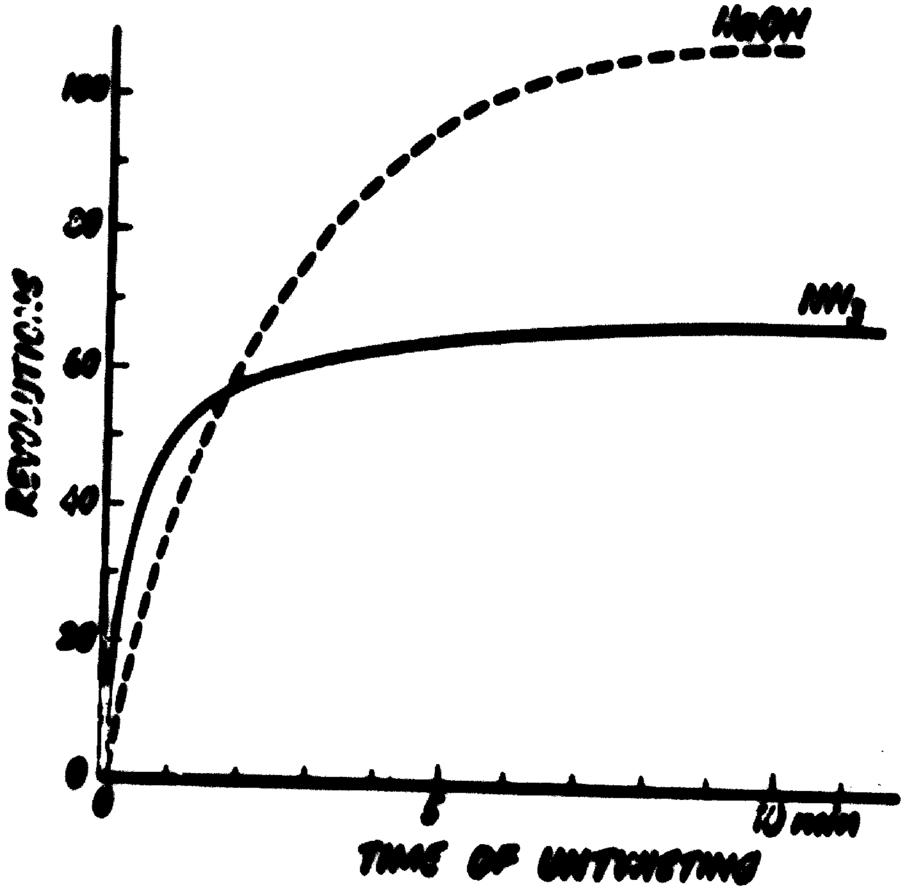
VARIETY	STRENGTH % GAIN	ELONGATION % LOSS
KARNAK	0.7	31.2
LENGUPA	1.5	10.3
PIMA - S1	5.8	45.5
WATSON MEBANE	17.1	40.6
EXPERIMENTAL STRAIN	27.2	44.1
ACALA 442	29.9	29.1
SUPIMA	30.2	21.5
TRIPLE HYBRID	35.0	5.3
SEA ISLAND	38.2	34.1
COASTLAND	52.0	26.4
DELTAPINE 15	52.8	30.3
BELGIAN CONGO	73.6	38.2

SLIDE 18

RESPONSE TO CROSSLINKING OF NORMAL (B) AND ROVING-MERCERISED (RM) COTTON IN SHEETING FABRIC

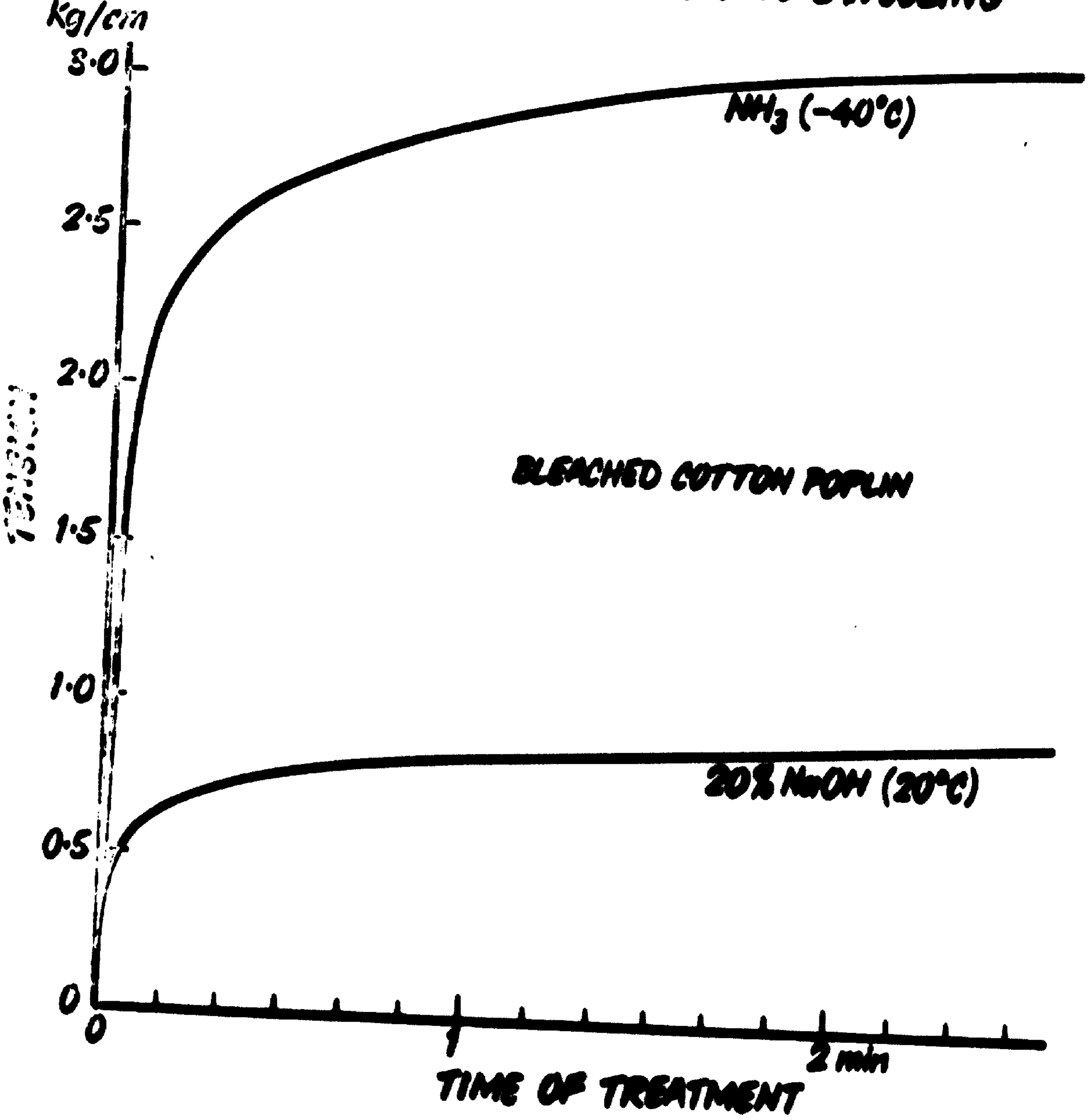
	RUN A1		RUN A3	
	B	RM	B	RM
TENSILE. FILL %	65	95	57	84
TEAR FILL %	75	113	44	71
DRY C.R.A. (WP+FILL)	285	287	307	300
RING WEAR, revs	2000+	2000+	1370	1080
ACCELEROTOR, 6min loss	12.8	16.3	17.4	24.6
FIXED RESIN %	2.8	3.3	6.0	6.0

SLIDE 19


MeOH
NH3
100
80
60
40
20
0
0
5
10 min
REVOLUTIONS
TIME OF UNTWISTING

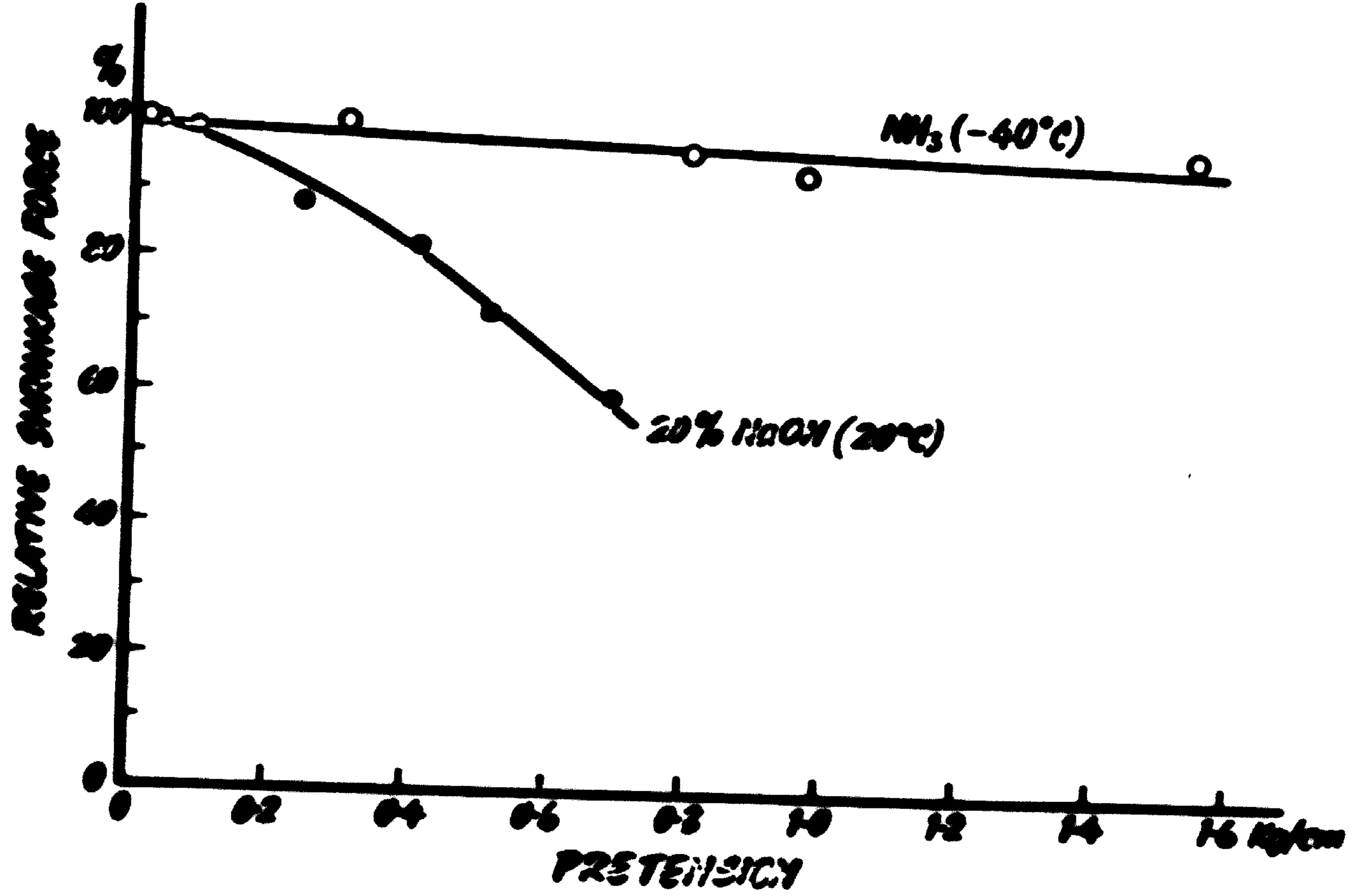
SLIDE 20

DEVELOPMENT OF TENSION DURING SWELLING



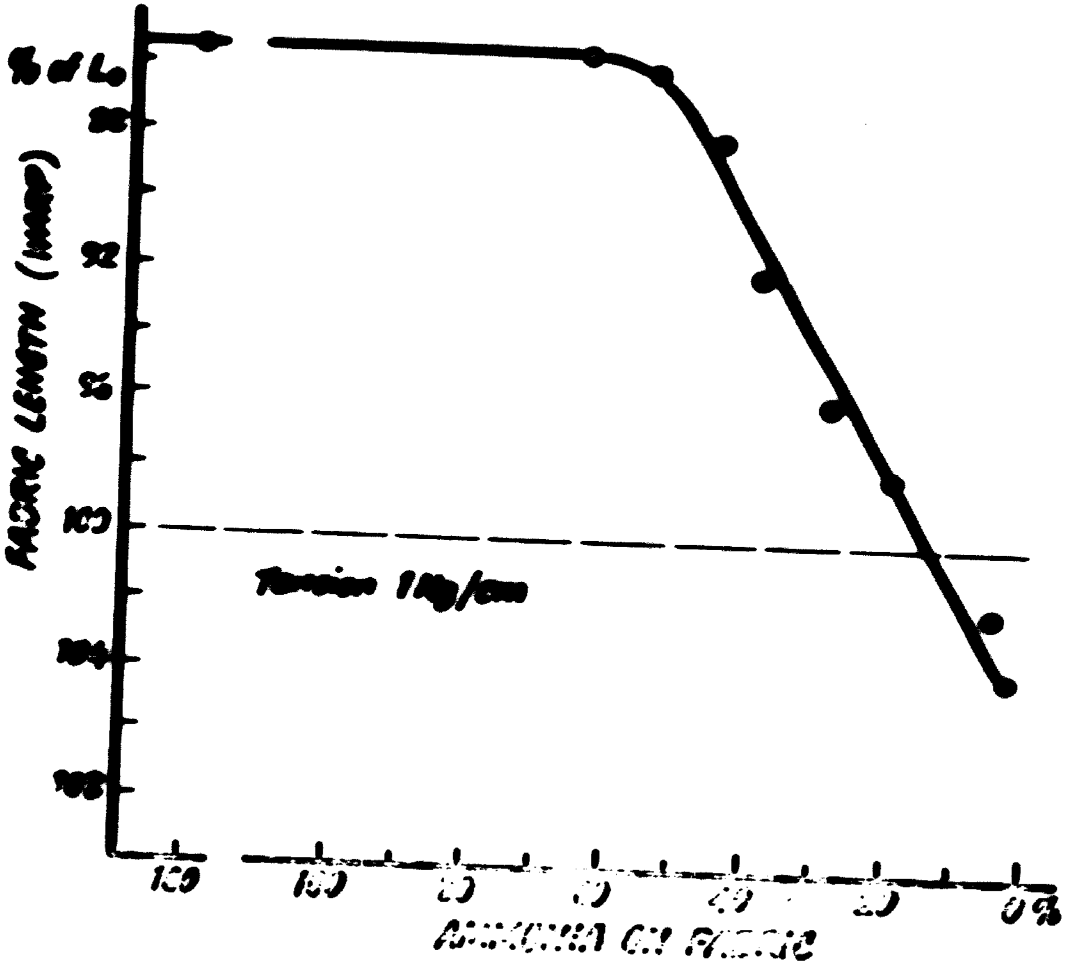
SLIDE 21

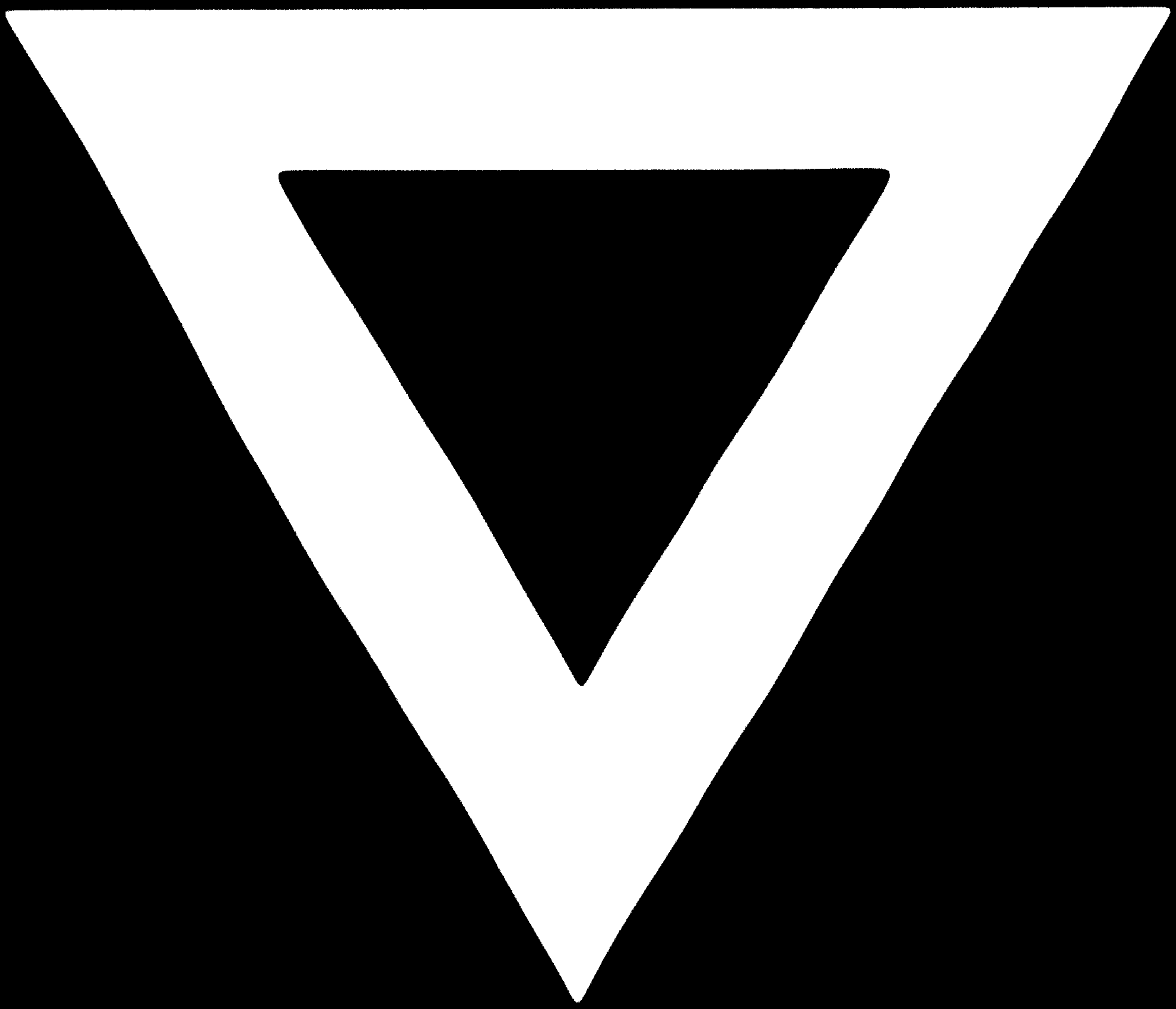
EFFECT OF PRETENSION ON SHRINKAGE FORCES



SLIDE 22

DEGREE OF RESTRETCHING OF COTTON POPLIN AS A FUNCTION OF AMMONIA CONCENTRATION ON THE FABRIC.





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