STUDIES ON THE CHEMICAL FINISHING OF COTTON CELLULOSIC FABRICS

BY

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DEDICATION

TO

NONYE

Who took a special care of the toddler I entrusted upon her all these months.

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SUMMARY

The aim of this project is to study some aspects of the crosslinking of cotton cellulose. Cotton fabrics are often subjected to various chemical finishing treatments to enhance their natural resilience. In the present work, crosslinking is accomplished by impregnating cotton with N - methylol urea precondensates, viz, dimethylol-dihydroxy-ethylene-urea- (IMDHEU) and dimethylol-ethylene urea (IMU).

For each of the resins used in the investigation, we established the most favourable resin concentration in the padding bath, that is, the concentration that gives highest crease-recovery, which was 9% for these particular resins. We further considered what effects the type and amount of catalyst would have on the fabric durable-press characteristics. We used here hydrates of magnesium chloride and zinc nitrate (Mg Clg. 6H20) and $Zn(NO_3)_2$. 6H20 and dimethyl sulphoxide (IMSO) as catalysts. It was observed that as in the case of resins, the degree of crosslinking increased with catalyst concentration.

However, significant crease recovery property was not achieved by the use of IMSO.

It has been shown that all chemical wrinkle-shedding operations invariably resulted in losses of some useful properties of the fabric. An attempt was therefore made to investigate the degree of deterioration with respect to the quantity and type of catalyst in the bath and the effects of ageing on the properties of the resin.

Other properties of the fabrics, such as extensibility, changes in glass transition temperature (Tg) and charring temperature, elastic recovery properties, abrasion resistance and the susceptibility of the padded fabric to the incidence of fishy odour were determined. In most cases, the changes or otherwise, in the afore-mentioned characteristics were verified in relation to those of the untreated samples.

CHAPTER ONE

1.1 Introduction

Usefulness, aesthetics and economic considerations have always motivated man to find ways of imparting onto cotton apparel the characteristics of smooth, freshly ironed, wrinkle resistant appearance during wear. There is great impetus for a systematic research and understanding of the mechanics of durable-press characteristics in cellulose. As for the protein fibres such as wool, sick, mohair, alpaca, cashmere, angora etc, their easy-care properties have always been attributes most fancied by both the manufactures and users alike.

The difference between the behaviour of the protein-based and the cellulose-basedfibres like jute, rayon, cotton and linen became clearer when the molecular architecture of their building blocks came to be better understood. Whereas cotton fibre is made of polymer molecules held together by many inter-molecular forces hydrogen bonds, and are composed of stiff back-bone structure, the wool molecules are highly crosslinked, highly folded and, therefore, exhibit enhanced extensibility and improved crease recoverability.

The pioneering work of reacting formaldehyde and cellulose in 1906 by Eschalis [1] and the resultant improved wrinkle resistance there from, has stimulated many years of research and speculation on the mechanism of their effects. The aim of all such work has always been geared towards finding products and processes which could give better results than this early formaldehyde precondensate. The overall result is that broadly speaking, achievement of dimensional stability tends to encompass both mechanical and chemical fields. The mechanical methods include the various calendering procedures such as chasing, frictioning, swissing etc, Sanforising and the Rigmel processes. However, it became apparent that for definetely permanent dimensional stabilisation of cotton goods, the chemical processes are more promising. This has resulted in a voluminous literature in this field. With introduction of the synthetic fibres of nylons and polyesters, it was realised that annealing them at about 218°C for not more than 30 minutes imparted onto them retained shape under normal use.

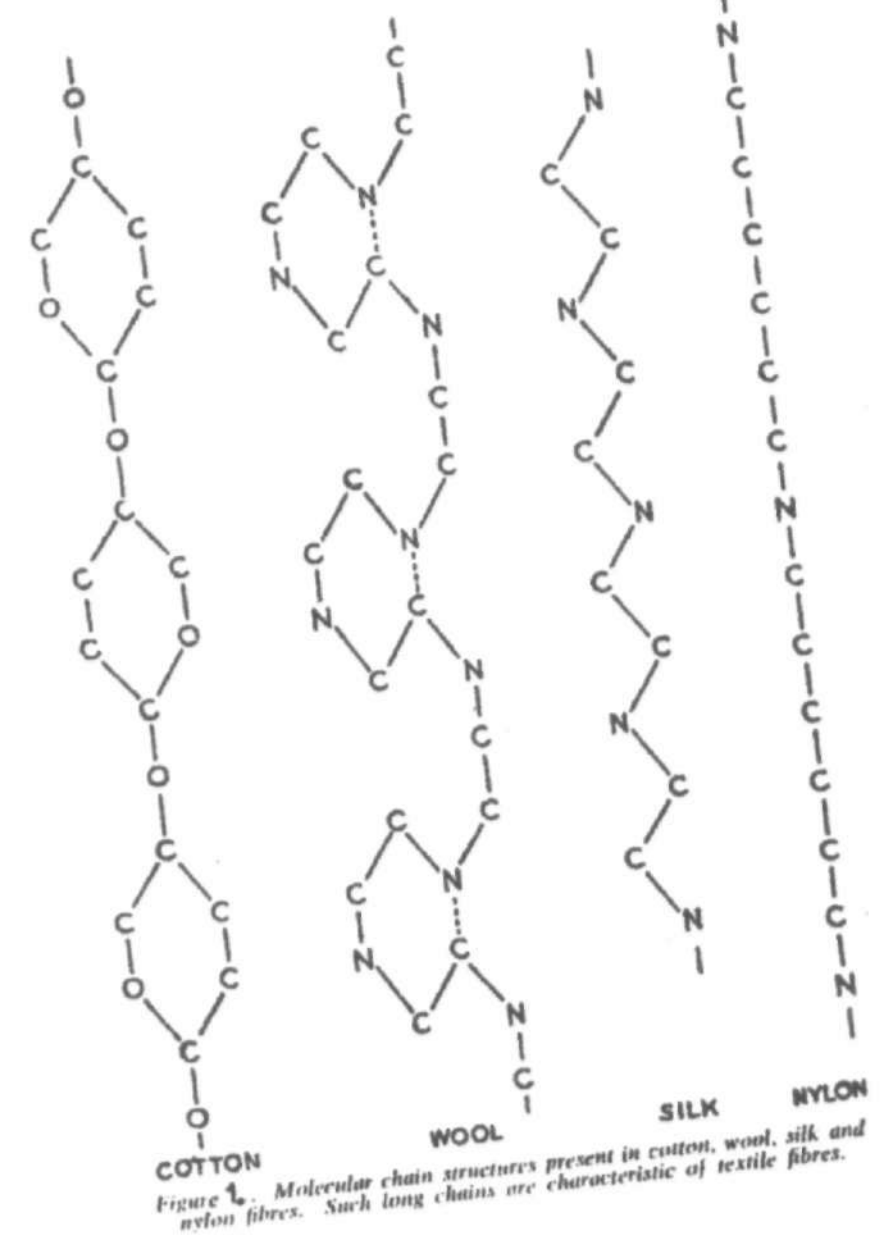


Figure 1. Molecular chain structures present in cotton, wool, silk and nylon fibres. Such long chains are characteristic of textile fibres.

1.2 Early Theories of Crease Recovery in Cellulosic Fabrics

Efforts made to explain the mode of action of crease-resistant finishes may be summarised thus:-

1.2.1: The Resin Deposition Theory:

Marsh [2] attributed these effects as arising from swelling the fibres by depositing resins between them. He maintained that such distended fibres would acquire woollike properties. Later it was believed that the resin particles inside the fibres mechanically inhibited intermolecular slippages resulting in irrecoverable deformation. Later it was argued that the resins altered the molecular entanglements or resulted in the formation of new sets of hydrogen bonds or some other secondary forces. Though the resin deposition theory has much to commend it and in fact, still has some adherents [3-6], it has in the main been superceded by the covalent crosslinking hypothesis.

1.2.2: The covalent crosslinking theory

This second theory was first advanced by Meunier and Guyot[7] in 1929 and gained popularity from the work of Cameron and Morton[8] in 1948. These authors maintained that a greater part of the crease recovery is due to the part of the precondensate which reacted bifunctionally with the cellulose to form a covalent link between them. There appears to be a lot of evidences in support of this latter theory. These include (i) observed insolubility of the treated fabric in the usual cellulose solvents such as cuprammonium hydroxide [9,10,11], copper chloride solution etc, (ii) reduced water and dye imbibition properties, (iii) the necessity for the crosslinker to be polyfunctional with respect to cellulose, (iv) observed increased absorption in the 11 μ region [12-14] indicating ether formation and (v) the fact that such agents are not effective on fully acety-lated cellulose, (the one in which all the hydroxyl groups have been blocked). Further, by circumstantial reasoning, one can liken crosslinked cellulose to wool or vulcanised rubber. In such a case, crosslinking is believed to impart improved resiliency by tying cellulose molecules together into a three-dimensional network so that inter-molecular creep is prevented and enables the deformed fibre to, as it were, "remember" to return to its original configuration.

The crosslinking theory has become accepted by most researchers.

1.3: Invention of Crosslinking Agents

In the wake of the crosslinking theory, it became clear that any compound with two or more functional groups that can react with cellulose is a potential crease-proofing agent. This led to the trial on a vast array of such compounds. These include phenolformaldehyde, melamine formaldehyde, urea formaldehyde precondensates; ketones, acetals, ketens, urons, trazines, carbonyls and isocyanates. These types of compounds can be represented by a general formula R - (x)n where R is a radical to which are attached two, three or more X-groups and X represents any of the functional groups stated above or some others.

The type of crease-proofing agent chosen depends not only on economic considerations but also on how its characteristics simulate what may be deemed the properties of an "ideal" resin. The desired qualities demand that such agents be (i) water-soluble, (ii) non toxic in the use or oh the treated - material (iii) effective at 5-10% concentration (iv) non chlorine retentive,

(v) durable to all types of washing at moderate temperatures

(vi) no reduction in light fastness of dyes,

(vii) achieves both wet and dry crease recovery,

(viii) no reduction in fabric strength and

(ix) not much change in fabric handle. While it is agreed that no single wrinkle-proofing agent satisfies all these conditions perfectly, the attempt has always been to approach them as much closely as practicable or to isolate the desired characteristics for a given resin, that tally with the conditions under consideration. For all practical purposes the methylol urea precondensates seem to feature a lot in many applications.

CHAPTER TWO

Chemistry and Mechanism of Crosslinking with N-methylol ureas

2.1: Behaviour of Crosslinking Agents with Cellulose

Though different compounds behave differently towards cellulose, some general statements can be made to illustrate their behaviours with cellulose. Marsh[15] has observed that there is the necessity for the resin to be distributed within the fibres and not on their surfaces, since surface resins only increased the stiffness of the treated cloth but did not contribute significantly to increase its crease-recovery. This idea has been corrborated by the works of Etzkorn [16 & 17] and Gagliadi and Gruntfest [18] who emphasized that the resin must be necessarily low-molecular weight, essentially monomeric to be of any use. This naturally gives an insight into the nature of the reactions.

Cotton cellulose is composed of long chain molecules of glucopyranosyl residues joined together by glucosidic linkages at 1,4 positions and having a chair conformation..

This conformation has resulted in highly ordered crystalline fibres. This high crystallinity controls the sites of the reactions; thus for reaction to take place between the crease-proofing molecules and the hydroxyl groups of the cellulose, the latter must be accessible.

According to the Fringed Micelle theory of the microstructure of cellullose, a polymer molecule traverses several crystalline and disordered regions.[18 & 19] The amorphous regions are by nature more accessible to the reagent than the crystalline areas. It follows therefore, that crosslinking reactions take place predominatly with glucopyranosyl unit hydroxyls in these areas or those at the surface or periphery of the fibres when the medium is of a lesser swelling power than mercerising caustic.[18] However, it has been observed that the three hydroxyls in a glucose unit are preferentially accessible; the hydroxyls at C-2 being more exposed than those at C-3 or C-6 for those reactions whose swelling capacity for cellulose is limited to that of water alone, as is the case with our present work.

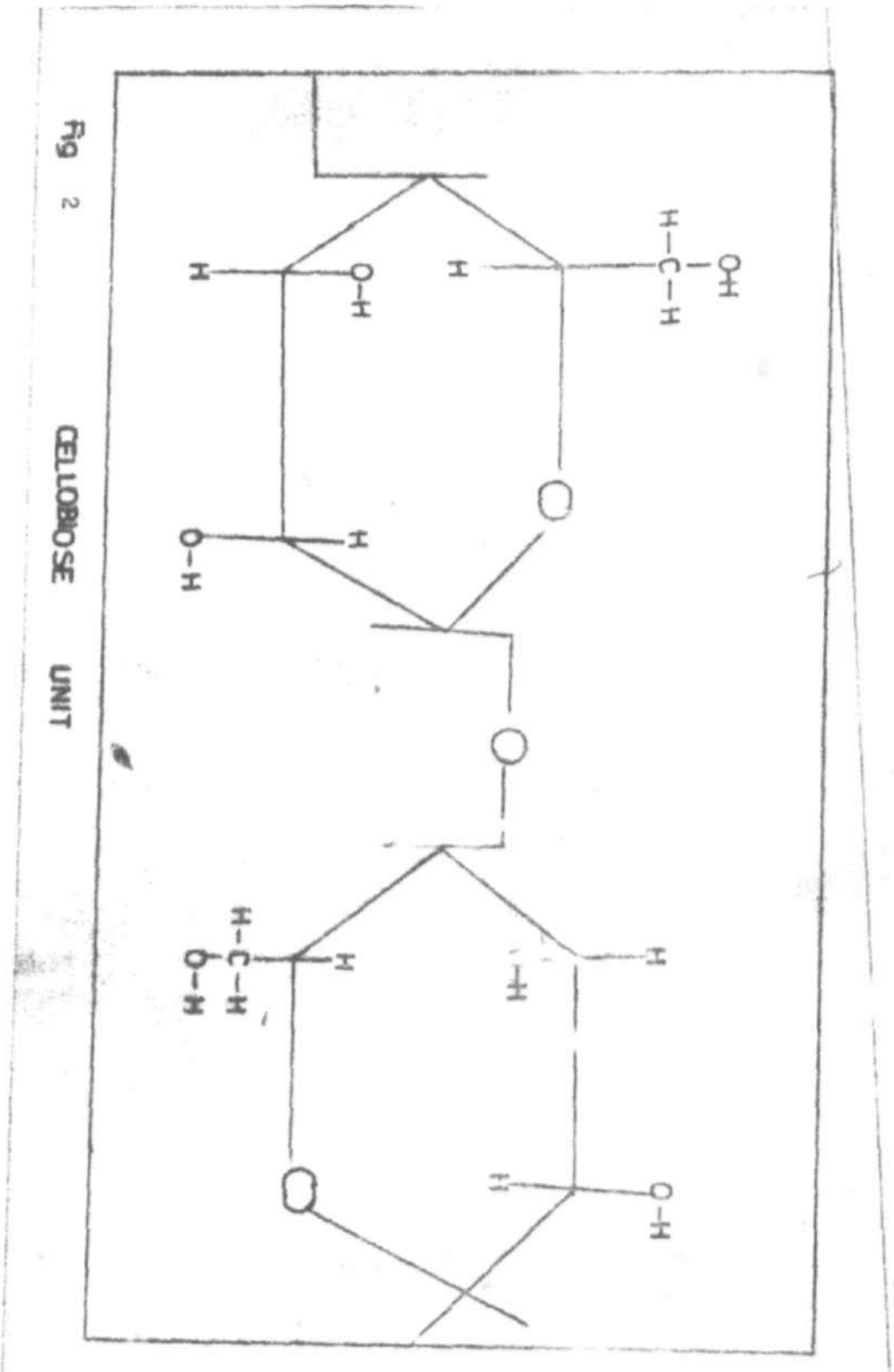


Fig 2 CELLOBIOSE UNIT

2.1.1: Physical Chemistry Associated with Crosslinking

The process of crosslinking is known to proceed in the following order:-

i Diffusion of the crosslinking molecules from solution phase to the cellulose/solution interphase.

ii. Adsorption of the crosslinking molecules from the inter face onto the cellulose surface;

iii. Diffusion/penetration of crosslinking molecules into the microstructure of cellulose;

iv. Reaction between crosslinking molecuIs and cellulose hydroxyls;

v. Partial degradation of cellulose

vi. Hydrolysis of some of the crosslinks formed. [20]

There is, usually for a given system, a gradual increase in adsorption up to a point and the rate decreases with increase in the concentration of the padding bath, especially for crosslinking molecules that tend to aggregate. This confirms the ascertion[14] that only simple mono molecules are adsorbed.

Similar observations have been recorded in the case of surfactants and dyes.[20] During the drying of the padded fabric, there is normally a gradual change in pH and the crosslinking molecules diffuse inside the fibres. At the higher temperatures of cure, polymerisation/crosslinking result and it is known that for DMDHEU and possibly N-methylol resins in general, there is no noticeable increase in crease-recovery by prolonging the time of chemisorption. This more than indicates that only those molecules which are chemisorbed on cellulose react further to form links during curing, and further shows DMDHEU in particular to be stable towards acid hydrolysis.[21]

2.2 Factors Influencing the Crosslinking Behaviour of the Crease-resist Finishes:

2.2.1 Physical Factors:

Crease resistance is not an inherent property of the cotton fabric, but is a composite property which results from a variety of factors, such as the stress-strain and elastic properties of the fibres, the yarn construction, weave, thickness and density of the goods, the extent of strain and stress induced during manufacture

and the presence or absence of a host of processing agents left on the fabric.

Apart from those outlined above, the wrinkle recovery achieved with a particular crosslinker also depends on the operating conditions viz:- the concentration of the padding bath; the higher the treating bath concentration, the larger the amount of the reagent that is bound to the cotton and higher the wrinkle resistance achieved, though there is always a limit to useful concentration values, [22] the batching period, the time and the temperature of cure. It has been found by analytical procedures that at least every 25th accessible anhydroglucose unit has to be inter-molecularly crosslinked when maximum crease recovery values are attained,[23] though the relationship between extent of crosslinking and wrinkle recovery is known to be logarithmic.[24]

2.3: Chemical Considerations:

2.3.1: Mild Acid Scouring:

One condition which must have to be strictly adhered to is that the material to be impregnated with resin must be as clean as practicable.

It is known [56] that residual alkalis left on the fabric can neutralise the acid catalysts. This results in undercure or non uniformity of cure. Further, other materials like starch, may interfere with the reactions [57] and must therefore be removed. Before the application of resin, a convenient size of the fabric is cut out, washed with 0.1% acetic acid, rinsed in cold water and then dried.

2.3.2: Nature of the Crosslinking Agent:

It was stated in section 2.1 that the appropriate reagent must be necessarily monomeric and small so that it can penetrate the microstructure of the fibres. This precludes most large potential molecules or those that easily polymerise on standing for a short time. Polymerised resin precondensates may become so large that they cannot diffuse into the fibres; they simply coat the fibre surfaces [25-27] or form crosslinkages composed of a number of polymeric side chains or perhaps even resin particles not bound to the cotton cellulose by primary valence bonds, but still embedded in the fibre.

Further, as for the N-methylol compounds the presence of the basic nitrogen atom beta to the ether oxygen plays a role in the reaction.

Even though the substituents making the nitrogen atom less basic inhibit hydrolysis, they also decrease the reactivity of such compounds. In the case of ureaformaldehyde (UF) precondensates the efficiency of the resin (UF) as a crease-proofing agent depends to a significant extent on the urea-formaldehyde ratio.[28 & 29]

2.3.3: Drying and Curing

Usually the impregnated fabric is given a moderate drying temperature (Ca 110°C). This enhances uniform penetration of the crease-proofing molecules and reduces the loss of volatile molecules e.g., free formaldehyde "split" by some N-methylol reagents. It also minimises surface-resin deposition ascribed to "migration" of reagents to fibre surfaces.[29-31] The method of drying employed varies considerably, but hot-air drying has been observed to have much to commend it. It is now known that the application of tension during drying and curing slightly reduced tensile strength losses.[32 & 33] Similarly, drying the fabric in a slack state has some favourable implications: apart from improving wrinkle-resistance of the fabric, it results in higher dimensional stability upon subsequent laundering.

The lengths of time and temperature of cure have profound and controlling influence on the degree of resiliency achieved, since most of the chemical reactions of crosslinking occur at this stage. Consequently, the degree of cure reached becomes of paramount importance since wrinkle recovery level, chlorine retention and finish durability, all depend on it.[34-37] Overcure, often associated with maximisation of reaction conditions always leads to partial or complete degradation of the cotton fabric as well as that of the impregnating agent. Undercure, on the other hand, results in incomplete chemical reactions. Again, there are varying curing media, but the most popular appears to be hot-air. Experiments have also been conducted by curing in ultrasonic, inert liquids, fluidbed, infra red, multifrequency, high frequency methods. Curing in superheated steam containing a high proportion of moisture has been claimed [38-40] to result in fabrics with higher retained abrasional resistance than those treated in dry heat.

2.3.4: Post Cure Treatment:

The after-treatment given to an impregnated fabric sample is as important as the method of applying the crosslinking agent.

Cured fabrics are therefore afterwashed to give quality finishes and this diminishes the incidence of formaldehyde evolution and the possibility of fish odour formation.[58 & 59] It has also been reported by Reid and others[60] that, apart from moderating acid-hydrolysis, which often results in lessened crease shedding performance, it also reduces the onset of chlorine damage when N-methylol compounds are used. Neutralisation of residual catalysts also prevents post-curing. It breaks down amine salts, thus permitting the free amines to come off the fabric during hot rinsing. The cured sample is usually given very dilute sodium carbonate afterwash followed by a copious rinsing in distilled water. It is then dried at room temperature.

2.4: Mechanism of Crosslinking Reactions

2.4.1: General

From the works of Rowlands et al[18] and Reeves[49] crosslinking reaction is taken to proceed through a set of reversible steps wherein the formation of a reasonance-stabilised intermediate is considered the rate-determing step. This also indicates that the backward reactions represent the mechanism of the hydrolysis of the crosslinked cellulose under same conditions.

However, it must be taken that at each stage the forward reaction is favoured:

i. $R C O N H C H_2 O H + H^+ = R C O N H C H_2 O^+ H_2$

ii. $R C O N H C H_2 O^+ H_2 = R C O N H C H_2^+ + H_2 O$

iii. $R C O N H C H_2^+ \longleftrightarrow R C O N^+ H = C H_2$

iv. $R C O \overset{+}{N} H C H_2 + Cell\ OH = R C O N H C H_2 \overset{+}{O}(H) - Cell$

v. $R C O N H C H_2 \overset{+}{O}(H) - Cell = R C O N H C H_2 - O - Cell + H^+$

2.4.2: Catalysis

Crosslinking reactions in durable-press (Dp) finishes can take place without catalysts, but this involves a prolonged time and still the product is rarely durable. In the presence of certain compounds, a better result is often achieved. Such compounds accelerate the rate of reaction and stabilise the finish, and are therefore designated as catalysts even though their functions are not strictly catalytic.

These groups of compounds include mineral acids and the so-called "latent" acids; so-called because though they are stable in the bath, under curing conditions, they release or form acids. Incidentally, the use of basic catalysts in crease-proofing formulations containing N-methylol compounds has not proved feasible in commercial practice.[41] The mineral or strong organic acids hydrolyse cellulose, and are rarely used as catalysts except on special occasion[42-46] and, in fact, they have been completely replaced by the "latent" acid catalysts.

These catalysts function by providing the acid necessary for the crosslinking reaction, eg, in the case of magnesium chloride hexahydrate. It is also known that when zinc nitrate hexahydrate is used as a catalyst there is complex formation with the cellulose by the zinc ion. The mechanism of the catalytic action involves stepping up the covalent linkage reactions and can be represented by the following two steps:

i) $\text{Cell} - O - R - O\,H + M = \text{Cell} - O - R - \overset{\overset{M}{\vert}}{O} - H$

ii) $\text{Cell} - O - R - \overset{\overset{M}{\vert}}{O} - H - + O\,H - \text{Cell} = \text{Cell}\,O - R - O - \text{Cell}$

in which (i) is the formation of an activated complex and M the

catalyst, which may be hydroxonium or metallic ion or any strong Lewis acid for that matter. Madan et al [50] have shown the catalytic effects of magnesium chloride hexahydrate to proceed in the following manner:-

(a) Decomposition of the salt

$$2Mg\,Cl_2 . 6H_2O = Mg_2\,O\,Cl_2 + 5\,H_2O + 2HCl$$

(b) Protonation of Crosslinking molecule

$$R\,C\,O\,N\,H\,C\,H_2\,O\,H + H^+ = R\,C\,O\,N\,H\,C\,H_2\,O^{+}\,H_2$$

$$= R\,C\,O\,N\,H\,C\,H_2^+ + H_2\,O$$

$$R\,C\,O\,N\,H\,C\,H_2^+ + Cell\,OH = R\,C\,O\,N\,H\,C\,H_2\,O\,Cell + H^+$$

2.5: Strength and Failure During Crosslinking:

Wherever there is gain in resiliency of the treated material, this invariably is accompanied by losses in tensile properties. Considerable amount of efforts have been directed towards finding methods and processes whereby this apparently inevitable loss can be controlled.

The methods employed range from scrupulous choice of reagents and conditions to methods of drying, curing, fabric construction and processing techniques. Nevertheless, it has been reported [51] that, as far as N-methylol reagents are considered, it is impossible to completely eliminate these losses; however they can be minimised.

2.5.1: Theory of Failure:

From rheological considerations an elastic recovery test is well defined geometrically and consequently one finds it reasonable to explain resiliency in that light. When a sample is subjected to a stretching force or extended under a load, the resultant response, extension etc, is generally the sum total of three separate components:

(i) the elastic deformation which is time-dependent and is instantaneously recovered on releasing the load.

(ii) the secondary creep comprises a time dependent viscous flow and elastic deformation, though the recovery is rather slow when the load is removed, and

(iii) the permanent creep is time-dependent, but there is no recovery on withdrawal of tension.

From rheological considerations it can be assumed that viscous deformation is due to slippage of chains and segments relative to each other and the function of crosslinking is therefore to reduce or inhibit creep. In fact, it is common knowledge that vulcanised rubber does not show creep.[67]

2.5.2: Causes of strength Losses in Crease-proofing Reactions:

Strength losses in crease resistance treatments have been attributable to factors arising from crosslinking embrittlement at the shorter times of cure and to acid hydrolysis and thermal degradation during the longer cure times.

With crosslinking the relative movement of molecular chains become more restricted, so that there is less opportunity for chain molecular motions contributing to the equalisation of stress distribution on individual chains. In such a case high local stress concentrations are built up and these increase the chances of rupture and hence failure.[51,52-54]

However, it is not possible, without damaging the fabric, to practically completely strip the treated fabric of all the bound resin so as to demonstrate quantitatively the strength losses due to crosslinking embrittlement alone.

It has been reported [55] that with cyclic ethylene urea formulations, as much as one half of the total tensile strength loss is due to factors other than the acid catalysts.
In some other instances, for example, where zinc nitrate hexahydrate catalyst is used, its decomposition at the temperature of cure results in the evolution of nascent oxygen and oxides of nitrogen which are injurious to cellulose.

2.6: Effects of Environment on CRA Results:

In evaluation of crease recovery test results, it is paramount that the environmental conditions prevailing be stated. This is because in case of cotton cellulose, as well as other natural fibre fabrics, environmental conditions exert substantial influences on their properties. Temperature seems to have a little effect on the deformation and recovery property of cotton and, although stress-relaxation has been known to be more rapid at higher temperatures,

the differences are not remarkable. [63 & 64]

Humidity, that is the moisture content of the testing atmosphere, has a more controlling impact: water is absorbed readily on hydroxyl groups and since this can break hydrogen-bonds, it increases the mobility of fibre structural elements. Consequently, the dry strongly-dydrogen-bonded fibre has higher initial modulus, lower extensibility and higher deformation recovery than the water-lubricated, more flexible wet fibre. [65,66] Other characteristics such as electrical conductivity and stress-relaxation also increase sharply with higher moisture regain.

Naturally crease recovery is much altered by changes in environmental pressure, but since tests are usually carried out at relatively constant laboratory atmospheric pressure conditions, the effect is often ignored. Air current/wind of course disturbs the smooth gradual recovery of test samples.

2.7: Survey of Wrinkle Test Methods:

Apart from the AATCC Method 66 procedures employed in this work, various other methods have been deviced to measure crease recovery in fabric samples.

The techniques range from highly improvised ones to those employing sophisticated equipments. A resume' of some of them is given here:-

(i) The fabric sample is given some crease by being subjected to a definite load for a given length of time;the load is removed. The sample is stood on a flat surface with the two ends, and as recovery proceeds, its height diminishes. Obviously this method will require that the compared samples must be of same density and construction and that the flat surface be perfectly smooth.

(ii) In this method, the test material is folded into two equal halves. It is then placed horizontally on one of the folded flaps while the other is allowed to rise. The height risen for stipulated length of time is recorded. While this shows some refinements over method (i) above, it is difficult to operate: the folded fabric halves may become interlocked so that they fail to separate. Further, the method calls for a completely drought-free atmosphere. In measuring the height attained after some time, some difficulty may arise from the thickness of the fabric.

(iii) Thirdly, in some cases, the fabric, already creased, is hung on a thin straight taut piece of wire; with the two loose ends pointing downwards on a plane mirror mounted with a linear or a circular scale. As recovery progresses, the two arms dilate the more and this is read off from their images on the scaled mirror. This method is considered good for most routine work, but personal judgement, arising from parallax etc. may introduce some error. Again, the thickness of the fabric determines to some extent the accuracy of the readings.

(iv) The AATCC method RA6 is another elaborate way of measuring CRA. This, like all the previous ones is for determining the appearance of textile fabrics made from any fibre or combination of fibres. The principle is as follows:- a test sample is wrinkled under standard atmospheric conditions in a standard wrinkling device under a pre-determined load for a prescribed period of time. The specimen is then reconditioned in standard atmosphere of textile testing and evaluated for appearance by comparison with 3 - dimensional reference standards. The accuracy of this method depends on the degree of experience of the evaluators.

Though it is a popular method employed in large industrial set-ups, and gives a fairly reliable result, it is time consuming.

(v) In some other instances, an incident ray of light is directed on the crest of the wrinkle. Reflected rays from this are made to focus on a scale and the movements of the reflected rays, as they traverse the scale give the crease recovery straight-away. In practice this is not easy.

(v) At the extreme end of sophisticated method, the force of recovery actuates an electronic stylus which records CRA automatically.

In essence, the method applied at any time and place depends not only on the economics and availability of instruments, but often times on the personal preferences of the technician.

2.8: Abrasion Resistance in Cotton Fabrics

Abrasion is defined as the wearing away of any part of a material by rubbing against another, while wear means the progressive loss of substance from the surface of a body

brought about by mechanical action. Abrasion has also been considered as wear caused by fine solid particles.[83] In use, there are many ways by which a fabric is abraided, eg. (i) elbows on the table, (ii) Under the arm by mutual rubbing, (iii) dry and wet conditions in a washing machine or during laundery, (iv) flexing at neck of shirts or elbows of sleeves. In fact there are so many causes of wear that it is impracticable to simulate them all perfectly in the laboratory. What could be said generally is that the life of a fabric is very much dependent on its resistance to abrasion.

Mechanisms operating in abrasion have been studied extensively for a wide range of materials including metals, [84] rubbers and plastics and it is surmised that abrasion resistance increases with increase in surface hardness. It has been established [85] that two extreme types of wear can occur in polymers viz:-

(i) plastic deformation and cutting by relatively sharp asperities;

(ii) plastic deformation and fatigue by more rounded asperities.

The latter is more likely to operate in fibre-fabric systems. Yet, some, [86-88] have proposed three forms of abrasion damage in fabrics.

These are:-

(i) frictional erosion

(ii) fibre slippage and

(iii) fibre rupture.

The abrasion resistance in clothes is much controlled by, not only the nature of the fibre (or polymer), but also by the structural features of fibres, yarns and fabric geometry etc. Treloar [89] has stated that the abrasion-resistance of twisted continuous filament yarn is enhanced. Filament yarns with 'solid' body have greater strength and upon twisting together, produce a coherent structure that is not easily deformed. Further, fine binding of the fibres resulting from higher twists or tighter weaves all are known to reduce tearing-out action and open-end spun yarns are superior in abrasion-resistance than the conventional ring-spun yarns. Similarly, higher sett fabrics are known to possess better overall wear resistance [90,91] whereas compact woven structures such as plain weaves, are less susceptible to abrasion damage than open loose ones, e.g. Matt, Hopsack, etc weaves where the fabric could be abraded by plucking, pulling or snagging of the floated threads.

However, it can be conveniently stated that nylon has the best resistance to abrasion, polyester is also excellent, especially as a blend, cotton, wool and high tenacity rayon such as "Durafil" are fairly good. The inclusion of 20% nylon in a cotton yarn will approximately double cotton's resistance to wear.

CHAPTER THREE

Materials and Experimental Methods

3.1: Materials

3.1.1: Greige fabric was supplied by Kaduna Textiles Limited (KTL) and had the following specifications:

Ends per centimeter	23
Picks per centimeter	33
Density, g/cm^3	0.0478
Thickness, mm.	0.32

3.1.2: Arko-fix (dimenthylol-dihydroxy-ethylene-urea)

- DMDHEU, was provided by Hoechst Nigeria Ltd.

Magnesium chloride hexahydrate - $Mg\ Cl_2 . 6H_2O$

Zinc nitrate hexahydrate - $Zn(NO_3)_2 . 6H_2O$

Dimethyl Sulphoxide (DMSO) - $(CH_3)_2\ S\ O$

All chemicals were of BDH grade.

3.1.3: Dimethylol urea (DMU) was prepared by reacting one mole of urea (60g) and two moles of 37% formaline (170.3g) for fifteen hours at pH of 7-8 and temperature of 28°C. The system was buffered with small quantity of monosodium -dihydrogen-phosphate. The syrupy precipitate was filtered, washed thrice with absolute alcohol and vacum-dried at 40°C.

3.2 Experimental Methods:

3.2.1: Pretreatment:

(a) Alkali Scouring: fabric was given mild scouring with 4% sodium hydroxide at bath temparature of 95°C for one hour, rinsed thoroughly with hot water and then cold-water washed until phenolphthalein test indicated absence of alkali.

(b) Bleaching:

Recipe':

Liquor Ratio 20:1

Weight of 20 volume Hydrogen peroxide - 74.4g.

Weight of fabric-186.0g

Weight of sodium silicate-93.0g

Weight of sodium carbonate-186.6g

Weight of Teepol (surfactant) 186.6g

The scoured fabric was open-kier bleached using the above formulation at a pH of 11.4 and temperature of about 85°C for seventy minutes. Bleached sample was first washed with hot water and then rinsed in running cold tap water for 2 minutes and finally dried at room temperature.

(c) Mild Acid Scouring:

The bleached sample was washed with 0.1% acetic acid solution, washed with distilled water and finally dried at room temperature.

3.2.2: Crease - Resist Treatment Method

The treatment method is similar to the Tootal, Broadhurst, Lee (or TBL) process which in essence is based on impregnating the cellulosic material with 5-16% aqueous solution of N-methylol urea resin and a latent-acid catalyst. In the present work this was accomplished by introducing the fabric into the formulation, waiting for some 30 minutes, with occasional working, removal from solution, pressing over a hand roller for four times. The treated sample was dried in a Gallenkamp size One BS Model-OV-16

oven for 6 minutes at 110°C. The dried sample was then cured at 150°C in same hot-air oven for 4 minutes.

The cured sample was given very dilute sodium carbonate afterwash, followed by a copious rinsing in distilled water. It was then dried at room temperature.

3.2.3: Conditioning:

All treated samples were conditioned for 24 hours in an atmosphere of about 65% r.h. and temperature of 25°C before any tests were made. This is necessary because atmospheric conditions are known to affect the properties of cotton materials. As a control, untreated fabric was also made to undergo all the washing, drying, exposure to curing temperature and conditioning.

3.2.4: Method of Test for determining Crease Recovery Angle.

The shirley crease Recovery tester was used to determine the crease recovery angle. The sample was folded in two and subject to a load of 2kg for 3 minutes. The load was removed and the fabric allowed to recover for a further 3 minutes;

the protractor of the crease recovery tester being shifted continuously to monitor the crease recovery angle at any given instance (ASTM 1295-67). At the end of this latter 3 minutes; the maximum recorded angle was noted. This was done for both the warp and the wetf directions and in each case two measurements were taken. The average values of the CRA for warp and weft were added for the particular sample. It is worth noting that in cutting out the test samples, care was taken to test same yarns in both warp and weft directions, so as to minimise variations in fabric properties arising from yarn and fabric constructions. The size of each test sample was kept as constant as practicable at 5cm length and 2,5cm width. Only dry crease recovery measurements were made.

3.2.5: Determination of Mechanical Properties:

(a) Breaking Load and Extension - at - Break percent.

Instron Table Model "1026" at crosshead speed of 100mm/min. and chart speed of 200mm/min. was used to measure the breaking load and extension-at-bread %. The gauge length was 5cm. This test was done for yarn as well as for the fabric. The results were expressed in specific stress units and N/m^2 respectively, and % extension at break % .

(b) Cylic Testing:

Using same Instron tensile testing machine, the effect of cyclic loading was performed only for the yarn using a gauge length of 5cm and chart to crosshead speed ratio of 5:1 and at maximum strain level of 8.5%, when rupture did not occur. The experiment was performed on the control sample and the specimen that showed maximum crosslinking based on the achieved CRA. The duration of action at each specific strain was 30 seconds and the recovery time from the start of unloading was 60 seconds.

·3.3.1: Thermal Analysis

Perkin - Elmer DSC-2 Differential Thermal Analyser was used. Five milligram samples were encapsulated in aluminium pans and samples were scanned at heating rate of 20°C/min. and range of 20m cal/sec. Scanning was done to beyond 600°K so as to include the known charring temperature of cotton cellulose.

3.3.2: Determination of Bound Resin

The treated samples were stripped in a Soxhlet extractor, using 0.2% hydrochloric acid for four-and-half hours at the boil. The amount of resin bound on to the fabric was determined.

3.3.3: Determination of Residual Formaldehyde by the "Sealed Jar" Method.

An accurately weighed resin-treated specimen was suspended by means of a thin aluminium foil over 50ml of distilled water. The jar was tightly covered and then left in an oven at 49°C for the sample to incubate for 20 hours. The jar was then removed from the oven, cooled for 45 min. and carefully opened to remove the sample. The jar was gently shaken so as to bring all condensed water/formaldehyde droplets at the sides of the jar in contact with the rest of the solution.

5ml of the solution was withdrawn and mixed with another 5ml of Schieff's reagent and the colour allowed to develop for 30 minutes. Reading in percentage transmittance were obtained using the Baush and Lomb Spectronic 20 at a wavelength of 550mμ. From a

calibration curve, the corresponding amount of formaldehyde in 5ml of the solution was determined and hence the total quantity of released formaldehyde for the sample weight. Since the coloured complex is not very stable, for each 5ml of solution two readings at interval of 5 minutes were taken. Further, for each specimen, three different 5ml solutions were withdrawn.

Calibration curve was constructed as follows:- 3.8ml of 37% formaldehyde was diluted with distilled water to make a litre solution. This gave 1500 ppm solution. With this standard, solution of 1 ppm,, 2 ppm,, 3 ppm,,and 4 ppm,, were prepared. Transmittance readings for these latter standard solutions were taken and the calibration curve drawn.

3.3.4: Abrasion Test

This was carried out with a flat abrasion tester. Test samples were abraded for 30 minutes using a speed of 30 cycles per minutes and a weight of 3kg.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Effects of Concentration of Padding Bath on Fabric Crease Recovery:

As noted in section 2.2.1, the crease recovery achieved by any given resin depends among other factors upon the concentration of the resin in the padding bath. However, the relationship between the quantity of the crosslinker in the bath and the wrinkle recovery improvement is neither completely linear nor exponential. There is always a limit to the extent of crosslinking and hence the crease resistance achieved. This is observed in Table I where there is a gradual increase in crease recovery angle with moderate DMDHEU resin concentration. From 2.1.1 It would be appreciated that under same catalyst concentrations and swelling conditions temperature and time of impregnation, the rate of diffusion of the reagent molecule unto the surface and its penetration into the matrix of the substrate contribute significantly to the quantity of the molecules available for crosslinking reaction. In the type of system under consideration the Fick's Laws hold:

$$J = \frac{DdC}{dx} \quad \text{--- (1)}$$

TABLE 1

Effect of DMDHEU resin concentration on some properties of resin-treated cotton fabrics

Sample Code	% Resin	CRA degrees	Yarn Specific stress g/tex	Fabric Breaking Load $N/m^2 \times 10^8$	Yarn % Ext. at Break %	Fabric % Ext. at Break %	Amount of Bound resin by stripping (g)	Glass Transition Temp ^{o}C Tg	Charring Temp ^{o}C	CRA ^{o} after stripping
		148	14.68	134.55	14.64	25.46	0.000	88	356	-
A	2	152	12.19	146.3	14.10	23.99	0.0065	95	364	141
B	4	166	14.38	116.97	13.70	24.53	0.0078	99	383	159
C	6	183	14.35	94.44	14.00	22.66	0.0111	89	381	174
D	8	186	11.08	114.53	13.20	22.26	0.0162	85	383	148
E	10	183	12.21	124.78	13.0	24.25	0.0132	87	376	170
F	12	174	13.55	105.56	15.15	22.66	0.0215	90	380	149
G	14	212	11.23	111.79	13.40	20.66	0.0161	91	380	169
H	16	196	7.23	113.43	12.13	20.26	0.0168	90	379	132
I	9	212	12.71	121.43	12.30	22.93	0.0264	87	380	132

TABLE II

Effect of DMU resin concentration on some properties of resin treated cotton fabrics

Sample Code	% Resin	CRA°	Yarn Specific Stress g/tex	Fabric Breaking Load $N/m^2 \times 10^6$	Yarn % Ext at Break %	Fabric % Ext at Break %	Amount of Bound resin by stripping (g)	Glass Transition Temp° Tg °C	CRA° after stripping
A	0	148	14.68	134.55	14.64	25.46	0	88	-
B	2	173	13.36	114.87	13.70	22.00	0.0144	89	130
C	4	200	12.92	125.41	11.60	21.40	0.0363	91	117
D	6	175	9.47	117.48	13.60	21.73	0.0432	90	153
E	8	219	10.03	115.56	11.75	22.27	0.0565	91	134
F	10	206	10.20	89.98	14.82	25.60	0.0557	88	131
G	9	222	8.77	95.57	11.56	22.66	0.0509	90	148

Relationship between CRA and the concentration of the paddin bath.

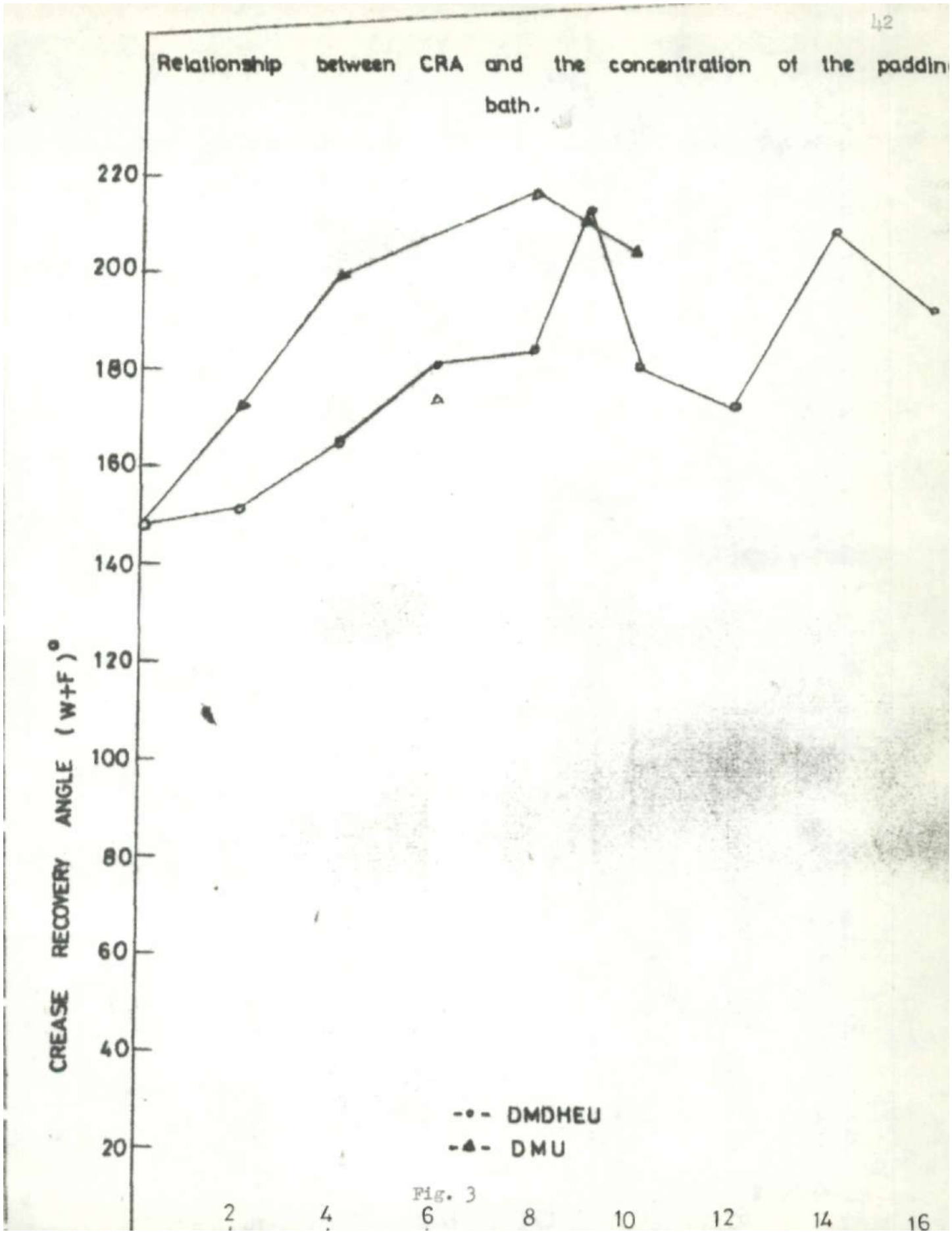


Fig. 3

Where J = diffusion flux or rate of accumulation of the reagent per unit area of the reference plane oriented normal to the X-axis;

D = diffusion coeficient

C - local reagent concentration at a point distance X from the origin of coordinates.

A second differential of Equation (1) gives Fick's second law, that is, Rate of accumulation $\frac{dc}{dt} = \frac{Dd^2C}{dx^2}$ (2)

What emerges from this is that at reasonable concentration levels, the rate of accumulation of the crease resistance reagent on the surface of fabric and hence penetration and subsequent crosslinking reaction depends to a large extent on the concentration of the padding bath. This perhaps explains why, with increasing bath concentration higher crease recovery was recorded as shown in tables I and II Fig.3.

The observed maximum value in the crease recovery angle for a certain resin concentration may be attributed to the gradual increase in adsorption tenable up to a point for a given resin-fabric system.

The initial adsorption concentration relationship can be described by the usual Langmuir type of equation. Beyond a specific concentration point however, there is a sudden decrease in adsorption. This point would signal the onset of molecular aggregation.

It is a truism that, for the molecules to participate in the crosslinking reaction, they must be of diffusible size. Aggregated molecules are thus excluded from taking part thus increasing the concentration of the padding solution indefinitely may not result in higher crease - recovery. Further, the crease recovery improvement may not necessarily be directly proportional to the number of crosslinkages in the fibre, but to the degree of restraint on slippage between the fibre elements given by the treatment, Consequently the initial crosslinkages should exert a greater effect per crosslink than the subsequent ones. This, therefore, introduces an upper limit to improvement attainable because once an amount of reagent enough to immobilise the fibre elements has been incorporated, additional crosslinages cannot further improve the wrinkle recovery of the fibre. This optimal resin concentration is known to correspond to a situation where every 25th available anhydroglucose unit is intermolecularly crosslinked.[25]

In terms of maximum crease-recovery angle for DMDHEU and DMU resins used in this experiment, the optimal concentration is 9% of the bath solution. As shown in Fig. 3 beyond this 9% resin concentration little improvement is achieved and economic considerations as well as deterioriation of other properties of the treated fabric do not justify further increase in resin concentration.

It is noted that for different agents, in this case DMU and DMDHEU, the crease recoveries achieved for equal amount of precondensate concentration are not the same; this is true even when one uses "molar add-ons". Again, it is appreciated that for two unidentical molecules, the rates of diffusion, penetration and crosslinking reactions cannot be unequivocally the same. The differences may arise from the sizes and orientation of the molecules, the constituent atoms and of course, the general chemical reactivities or otherwise of the functional groups they bear. Some compounds are less reactive with cellulose than others. The less reactive ones are more likely to form a large number of side groups on the cellulose chains than the reactive ones; that is, for the former there is, as it were, wastage of material. In the case of DMU and DMDHEU, it is observed that for equal concentrations, higher crease recovery angles are generally recorded at each stage by DMU. This might be explained

in terms of the smaller size of DMU as compared to DMDHEU, which perhaps makes for better diffusion, penetration etc of DMU. The chemistry of the two compounds shows DMU to be more reactive than the cyclic DMDHEU. For the acid catalysed crosslinking reactions under review the presence of the basic nitrogen atom beta to the ether oxygen renders DMU more reactive than the less basic DMDHEU N-atom. This perhaps contributes significantly to the observed differences in crosslinking at any given resin concentration. However, since crosslinking and hydrolysis of the cellulose-N-methylol reaction are reversible, the basic nitrogen in DMU would necessarily make such linkages less durable to acid hydrolysis. This seems to agree with the observations in Tables 1 and 11 where using similar stripping conditions, the DMU treated fabrics lost virtually all the resin whereas DMDHEU crosslinked sample retained residual crosslinkages even under drastic stripping conditions.

Nevertheless, considering CRA per se DMU and DMDHEU would be recommended as the results from the present work, though slightly lower, compare somewhat favourably with other results. [72,73,74 & C]

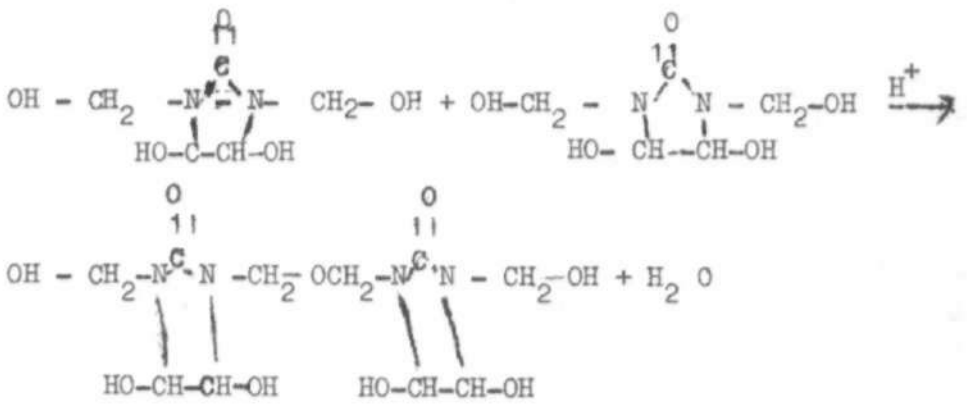
The slightly lower values may be due to the mode of impregnation. Whereas the other workers [72,73,74] used padding mangles which give higher expression, ours here was done slack by simple immersion.

TABLE III

Effect of catalyst concentration on properties of 9% DMDHEU resin treated cotton fabric.(Bath was prepared and used after 5 days to verify the effect of ageing)

Catalyst Concentration $MgCl_2$	Specific Stress g/tex	$CR^{\circ}A$ $(W+F)^{\circ}$	Fabric Breaking Load $N/m^2 \times 10^6$	Yarn % Ext. at break %	Fabric % Ext. at break %	T_g °C
0	14.68	148	134.55	14.6	25.46	88
10	6.85	155	99.99	8.9	25.06	79
15	8.82	156	103.07	13.6	21.86	77
20	7.58	162	97.68	8.36	23.06	78
25	7.76	159	118.52	9.2	21.68	80
30	6.05	159	140.36	11.44	26.13	80

It will be noted also from Table III that where the padding solution is stored for some time (here five days), before application, there is a drastic reduction in the wrinkle-shedding obtained. It is known that though DMDHEU - catalyst system is relatively stable and keeps better than other resin recipe, yet there is always the instance of self-polycondensation if left for a considerable length of time. The result of this is that dimers, trimers, tetramers etc are formed with consequently progressive losses in crosslinking sites. This thus reduces the potency of such a system of a crease recovery agent.



Dimer

TABLE IV

Effect of catalyst type and concentration on fabric properties

Catalyst	% Concentration	CR°A (W+F)°	Yarn Specific stress g/tex	Fabric Breaking load N/m² x 10^6	Yarn % Ext. at Break %	Fabric % Ext. at break %	Amount of Bound Resin	T °C g	CRA° after stripping (W + F)°
Magnesium Chloride hexahydrate	0	148	14.68	134.55	14.60	25.46		88	
	10	150	13.12	134.83	13.40	23.99		90	
	15	163	15.13	156.48	13.70	25.33		84	
	20	176	9.01	130.4	15.70	26.66		91	
	25	196	-	-	-	-			
	30	222	12.70	121.43	12.60	22.93		87	
Zinc nitrate hexahydrate	0	148	14.68	134.93	14.60	25.46	00	88	148
	10	140	8.22	122.93	9.33	26.40	0.0224	93	142
	15	155	11.64	142.05	13.07	24.60	0.0644	86	133
	20	180	13.25	96.11	13.06	23.82	0.0665	82	141
	25	167	7.93	94.13	14.8	24.54	0.0675	87	143
	30	176	8.89	105.53	10.7	24.00	0.0786	87	143
Dimethyl Sulphoxide	0	148	14.68	134.93	14.60	25.46	0	88	148
	10	144	11.51	128.47	17.70	24.93	0.0532	84	103
	15	132	11.92	103.88	16.3	21.33	0.0440	86	98
	20	130	15.43	130.24	16.3	23.06	0.0390	85	98
	25	129	14.79	118.96	16.60	24.80	0.0407	93	108
	30	143	12.2	131.71	11.5	23.99	0.0652	82	109

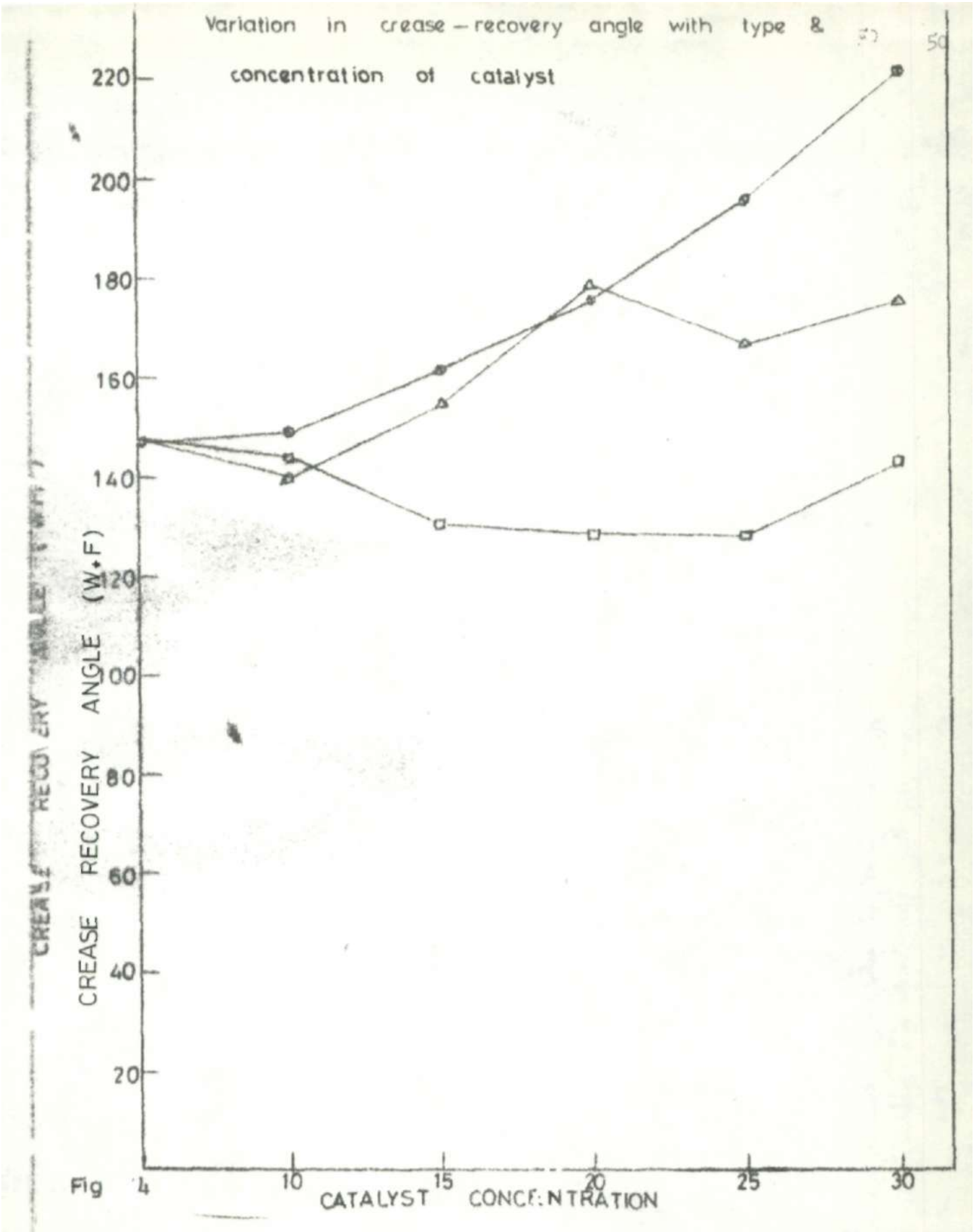

Variation in crease – recovery angle with type & concentration of catalyst
CREASE RECOVERY ANGLE (W+F)
220
200
180
160
140
120
100
80
60
40
20
4
10
15
20
25
30
CATALYST CONCENTRATION

Fig 4

Further, with each polymerisation, the resin gets bulkier and of course less diffusible. These may be the reasons for the reduced crosslinking observed in the present work. However, as evident from the results, some degree of crease recovery is still achieved and the fact that they intend to aqualise seems to indicate that for a given resin/catalyst combination, there is a ceiling to self-polycondensation at same temperature conditions no matter the catalyst concentrations; so long the amount of the precondensate remains constant.

DMDHEU was chosen specifically for this experiment because it is known to be more stable than the other resins such as dimethylol urea. In fact, in the latter case, sometimes it becomes expedient to stabilise it in form of the methoxy-urea. However, the active compound is usually regenerated at the curing conditions.

4.2 Effect of type and concentration of catalyst on the CRA° of cotton fabric:

Crease recovery reactions are often carried out in the presence of acids or acid-liberating compounds whose function is supposedly to provide the acidity necessary for the cross-linking reactions

the general mechanism of the catalysis is already given in 2.4.2

From Table IV and Fig. 4 certain deductions are apparent. In the case of the latent acid catalysts, magnesium chloride and zinc nitrate, there is a gradual increase in crosslinking with catalyst concentration in the padding solution. This can be explained in terms of rate of diffusion of the resin molecules into the fibres, that is there is enhanced adsorption of crosslinking molecules with increases in catalyst concentration. This results from the modification of water structure by the metal ions. Dissolved ions are assumed to carry around each of them a number of rigidly bound water molecules.[73] The hydrated ions by virtue of its strong electrostatic field, forms an envelope of a moltern zone in which there is more orientation disorder than in the hydration zone as well as in bulk water. When cellulose is immersed in water, the water initially adsorbs onto the cellulose surface, forming a monolayer of strongly bound water molecules. The energy of interaction of this water with cellulose is of the same order of magnitude as for hydrogen bonding. In a system containing cellulose, metal ions water and crosslinking agent, the charged ion probably disturbs the monolayer of water on cellulose surface.

The disturbance is expected to increase with the concentration of the metal ion in solution and since this disturbance brings the crosslinking agent more in contact with surface: it follows that diffusion, penetration and crosslinking reactions would increase with the quantity of the ions in solution. This perhaps explains the observed rise of crease recovery with catalyst concentration.

It is seen from Fig 4 that at almost all the concentrations verfied mangesium chloride hexahydrate gives higher crosslinking than zinc nitrate hexahydrate. Perhaps the reason may be due to the higher electronegativity of magnesium which means it would attract more water molecules to itself in solution than the larger zinc ion.

TABLE V

Properties of yarns withdrawn from 9% DMDHEU resin treated fabrics in the presence of various catalysts

	Magnesium chloride 30%	Zinc nitrate 20%	Dimethyl Sulphoxide	
			20%	30%
Specific stress g/tex	12.70	13.25	15.43	12.22
Extension at break % (Yarn)	12.6	13.06	16.3	11.5
CRA° (W + F)° fabric	222	180	143	
CRA° for untreated (W+F) sample	148.0	148.0	148.0	148.0

TABLE VI

(DMSO)

% Resin DMDHEU	9	10	11	12
CRA° (W+F)	130	139	141	137

This indicates that magnesium ion provides more opportunity for the precondensate molecules to come into closer proximity with the fibre and hence better chances of crosslinking. Further, in terms of acidity function, again, magnesium chloride will provide a lower pH value than zinc nitrate and since the crosslinking reactions are acid-catalysed, then this gives added credence to the observations in fig. 4.

It is known that the strength losses of cotton fabrics given a durable press treatment with N-methylol reactant and magnesium chloride or zinc nitrate catalysts arise from molecular degradation caused by the catalyst in addition to crosslink embrittlement caused by the crosslinks. This implied that if crosslinking is achieved in the absence of an acid liberating catalyst or in the presence of a metal salt-supplying cation (other than proton) necessary for the crosslinking reaction, at least those strength losses due to molecular degradation of cotton cellulose can be avoided. DMSO was tried as one such catalyst but the data indicate poor crosslinking performance. More work is required to investigate the possibility of using non acid catalysts for the resin finishing of cotton cellulose.

Changes in the breaking load of same yarn with type & concentration of resin bath

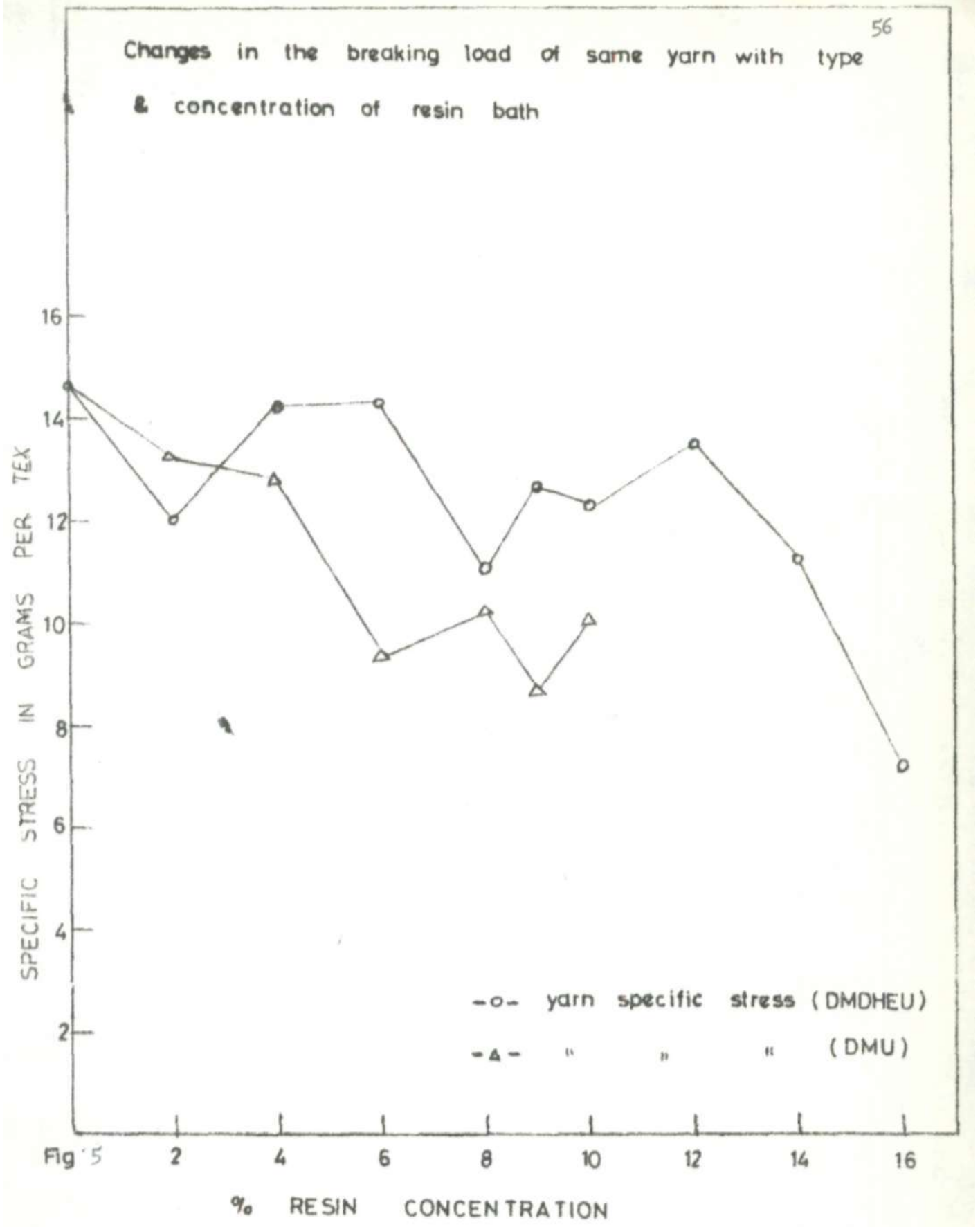


Fig 5

Changes in fabric breaking load with type & concentration of resin

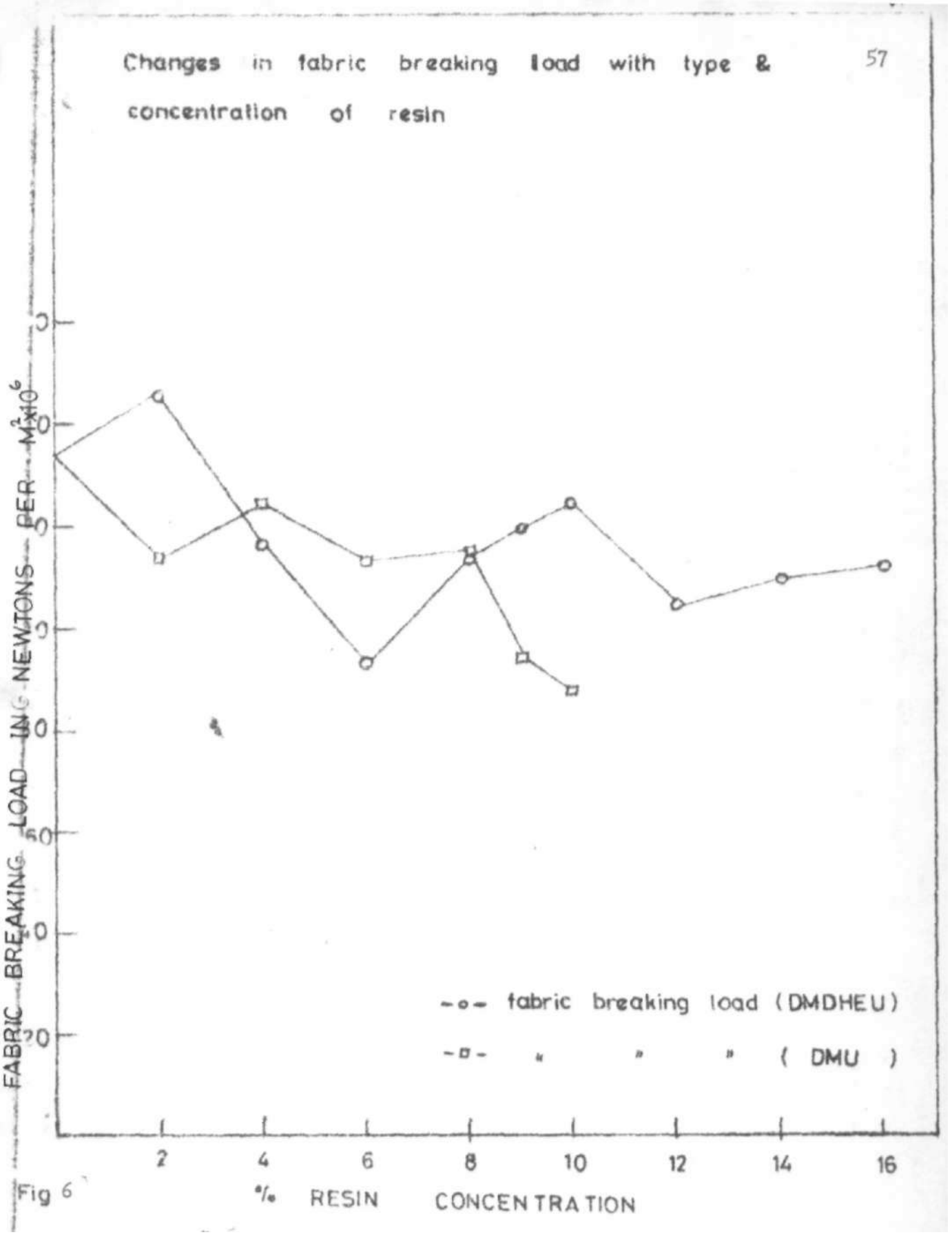
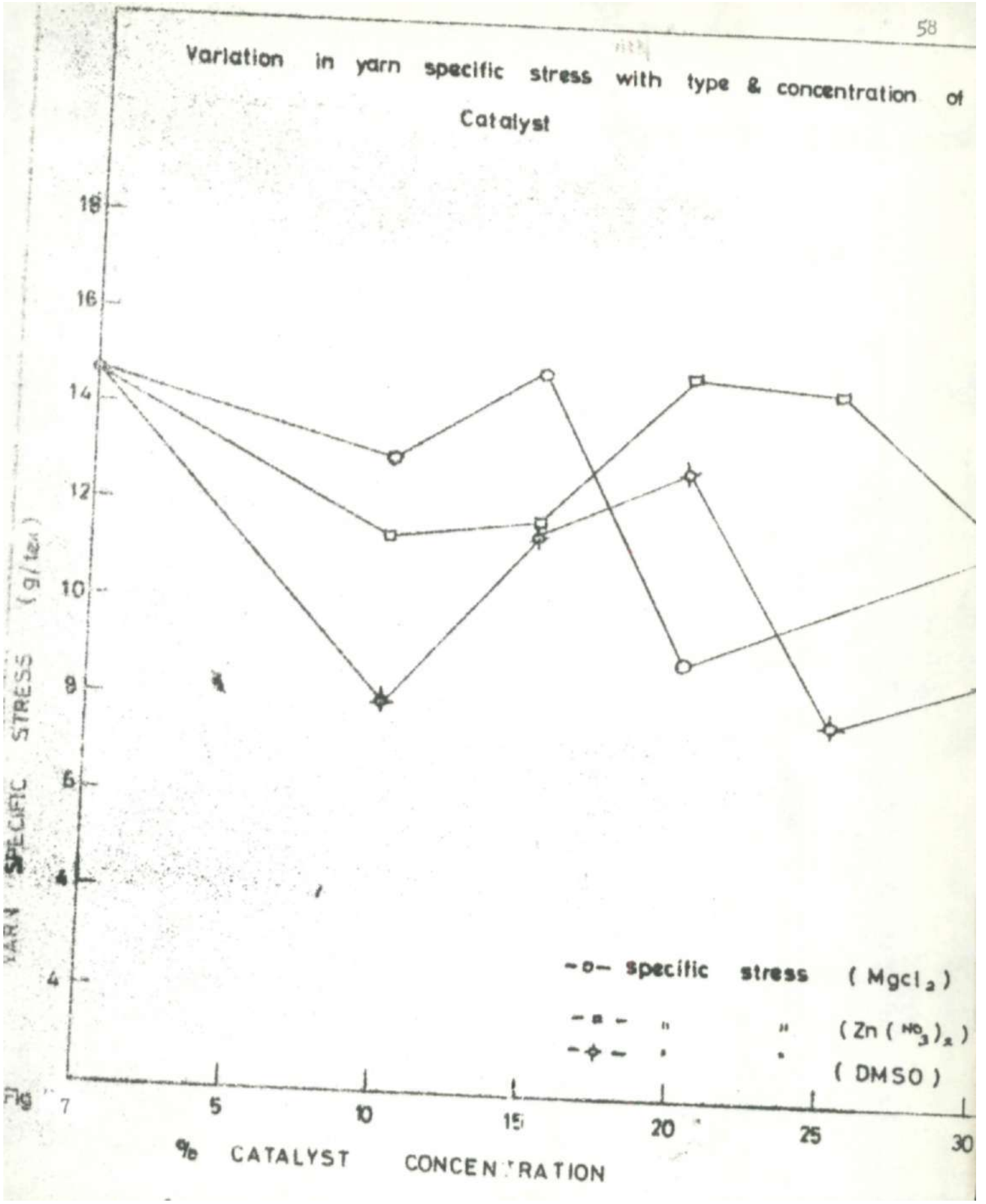


Fig 6

Variation in yarn specific stress with type & concentration of Catalyst



Fig

Further since DMSO is a dehydnating agent, it would be possible to postulate that crosslinking reactions are not feasible when the fibres are in their collapsed state. In fact, swelling enhances crosslinking. For the latter experiment no advantages were recorded even at increased resin concentrations (Table VI)

4.3: Achievement of Resiliency and Losses in Tensile Properties after Resin Treatment:

It is obvious from Table 1 - V and Figs 5-7 that whenever there is an increase in resiliency of the cotton cellulose after resin treatment, this is invariably followed by losses in tensile strength. This is evident from the yarn and fabric strength values before and after resin treatments. In general, the strength losses increase with the rise of resiliency achieved, although the relationship is not strictly linear.

With the two resins under consideration the extent of deteroriation in tensile property is, again, not identical. In almost all the resin concentrations, the fabric treated with DMU suffered more losses than that crosslinked with DMDHEU.

Since a part of strength losses in wrinkle recovery application is due to crosslinking embrittlement and since it has been noted that for any specific resin concentration, DMU forms more crosslinks, then the observed higher losses due to DMU treatment appears to be consistent. It is known that DMU treated fabric, "splits" more free formaldehyde than DMDHEU crosslinked fabrics. At conditions of cure, that is, at 150°C, part of this free formaldehyde further-crosslink with the cellulose molecules. Formaldehyde linkages are more taut than those of DMU or DMDHEU and of course more effective as crease recovery device, but at the same time it results in higher tensile strength losses. This latter observation might well have contributed to the differences in tensile properties of the two fabric samples.

For N-methylol crosslinkages of cellulose, more than one half of the strength losses arise from acid hydrolysis.[55] DMDHEU-cellulose bonds are less susceptible to acid hydrohysis than DMU-cellulose links. Furthermore, the resultant higher reduction in degree of polymeriasation in the case of DMU also vindicates the above mentioned observations.

4.3.1: Effects of Type and Concentration of Catalysts on the Tensile Properties of the fabrics/yarn

Since crosslinking increases with the concentration of the catalyst for a given quantity of resin in solution, the decline in tensile properties, to some reasonable extent follows that trend ; that is the higher the catalyst concentration, the more the tensile strength losses observed; details are shown in Table IV and Figs 5-7 This is particularly the case with magnesium chloride and zinc nitrate catalysts which are acid-liberating. Moreover, the hydrolytic potential of the liberated acid is expected to rise with the concentration of the protons in the soultion, therefore the higher the catalyst concentration, the more hydrolysis will be evidenced by the cellulose fabric. However, more subtleties are involved and in the case of zinc nitrate, it is known that what actually exists in practice could be solution of zinc ions in cellulose solvent. Under such conditions the zinc nitrate easily decomposes to yeild nascent oxygen and oxides of nitrogen at the curing temperature. These gases have detrimental effects on cellulose and generally result in more degradation of cellulose molecule than either mere crosslinking embrittlement or acid hydrolysis. If strength losses are due only to hydrolysis and crosslinkages, magnesium chloride catalyst would be expected to give less retained strength.

From our observations here, the reverse appears to be the case. As stated earlier, in the presence of DMSO as a catalyst little or no crease recovery is achieved, that is, little, if any crosslinks are formed. In fact there is observed decrease in the natural resilience of cellulose. It is possible that at the high temperature of cure oxidative degradation also contributes to some significant extent. However, there is more retained tensile strength in the case of $M_g Cl_2$ than either for DMSO or Zn $(NO_3)_2$ while the latter appears most culpable. It can also be seen that for a given catalyst there is optimal catalyst concentration with regards to resiliency achieved at a specific resin value, and retained strength (Table V!).

Cellulose fibres are already laid as almost taut parallel rods. With crosslinking, plastic deformation is inhibited. This results in reduced extensibility of the composite fibres. This means that extensions at break % of the fabric, yarn etc would decrease with crosslinking density. Details of the results are given in Tables 1,II& VI These results show progressive decrease in extension-at-break % of the . cotton cellulose with improvement in the crease recovery angle. Nevertheless, the difference between the treated and the untreated fabric do not appear significant, which in terms of usefulness of the

Using same yarn, but different resins: changes in % extn at break with resin concentration.

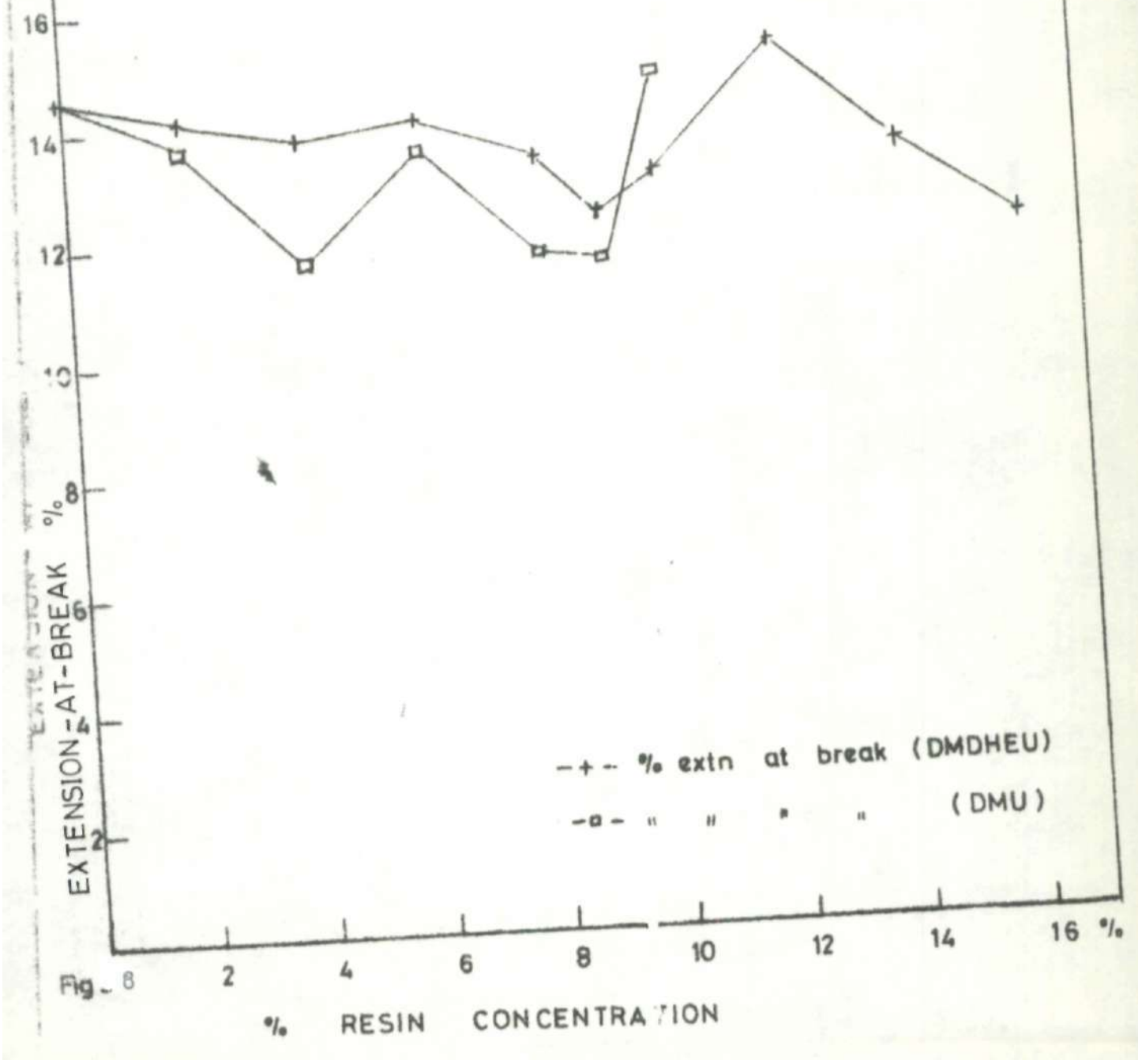


Fig. 8

Effect of type & concentration of catalyst on yarn extn. at break.

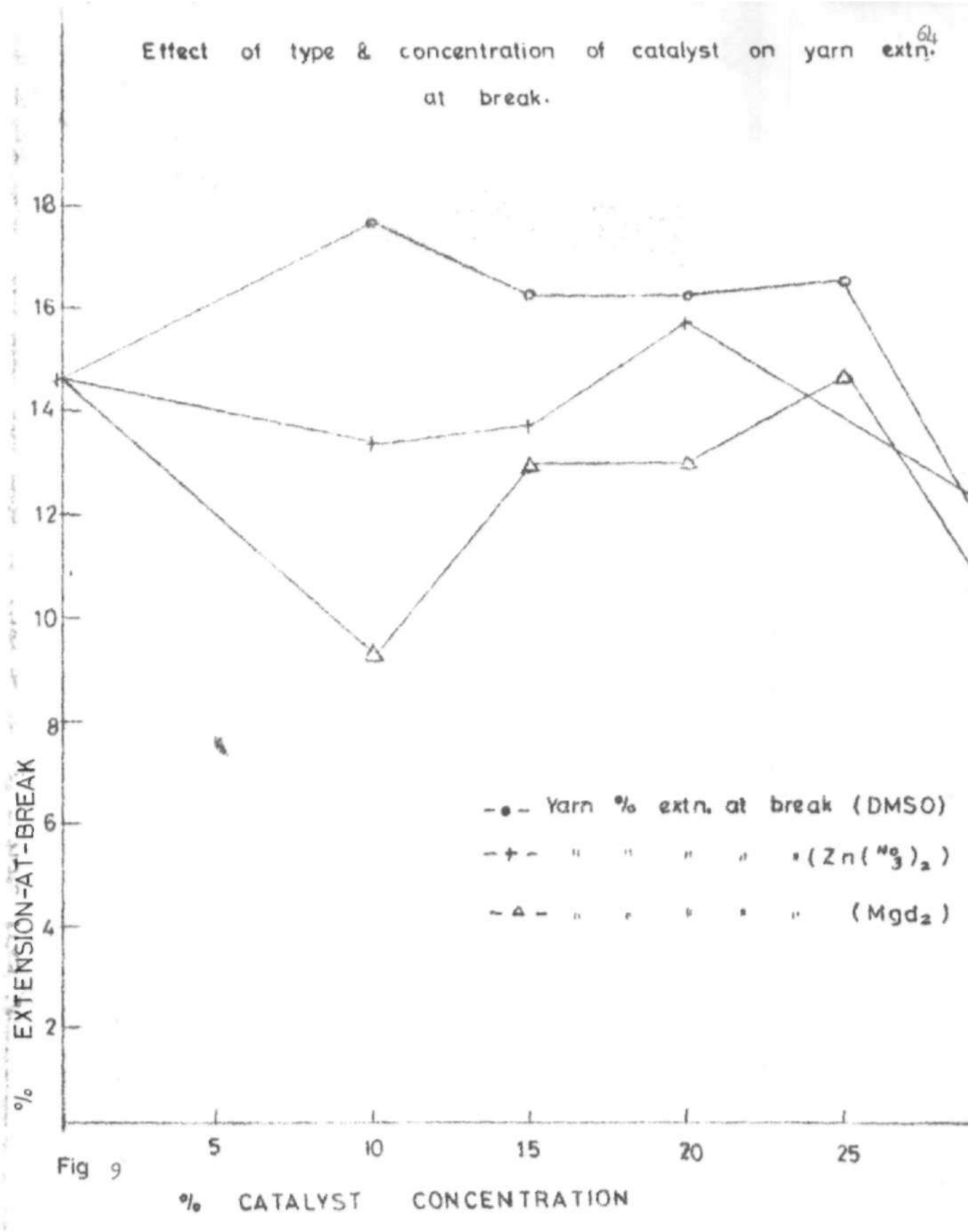


Fig 9

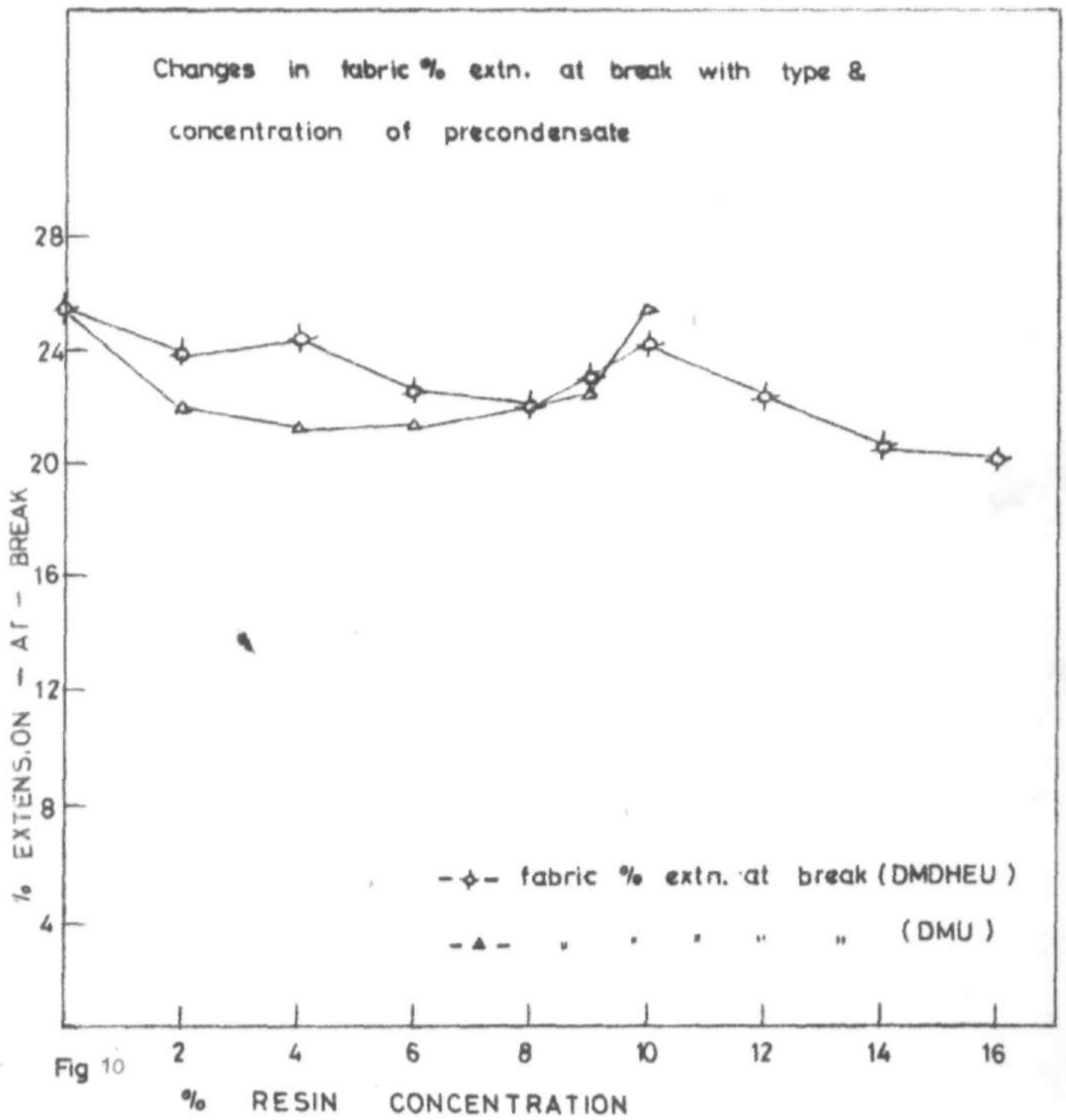

Changes in fabric % extn. at break with type & concentration of precondensate
% EXTENSION AT BREAK
28
24
20
16
12
8
4
-◇- fabric % extn. at break (DMDHEU)
-▲- " " " " " (DMU)
2
4
6
8
10
12
14
16
% RESIN CONCENTRATION

Fig 10

material is an advantage. As for DMSO catalyst however, there is an appreciable gain in fabric extensibility. The reason for this must be due to the catalyst actin as a "lubricant".

4.3.2: Stability of DMDHEU resin and Properties of fabric treated with Aged resin.

It is expected that ageing the crosslinking recipe would result in the formation of longer resin-cellulose linkages. Longer linkages would result in the fabric suffering lesser tensile strength losses, since longer crosslinks would permit molecular slippages and hence better load distribution and higher elongation.[24 & 76] In the present work, the deteroriation in the breaking load observed for the fabric in Table III is more compared to the data in Table IV; which should not have been the case. The plausible reason for this discrepancy may be found in the greater size of the polycondensate after dimerisation etc., which may have resulted in a greater fraction of the resin crosslinking at the fibre surfaces. Surface resins increase fabric stiffness and consequently its brittleness. This, perhaps, more than offsets whatever tensile strength retention that would have accrued from longer crosslink bridges.

When the treating solution was shelved for five days before padding (Table IV), there was still noticeable loss in extensibility: inextensibility and brittleness are of course opposite faces of the same coin.

TABLE VII

Elastic Recovery

Cycle	Fabric details	IE^R %	TER %	Load (g)
First	Untreated	50.0	66.10	230
	Treated	58.0	70.0	203
Fourth	Untreated	72.5	74.25	185
	Treated	87.0	90.95	187

4.4 Elastic Recovery (cyclic) tests:

Results of the elastic recovery test of the yarns are given in Table VII. Resination of cotton cellulose enhances its elastic recovery. This observation comforms with the increased crease recovery recorded (Tables I & II, Figs 3-4) after such treatment and further shows that there is a uniform distribution of crosslinks along the cellulose fibre.

The load required to maintain the yarns at constant strain level diminishes with increase in number of cycles. Table VII further shows that there is appreciable decrease in the load after the fourth cycle for the untreated fabric. The smaller change in load between the first and fourth cycles for the treated fabrics indicates reduction in frictional restraint within the fibre structure. It is thus noted that treated cellulose sample responds more readily to mechanical conditioning than untreated ones; as evidenced from the former showing almost complete elastic recovery at the end of the fourth cycle.

TABLE VIII

Results of Abrasion tests and Air Permeability, Pa, values

Sample Code	% Catalyst concentration ($Mg Cl_2$)	Original Wt. of fabric	Pre Abrasion Pa.	Post-Abrasion wt.	Post Abra-sion Pa.	% wt. Loss/min.
A	10	0.3833	0.26	0.3692	2.3	0.04
B	15	0.3813	1.5	0.3730	2.3	0.02
C	20%	0.3883	2.1	0.3728	2.27	0.045
D	30%	0.4384	1.7	0.4476	1.25	0.01

TABLE IX

Results of abrasion test&air permeability values

Sample Code	% Resinconc-n	Original weight of fabric	Pre-Abrasion Air Permeability Pa	Post-Abrasion wt.	Post-Abrasion Pa	% Wt. Loss/min	CRA° (W+F)
C	6%	0.4605	0.42	0.4522	0.41	0.19	183
D	8%	0.4678	1.70	0.4544	2.5	0.03	186
E	10%	0.4706	-	0.4272	-	0.10	183
F	12%	0.4528	0.42	0.4426	0.42	1.02	174
G	14%	0.4718	1.22	0.4413	1.23	0.06	212
H	16%	0.4785	1.23	0.4451	1.25	0.06	196
I	9%	0.4384	1.3	0.4275	1.25	0.025	222
O	0%	0.4520	1.7	0.4476	1.25	0.01	148

Relationship between fabric abrasion-resistance and concentration of the resinating solution

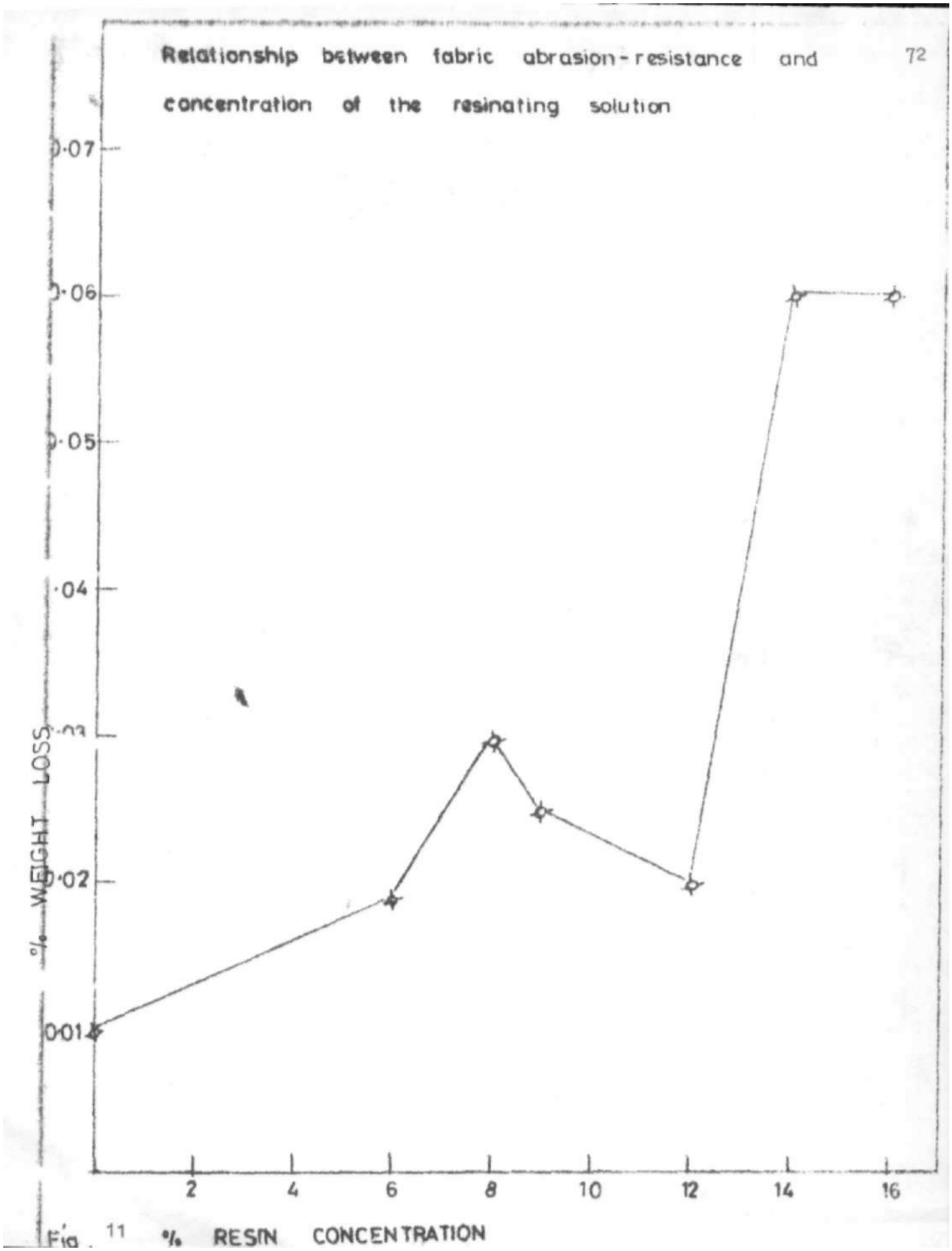


Fig. 11

Abrasion resistance & degree of crosslinking of cotton cellulose

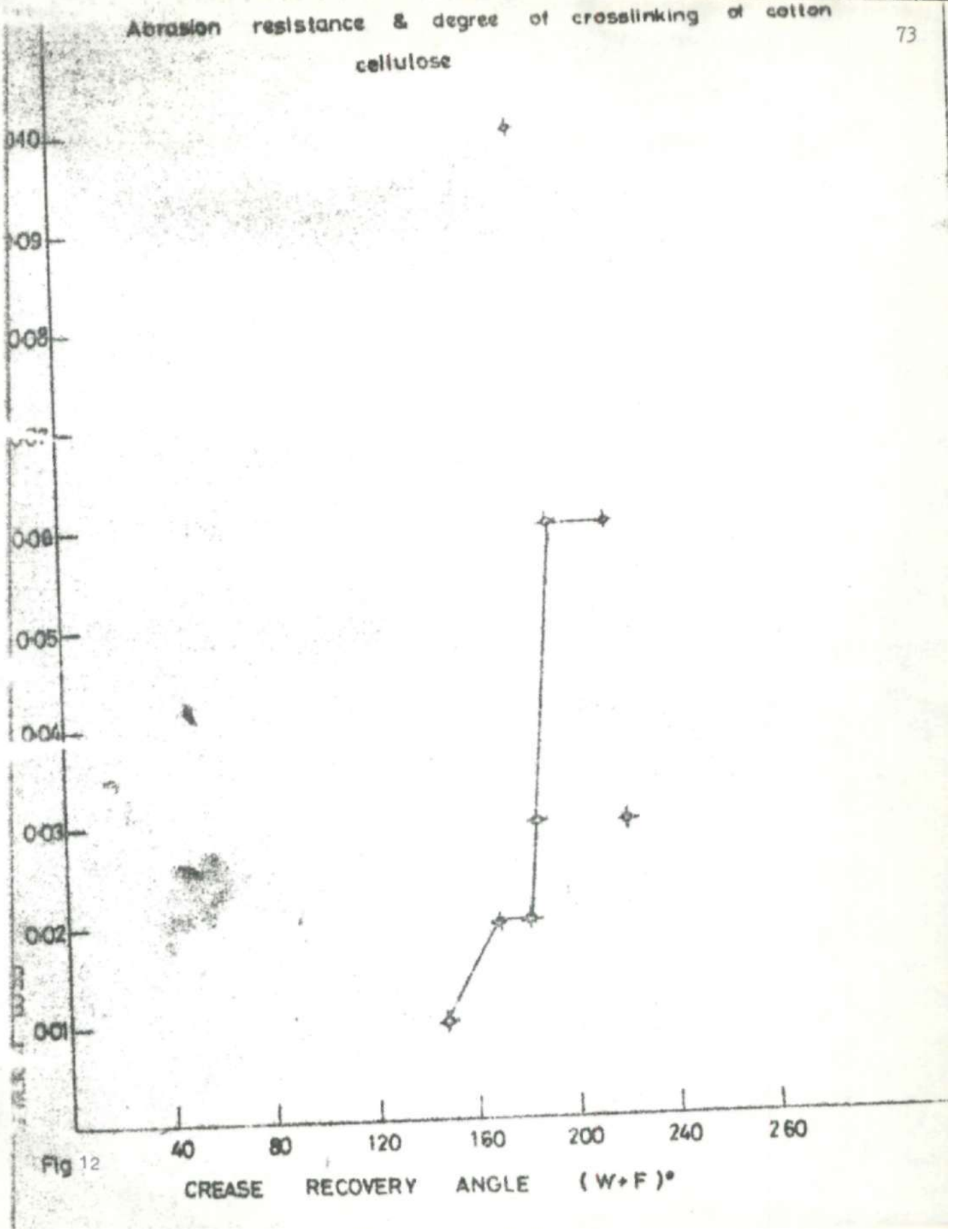


Fig 12

4.5: Abrasion - Resistance by Resinated fabrics

Usually wrinkle-recovery treatment leads to losses in abrasion resistance in cotton fabrics.[92 & 93] This is partly because crosslinking results in the weakening of the fibre molecules as already highlighted and partly due to the fact that it makes the fibres stiff, thereby reducing the fibre extensibility and hence decreasing the chances of load distribution whilst raising inter fibrillar friction.

Data plotted in Figs. 11 & 12 indicate that resination results in reduction of abrasion resistance and it is also discerned that there is some good correlation between deteroriation in tensile properties and susceptibility to abrasion.

4.6: Crease Recovery, Glass Transition and Charring Temperatures: Effects of crosslinking.

Usually crosslinking increases the glass transition temperature (T_g) of most polymers especially when their amorphous content is high. As for cellulose, the rise is not significant (Tables 1-II) and the small increase rapidly levels up; the reason may be due to the fact that the polar nature of the cellulose molecules and the polycrystalline structure of the fibres made the observable T_g much smaller than would have been the case with amorphous or less polar polymers.[75]

However, the observations that no reasonable correlation appears to exist between the degree of crosslinking and the temperature at which the molecules char seem to be in agreement with known facts: the forces between cellulose molecules in dry cotton are so strong that the fibres exhibit neither thermoplasticity, nor second order transition temperature. The amount of energy that would be necessary to break inter molecular bond is perhaps so high that the molecules decompose before second order transition is reached. Similar situations have been observed by other workers.[63,64 &C]

TABLE X

Free formaldehyde values of DMDHU & DMU-resin treated fabrics

DMDHEU				DMU			
(ii) % Resin	Weight of fabric (g)	PPM HCHO on Weight of fabric	PPM HCHO pergram of fabric	% Resin	Weight of fabric	PPM HCHO on wt. of fabric	PPM HCHO per gram of fabric
2	0.7181	57.44	79.99	2	0.5336	173.25	324.68
4	0.3581	97.04	270.99	4	0.4056	341.37	841.64
6	0.4610	176.25	382.32	6	0.4034	383.74	946.10
8	0.4846	135.16	278.91	9	0.4426	329.98	745.55
10	0.4191	92.46	220.62	10	0.4348	355.04	816.56
12	0.4650	200.00	430.11	11	0.4678	349.29	746.67
14	0.4233	97.45	230.21				
16	0.4233	97.45	230.21				
16	0.4088	159.00	388.94				
9	0.3406	146.80	431.00				

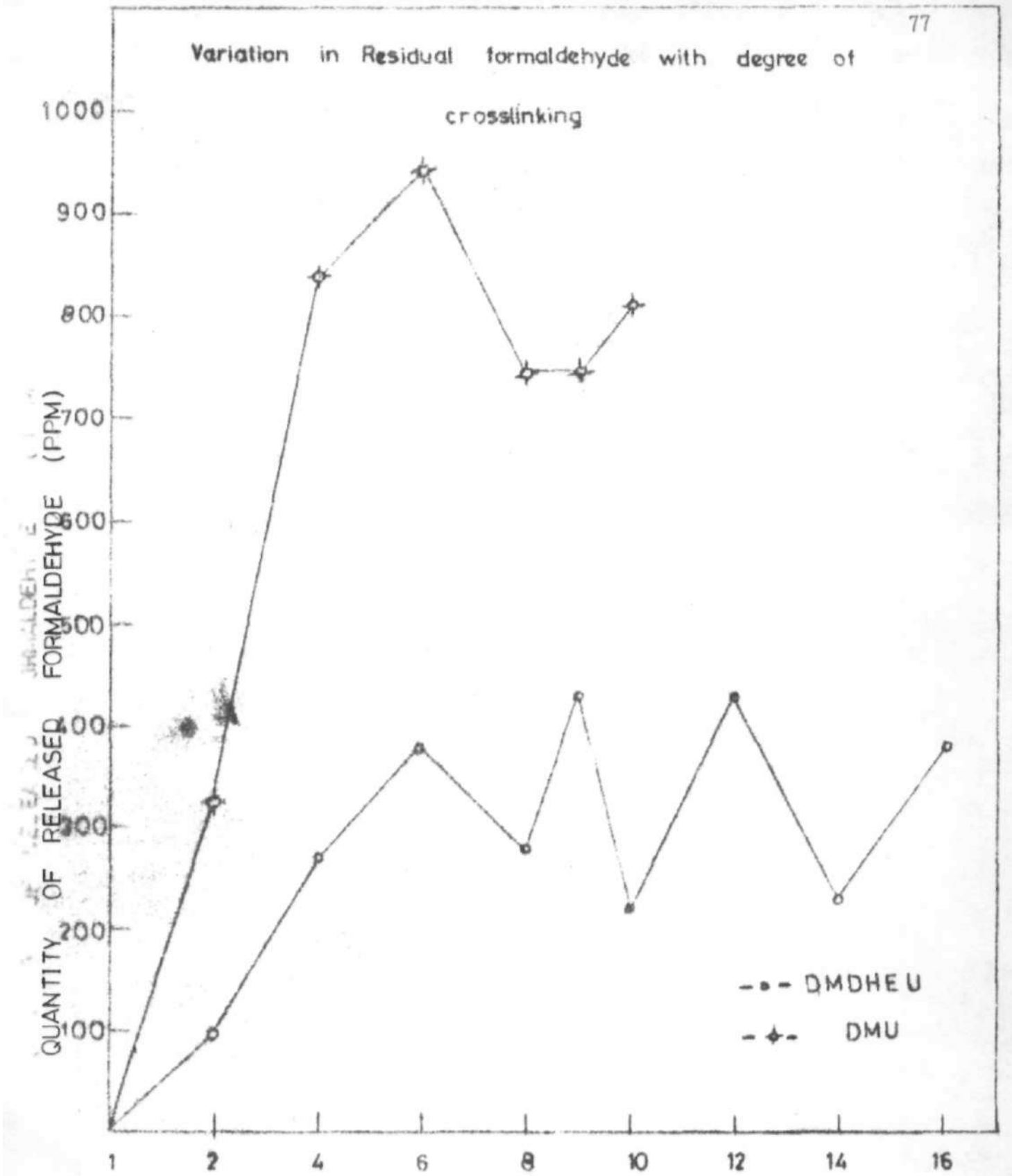

Variation in Residual formaldehyde with degree of crosslinking
QUANTITY OF RELEASED FORMALDEHYDE (PPM)
1000
900
800
700
600
500
400
300
200
100
DMDHEU
DMU
1
2
4
6
8
10
12
14
16
% RESIN CONCENTRATION

Fig 13

Calibration curve for the determination of released formaldehyde by resinated fabric

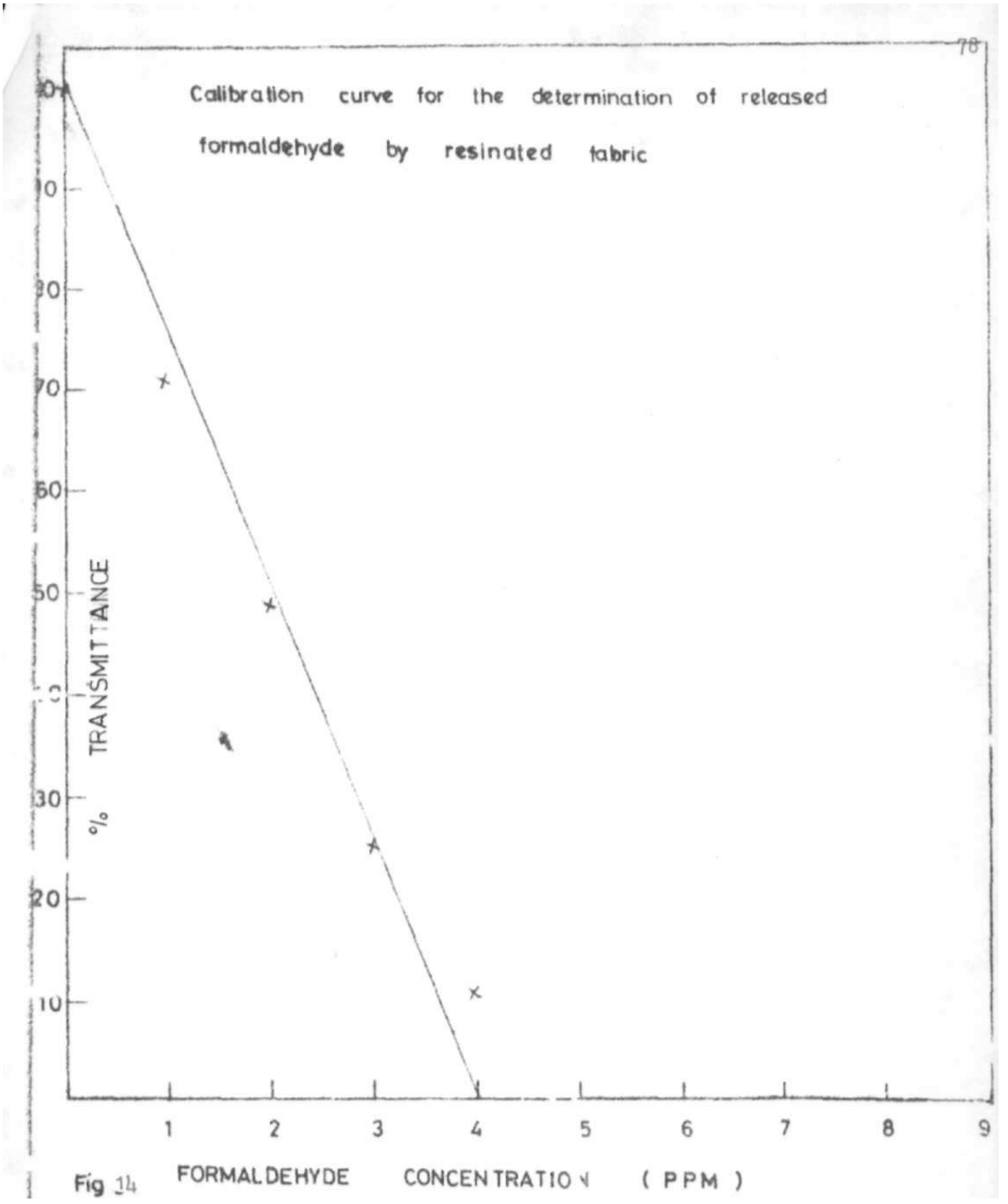
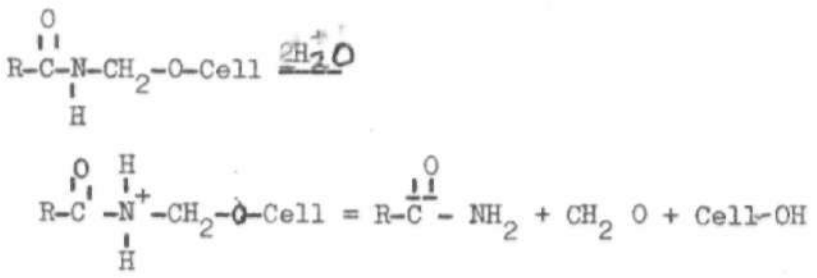


Fig 14

4.7 Formaldehyde Release by Resin treated fabrics:

It is seen from Table X and Fig. 9 that quite a substantial amount of formaldehyde is released by the treated fabrics under warm humid conditions, especially, as acid catalysts have been employed. The residual formaldehyde arises from surface resins as well as from partial hydrolysis of the crosslinks.[78] The mechanism of the releases due to surface resins, as well as those emanating from partial hydrolysis could by postulated as follows:-



It will be observed from Table IX that beyond 6% resin concentration, the amount of split formaldehyde appears to level up. Further, for the two resins under consideration, the quantity released by D.M.U. is considerably higher than that from DMDHEU treated fabric.

If only surface resins were solely responsible, the observations could perhaps not be easily justified. It is worth noting that the values got from our experiments here perhaps do not differ too markedly from other works. [79,80,81 & 82]

4.8 Conclusions:

The following conclusions may be drawn from this work:-

i. Cotton fabrics responded to wrinkle recovery treatment induced by chemical crosslinking with DMU and DMDHEU resins.

ii. The degree of improvement in crease recovery (resiliency) is influenced by the concentration of the padding bath. However, there is a limit to the bath concentrations, beyond which no further increase in crease recovery is achieved, 9% concentration appears optimal.

iii. The achieved CRA varies with the nature, ie., the chemical reactivities or otherwise of the precondensate in question with respect to cellulose and depends to some significant extent on the stability or durability of the crosslinks formed.

iv. The type and quantity of the catalyst employed exerts a lot of influence: the higher the concentration, the better durable press obtained, though, again, for each catalyst, there is an optimum amount in terms of CRA, tensile strength losses, percentage extension at break % etc. In our work here, magnesium chloride concentration of 30% on the weight of the precondensate is most favourable. For zinc intrate, it is 20% though 25% may be recommended, while dimethyl sulphoxide did not enhance CRA of the fabric at all concentrations. Such a catalyst may require the presence of a co-catalyst.

v. In all cases considered, gain in wrinkle shedding is invariably accompanied by deterioration in physical and other properties of the fabric. There is noticeable losses in tensile strength of both the yarn and the fabric. Tensile strength decreases with the degree of crosslinking as well as the catalyst concentration.

vi. For the two resins, DMDHEU treated fabric has higher strength retention than that impregneted with DMU;

vii. Comparing the effect on tensile strength by the catalysts, magnesium chloride has less detrimental effect than zinc nitrate. Though dimenthl sulphoxide resulted in little or no crease recovery improvement, yet there is still decline in the fabric tensile strength. Nevertheless, its effect is intermediate between that of magnesium chloride and zinc nitrate.

viii Crosslinking of cotton cellulose does not change the T_g markedly;

ix. If a padding formulation is shelved for five days (here in case of DMDHEU - catalyst system), Its potency as a crosslinker is adversely reduced, relatively lower deleterious effect on tensile strength is recorded and extensibility is impaired.

x. Fabric treated with N-methylol urea compounds split free formaldehyde under warm moist conditions (fishy odour). The quantity of residual formaldehyde on the fabrics also depends on the treating resin. DMU impregnated sample releases more than the specimen crosslinked with DMDHEU and the quantity depends on the degree of crosslinks on the material.

xi. Resinated yarns are more elastic at any level of deformation than untreated ones.

xii. Crease recovery treatment reduces abrasion resistance.

xiii. It must be appreciated that imparting crease recovery characteristics in cellulose fabrics is a compromise between the level of resiliency desired and the concomittant losses in useful textile properties. Economic considerations are also of paramount importance.

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