

The Introduction of Chlorotriazine Cross Links into Paper

A thesis submitted to the Victoria University of Manchester
for the degree of

Doctor of Philosophy

by

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January 1965

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The author graduated in the Department of Textile Chemistry with a B.Sc.Tech.(Hons.) in 1961. He has since been engaged in the present work on a British Industrial Plastics Scholarship.

None of the work referred to in this thesis has been submitted for application for another degree in this or any other University.

A b s t r a c t

The tensile strength of paper falls when the paper is immersed in water due to the disruption of secondary valence forces between the fibres. This effect has been reduced by treatment of the paper with chlorotriazines to form covalent cross-links in the paper. It has been found that the conditions for drying the paper after treatment are critical in determining the efficiency of cross-linking. The range of compounds available for cross-linking has been limited by their low water solubility and attempts to overcome this difficulty have been unsuccessful.

The effects of inter- and intra-fibre cross-linking on the mechanical properties of paper have been discussed. From comparisons of the mechanical properties of treated and untreated papers it is believed that the changes in these properties are due to inter-fibre cross-links.

The importance of conformability on the bonding capacity of the fibres has been demonstrated by the introduction of cross-links into the fibres before sheet formation.

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CHAPTER I

I N T R O D U C T I O N

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Paper is made from an aqueous dispersion of short cellulosic fibres by draining the water followed by pressing and drying the resultant sheet. To give a high degree of strength to paper it is necessary to pretreat the fibres by beating, in which the fibres are cut and crushed in the presence of water. The mechanism by which the beating process improves the strength of paper is still not fully understood although many theories have been put forward to explain it.

It was originally considered⁽¹⁾ that during the beating operation the fibres were cut and fibrillated and at the same time a cellulose hydrate was formed on the surface layers of the fibrils, providing a strong adhesive which cemented the structure together on drying. No evidence has been found to support the concept of a chemical hydrate of cellulose and the only water that is attached to cellulose is considered to be held by physical means during the swelling of the fibres. Strachan⁽²⁾ considered that coherence of the sheet was due to intermingling and tangling of the fibrils. As the degree of fibrillation increased along with the plasticity of the fibres, the strength of the resulting paper should increase. This

theory was found to be insufficient to explain all the observed effects of beating, such as the loss of strength of paper on wetting, and shortly afterwards the present theory began to develop.

In 1929 Urquhart⁽³⁾ had suggested that, during formation, plant cellulose had precipitated from water and therefore some water would remain attached to the hydroxyl group. On drying the water would be removed and the residual secondary valencies would be taken up by the hydroxyl groups, forming intermolecular bridges. Campbell⁽⁴⁾ extended this idea and proposed that during the beating operation the surface layers of the fibrils were partially in solution and the molecules of adjacent fibres were able to orientate themselves, thus enabling interfibre bonds to be formed, which were later suggested by Clarke^(4a) to be hydrogen bonds. As the paper sheet dries the number of these bonds would increase. He also drew attention to the high surface tension forces arising on drying resulting in high compacting pressures in the paper. This effect is emphasized by the higher plasticity of the fibres as the degree of beating rises. During the beating process the primary and outer secondary walls are ruptured and partially removed causing the fibre to swell. At the same time, together with the flexing of the fibres due to the action of the beater itself, the bonds between the amorphous polysaccharide phase between the inner and outer surfaces of the coaxial cellulose layers are broken and internal fibrillation

takes place. The highly swollen fibres permit greater deformation to take place under drying forces, thus increasing the area of contact of the fibres and fibrils during bonding. All of the evidence available today points to Campbell's theory being correct.

Gallay⁽⁵⁾ has questioned the importance of high extents of fibrillation to produce greater strength and degrees of bonding in paper. He maintains that the base of the fibril attached to the main fibre is weakened as beating continues and will thus decrease the final strength of the paper. He argues that the increase in strength is developed when the primary wall is removed increasing the flexibility of the fibre. He suggests that after the primary wall is removed, the S_1 layer becomes 'tacky' and further beating breaks up the crystalline regions of the cellulose, thus increasing the bonding capacity. He suggests that fibre entanglement plays a significant part in paper strength. He has illustrated this by comparing two sets of sheets, one air dried, and the other solvent exchanged for 10 min. in ethanol and ether followed by drying over calcium chloride for 30 min. After beating the ratio of strength of the extracted sheets to the normal sheets rose from 6 % to 30 %. In view of the short periods of solvent exchange it would be expected that some water would remain in these sheets thus contributing to the strength.

Just as hydrogen bonding in paper will impart high strength,

it is the reason for the almost total loss of strength when paper is immersed in water. Water, or any liquid of a high hydrogen bonding capacity, can penetrate the bonded areas of the paper and replace the hydrogen bonds between the cellulose molecules with bonds between the cellulose and the liquid. To improve the strength of paper it is necessary to protect the hydrogen bonds by introducing insoluble films around the bonded areas or by the introduction of covalent crosslinks between the fibres which are stable to water.

For the present investigation it was decided to use compounds capable of forming covalent inter-fibre cross-links in the paper.

The most common method of increasing the wet strength of paper is by the use of resins of the urea- and melamine-formaldehyde types. The mechanism by which these resins impart wet-strength is uncertain. Although they probably do form some covalent bonds with the cellulose, they also condense to form solid deposits inside and between the fibres. The resin would thus restrict wetting and swelling and prevent the penetration of water into the bonded areas of the paper thus contributing to the wet-strength of the paper.

The complexity of the reactions described above make the uses of resins unsuitable for investigating the effects of cross-links alone on the mechanical properties of paper.

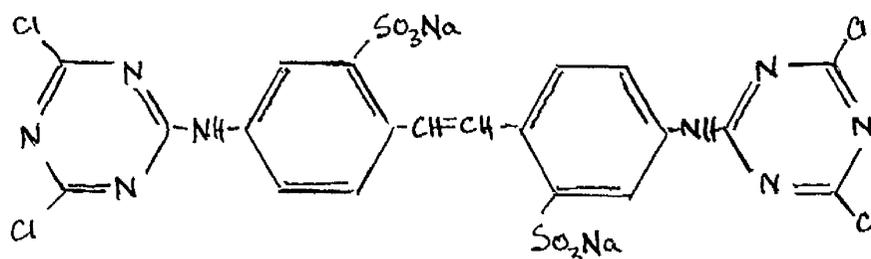
Fibres which have previously been oxidised with sodium meta periodate are capable of producing wet strength paper.

Zeronian⁽⁶⁾ has suggested that the improvement of the mechanical properties of wet periodate oxycellulose paper is due to inter-fibre hemi-aldol or hemi-acetal cross-links.

It was decided to use difunctional compounds of low molecular weight which were known to be capable of reacting with the hydroxyl groups of cellulose with no possibility of polymerisation. There are many compounds fulfilling these conditions but the majority of them, such as diacid chlorides and diisocyanates, are too reactive and it would be necessary to use organic solvents for their application. In recent years dyestuffs capable of chemical reaction with cellulosic fibres have been produced with several types of reactive groupings. These dyestuffs will react with cellulose, in an alkaline medium, with only a low degree of reaction with the water in the system. The reactive entity in many of these dyestuffs is either cyanuric chloride or divinyl sulphone and it was decided to attempt to prepare compounds, capable of reacting with paper fibres, based on cyanuric chloride.

When the investigation started, the only literature regarding the reactions of chlorotriazines with cellulose was concerned with their application to textile materials. It was considered that, in order to obtain cross-linking of the paper fibres, it would be necessary to prepare derivatives containing two chloro-s-triazine rings linked through an aromatic diamine containing sulphonic acid groups to impart solubility. The

compound selected was the disodium salt of 1:1'-di(2:4-dichloro-1:3:5-triazin-6-yl) diamino stilbene 3:3'disulphonic acid:



produced on drying, pulled the fibres together. This method proved unsuccessful and it was found necessary to treat paper sheets with alkaline solutions of the compound, followed by drying at 100°C under conditions permitting unrestricted evolution of the steam produced. The high increase of wet tensile strength of the paper treated in this manner, together with its resultant insolubility in cuprammonium hydroxide solutions indicates that interfibre cross-links are probably present. The insolubility of papers treated with wet-strength resins in cuprammonium hydroxide can be explained by the protection of the fibres by a thin film of resin or by cross-linking. In the case described above where no polymerisation can take place the insolubility must be due to some form of cross-links in the fibre structure.

The effects of using unsubstituted aliphatic diamines, instead of sulphonated aromatic diamines, and replacing the chlorine atoms in the triazine ring with sulphonic acid groups has been investigated but only limited success has been obtained.

CHAPTER II

Survey of Previous Work on the Improvement of the Mechanical Properties of Paper by the Introduction of Reactive Chemical Groups.

I. Introduction

Before the improvement of the mechanical properties of paper can be discussed, the present day knowledge of the relationship between the mechanical properties of paper and its structure will be reviewed. This will be followed by a historical account of methods of producing wet-strength paper leading up to the use of wet-strength resins and methods of forming covalent bonds between paper fibres. Finally, the use of cyanuric chloride in the preparation of reactive dyes and possible uses in forming covalent bonds in paper is discussed.

II. The Mechanical Properties of Paper

The experimental methods which have been devised to investigate the mechanical properties of paper will be reviewed before the individual theories to explain them are discussed.

Nordman⁽⁷⁾, working on the principle that only free surfaces scatter light, has investigated inter-fibre bonding by measuring changes in light scattered as the free surface area of the fibres change during straining. Although optical

contact has been taken as a measure of bonded area, it does not follow that the whole area is bonded. Optical contact can occur when fibres are separated by several hundred Angstrom units but hydrogen bonds and other secondary valence forces act at distances of five Angstrom units or less. There does appear to be, however, a direct correlation between the area of optical contact and area of bonding, for example, dry compression of a sheet neither decreases the optical scattering nor increases strength. He followed the changes in scattering during straining, obtaining the curves shown in Fig. 1.

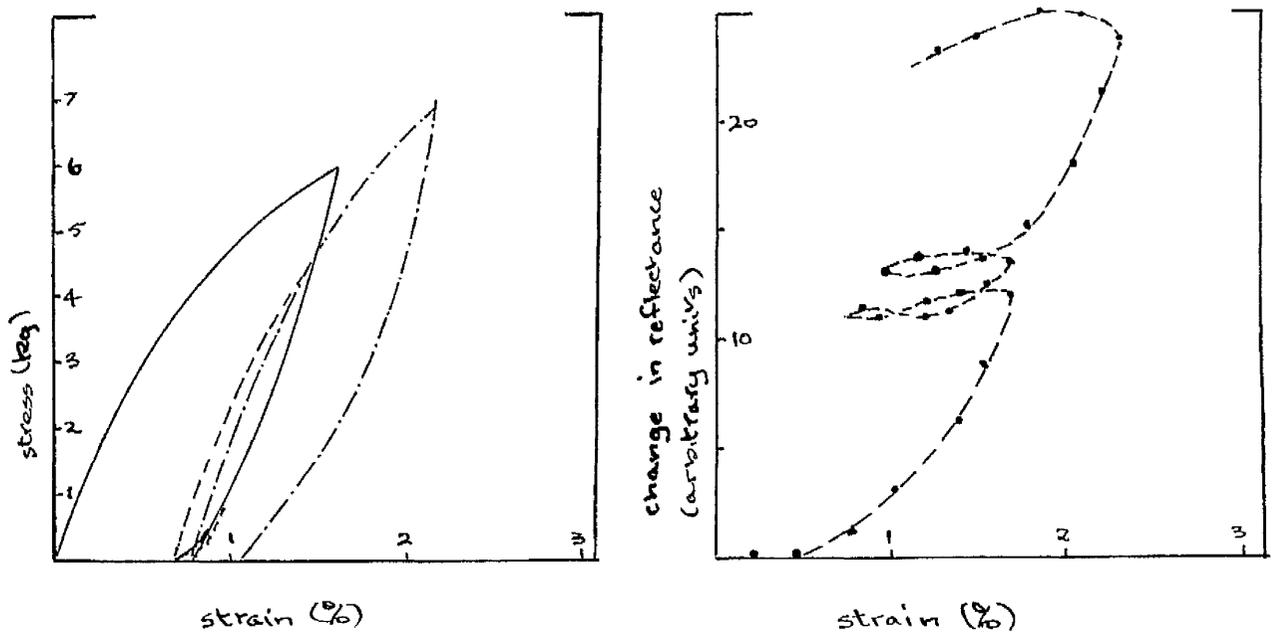


Fig. 1 Comparison between stress/strain curves and a corresponding curve showing change in reflectance

He found that the scattering coefficient began to increase at almost the same strain as the slope of the stress-strain curve changed from the elastic region to the plastic region. On releasing the stress, the scattering coefficient continued to rise, at a slower rate, until the straining cycle was almost complete when it started to decrease slightly. On repeating the cycle to the same strain there was very little increase in scattering, but if the paper was raised to a higher strain value a further rise in the scattering coefficient was noted. He suggests that as there is no increase in scattering on stress relaxation, the bonds broken on straining do not recover to any appreciable extent. On examining the reflectance of a given area of a sample during straining, Nordman found that the scattering increased irregularly. He says that this is due to redistribution of stresses in the area of bond breakage. As the bonds break some stresses in that area are relieved and, as a result, the rate of bond breakage would decrease.

Page⁽⁸⁾ has examined the individual areas of contact of a paper sheet using the light microscope under conditions of polarised vertical illumination. In normal vertical illumination no light will be reflected in areas of optical contact as the two surfaces which are in contact are equal but in antiphase and interfere to give zero intensity. In regions of close proximity (but not optical contact) interference fringes are produced, the effect of which can be minimised by using polarised illumination

with a crossed analyser. To reduce the light scattered from surrounding fibres, Page used sheets containing 70 % dyed fibres.

He has concluded that areas of optical contact are of the same magnitude as the bonded sites after accumulating a considerable amount of evidence. The fact that when paper sheets are strained there is no detectable change in size or shape of areas of optical contact, is the most convincing piece of evidence. It would be expected that mere optical contact would change under the slightest strain.

Page and coworkers⁽⁹⁾ have gone on to investigate the geometrical arrangements of the fibre-to-fibre bonds, and to assess the variables that will change them. They have proposed exact definitions for distances between bonds. The distance between the centres of bonded crossings is defined as "intercrossing distance" (I.C.D.), and the distance, measured in the direction of the fibre, between the projection of the bonds on the fibre axis as "projected interbond distance" (P.I.B.D.). Thus the P.I.B.D. is a more accurate measure of free fibre length. Working with a bleached spruce sulphite pulp, they have measured the decrease in I.C.D. and P.I.B.D. after beating the pulp for 20 min. in a Valley beater. They found that I.C.D. decreased from 81.0μ to 59.0μ and P.I.B.D. decreased from 34.0μ to 13.2μ . They have assumed that the fibres in the body of the sheet display on both sides bonding similar to that measured for the single side observed. This leads to negative figures

for P.I.B.D. and serves to show how small the unbonded areas actually are.

Page and coworkers⁽¹⁰⁾ have made a quantitative examination of bond breakage during rupture of the paper strip. On relating the loss in bonded area to the energy required for hydrogen bond breakage in that area, they found it to be smaller than the energy loss in straining by several orders of magnitude, thus indicating that Nordman's results are only a correlation. They also found, contrary to expectation, that over 80 % of the loss in bond area was due to partial breakage of fibre-to-fibre bonds, and not due to complete severance of those bonds.

Corte and his coworkers⁽¹¹⁾ carried out some investigations into the importance of fibre bonding, with special reference to hydrogen bonds, during rupture. They stated that the interfibre bonds in paper are hydrogen bonds and that, when paper ruptures, it is due to the rupture of these bonds. They deuterated samples of pulp and paper to determine the percentage of free hydroxyl groups remaining after beating and after sheetmaking. In this manner they determined the number of hydrogen bonds involved in fibre-to-fibre bonds. From infra-red data they then calculated the average bonding energy of the hydrogen bond to be 4.5 kcal/mole OH. These two values enabled them to calculate the energy required to rupture the paper. This figure was compared with an experimental figure determined by plotting rupture energy against test specimen length. The resulting

straight line gave a positive intercept on the rupture energy axis at zero test length. This enabled the fraction of energy required for the rupture zone to be calculated. On comparison of the two results remarkably good agreement was obtained but the experimental value was always higher than the theoretical figure. They attributed these differences to: -

- a) Deformation of the fibres in the rupture zone.
- b) Increase of temperature.
- c) Uncertainties in the calculations.

The positive intercept on the rupture energy axis obtained by Corte when rupture energy is plotted against test length has been observed by Craven⁽¹²⁾.

The part played by fibre failure in tensile tests has been examined with the zero span tester. In this test the fibres are able to span both jaws of the tester. This gives a measure of the strength of randomly oriented fibres. Assuming that the fibres in the paper specimen are Hookean up to the point of rupture, Van den Akker and coworkers⁽¹³⁾ have calculated that the breaking load would be 37.5 % of that load observed if all the fibres were aligned in the direction of loading. This theory has compared well with experimental results.

If the failure of paper at spans greater than the fibre length is due to bond breaks, then tensile strength must be related to the degree of interfibre bonding. Jacobsen⁽¹⁴⁾ has called the ratio of the normal span (multiplied by a hundred)

to zero span tensile strength the percentage adhesion.

The validity of the zero span tensile test has been questioned by Hopkins and Ranger⁽¹⁵⁾ because of differences in the method of testing. When a normal test strip is strained it undergoes lateral contraction, whereas in the zero span test the specimen is constrained by the jaws and no contraction can take place. They have shown that, even if fracture were determined wholly by fibre failure, the zero span test would still yield a value 30 % higher than the normal span. It is accepted procedure for carrying out tests, in which the rate of strain is variable, to maintain a constant time of test. This would result in the strain rate at fracture, for the zero span test, being far higher than the normal span and again raising the result for that test.

Wink and Van Eperen⁽¹⁶⁾, with an improved zero span tensile tester, have demonstrated that processes which would increase the normal span tensile strength have very little effect on zero span tensile strength. They have illustrated this with figures for increased wet pressing, increased drying pressure of handsheets, increased degree of beating and the addition of starch. In every case the rise in zero span tensile strength was small compared with the rise in normal span tensile strength. In two cases they added Hyamine - a debonding agent - to the pulp at different degrees of beating. In both cases there was a large fall in normal span tensile strength and a comparatively

low decrease in zero span strength.

The importance of fibre rupture in the failure of a test specimen has been examined by Van den Akker and coworkers⁽¹³⁾. They prepared sheets incorporating a small percentage of dyed fibres. They then searched the ruptured strips in order to find the number of dyed fibres that had broken. They found that beating increased the percentage of broken dyed fibres from 40 to 70. They showed that additions which increased the tensile strength of the paper increased the proportion of broken fibres, while those that decreased the tensile strength had the opposite effect. Van den Akker and coworkers did observe that many fibres broke after rupture had begun, and it still seems probable that inter-fibre bond breakage is the most important factor in the tensile strength of paper.

The wide range of experimental evidence regarding the mechanical properties of paper have led to a correspondingly wide range of theories to explain these properties. The visco-elastic nature of paper has led many workers, notably Steenberg et al.⁽¹⁷⁾, to formulate models consisting of springs and dashpots. The original models used ideal elastic springs and ideal viscous liquids in the dashpots and, by using models of varying complexity, some properties could be simulated. With the use of varying non-Newtonian fluids in the dashpots and arbitrary values for the elastic moduli of the springs, a model can be obtained to follow the prerupture

behaviour of paper. For these systems to work, however, the springs cannot break and the pistons cannot come out of the dashpots. Under these conditions fracture cannot occur and the method is unsatisfactory.

Rance⁽¹⁸⁾ argued that the mechanical properties of paper could only be interpreted in terms of its structure. He considered that the primary events occurring during straining are (a) elastic deformation of the fibres and (b) severance of interfibre bond areas. He accounted for viscoelastic flow and plastic deformation by regarding them as secondary effects resulting from the primary events. As investigations into the rheological properties of paper have provided more information of its structure, modifications have had to be made to Rance's theory. Most workers are, however, still using his basic ideas to produce more complex theories.

The importance of parts played by fibres and interfibre bonds has been the main cause of dispute among workers in this field. The importance of interfibre bonding has been considered by Nissan⁽¹⁹⁾ who has propounded a theory of the strength of paper based on a hydrogen bonded network of fibres. Considering a randomly orientated, isotropic network of hydrogen bonds at infinitesimal strains, and using a Morse function to represent the potential energy of a hydrogen bond, he has deduced an equation to represent the initial modulus of a hydrogen bonded solid. The theory has been developed to allow the values for

hydrogen bond energies to have a statistical distribution about a mean, and to make the hydrogen bonds interdependent to some extent. Nissan and Sternstein⁽²⁰⁾ believe that these models explain most of the stress-strain behaviour of paper, and that the viscoelastic properties of paper are not due to separate elements but to one integrated unit - the hydrogen bond. They propose that the various flow properties ^{of} paper will become amenable to study by classical methods of chemical kinetics.

In a later paper Nissan and Sternstein⁽²¹⁾ have worked out the ratio of hydrogen bonds active during straining (n_E) to the total number of bonds (n_T). From this ratio they have arbitrarily derived an expression relating the elastic modulus to the effective number of hydrogen bonds $E = 7600 n_E^{1/2}$. From this they have estimated the actual area of the bond compared with the normal area measured by Page's technique and obtained values for the strength of the hydrogen bond to be 10^{-4} to 10^{-6} dynes. They have formulated a theory to predict these values giving $E = 7700 n_E^{1/2}$ and the strength of the hydrogen bond as 10^{-5} dynes. The molecular theories for the properties of paper propounded by Nissan et al. have been criticized by Page⁽²⁷⁾, who claimed that the assumptions they have made are oversimplified and that not enough tests have been carried out to confirm these theories.

Carte and Kallmes⁽²²⁾ have investigated the role of interfibre bonding in a different manner. They have attempted

to relate the structure of paper to the shape of the fibres and geometric laws. They considered a large number of fibres characterised by dimensions and shape in an irregular network using statistical geometry. Their aim was to enable dependent variables, such as the number of fibre-fibre crossings and number of spaces, to be calculated from independent variables, such as length and width of the fibres, which could be chosen as required. They started by preparing very thin two-dimensional handsheets of $2\frac{1}{2}$ g.m.⁻² basis weight in which the fibres would be randomly distributed. They then went on to study orientation and flocculation in two-dimensional sheets, and later to consider three-dimensional networks as multiplanar (M.P.) sheets made up of piles of two-dimensional sheets.

From these investigations they have proceeded to an examination of the mechanical properties of two-dimensional sheets. They found that, as the sheets were strained, the process was accompanied by a series of clicks and, by simultaneous recording of both strain and number of clicks, showed that each click corresponded to a bond failure. The bond failure occurred randomly over the test specimen at first and gradually concentrated into an apparently weaker area as rupture took place. They have developed a theory to predict the number of bond failures, in a zone of fracture, required for a sheet to break. They have had to assume that, all the fibre crossings in the area of rupture were initially bonded and

and that no fibres failed. The agreement between theory and experiment~~al~~ has been very good despite the limitations of the method.

Kallmes⁽²³⁾ has extended the work on the geometric properties of multiplanar sheets to formulate a theory of the elasticity of paper. To achieve this, the bonded areas of the paper are assumed to be rigid and undergo no rotation and that the extension of the sheet takes place through deflection of the unbonded portions of the fibres between fibre-fibre bonds. Many more approximations have had to be made, but experimental figures for the elastic moduli of fibres made into multiplanar sheets agree quite well with those calculated from the theory.

Van den Akker⁽²⁴⁾ has studied the mechanical properties of paper when dried under strain and the forces which act on the dry web when it is subjected to further strain. He has examined these properties in both the elastic and plastic regions of the stress-strain curve. Like Kallmes he has assumed that the interfibre bonds are rigid, but he has allowed for angular displacement as the sheet is strained. He has derived expressions for Young's Modulus, Poisson's Ratio and Modulus of Rigidity in terms of suitable fibre and sheet parameters. This has enabled him to predict satisfactorily the value of Young's Modulus for handsheets that had been dried under constant strain. He went on to consider the plastic region of

the stress-strain curve where the failure of interfibre bonds becomes an increasingly dominant factor in the shape of the curve. He argued that the stresses in the bonds could be attributed to three main sources: (a) stresses due to flexure of fibre segments, (b) stresses resulting from anisotropic shrinkage of fibre segments and (c) stresses due to longitudinal tension in the fibres. He has made a preliminary investigation into the relative importance of these forces in the plastic region, but considered that, at the present stage, the phenomena are too involved for a reasonably accurate mathematical theory.

Hopkins and Ranger⁽¹⁵⁾ claim that fibre failure is a more important factor in the rupture of paper than is generally recognised. They have suggested that the bonded areas rupture by peeling rather than shearing. Fibres at right-angles to the direction of strain will undergo compression owing to the lateral contraction of the specimen. The slenderness of the fibres will cause those under compression to buckle and the resulting stresses will allow peeling to occur in the areas affected. The stress required for bond failures to start in this manner is far less than that required for shearing although the total energy requirement for rupture is the same in both cases. They said that this mechanism is necessary to explain the changes of opacity of paper under strain originally observed by Rance. Rance⁽²⁵⁾ observed that, when a cross directional strip of tracing paper is strained, the regions of increased opacity

form a network of lines at characteristic angles to the direction of tension. Hopkins and Ranger assumed the strain lines to be started by the peeling of one bond or a small group of bonds resulting in a small local area of deformation, thus raising the stress level in the immediate vicinity. Eventually the progress of the lines is stopped by fibres under tension and the rising stress level initiates the process elsewhere. They claim that these factors lead to a higher proportion of fibre failure to bond failure during rupture.

Page and Tydeman⁽²⁶⁾ have developed a theory, from their experimental observations of fibre bonding, concerning the shrinkage of paper and its relationship to mechanical properties. If only the centres of bonded crossings are fixed, although the longitudinal shrinkage of fibres on drying is only 1 - 2 % compared with 20 - 30 % for the transverse shrinkage, there should not be any sheet shrinkage on drying. Shrinkage can, however, be considerably higher than the expected longitudinal shrinkage and Page and Tydeman deduced that the fibres must diminish in length for this effect to occur. By incorporating dyed fibres in the sheets, they found that, even for shrinkages as high as 12 %, the longitudinal shortening of the fibres was the same as the shrinkage of the sheet. Steenberg's original idea, that high shrinkage might be due to microcreping of fibres between bonds, was pointed out to be invalid, as the sheets showing the highest shrinkage were highly beaten and

had very little, if any, free fibre length. They have concluded that the interfibre-bonding is sufficiently strong, before shrinkage is complete, for the transverse shrinkage of one fibre at a crossing to cause longitudinal shrinkage in another fibre at that crossing. Their experimental evidence indicates that the shrinkage is due to microcompressions in the bonded areas themselves, illustrating this with fibres curled to align in both the machine- and cross direction. The MD fibres showed no sign of microcompressions. They also found that, after shrinkage, the bonded areas diminished in size and, as there was no relative movement of the fibres at the crossings, the unbonded segments should also shorten to retain the shape of the structure.

They have applied their observations on microcompressions to formulate a theory of the elasticity of paper in which stretching of the paper pulls out the kinks and microcompressions. They show that while the kinks are reasonably small they can still have an elastic modulus. As they increase in size, they lower the yield point owing to stress concentrations introduced into the kink, resulting in permanent set. They have also emphasised the importance of bond breakage. As the bond slowly breaks the microcompressions are released allowing greater extension and permanent set in the paper.

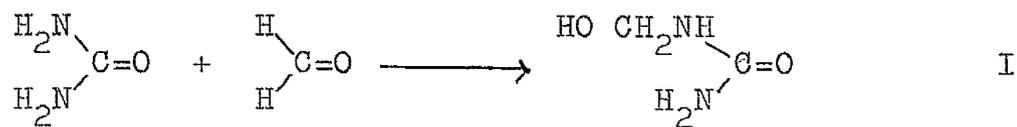
III. The Effect of Water on the Mechanical Properties of Paper and Means of Reducing these Effects.

The importance of hydrogen bonds and Van der Waals forces in paper has been demonstrated by Broughton and Wang⁽²⁸⁾ who studied the effect of immersion in liquids of various hydrogen bonding capacities. They found that the greater the hydrogen bonding capacity of the liquid, the lower the tensile strength of the paper which had been wetted in that liquid. Water, which has a high capacity for hydrogen bond formation, is frequently in contact with paper and many attempts have been made to reduce the resulting loss in strength.

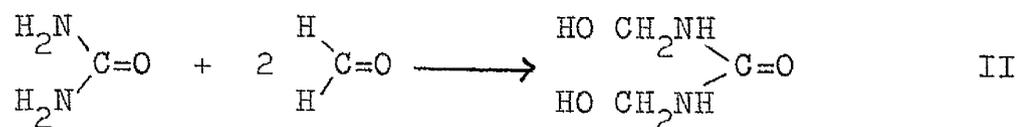
The manufacture of vegetable parchment is probably the oldest method of improving the wet strength of paper. Strong sulphuric acid is used to gelatinise and fuse the paper into an almost homogenous sheet after which it is washed, neutralised and dried. This paper combines wet strength with resistance to oils and greases and is used mainly as a greaseproof paper. Other processes have utilised animal glue or gelatin applied by surface sizing techniques followed by treatment of the paper with tanning agents such as alum, formaldehyde or glyoxal which cross link the proteins rendering them insoluble in water. Starches, polyvinyl alcohol, viscose solutions applied with precipitating agents have been used to prepare wet strength papers of temporary nature where absorbency is required.

It was not until the advent of synthetic resins that papers with permanent wet strength and good absorbent properties could be produced economically. They were originally used in the textile industry to impart crease resistance to fabrics and later applied to paper. It was not until they were developed so they could be added to the beater with high retentions of resin on the pulp, that they were used on a large scale. The resins used, mainly condensation products of urea and formaldehyde or melamine and formaldehyde, are prepared as water soluble derivatives of low molecular weight and polymerised after the paper has been made. The mechanism by which these resins polymerise is still uncertain although in recent years a considerable amount of work has been done on the topic. A comprehensive review⁽²⁹⁾ of the literature on the mechanism of urea-formaldehyde polymerisation is given in a paper by Glanert. The mechanisms of these processes are believed to be as follows: -

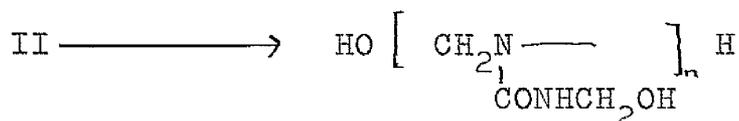
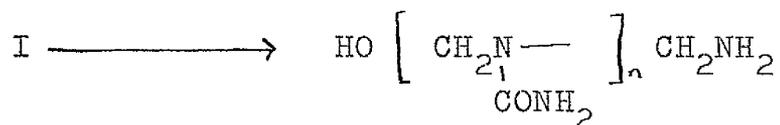
a) Urea-Formaldehyde



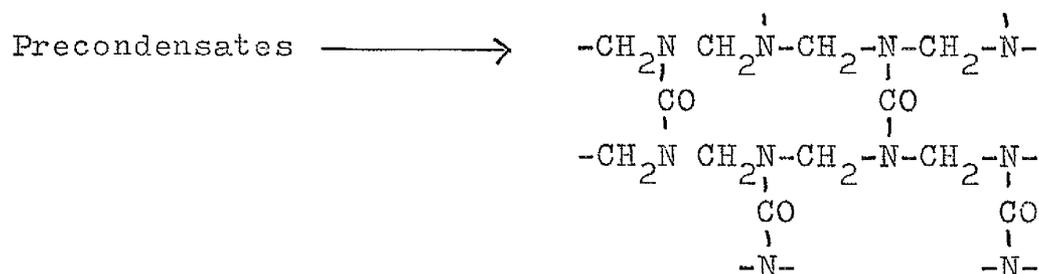
or



These compounds are then condensed further to give low molecular weight compounds with very few crosslinks.

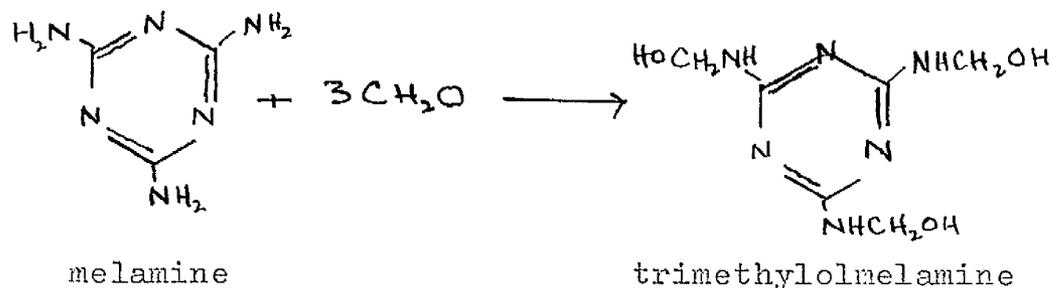


These are the water soluble precondensates applied to the fibres. On heating further condensation takes place to give the insoluble, cross-linked network.



In practice formaldehyde is lost during the heating and a more open network results.

b) Melamine-Formaldehyde



From here the process is similar to the urea-formaldehyde mechanism. The melamine precondensates are too unstable to be stored as liquids and are frequently made into methyl ethers

or spray dried to improve stability.

Less is known about the mechanism by which wet strength is produced in paper. Although there is some support for the idea that the precondensate or polymerised resin reacts with the fibres in textiles to form chemical cross-links, the majority of evidence available seems to indicate that the increased wet strength is due to the polymerisation of the resin within and around the fibres and is mainly a physical effect.

Jurecić et al.⁽³⁰⁾ have made possible the most comprehensive investigation into the development of wet strength. They compared the rates of development of wet strength in resin treated papers made from cellulose fibres or glass fibres. They plotted the log of the initial rate of cure against the reciprocal of the absolute temperature to give an Arrhenius plot. From the slopes of these lines the activation energies associated with the development of wet strength were calculated. The values for cellulosic fibres were approximately 22.6 kcals. and glass fibres 23.8 kcals. compared with 19 - 21 kcals. for the neutral condensation of urea-formaldehyde resins.

In a later paper⁽³¹⁾ they measured the effect of prolonged soaking in water on the wet strength of the resin treated paper. From the rates of decrease of wet strength, they calculated the activation energy to be approximately 23 kcals./mole. They attributed the loss in wet strength either to the gradual permeation of water through the resin film into the bonded areas

of the paper or to the hydrolytic cleavage of the cross linked structure of the resin. They assumed the activation energy of diffusion of water through the resin film between the bonded areas of the paper to be about the same as the diffusion through a plastic membrane for which the activation energy is known to be about 10 kcal./mole. Thus they say that the wet strength is due to a reversible condensation of the resin into a cross-linked structure within and on the surface of the fibre walls. The polymerisation is a reversible process and prolonged exposure to water or water vapour will remove the wet strength property from the paper. They have provided more evidence for this theory by placing cured and uncured resin treated papers in a desiccator at 100% r.h.. They found that both types of paper tended towards the same ultimate wet strength.

In an attempt to resolve the question of chemical linkage between the resin and cellulose they heated a methyl glucopyranoside with urea-formaldehyde resin in an open tube for 12 hours. They obtained a cross-linked product but the glucoside was easily quantitatively extracted with cold water. The fact that cellulose ether bonds are highly resistant to hydrolysis makes the possibility of a chemical reaction between the glucoside and the resin highly unlikely.

Fineman⁽³²⁾ believes that the high dry strength of paper is due to the presence of hemicelluloses between the fibres providing cross-links through hydrogen bonds, and that the loss

of strength on wetting is due to the swelling of the hemi-celluloses rupturing the bonds between the fibres. He has suggested that the polycondensation of resins in the hemi-celluloses prevents swelling and thus raises the wet-strength of the paper. He has also proposed that monomeric compounds such as formaldehyde and glyoxal react with the hemicellulose to produce crosslinked copolymers which will also raise the wet-strength.

Although the majority of modern methods for improving the wet strength of paper utilise the addition of resin to the fibres followed by some form of heat treatment, several processes have been devised to achieve the same effect with monomeric compounds. As these compounds cannot polymerise the increased wet strength must be due to chemical cross-linking between the fibres.

Formaldehyde was the earliest compound to be used in this manner and a considerable amount of work has been done in order to determine the mechanism of reaction of formaldehyde with cellulose. The majority of work has been done on textile materials where emphasis has been laid on infra-fibre cross-linking as opposed to inter-fibre cross-linking which is probably required for it to be an effective means of producing wet strength in paper.

Stamm et al.⁽³³⁾ have investigated the effect of catalysed heat treatment and formaldehyde on the dimensional stability

of wood and paper. For the work with formaldehyde they examined the effect of treatment with formaldehyde in the vapour and liquid phase, with and without various catalysts and determined the temperature and time of cure required to bring about optimum reduction in swelling. They found that the rate of cross-linking was independent of reactant concentration but varied with the nature and concentration of the catalyst and also with the temperature and time. They did not draw any conclusions as to whether the formaldehyde was involved in inter- or intra-fibre cross-linking although they found very little embrittlement of the paper provided the treatment did not reduce the swelling by more than 40 %. This does not, however, indicate that the treatment had resulted in inter-fibre cross-linking as embrittlement is probably caused by cross-linking within the fibres and degradation of the fibres due to acid catalysts.

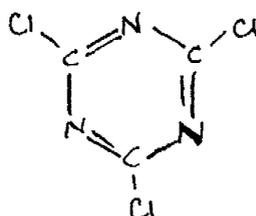
The effect of making paper from pulp which has been oxidised with sodium metaperiodate or which has been treated with periodate oxidised starch has been studied in some detail. The earliest workers suggest that the resulting wet strengths from these treatments are probably due to chemical cross-linking of the fibres, were Schur and Levy⁽³⁴⁾ although they did not suggest how these cross-links might be formed. Zeronian⁽⁶⁾ has reviewed the work done in this field and together with his investigations into the mechanical properties of paper made from periodate oxidised pulp, the nature of the

reaction seems to be the formation of hemiacetal or hemi-aldol cross-links. Glyoxal, another wet strength agent frequently mentioned in the literature, seems to react in the same manner.

Lagally⁽³⁵⁾ has postulated a cross-linking mechanism for cellulose fibres by means of orthotitanic acid. They have studied the hydrolysis of alkylolamine titanates in the presence of sugars and amines with electron-donating groups to stabilise the resulting orthotitanic acid. Orthotitanic acid $Ti(OH)_4$ is not stable because four OH groups are not sufficient to satisfy the coordination requirements of the titanium ion which has a coordination number of six with respect to oxygen. In the absence of other electron donating groups to surround the ion, the orthotitanic acid would polymerise sharing hydroxide groups between Ti^{++} ions. Lagally says that cellulose is covered with OH^- ions which can coprecipitate with the titanic acid forming strong bonds between the fibres. His figures for increased wet-strength do indicate that some stabilisation of the paper has taken place.

IV. The Properties of Cyanuric Chloride.

Cyanuric chloride was discovered by Serullas⁽³⁶⁾ in 1827 and was believed to be an isomer or trimer of cyanogen chloride for several years. Its structure is now known to be: -



It is generally manufactured by passing cyanogen chloride vapour over a charcoal catalyst, activated with an alkaline earth chloride, at temperatures from 250° - 480°C .

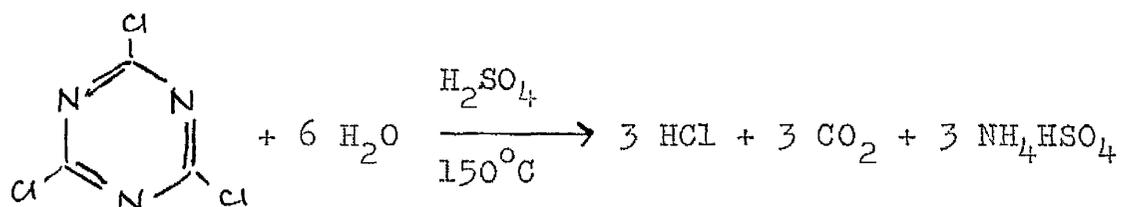
Cyanuric chloride is the acid chloride of cyanuric acid and the chlorine atoms are more reactive than an alkyl halide but less reactive than acyl halides. This depends on the acyl halide and although it is less reactive than acetyl chloride, it is more reactive than stearoyl chloride. Before discussing the reactions of cyanuric chloride involved in dyestuff preparation and cellulose derivatives, the basic chemical properties will be summarized⁽³⁷⁾.

(i) Hydrolysis

Cyanuric chloride is stable in water at 0°C for at least 12 hours but is readily hydrolysed as the temperature is raised. From the evidence available⁽³⁹⁾ it appears that the hydrolysis does not stop at the hydroxy chloro-s-triazine stage, but that the second and third chlorine atoms are hydrolysed as readily as the first one.

Cyanuric chloride is only hydrolysed by nitric and sulphuric acids at room temperature after prolonged treatment. On heating with sulphuric acid at 150°C the triazine ring is

destroyed.



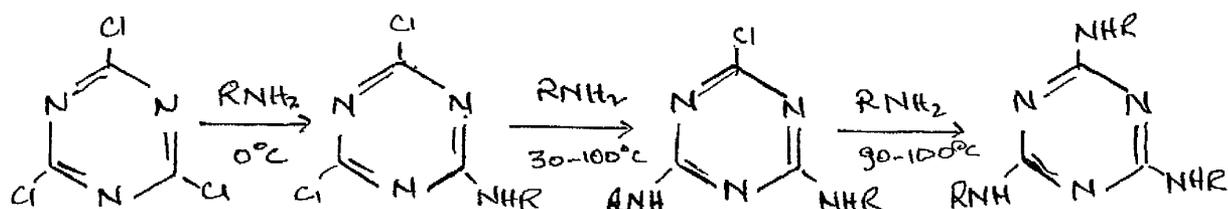
(ii) Reaction with Hydroxy Compounds

Cyanuric chloride reacts with alkaline earth alkoxides or with alcohols in the presence of a basic acceptor to form mono-, di- and trialkyl esters of cyanuric acid. In the majority of cases the di- or trialkyl esters are obtained and in order to carry out a stepwise replacement it is preferable to use sodium carbonate or sodium hydroxide.

Warren et al.⁽³⁸⁾ have studied the reaction of cyanuric chloride with cellulose. They pretreated cotton linters or yarn with alkali, centrifuged to remove the excess liquor and reacted the alkali cellulose with cyanuric chloride in various solvents. They obtained a degree of substitution of 1.9 anhydro-glucose units/triazine ring when the yarn had been pretreated with 13 - 14 % sodium hydroxide solution and reacted with cyanuric chloride in xylene. Several patents in the early 1930's have described a similar process in which the resulting ester is reacted with an aromatic amine, diazotised and coupled with β naphthol⁽⁴⁰⁾.

(iii) Reactions with Amino Compounds

In many cases it can be said that cyanuric chloride reacts with amino compounds in three steps: -

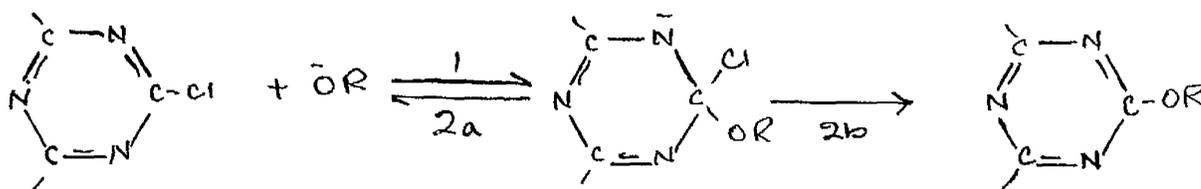


This mode of reaction, however, applies only to aqueous solutions and not to other solvents. The extent of reaction varies with different amines, some substituting all three chlorine atoms at 0°C and others not reacting at 100°C. The reactivity of aromatic amines towards cyanuric chloride is greatly reduced if the basic character of the amino group is weakened by negative substituents in the ring.

The ability of the three chlorine atoms to be substituted in successive steps has been of great advantage in the preparation of dyes and dye intermediates. It has allowed the combination of several dye units to form more complex dyes which have been claimed to have superior properties, such as fastness and brightness, lacked by the original colours. More recently, by substitution of only one or two chlorine atoms, dyestuffs have been prepared which are capable of forming covalent bonds with cellulose fibres. The existence of these bonds has been proved by Baumgarte⁽⁴¹⁾ who studied the reaction

of reactive dyes with cellulose model compounds such as cellobiose etc.. By using paper chromatography he isolated definite chemical derivatives of the dyes.

A considerable amount of work has been done on the mechanism of dyeing with reactive dyes. It is now generally accepted that the carbon atoms in the triazine ring have low electron densities due to the electron withdrawing effect of the nitrogen atoms, and are attacked by nucleophilic reagents to give a complex which dissociates almost immediately eliminating either the reactive group or the nucleophilic reagent, i.e.: -



The dissociation stage of the reaction is extremely fast, the rate determining step being 1 and the reaction can be regarded as SN_2 .

The high ratio of reaction between fibre and dye to hydrolysis of the dye can be partially attributed to the high concentration of cellulosate ion with respect to hydroxide ion inside the fibre. The rate constant for the reaction between the dye and cellulose is also higher than that for the hydrolysis of the dye. These conditions only apply to dye molecules inside

or on the surface of the fibre. Any dye remaining in the solution outside the fibres is, of course, hydrolysed. This effect is not so important in dyeing as there are ways of ensuring that adequate diffusion of the dye into the fibre takes place before adding alkali to the system. In order to cross-link paper fibres, however, it is necessary to get the cross-linking compound adsorbed on the surfaces of the fibres with a minimum of penetration.

Paper has been treated with chlorotriazine compounds in order to improve its wet and dry tensile strengths. The patent⁽⁴²⁾ describes the use of compounds combining one triazine ring compared with two rings which it was proposed to use for the present work. In the process described the paper was impregnated with the reactive compound and sodium carbonate or bicarbonate and dried at 90 - 100°C on a drum drier. Wet strengths of 50 % have been obtained with these dichlorotriazine derivatives. They have also given two examples in which the chlorine atoms in the triazine ring are replaced by sodium sulphate or phenoxy groups reducing the reactivity of the compounds.

CHAPTER III

Experimental Methods

1. Experimental Approach

This chapter covers the synthesis of derivatives of cyanuric chloride and their application to pulp and paper together with the subsequent physical and chemical evaluation of the paper.

When the project was started it was believed that, in order to obtain compounds capable of spanning the distance between two fibres, it would be necessary for the compounds to have two chlorotriazine rings at opposite ends of the molecule, thus most of the syntheses described are concerned with compounds of this type. Variations in the length of the cross-linking agent could have been facilitated if aliphatic diamines could have been used to separate the triazine rings. These compounds are, however, insoluble in water and attempts were made to replace the chloride groups in the triazine ring with sulphonate groups which although they would decrease the reactivity slightly, should impart water solubility. Sulphonation of aliphatic amino derivatives of cyanuric chloride, however, did not impart water solubility to these compounds.

The reactions have been followed by titration of the hydrochloric acid produced with sodium carbonate, the generation

of one equivalent of hydrochloric acid for each equivalent of cyanuric chloride present being taken as the end of the reaction. Elemental analyses of the products have confirmed this although the difficulties in determining sulphur make the figures too unreliable to be taken alone.

The cross-links were to be introduced by dyeing the pulp with reagent and adding alkali to the sheet machine before formation, followed by pressing and air-drying. This process proved to be unsuccessful and the methods of applying the reagent and drying the paper were varied until the present technique of surface sizing the paper with a mixture of reagent and alkali followed by drying on a drum drier was evolved.

The physical properties measured included breaking load, extension at break, initial modulus, rupture energy and elastic recovery (immediate plus delayed). The extent of cross-linking was impossible to determine absolutely, but arbitrary figures were used for comparative purposes from the nitrogen contents of the treated paper.

The effect of internal cross-linking on the conformability of different fibres was investigated to a limited extent. Pulp was dyed with a cross-linking agent and then reacted by heating with alkali before sheet making. The change in conformability was examined by measurements of drainage-time, air porosity, sheet density and tear together with tensile properties measured on the Instron.

2. Syntheses

i) Amino Derivatives of Cyanuric Chloride

a) Preparation of bis-4:4'-(2":4"-dichloro-6"-s.triazinylamino) stilbene-2:2'-disulphonic acid

The method used was similar to that described by Fierz-David and Matter⁽³⁹⁾ for the reaction of cyanuric chloride with aminonaphthalene sulphonic acids. 4:4' diamino stilbene-2:2'-disulphonic acid (0.05 mole) was dissolved in the minimum amount of N sodium hydroxide and added to a suspension of cyanuric chloride (0.10 mole) in 100 ml acetone. The mixture was stirred at 0-5°C, the temperature being maintained by cooling the reaction flask in an ice/salt bath. N sodium carbonate was added from a burette to maintain the reaction mixture at pH 4 and the reaction was considered to be complete when the theoretical amount of sodium carbonate had been added (100 mls.). The reaction mixture was acidified with concentrated hydrochloric acid, filtered, washed with cold, distilled water and finally filtered again. The product was dried in vacuo over silica gel and sodium hydroxide pellets to absorb hydrogen chloride vapour.

b) Preparation of bis 1:4-(2":4"-dichloro-6"-s.triazinylamino) benzene-2-sulphonic acid

This compound was prepared in a similar manner to (a) using the sodium salt of 1:4-diamino benzene-3-sulphonic acid. It was found that as the reaction proceeded the viscosity rose

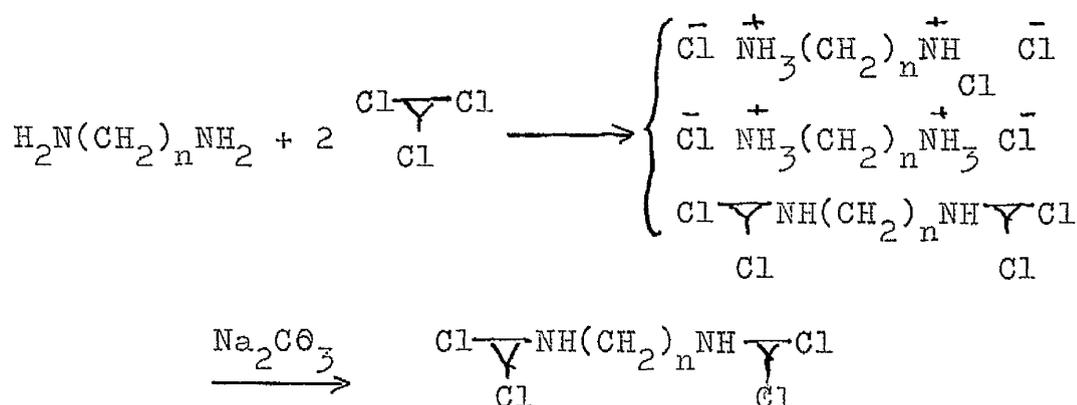
probably due to association of the product molecules.

c) Preparation of (2:4-dichloro-6-s-triazinylamino) benzene-3-sulphonic acid

The compound was prepared in a similar manner to (a) but equimolar proportions of sodium metanilate and cyanuric chloride were used.

d) Preparation of Aliphatic Diamino Derivatives of Cyanuric Chloride

The techniques used are derived from those described by Thurston et al.⁽⁴³⁾. In these cases the amine itself was used as a base for the first stage of the reaction, the amine salt then being hydrolysed with sodium carbonate to enable the second stage to occur:



A solution of 0.01 mole of diamine in water (50 mls) was added to a suspension of cyanuric chloride (0.02 mole) in acetone (50 mls) and the mixture stirred at 0-5°C until the pH

fell to between 4-5. Sufficient N sodium carbonate was added to enable the reaction to go to completion after which the insoluble product was filtered off and dried in vacuo over silica gel and sodium hydroxide.

ii) Preparation of dihydroxy Derivatives of Cyanuric Chloride

It was intended to prepare derivatives of poly-ethylene glycols of varying molecular weights in order to vary the chain lengths of the cross-linking agent. Although monohydric alcohol derivatives of cyanuric chloride have been prepared, it was found that, using dihydric alcohols, the reaction could not be stopped after the first chlorine in the triazine ring had reacted and polymerisation took place. It was found that, even on reducing the temperature to -10°C and with no alkali addition, both chlorine atoms in the triazine ring were removed at the same time.

iii) Sulphonation of some Chloro-s.triazine Derivatives

In view of the lack of water solubility of the aliphatic diamine derivatives of cyanuric chloride it was thought that the sulphonation of the triazine rings in these compounds would render them water-soluble.

The methods used were similar to those covered by Atkinson et al.⁽⁴⁴⁾ and may be divided into two types, both using sodium sulphite as the sulphonating agent:

- a) Sulphonation of cyanuric chloride followed by reaction with diamine,
- b) Sulphonation of the chloro triazine derivative itself.

It was found that although the reactions involving aromatic diamines containing sulphonic acid groups were quite successful, those utilizing aliphatic diamine did not yield water-soluble products.

A) Sulphonation of Cyanuric Chloride

Cyanuric chloride (0.05 mole) dissolved in 70 mls tetrahydrofuran was added to a solution of sodium sulphite (0.15 mole) in 100 mls water over 15 minutes at 0-5°C. The reaction mixture was then stirred for 1 hr. and the temperature allowed to rise to 15°C. Salt (55 g) was added to the solution and the precipitate was filtered off and washed with saturated brine and dried in vacuo over silica gel.

B) Preparation of 1:3-disulpho-5-(3'-sulphoanilino)s.triazine

Cyanuric chloride (0.05 mole) was dissolved in tetrahydrofuran (50 ml.) and a solution of sodium sulphite (0.1 mole) in water (80 ml.) was added over 20 min. at 0-5°C. A neutral solution of sodium metanilate (0.05 mole) in water (70 ml.) was then added and the mixture stirred for 1 hr. and the temperature allowed to rise to 15°C. Salt (20 g) was then added and the product filtered off and dried in vacuo over silica gel.

C) Preparation of bis 1:6-(3':5'-disulpho-s.triazinylamino)hexane

Cyanuric chloride (0.05 mole) was dissolved in 50 ml. tetrahydrofuran and a solution of sodium sulphite (0.1 mole) in 100 ml. water was added over 20 min. at 0-5°C. Hexamethylene diamine (0.025 mole) in 100 mls. water was then added and the temperature being allowed to rise to 15°C over 1 hr., the reaction mixture being maintained at pH 4 by the addition of N sodium carbonate. After the addition of the diamine the reaction mixture began to cloud and precipitation took place. Both of the reactants were water soluble and consumption of the sodium carbonate indicated that reaction had taken place to form a water insoluble product.

3. Preparation of Pulp

In all cases where handsheets have been made, unless otherwise stated, a bleached sulphite pulp has been used.

The Medway beater was allowed to run empty for 3 minutes, the stock (130 g air dry pulp in 3.5 litres of distilled water) was added and 'brushed' for 3 minutes. The bedplate was then raised, a 20 pound weight being placed on the bedplate lever at 6 inches distance, and the pulp beaten for 90 seconds to a freeness of about 30°SR. The pulp was placed in a container with a screw cap and kept in a refrigerator at 5°C until used.

4. Dyeing of Pulp with Cross-linking Agents

A sample of the pulp equivalent to 24 gm. bonedry fibre was suspended in 2 litres of distilled water and a predetermined amount of cross-linking agent, to give up to 5 % on the dry weight of fibre, was added. The mixture was disintegrated for 1000 revolutions in the standard disintegrator, allowed to stand for 10 minutes after which salt (30 gm) was added and the mixture disintegrated for a further 1000 revolutions and allowed to stand for another 30 minutes. The pulp was then finally disintegrated for 250 revolutions before being diluted to 7 litres with distilled water. The consistency was then determined in the standard manner and the calculated volume of distilled water added to reduce the consistency to 0.3 %.

5. Preparation of Sheets

The pulp was formed into sheets of basis weight 60 g.m.⁻² using the method of the Technical Section of the Paper Makers Association of Great Britain and Ireland⁽⁴⁵⁾. The sheet-machine used had a backwater tank which could recirculate the water drained off during the formation of the sheet, thus reducing the amount of distilled water required. Sufficient sodium carbonate (100-200 g) was added to the backwater tank to cause reaction between the cross-linking agent and the cellulose. During the first attempts at cross-linking the sheets were pressed in

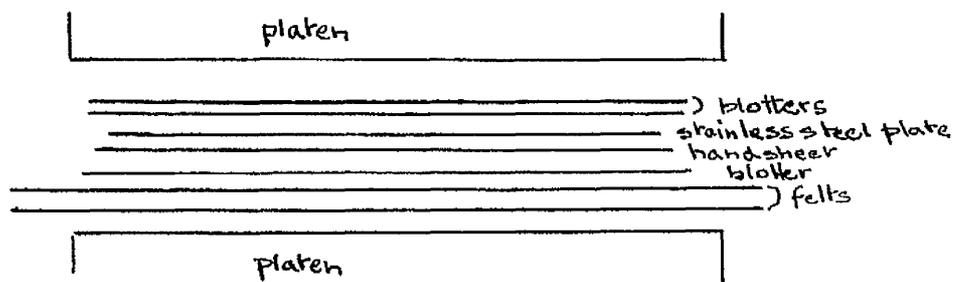
the standard manner and dried by exposure to air at 65 % r.h. and 20°C, but this method was altered later. The number of sheets prepared from a given sample of pulp varied between 8 and 12.

6. Dyeing of Sheets with Cross-linking Agent

The sheets were dyed in pairs in a photographic developing dish containing a solution of cross-linking agent (0.12 g) in 750 mls. water. After 10 minutes salt (15 g) was added. The sheets were then allowed to stand for a further 30 mins. after which sodium carbonate (20 g) was added. The sheets were removed after 2 minutes and were dried between blotters in the Palmer Drier.

7. Comparison of Drying Techniques

When the air drying of handsheets was found to be unsuccessful, it was decided to dry at elevated temperatures in a plastics press. The arrangement of the sheet with blotters is shown below:



Each sheet which had been formed from the treated pulp or dyed as described above was dried separately. The temperature in both platens was varied with either the upper or lower platen at 105°C and the other at 70°C. It was found that, in all cases, the steam generated by the drying sheet could not escape and the chlorotriazine compound was reacting before the fibres in the sheet were in close enough contact for cross-linking to take place.

The Palmer Drier did not prevent the escape of steam during drying and sheets dried in this manner showed the properties desired. When handsheets were used, however, the anisotropic stresses introduced during drying caused the sheets to cockle. The machine made paper which was used in later experiments did not have this disadvantage when dried in the machine direction. The sheets were circulated twice between two blotters, when the majority of the water was removed, and a third time without blotters. The temperature of the drum was maintained at 100-105°C.

8. Surface Sizing of Paper with Chlorotriazines

This technique proved to be the most successful in producing papers of high wet strength. To obviate the need for making handsheets it was decided to use machine made paper from cotton linters pulp. Sheets of foolscap size were

impregnated in a solution containing 3 g cross-linking agent, 30 ml N sodium carbonate and 570 ml. water. The excess liquor was squeezed out in an 'Acme' wringer and the paper dried in the Palmer drier as described above. To obtain high extents of reaction it was necessary, owing to the limited solubility of the compounds used, to repeat the process until the desired amount of reagent had been applied.

In order to observe the mechanical effects of the treatment on the paper, duplicate sheets were immersed in water after treatment and redried in the Palmer Drier before testing.

9. Introduction of Intra-Fibre Cross-links into Paper

A series of experiments were carried out in which only intra-fibre cross-links were formed to compare the effect of this form of cross-linking on the mechanical properties of the resultant paper. As this necessitated cross-linking before the sheets were formed, the conformability of the fibres was altered and thus no direct comparison of paper containing inter- and intra-fibre cross-links could be made. The experiments did, however, furnish some data upon the relationship between the conformability of the fibres and the mechanical properties of paper.

Three fibre sources were used: esparto grass, cotton linters and a bleached sulphate. They were all beaten to approximately

30° SR in the Clough Beater before treatment.

The cross-linking agent (5 g) was dissolved in 500 ml. water together with 15 g sodium chloride. Pulp (30 g) was added and the whole diluted to 1500 ml. and stirred for 1 hr.. 10 N sodium hydroxide (20 ml.) was added and the mixture then heated to 90°C and maintained at that temperature for 30 mins.. The pulp was then allowed to cool to room temperature, diluted to 2 l. and disintegrated for 5000 revolutions. After dilution to 0.3 % consistency sheets were formed, pressed and dried in the manner normally employed, the temperature of the stock and the draining time during sheet formation being noted. For comparative purposes further sets of sheets were made by the same method without the addition of cross-linking agent.

10. Reaction of Cyanuric Chloride with Cellulose

Several attempts have been made to react cyanuric chloride with cellulose fibres followed by sheet formation and further reaction to introduce inter-fibre cross-links into the paper.

i) Cotton linters (4 g) were dried over phosphorus pentoxide for 5 days and then refluxed with cyanuric chloride (4 g) in 300 ml. A.R. benzene (dried by azeotropic distillation) for 90 mins. Hydrochloric acid liberated during the reaction was passed, via the condenser, into a conical flask and titrated against 0.025 N sodium hydroxide. After 90 mins. the amount of

hydrochloric acid collected corresponded to 1 triazine ring/4600 anhydroglucose units which, considering the limitations of the experiment, was not significant.

ii) A sheet of cotton linters paper was immersed in 300 ml. 3 % solution of cyanuric chloride in xylene, pressed between two blotters and oven-dried at 140°C. The sheet was then impregnated with 1 % sodium carbonate and redried at 140°C. Another sheet was treated in the same manner without the addition of cyanuric chloride for comparative purposes.

11. Determination of Moisture Content and Basis Weight

The basis weights and moisture contents of the paper treated and conditioned for a minimum of 24 hours at 65 % r.h. (in later experiments 50 % r.h.) and 20°C were determined by cutting a specimen of size 4.17 x 10 cm, using a template and razor blade, from each sheet. The specimen was weighed on an analytical balance using tared weighing bottles and then heated in an oven at 110°C for 4 hours. The new weight of the sample was then determined and the moisture content of the paper, expressed as percentage moisture on the air dry weight of fibre, and basis weight could then be calculated. These samples were not used in any further testing.

12. Determination of Thickness and Sheet Density

A deadweight thickness tester, made by Kelvin and Hughes Ltd., was used. When handsheets were being tested the recommended method⁽⁴⁵⁾ was used. In the case of machine made paper the thickness of a number of 4.17 x 10 cm specimens was measured, the thickness of the sheet being determined by dividing the total thickness by the number of samples in the pad. The results were expressed in millimeters.

The density of the paper under examination was determined by calculating the average basis weight of the paper and dividing by the average thickness of the paper. The results were expressed as grams per cubic centimetre.

13. Load-Extension Measurements on Dry Sheets

Load-extension curves of specimens of 1.5 cm width and 10 cm length, cut on a ^ugillotine, at 65 % r.h. (50 % r.h. in later experiments) and 20°C were measured in the Instron testing machine at a constant rate of extension of 1.0 cm/min. At least 6 specimens were tested from each sample of paper. Where the sample broke at either of the jaws the result was rejected. Some of the load-extension curves obtained show a 'toe'. This region was ignored and the origin of the curve was taken as the point where the line extrapolated from the initial slope (after the toe) of the curve cut the extension axis at zero load. The

initial modulus, breaking load and breaking extension, corresponded to the initial slope, the maximum load obtained, and the extension at this load respectively. The rupture energy was calculated from the area under the curve which was measured with a planimeter. The area under the 'toe' was calculated to be about 0.1 % of the area under the rest of the curve.

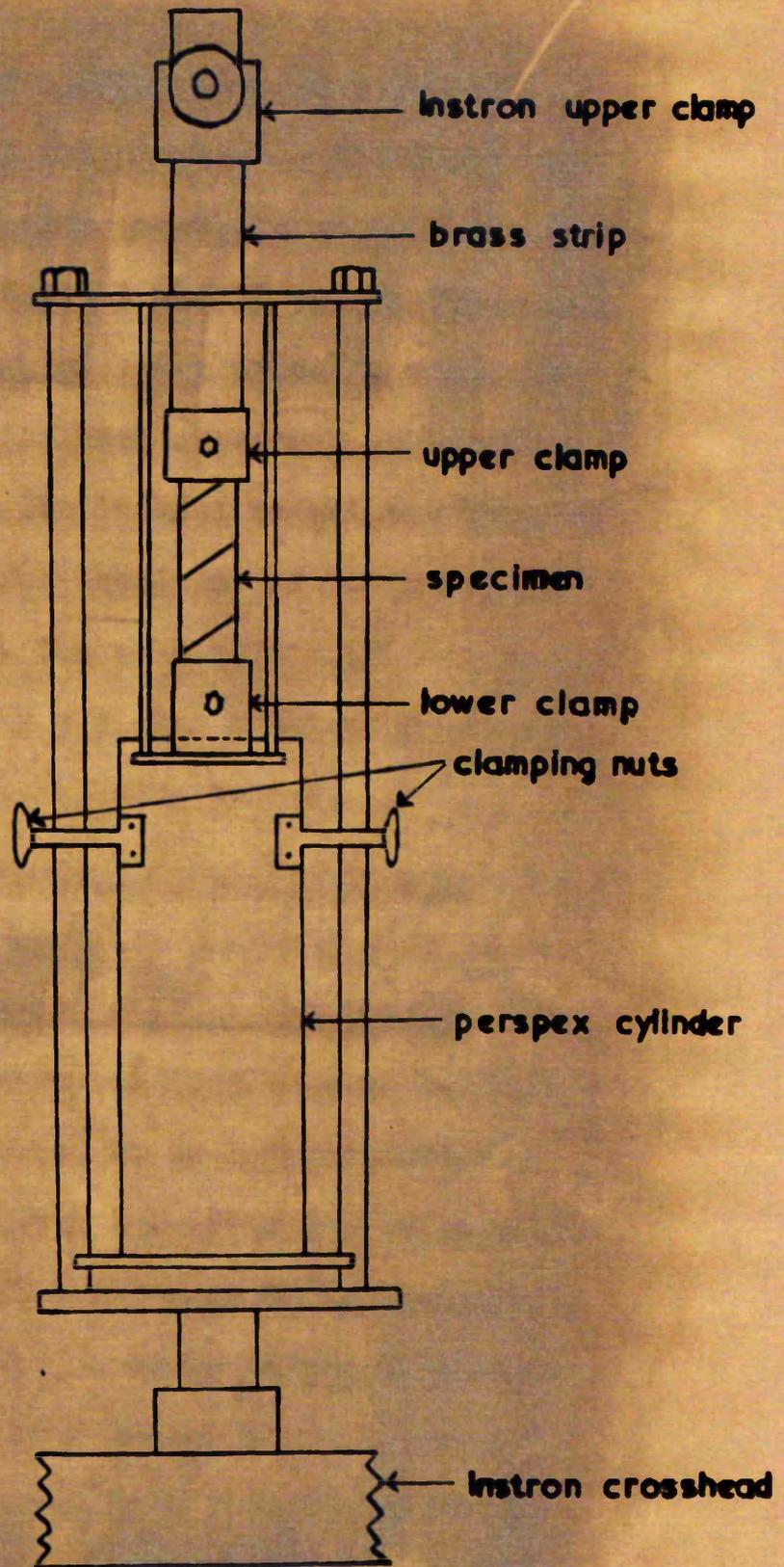
Breaking loads, initial moduli and rupture energies were measured in units of g, g, and g cm.cm^{-1} , respectively. The breaking loads have also been expressed as breaking lengths with units of metres. The initial moduli and rupture energies have been calculated for specimens of 1.5 cm width and of basis weight 70 g.m^{-2} . The mean values of each series of tests have been multiplied by a factor obtained by dividing 70 by the basis weight of the paper being tested.

14. Load-Extension Measurements on Wet Sheets

Load-extension curves of specimens of 1.5 cm width and 10 cm length were measured on an Instron tester at a constant rate of extension of 1 cm/min. after immersion of the specimen for 1 minute in distilled water at 20°C . The ends of the strips were bound with adhesive paper to reduce the number of jaw breaks. The apparatus used for wetting the paper is described more fully by Zeronian and is illustrated in Fig. 2. The load cell was calibrated with the upper clamp immersed in water and

FIG. 2

APPARATUS ATTACHED TO INSTRON FOR TENSILE TESTS
ON WET SPECIMENS



the calibration weight placed on top of the jaw clamps instead of between the jaws. In this way the weight was not immersed in water. The specimen was fitted between the clamps and the cylinder containing distilled water was raised. After one minute the test was started with the specimen still immersed in the water. The dimensions of the apparatus were such that a specimen of 10 cm length could be extended 65 % before the upper clamp emerged from the water.

The origins of the load extension curves were found by the method used for dry paper (see section 13). At least 6 specimens were tested from each sample of treated paper. The properties derived from the curves were expressed in the same units as those for the dry paper.

15. Recovery Measurements on Air-Dry Sheets

Specimens of 1.5 cm width and 10 cm length were tested on the Instron under the same conditions of humidity and temperature as described in section 13. The tests were carried out on 4 specimens from each sheet. Each specimen was extended in successive steps, increasing the strain by 0.25 % for each step until the sample broke. Before the test started the controls on the Instron were set so that the crosshead would go into reverse and return to its original position when it had travelled a predetermined amount. When the cross-

head started to return it was accelerated by using the fast speed return. Zeronian has used a period of 3 minutes for the specimen to recover as sufficient time for delayed recovery to take place. During the recovery period the Instron controls were altered for the next cycle. From the chart (see Fig. 3) the following distances were measured. The original slack in the specimen (A), the extension of the specimen (B) and the slack that appeared in the cycle that followed (C). Then:

$$\% \text{ Strain} = \frac{100 B}{10 + A} \quad \text{and} \quad \% \text{ Recovery} = \frac{B - C + A}{B} \times 100.$$

From these results % recovery v. % strain graphs were plotted.

16. Nitrogen Determinations

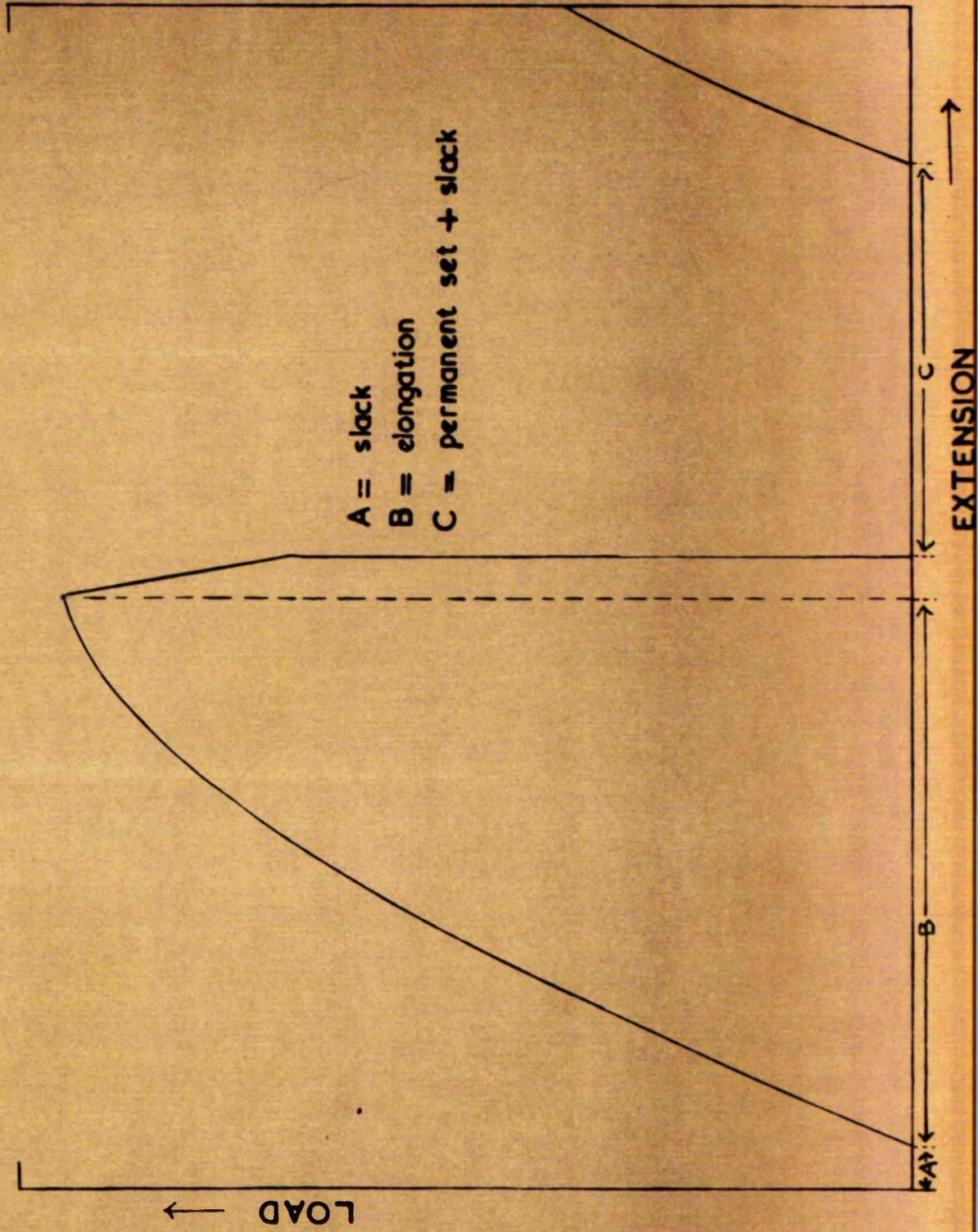
i) Nitrogen Content of Reagents

Approximately 5 mg of the compound under investigation was weighed accurately into a micro Kjeldahl digestion flask together with 5 ml concentrated A.R. sulphuric acid. The boiling point of the sulphuric acid was raised by the addition of 1.5 g of a mixture of 2 % A.R. copper sulphate in anhydrous A.R. sodium sulphate. The contents of the flask were digested for 3 hours when the solution turned to a pale green colour.

The distillation differed from the standard micro procedure in that a macro distillation unit made by the Loughborough Glass Co. was used. The contents of each flask were transferred into the distillation flask and 1.5 ml of

FIG. 3

MEASUREMENT OF ELONGATION COMPONENTS IN A LOADING
AND UNLOADING CYCLE ON PAPER



10 N sodium hydroxide were added. The mixture was then steam distilled for 15 minutes into 10 mls 2 % boric acid solution. The ammonium borate formed was titrated against 0.02 N hydrochloric acid using a mixture of methylene blue and methyl red (0.125 g methyl red and 0.083 g methylene blue in 100 mls ethanol) as an indicator.

ii) Nitrogen Content of Paper

The sample of paper (approximately 200 mg) was cut into pieces of approximately 0.2 x 1.0 cm, care being taken not to touch the paper. The paper was then digested and distilled by the same procedure as outlined above.

17. Determination of Tearing Resistance

The tearing resistance was determined on a Marx-Elmendorf Tearing Tester using two specimen for each test. There was insufficient paper for the recommended 5 tests and the results have been obtained from 3 or 4 tests for each set of sheets. The results have been expressed as a 'tearing factor', i.e. the ratio of the tearing resistance in grams to the substance of the paper in gsm.

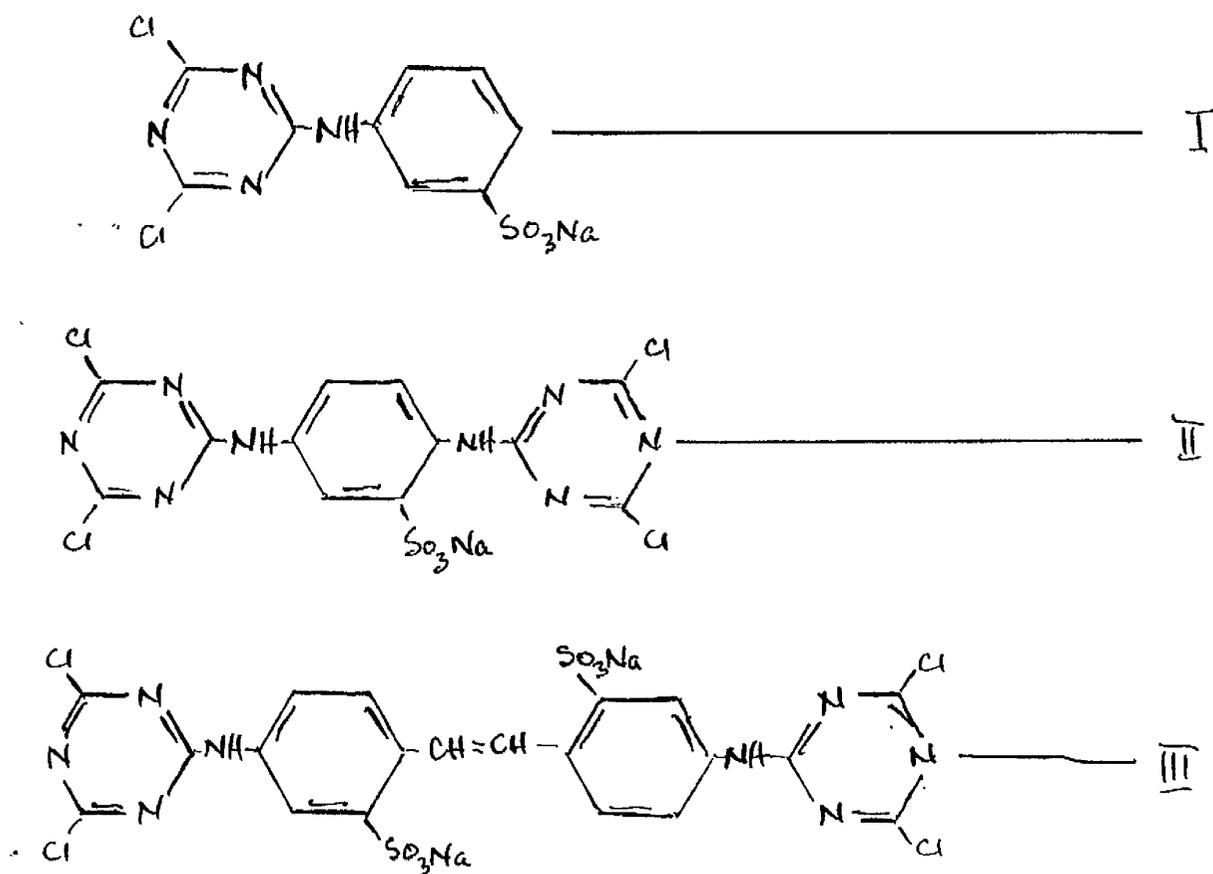
18. Determination of Air Permeability

The air permeability of handsheets was measured on a Bendtsen Smoothness and Porosity Tester. Three measurements were made on each half sheet, six half-sheets being tested in all. The results were recorded as mls./min. over 10 cm² paper.

CHAPTER IV

Results

The compounds used in most of the cross-linking work have been represented in the following manner:



Pages 64 and 65 have been interchanged

Table I

Mechanical Properties of Paper treated with Alkali (Machine Direction) Tests at 50 % r.h. and 20°C.

| No. of treatments | 0 | 1 | 2 | 3 | 5 | 7 |
|--|------|------|------|------|------|------|
| <u>Tensile Strength</u> (m) | 3362 | 2724 | 2421 | 2363 | 2157 | 2155 |
| Standard deviation (m) | 114 | 133 | 63 | 90 | 63 | 67 |
| Coefft.of variation (%) | 3.4 | 4.9 | 2.6 | 3.8 | 2.9 | 3.1 |
| <u>Breaking Extension</u> (%) | 1.65 | 1.98 | 1.90 | 1.98 | 1.94 | 1.92 |
| Standard deviation (%) | 0.17 | 0.11 | 0.08 | 0.18 | 0.07 | 0.07 |
| Coefft.of variation (%) | 10.3 | 5.6 | 4.2 | 9.1 | 3.6 | 3.6 |
| <u>Initial Modulus</u> (g x 10 ⁻⁵) | 5.09 | 1.99 | 1.89 | 1.73 | 1.68 | 1.59 |
| Standard dev. (g x 10 ⁻⁵) | 0.33 | 0.18 | 0.10 | 0.10 | 0.08 | 0.10 |
| Coefft.of variation (%) | 6.4 | 8.9 | 5.5 | 5.5 | 4.9 | 6.0 |
| <u>Rupture Energy</u> (g.cm.cm ⁻¹) | 47.6 | 40.1 | 33.9 | 35.4 | 31.2 | 31.0 |
| Standard dev. (g.cm.cm ⁻¹) | 4.3 | 6.7 | 2.9 | 3.6 | 2.2 | 2.3 |
| Coefft.of variation (%) | 9.4 | 16.7 | 8.7 | 10.1 | 7.2 | 7.5 |

Table II

Mechanical Properties of Paper Treated with Alkali (Cross Direction) Tests at 50 % r.h. and 20°C.

| No. of treatments | 0 | 1 | 2 | 3 | 5 | 7 |
|--|------|------|------|------|------|------|
| <u>Tensile Strength</u> (m) | 3403 | 2298 | 2204 | 2102 | 1910 | 1808 |
| Standard deviation (m) | 107 | 71 | 73 | 55 | 78 | 16 |
| Coefft.of variation (%) | 3.1 | 3.1 | 3.3 | 2.6 | 4.1 | 0.9 |
| <u>Breaking Extension</u> (%) | 1.83 | 2.99 | 2.84 | 2.78 | 2.65 | 2.32 |
| Standard deviation (%) | 0.12 | 0.16 | 0.20 | 0.14 | 0.29 | 0.08 |
| Coefft.of variation (%) | 6.5 | 5.4 | 7.0 | 5.0 | 10.9 | 3.4 |
| <u>Initial Modulus</u> (g x 10 ⁻⁵) | 5.26 | 1.38 | 1.38 | 1.30 | 1.19 | 1.17 |
| Standard dev. (g x 10 ⁻⁵) | 0.34 | 0.08 | 0.07 | 0.06 | 0.06 | 0.03 |
| Coefft.of variation (%) | 6.4 | 6.1 | 4.8 | 4.3 | 4.7 | 2.2 |
| <u>Rupture Energy</u> (g.cm.cm ⁻¹) | 39.9 | 54.7 | 46.4 | 44.1 | 40.2 | 30.9 |
| Standard dev. (g.cm.cm ⁻¹) | 3.8 | 4.3 | 7.8 | 3.3 | 4.6 | 1.5 |
| Coefft.of variation (%) | 9.6 | 7.9 | 16.8 | 7.4 | 11.5 | 4.7 |

Table III

Mechanical Properties of Paper Treated with I (Machine Direction)
Tests at 50 % r.h. and 20°C.

| | | | | | | |
|--|------|------|------|------|------|------|
| Reagent (%) | 0.52 | 0.83 | 1.11 | 1.47 | 2.16 | 2.51 |
| <u>Tensile Strength</u> (m) | 2647 | 2809 | 2829 | 3167 | 3325 | 3252 |
| Standard deviation (m) | 130 | 124 | 156 | 98 | 73 | 88 |
| Coefft.of variation (%) | 4.9 | 4.4 | 5.5 | 3.1 | 2.2 | 2.7 |
| <u>Breaking Extension</u> (%) | 1.94 | 2.15 | 2.12 | 2.25 | 2.39 | 2.22 |
| Standard deviation (%) | 0.23 | 0.22 | 0.36 | 0.15 | 0.20 | 0.17 |
| Coefft.of variation (%) | 11.9 | 10.2 | 17.0 | 6.7 | 8.4 | 7.7 |
| <u>Initial Modulus</u> (g x 10 ⁻⁵) | 4.04 | 4.02 | 3.94 | 4.07 | 3.87 | 3.86 |
| Standard dev. (g x 10 ⁻⁵) | 0.21 | 0.34 | 0.21 | 0.44 | 0.13 | 0.15 |
| Coefft.of variation (%) | 5.3 | 8.4 | 5.4 | 10.9 | 3.3 | 4.0 |
| <u>Rupture Energy</u> (g.cm.cm ⁻¹) | 39.0 | 44.6 | 42.3 | 52.8 | 58.1 | 51.9 |
| Standard dev. (g.cm.cm ⁻¹) | 4.1 | 5.5 | 6.0 | 3.4 | 6.9 | 5.4 |
| Coefft.of variation (%) | 10.4 | 12.4 | 14.1 | 6.5 | 11.9 | 10.4 |

Table IV

Mechanical Properties of Paper Treated with I (Cross Direction)
Tests at 50 % r.h. and 20°C.

| | | | | | | |
|--|------|------|------|------|------|------|
| Reagent (%) . | 0.48 | 0.69 | 0.89 | 1.65 | 1.86 | 2.64 |
| <u>Tensile Strength</u> (m) | 2280 | 2459 | 2634 | 2741 | 2708 | 2918 |
| Standard deviation (m) | 75 | 66 | 74 | 49 | 89 | 114 |
| Coefft.of variation (%) | 3.3 | 2.7 | 2.8 | 1.8 | 3.3 | 3.9 |
| <u>Breaking Extension</u> (%) | 2.11 | 2.79 | 3.12 | 3.09 | 2.81 | 2.63 |
| Standard deviation (%) | 0.32 | 0.22 | 0.20 | 0.16 | 0.27 | 0.28 |
| Coefft.of variation (%) | 5.2 | 7.9 | 6.4 | 5.2 | 9.6 | 10.6 |
| <u>Initial Modulus</u> (g x 10 ⁻⁵) | 3.50 | 3.21 | 3.18 | 3.19 | 2.96 | 3.06 |
| Standard dev. (g x 10 ⁻⁵) | 0.13 | 0.09 | 0.10 | 0.10 | 0.15 | 0.17 |
| Coefft.of variat.(g x 10 ⁻⁵) | 3.7 | 2.8 | 3.2 | 3.2 | 5.2 | 5.6 |
| <u>Rupture Energy</u> (g.cm.cm ⁻¹) | 48.7 | 53.3 | 63.9 | 62.9 | 57.2 | 59.1 |
| Standard dev. (g.cm.cm ⁻¹) | 3.9 | 4.8 | 3.4 | 10.1 | 4.0 | 12.9 |
| Coefft.of variation (%) | 9.3 | 9.0 | 5.3 | 16.1 | 7.0 | 21.8 |

Table V

Mechanical Properties of Paper Treated with II (Machine Direction) Tests at 50 % r.h. and 20°C.

| | | | | | | |
|--|------|------|------|------|------|------|
| Reagent (%) | 0.37 | 1.04 | 1.36 | 1.90 | 2.17 | 3.23 |
| <u>Tensile Strength</u> (m) | 2591 | 2636 | 3066 | 3110 | 3194 | 3316 |
| Standard deviation (m) | 44 | 126 | 49 | 93 | 89 | 73 |
| Coefft.of variation (%) | 1.7 | 4.8 | 1.6 | 3.0 | 2.8 | 2.2 |
| <u>Breaking Extension</u> (%) | 2.16 | 1.89 | 2.29 | 2.23 | 2.20 | 2.13 |
| Standard deviation (%) | 0.17 | 0.04 | 0.13 | 0.10 | 0.11 | 0.21 |
| Coefft.of variation (%) | 7.7 | 2.2 | 5.8 | 4.4 | 5.2 | 9.7 |
| <u>Initial Modulus</u> (g x 10 ⁻⁵) | 3.66 | 3.68 | 3.65 | 3.49 | 3.48 | 3.53 |
| Standard dev. (g x 10 ⁻⁵) | 0.11 | 0.14 | 0.17 | 0.11 | 0.11 | 0.20 |
| Coefft.of variation (%) | 3.0 | 3.7 | 4.7 | 3.2 | 3.3 | 5.8 |
| <u>Rupture Energy</u> (g.cm.cm ⁻¹) | 44.6 | 37.7 | 50.8 | 50.1 | 50.2 | 50.5 |
| Standard dev. (g.cm.cm ⁻¹) | 2.7 | 1.9 | 3.9 | 3.8 | 4.7 | 5.5 |
| Coefft.of variation (%) | 6.2 | 5.1 | 7.7 | 7.6 | 9.3 | 10.9 |

Table VI

Mechanical Properties of Paper Treated with II (Cross Direction)
Tests at 50 % r.h. and 20°C.

| | | | | | | |
|--|------|------|------|------|------|------|
| Reagent (%) | 0.52 | 0.86 | 0.90 | 1.54 | 2.27 | 2.70 |
| <u>Tensile Strength</u> (m) | 2313 | 2438 | 2527 | 2820 | 2686 | 2730 |
| Standard deviation (m) | 99 | 51 | 86 | 68 | 180 | 63 |
| Coefft.of variation (%) | 4.3 | 2.1 | 3.4 | 2.4 | 6.7 | 2.3 |
| <u>Breaking Extension</u> (%) | 2.62 | 3.00 | 2.92 | 3.20 | 2.78 | 2.85 |
| Standard deviation (%) | 0.21 | 0.31 | 0.30 | 0.18 | 0.14 | 0.15 |
| Coefft.of variation (%) | 7.9 | 10.3 | 10.2 | 5.6 | 5.0 | 5.4 |
| <u>Initial Modulus</u> (g x 10 ⁻⁵) | 2.84 | 2.71 | 2.74 | 2.70 | 2.61 | 2.51 |
| Standard dev. (g x 10 ⁻⁵) | 0.12 | 0.09 | 0.12 | 0.21 | 0.04 | 0.07 |
| Coefft.of variation (%) | 4.1 | 3.4 | 4.5 | 7.6 | 1.7 | 2.7 |
| <u>Rupture Energy</u> (g.cm.cm ⁻¹) | 46.4 | 58.4 | 55.5 | 67.6 | 54.9 | 55.6 |
| Standard dev. (g.cm.cm ⁻¹) | 6.1 | 5.0 | 6.4 | 5.9 | 3.2 | 6.4 |
| Coefft.of variation (%) | 13.1 | 8.5 | 11.5 | 8.7 | 5.9 | 11.6 |

Table VII

Mechanical Properties of Paper Treated with III (Machine Direction) Tests at 50 % r.h. and 20°C.

| | | | | | | |
|--|------|------|------|------|------|------|
| Reagent (%) | 0.58 | 0.84 | 1.27 | 1.71 | 2.07 | 2.65 |
| <u>Tensile Strength</u> (m) | 2776 | 3177 | 3175 | 3404 | 3539 | 3578 |
| Standard deviation (m) | 108 | 54 | 57 | 89 | 67 | 100 |
| Coefft.of variation (%) | 3.9 | 1.7 | 1.8 | 2.6 | 1.9 | 2.8 |
| <u>Breaking Extension</u> (%) | 1.98 | 2.25 | 2.10 | 2.11 | 2.19 | 2.01 |
| Standard deviation (%) | 0.19 | 0.13 | 0.13 | 0.11 | 0.18 | 0.03 |
| Coefft.of variation (%) | 9.6 | 5.8 | 6.0 | 5.1 | 8.1 | 1.6 |
| <u>Initial Modulus</u> (g x 10 ⁻⁵) | 4.07 | 4.31 | 4.28 | 4.40 | 4.28 | 4.44 |
| Standard dev. (g x 10 ⁻⁵) | 0.18 | 0.24 | 0.11 | 0.18 | 0.19 | 0.19 |
| Coefft.of variation (%) | 4.4 | 5.6 | 2.6 | 4.0 | 4.5 | 4.3 |
| <u>Rupture Energy</u> (g.cm.cm ⁻¹) | 42.1 | 53.9 | 49.7 | 53.6 | 56.6 | 49.2 |
| Standard dev. (g.cm.cm ⁻¹) | 3.7 | 4.3 | 4.1 | 3.9 | 5.0 | 4.5 |
| Coefft.of variation (%) | 8.7 | 8.0 | 8.2 | 7.2 | 8.8 | 9.2 |

Table VIII

Mechanical Properties of Paper Treated with III (Cross Direction) Tests at 50 % r.h. and 20°C.

| | | | | | | |
|--|------|------|------|------|------|------|
| Reagent (%) | 0.59 | 0.81 | 1.21 | 1.75 | 2.03 | 2.69 |
| <u>Tensile Strength</u> (m) | 2484 | 2543 | 2784 | 2867 | 3098 | 3301 |
| Standard deviation (m) | 57 | 86 | 42 | 75 | 68 | 83 |
| Coefft.of variation (%) | 2.3 | 3.4 | 1.5 | 2.6 | 2.2 | 2.5 |
| <u>Breaking Extension</u> (%) | 2.63 | 2.51 | 2.68 | 2.40 | 2.68 | 2.74 |
| Standard deviation (%) | 0.21 | 0.30 | 0.12 | 0.26 | 0.17 | 0.17 |
| Coefft.of variation (%) | 8.1 | 11.8 | 4.6 | 10.8 | 6.3 | 6.3 |
| <u>Initial Modulus</u> (g x 10 ⁻⁵) | 3.19 | 3.24 | 3.30 | 3.40 | 3.50 | 3.62 |
| Standard dev. (g x 10 ⁻⁵) | 0.15 | 0.20 | 0.12 | 0.10 | 0.09 | 0.16 |
| Coefft.of variation (%) | 4.6 | 6.2 | 3.5 | 2.8 | 2.6 | 4.4 |
| <u>Rupture Energy</u> (g.cm.cm ⁻¹) | 51.1 | 49.6 | 57.5 | 53.6 | 62.8 | 68.3 |
| Standard dev. (g.cm.cm ⁻¹) | 5.6 | 9.2 | 3.0 | 7.7 | 5.3 | 6.4 |
| Coefft.of variation (%) | 10.9 | 18.5 | 5.3 | 14.3 | 8.4 | 9.4 |

Table IX

Mechanical Properties of Paper Treated with Alkali (Machine Direction) Specimens soaked in distilled water at 20°C for 1 minute before start of test.

| No. of treatments | 0 | 1 | 2 | 3 | 5 | 7 |
|--|-------|-------|-------|-------|-------|------|
| <u>Tensile Strength</u> (g) | 147 | 60 | 57 | 61 | 66 | 77 |
| Standard deviation (g) | 21 | 6.6 | 9.9 | 5.0 | 3.0 | 3.9 |
| Coefft.of variation (%) | 14.0 | 11.0 | 17.4 | 8.2 | 4.5 | 5.1 |
| <u>Breaking Extension</u> (%) | 0.80 | 0.78 | 1.04 | 1.07 | 1.47 | 1.54 |
| Standard deviation (%) | 0.17 | 0.09 | 0.27 | 0.11 | 0.13 | 0.15 |
| Coefft.of variation (%) | 21.0 | 11.9 | 25.9 | 9.8 | 8.9 | 9.5 |
| <u>Initial Modulus</u> (g x 10 ⁻⁴) | 3.08 | 1.08 | 0.83 | 0.82 | 0.69 | 0.70 |
| Standard dev. (g x 10 ⁻⁴) | 0.62 | 0.11 | 0.11 | 0.08 | 0.04 | 0.64 |
| Coefft.of variation (%) | 20.1 | 11.8 | 13.2 | 9.9 | 6.3 | 5.4 |
| <u>Rupture Energy</u> (g.cm.cm ⁻¹) | 1.03 | 0.30 | 0.39 | 0.44 | 0.65 | 0.73 |
| Standard dev. (g.cm.cm ⁻¹) | 0.079 | 0.073 | 0.176 | 0.045 | 0.107 | 0.12 |
| Coefft.of variation (%) | 7.7 | 23.3 | 45.1 | 10.3 | 16.4 | 1.6 |

Table XI

Mechanical Properties of Paper Treated with I (Machine Direction) Specimens soaked in distilled water at 20°C for 1 minute before start of test.

| | | | | | | |
|--|------|------|------|------|------|------|
| Reagent (%) | 0.52 | 0.83 | 1.11 | 1.47 | 2.16 | 2.51 |
| <u>Tensile Strength</u> (g) | 303 | 894 | 1187 | 1419 | 1648 | 1695 |
| Standard deviation (g) | 26.6 | 51.9 | 51.0 | 131 | 85.7 | 197 |
| Coefft.of variation (%) | 8.8 | 5.8 | 4.3 | 9.2 | 5.2 | 11.6 |
| <u>Breaking Extension</u> (%) | 1.33 | 3.34 | 3.90 | 3.88 | 4.00 | 3.78 |
| Standard deviation (%) | 0.20 | 0.27 | 0.21 | 0.29 | 0.26 | 0.43 |
| Coefft.of variation (%) | 15.0 | 8.1 | 5.4 | 7.5 | 6.5 | 11.4 |
| <u>Initial Modulus</u> (g x 10 ⁻⁴) | 3.31 | 5.28 | 5.89 | 6.41 | 7.16 | 7.92 |
| Standard dev. (g x 10 ⁻⁴) | 0.27 | 0.25 | 0.32 | 0.44 | 0.47 | 0.53 |
| Coefft.of variation (%) | 8.2 | 4.7 | 5.4 | 6.8 | 6.6 | 6.7 |
| <u>Rupture Energy</u> (g.cm.cm ⁻¹) | 2.27 | 19.1 | 28.4 | 31.6 | 40.1 | 39.3 |
| Standard dev. (g.cm.cm ⁻¹) | 0.33 | 2.3 | 2.8 | 0.9 | 5.1 | 1.8 |
| Coefft.of variation (%) | 14.7 | 11.9 | 9.7 | 2.9 | 12.6 | 4.5 |

Table X

Mechanical Properties of Paper Treated with Alkali (Cross Direction) Specimens soaked in distilled water at 20°C for 1 minute before start of test.

| No. of treatments | 0 | 1 | 2 | 3 | 5 | 7 |
|--|-------|------|-------|-------|-------|-------|
| <u>Tensile Strength</u> (g) | 149 | 62 | 59 | 63 | 63 | 69 |
| Standard deviation (g) | 6.0 | 7.6 | 3.5 | 5.9 | 4.7 | 5.5 |
| Coefft.of variation (%) | 4.0 | 12.3 | 6.0 | 9.3 | 7.4 | 7.9 |
| <u>Breaking Extension</u> (%) | 0.90 | 1.08 | 1.29 | 1.50 | 1.63 | 1.76 |
| Standard deviation (%) | 0.10 | 0.19 | 0.17 | 0.21 | 0.02 | 0.20 |
| Coefft.of variation (%) | 11.1 | 17.3 | 13.2 | 13.9 | 1.4 | 11.4 |
| <u>Initial Modulus</u> (g x 10 ⁻⁴) | 3.42 | 0.75 | 0.64 | 0.62 | 0.59 | 0.59 |
| Standard dev. (g x 10 ⁻⁴) | 0.36 | 0.07 | 0.08 | 0.06 | 0.07 | 0.06 |
| Coefft.of variation (%) | 10.5 | 9.1 | 12.3 | 8.9 | 12.5 | 10.0 |
| <u>Rupture Energy</u> (g.cm.cm ⁻¹) | 0.98 | 0.46 | 0.44 | 0.62 | 0.67 | 0.77 |
| Standard dev. (g.cm.cm ⁻¹) | 0.075 | 0.13 | 0.096 | 0.081 | 0.029 | 0.126 |
| Coefft.of variation (%) | 7.7 | 28.3 | 21.8 | 13.1 | 4.4 | 16.5 |

Table XII

Mechanical Properties of Paper Treated with I (Cross Direction)
Specimens soaked in distilled water at 20°C for 1 minute
before start of test.

| | | | | | | |
|--|------|------|------|------|------|------|
| Reagent (%) | 0.48 | 0.69 | 0.89 | 1.65 | 1.86 | 2.64 |
| <u>Tensile Strength</u> (g) | 331 | 763 | 973 | 1182 | 1348 | 1609 |
| Standard deviation (g) | 9.6 | 2.9 | 19.5 | 42.6 | 68.7 | 14.4 |
| Coefft.of variation (%) | 2.9 | 3.8 | 2.0 | 3.6 | 5.1 | 0.9 |
| <u>Breaking Extension</u> (%) | 2.85 | 4.24 | 4.87 | 4.96 | 5.08 | 4.80 |
| Standard deviation (%) | 0.11 | 0.34 | 0.14 | 0.26 | 0.10 | 0.09 |
| Coefft.of variation (%) | 3.9 | 7.9 | 2.9 | 2.9 | 2.0 | 1.9 |
| <u>Initial Modulus</u> (g x 10 ⁻⁴) | 2.29 | 3.28 | 3.70 | 4.13 | 4.28 | 5.42 |
| Standard dev. (g x 10 ⁻⁴) | 0.32 | 0.52 | 0.27 | 0.29 | 0.24 | 0.54 |
| Coefft.of variation (%) | 14.1 | 16.0 | 7.2 | 7.1 | 5.7 | 10.0 |
| <u>Rupture Energy</u> (g.cm.cm ⁻¹) | 6.05 | 19.5 | 27.8 | 33.9 | 39.4 | 45.2 |
| Standard dev. (g.cm.cm ⁻¹) | 0.47 | 1.6 | 1.6 | 1.6 | 3.6 | 1.8 |
| Coefft.of variation (%) | 7.7 | 8.0 | 5.9 | 4.6 | 9.1 | 3.9 |

Table VIII

Mechanical Properties of Paper Treated with II (Machine Direction) Specimens soaked in distilled water at 20°C for 1 minute before start of test.

| | | | | | | |
|--|------|------|------|------|------|------|
| Reagent (%) | 0.37 | 1.04 | 1.36 | 1.90 | 2.17 | 3.23 |
| <u>Tensile Strength</u> (g) | 697 | 1109 | 1312 | 1550 | 1804 | 1935 |
| Standard deviation (g) | 30.7 | 68.8 | 89.2 | 132 | 119 | 92.9 |
| Coefft.of variation (%) | 4.4 | 6.2 | 6.8 | 8.5 | 6.6 | 4.8 |
| <u>Breaking Extension</u> (%) | 2.94 | 3.84 | 3.83 | 3.75 | 3.86 | 3.50 |
| Standard deviation (%) | 0.23 | 0.25 | 0.14 | 0.26 | 0.16 | 0.14 |
| Coefft.of variation (%) | 7.8 | 6.5 | 3.7 | 6.9 | 4.1 | 4.0 |
| <u>Initial Modulus</u> (g x 10 ⁻⁴) | 3.58 | 5.33 | 5.55 | 7.12 | 7.60 | 8.75 |
| Standard dev. (g x 10 ⁻⁴) | 0.19 | 0.50 | 0.56 | 0.21 | 0.49 | 0.82 |
| Coefft.of variation (%) | 5.3 | 9.4 | 10.1 | 2.9 | 6.5 | 9.4 |
| <u>Rupture Energy</u> (g.cm.cm ⁻¹) | 12.1 | 26.2 | 28.6 | 32.8 | 41.6 | 39.4 |
| Standard dev. (g.cm.cm ⁻¹) | 1.4 | 3.5 | 1.7 | 3.1 | 5.8 | 5.2 |
| Coefft.of variation (%) | 11.3 | 13.4 | 6.0 | 9.4 | 14.0 | 13.1 |

Table XIV

Mechanical Properties of Paper Treated with II (Cross Direction)
Specimens soaked in distilled water at 20°C for 1 minute before
start of test.

| | | | | | | |
|--|------|------|------|------|------|------|
| Reagent (%) | 0.52 | 0.86 | 0.90 | 1.54 | 2.27 | 2.70 |
| <u>Tensile Strength</u> (g) | 579 | 821 | 1112 | 1419 | 1529 | 1637 |
| Standard deviation (%) | 29.0 | 72.2 | 74.5 | 56.8 | 78.0 | 57.3 |
| Coefft.of variation (%) | 5.0 | 8.8 | 6.7 | 4.0 | 5.1 | 3.5 |
| <u>Breaking Extension</u> (%) | 3.86 | 3.90 | 4.89 | 5.02 | 5.09 | 4.94 |
| Standard deviation (%) | 0.13 | 0.29 | 0.26 | 0.16 | 0.23 | 0.26 |
| Coefft.of variation (%) | 3.4 | 7.4 | 5.3 | 3.2 | 4.5 | 5.3 |
| <u>Initial Modulus</u> (g x 10 ⁻⁴) | 2.64 | 3.06 | 3.51 | 4.47 | 4.62 | 5.67 |
| Standard dev. (g x 10 ⁻⁴) | 0.20 | 0.36 | 0.45 | 0.25 | 0.27 | 0.48 |
| Coefft.of variation (%) | 7.6 | 11.7 | 12.9 | 5.7 | 5.9 | 8.5 |
| <u>Rupture Energy</u> (g.cm.cm ⁻¹) | 14.1 | 19.3 | 31.1 | 42.0 | 44.2 | 47.5 |
| Standard dev. (g.cm.cm ⁻¹) | 1.2 | 4.1 | 5.2 | 5.0 | 4.7 | 3.8 |
| Coefft.of variation (%) | 8.3 | 21.5 | 16.6 | 12.0 | 10.6 | 8.0 |

Table XV

Mechanical Properties of Paper Treated with III (Machine Direction) Specimens soaked in distilled water at 20°C for 1 minute before start of test.

| | | | | | | |
|--|------|------|------|------|------|------|
| Reagent (%) | 0.58 | 0.84 | 1.27 | 1.71 | 2.07 | 2.65 |
| <u>Tensile Strength</u> (g) | 797 | 1103 | 1265 | 1628 | 1810 | 2030 |
| Standard deviation (g) | 14.3 | 73.9 | 106 | 76.5 | 43.4 | 69.0 |
| Coefft.of variation (%) | 1.8 | 6.7 | 8.4 | 4.7 | 2.4 | 3.4 |
| <u>Breaking Extension</u> (%) | 3.38 | 3.66 | 3.78 | 4.05 | 4.28 | 4.23 |
| Standard deviation (%) | 0.21 | 0.34 | 0.20 | 0.04 | 0.34 | 0.20 |
| Coefft.of variation (%) | 6.1 | 9.3 | 5.2 | 1.0 | 7.9 | 4.8 |
| <u>Initial Modulus</u> (g x 10 ⁻⁴) | 5.51 | 6.09 | 6.76 | 8.07 | 8.49 | 8.75 |
| Standard dev. (g x 10 ⁻⁴) | 0.34 | 0.52 | 0.48 | 0.43 | 0.87 | 0.76 |
| Coefft.of variation (%) | 6.1 | 8.5 | 7.1 | 5.3 | 10.2 | 8.7 |
| <u>Rupture Energy</u> (g.cm.cm ⁻¹) | 17.5 | 26.2 | 28.9 | 40.6 | 46.9 | 50.4 |
| Standard dev. (g.cm.cm ⁻¹) | 1.3 | 4.3 | 1.9 | 2.8 | 5.3 | 2.3 |
| Coefft.of variation (%) | 7.2 | 16.5 | 6.5 | 6.9 | 11.2 | 4.6 |

Table XVI

Mechanical Properteis of Paper Treated with III (Cross Direction)
Specimens soaked in distilled water at 20°C for 1 minute before
start of test.

| | | | | | | |
|--|------|------|------|------|------|------|
| Reagent (%) | 0.59 | 0.81 | 1.21 | 1.75 | 2.03 | 2.69 |
| <u>Tensile Strength</u> (g) | 615 | 877 | 1106 | 1359 | 1567 | 1862 |
| Standard deviation (g) | 16.6 | 37.7 | 85.2 | 32.6 | 121 | 147 |
| Coefft.of variation (%) | 2.7 | 4.3 | 7.7 | 2.4 | 7.7 | 7.9 |
| <u>Breaking Extension</u> (%) | 3.98 | 4.12 | 4.54 | 4.89 | 4.93 | 4.97 |
| Standard deviation (%) | 0.38 | 0.41 | 0.49 | 0.10 | 0.55 | 0.17 |
| Coefft.of variation (%) | 9.5 | 9.9 | 10.9 | 2.0 | 11.1 | 3.4 |
| <u>Initial Modulus</u> (g x 10 ⁻⁴) | 3.19 | 3.24 | 3.30 | 3.40 | 3.50 | 3.62 |
| Standard dev. (g x 10 ⁻⁴) | 0.15 | 0.20 | 0.12 | 0.10 | 0.09 | 0.16 |
| Coefft.of variation (%) | 4.6 | 6.2 | 3.5 | 2.8 | 2.6 | 4.4 |
| <u>Rupture Energy</u> (g.cm.cm ⁻¹) | 16.2 | 22.7 | 29.4 | 38.4 | 44.8 | 54.1 |
| Standard dev. (g.cm.cm ⁻¹) | 1.6 | 2.2 | 5.9 | 2.7 | 9.2 | 3.6 |
| Coefft.of variation (%) | 9.7 | 9.5 | 20.2 | 7.0 | 20.5 | 6.6 |

Table XVII

Mechanical Properties of Paper Treated with III (Machine Direction)
Before wetting. Tests at 65 % r.h. and 20°C.

| | | | | | | |
|--|------|------|------|-------|-------|------|
| Reagent (%) | 0.02 | 0.03 | 0.10 | 0.125 | 0.225 | 0.36 |
| <u>Tensile Strength</u> (kg) | 3.29 | 3.07 | 3.19 | 3.17 | 3.04 | 2.99 |
| Standard deviation (kg) | 0.08 | 0.12 | 0.09 | 0.06 | 0.09 | 0.06 |
| Coefft.of variation (%) | 2.4 | 3.9 | 2.0 | 1.9 | 3.0 | 2.0 |
| <u>Breaking Extension</u> (%) | 2.28 | 2.38 | 2.44 | 2.37 | 2.53 | 2.63 |
| Standard dev. (%) | 0.25 | 0.18 | 0.12 | 0.22 | 0.15 | 0.18 |
| Coefft.of variation (%) | 9.2 | 7.6 | 4.9 | 9.3 | 5.9 | 6.8 |
| <u>Initial Modulus</u> (g x 10 ⁻⁵) | 4.68 | 4.52 | 4.75 | 4.74 | 4.11 | 3.97 |
| Standard dev. (g x 10 ⁻⁵) | 0.42 | 0.44 | 0.29 | 0.32 | 0.31 | 0.08 |
| Coefft.of variation (%) | 9.0 | 9.7 | 6.1 | 6.8 | 7.6 | 2.0 |

Table XVIII

Mechanical Properties of Paper Treated with III (Machine Direction) After Wetting. Tests at 65 % r.h. and 20°C.

| Reagent (%) | 0.02 | 0.03 | 0.10 | 0.125 | 0.225 | 0.36 |
|--|------|------|------|-------|-------|------|
| <u>Tensile Strength</u> (kg) | 3.07 | 3.01 | 2.93 | 3.20 | 3.05 | 2.96 |
| Standard deviation (kg) | 0.10 | 0.05 | 0.09 | 0.08 | 0.10 | 0.12 |
| Coefft.of variation (%) | 3.3 | 1.7 | 3.1 | 2.5 | 3.3 | 4.1 |
| <u>Breaking Extension</u> (%) | 2.06 | 2.39 | 2.37 | 2.56 | 2.39 | 2.29 |
| Standard deviation (%) | 0.21 | 0.19 | 0.29 | 0.20 | 0.21 | 0.24 |
| Coefft.of variation (%) | 10.2 | 7.9 | 12.2 | 7.8 | 8.8 | 10.5 |
| <u>Initial Modulus</u> (g x 10 ⁻⁵) | 4.44 | 4.21 | 4.23 | 4.31 | 4.18 | 3.98 |
| Standard dev. (g x 10 ⁻⁵) | 0.12 | 0.46 | 0.35 | 0.34 | 0.25 | 0.13 |
| Coefft.of variation (%) | 2.7 | 10.7 | 8.3 | 7.9 | 6.0 | 3.3 |

Table XIX

Mechanical Properties of Paper Treated with III (Cross Direction) Before Wetting. Tests at 65 % r.h. and 20°C.

| Reagent (%) | 0.02 | 0.03 | 0.10 | 0.125 | 0.225 | 0.36 |
|--|-------|------|------|-------|-------|------|
| <u>Tensile Strength</u> (kg) | 2.52 | 2.53 | 2.63 | 2.58 | 2.57 | 2.44 |
| Standard deviation (kg) | 0.07 | 0.7 | 0.10 | 0.05 | 0.06 | 0.13 |
| Coefft.of variation (%) | 2.8 | 2.8 | 3.8 | 1.9 | 2.3 | 5.3 |
| <u>Breaking Extension</u> (%) | 3.04 | 3.17 | 3.14 | 3.37 | 3.11 | 3.15 |
| Standard deviation (%) | 0.3,4 | 0.42 | 0.34 | 0.13 | 0.40 | 0.31 |
| Coefft.of variation (%) | 11.2 | 13.2 | 10.8 | 3.9 | 12.9 | 9.8 |
| <u>Initial Modulus</u> (g x 10 ⁻⁵) | 2.98 | 2.79 | 3.12 | 3.03 | 3.04 | 2.86 |
| Standard dev. (g x 10 ⁻⁵) | 0.06 | 0.39 | 0.08 | 0.14 | 0.14 | 0.09 |
| Coefft.of variation (%) | 2.0 | 14.0 | 2.6 | 4.6 | 4.6 | 3.1 |

Table XX

Mechanical Properties of Paper Treated with III (Cross Direction) After Wetting. Tests at 65 % r.h. and 20°C.

| | | | | | | |
|--|------|------|------|-------|-------|------|
| Reagent (%) | 0.02 | 0.03 | 0.10 | 0.125 | 0.225 | 0.36 |
| <u>Tensile Strength</u> (kg) | 2.57 | 2.55 | 2.67 | 2.38 | 2.66 | 2.54 |
| Standard deviation (kg) | 0.07 | 0.11 | 0.07 | 0.07 | 0.05 | 0.09 |
| Coefft.of variation (%) | 2.7 | 4.3 | 2.6 | 2.9 | 1.9 | 3.5 |
| <u>Breaking Extension</u> (%) | 3.45 | 3.03 | 3.28 | 3.16 | 3.39 | 3.04 |
| Standard deviation (%) | 0.21 | 0.52 | 0.22 | 0.26 | 0.30 | 0.20 |
| Coefft.of variation (%) | 6.1 | 17.2 | 6.7 | 8.2 | 8.8 | 6.6 |
| <u>Initial Modulus</u> (g x 10 ⁻⁵) | 3.15 | 3.18 | 3.23 | 2.82 | 3.07 | 2.86 |
| Standard dev. (g x 10 ⁻⁵) | 0.30 | 0.06 | 0.24 | 0.10 | 0.21 | 0.22 |
| Coefft.of variation (%) | 9.5 | 1.9 | 7.4 | 3.5 | 6.8 | 7.7 |

Table XXI

Recoveries (immediate and delayed) of Paper Treated with Alkali.
Samples conditioned at 50 % r.h. and 20°C.

| | <u>Machine Direction</u> | | | | | |
|-------------------------|--------------------------|------|------|------|------|------|
| No. of Treatments | 0 | 1 | 2 | 3 | 5 | 7 |
| <u>Recovery (%) at:</u> | | | | | | |
| 0.75 % strain | 88.1 | 83.6 | 81.4 | 81.2 | 84.5 | 84.5 |
| 1.00 % strain | 82.0 | 75.9 | 74.0 | 74.3 | 76.8 | 77.6 |
| 1.25 % strain | 71.0 | 66.1 | 63.7 | 64.4 | 67.6 | 68.5 |
| 1.50 % strain | - | - | - | - | - | 55.2 |

| | <u>Cross Direction</u> | | | | | |
|-------------------------|------------------------|------|------|------|------|------|
| No. of Treatments | 0 | 1 | 2 | 3 | 5 | 7 |
| <u>Recovery (%) at:</u> | | | | | | |
| 0.75 % strain | 86.7 | 84.7 | 84.7 | 83.9 | 81.6 | 80.2 |
| 1.00 % strain | 80.8 | 78.9 | 79.2 | 76.0 | 75.7 | 74.3 |
| 1.25 % strain | 73.4 | 70.8 | 71.4 | 69.8 | 68.9 | 67.8 |
| 1.50 % strain | 62.8 | 59.6 | 61.1 | 59.7 | 60.0 | 59.9 |

Table XXII

Recoveries (immediate and delayed) of Paper Treated with I.
Samples conditioned at 50 % r.h. and 20°C.

| | <u>Machine Direction</u> | | | | | |
|-------------------------|--------------------------|------|------|------|------|------|
| Reagent (%) | 0.52 | 0.83 | 1.11 | 1.47 | 2.16 | 2.51 |
| <u>Recovery (%) at:</u> | | | | | | |
| 0.75 % strain | 88.4 | 87.5 | 85.6 | 86.7 | 88.8 | 88.6 |
| 1.00 % strain | 80.8 | 77.3 | 79.2 | 80.9 | 84.4 | 84.0 |
| 1.25 % strain | 72.4 | 66.8 | 70.7 | 73.6 | 78.3 | 79.1 |
| 1.50 % strain | 62.8 | 56.6 | 58.9 | 64.3 | 70.0 | 73.5 |

| | <u>Cross Direction</u> | | | | |
|-------------------------|------------------------|------|------|------|------|
| Reagent (%) | 0.48 | 0.69 | 1.65 | 1.86 | 2.64 |
| <u>Recovery (%) at:</u> | | | | | |
| 0.75 % strain | 85.0 | 86.3 | 86.9 | 89.1 | 89.7 |
| 1.00 % strain | 80.3 | 80.7 | 82.7 | 85.6 | 86.4 |
| 1.25 % strain | 73.2 | 74.2 | 77.8 | 81.5 | 82.7 |
| 1.50 % strain | 60.2 | 66.4 | 71.4 | 75.9 | 78.4 |

Table XXIII

Recoveries (immediate and delayed) of Paper Treated with II.
Samples conditioned at 50 % r.h. and 20°C.

| | <u>Machine Direction</u> | | | | | |
|-------------------------|--------------------------|------|------|------|------|------|
| Reagent (%) | 0.37 | 1.04 | 1.36 | 1.90 | 2.17 | 3.23 |
| <u>Recovery (%) at:</u> | | | | | | |
| 0.75 % strain | 84.7 | 82.7 | 86.7 | 89.6 | 88.9 | 87.8 |
| 1.00 % strain | 78.3 | 77.9 | 80.7 | 85.6 | 84.7 | 86.3 |
| 1.25 % strain | 70.2 | 70.9 | 73.6 | 80.7 | 80.7 | 82.6 |
| 1.50 % strain | 61.0 | 61.8 | 65.3 | 73.7 | 74.3 | 75.6 |

| | <u>Cross Direction</u> | | | | | |
|-------------------------|------------------------|------|------|------|------|------|
| Reagent (%) | 0.52 | 0.86 | 0.90 | 1.54 | 2.27 | 2.70 |
| <u>Recovery (%) at:</u> | | | | | | |
| 0.75 % strain | 85.0 | 87.1 | 87.7 | 87.6 | 89.0 | 89.6 |
| 1.00 % strain | 78.5 | 83.0 | 83.8 | 85.4 | 85.2 | 86.8 |
| 1.25 % strain | 70.7 | 76.6 | 78.8 | 82.3 | 80.7 | 83.8 |
| 1.50 % strain | 59.5 | 69.3 | 73.1 | 77.3 | 75.1 | 79.9 |

Table XXIV

Recoveries (immediate and delayed) of Paper Treated with III.
Samples conditioned at 50 % r.h. and 20°C.

| | <u>Machine Direction</u> | | | | | |
|-------------------------|--------------------------|------|------|------|------|------|
| Reagent (%) | 0.34 | 0.99 | 1.69 | 1.88 | 2.23 | 2.80 |
| <u>Recovery (%) at:</u> | | | | | | |
| 0.75 % strain | 84.3 | 85.4 | 86.1 | 86.3 | 87.6 | 89.2 |
| 1.00 % strain | 77.8 | 80.4 | 80.6 | 80.8 | 82.4 | 85.4 |
| 1.25 % strain | 67.7 | 71.6 | 72.7 | 74.2 | 75.0 | 79.7 |
| 1.50 % strain | - | 58.6 | 62.4 | 64.3 | 65.4 | 71.7 |

| | <u>Cross Direction</u> | | | | | |
|-------------------------|------------------------|------|------|------|------|------|
| Reagent (%) | 0.44 | 0.88 | 1.18 | 1.55 | 2.05 | 2.55 |
| <u>Recovery (%) at:</u> | | | | | | |
| 0.75 % strain | 82.2 | 87.2 | 89.5 | 86.8 | 86.2 | 90.3 |
| 1.00 % strain | 79.8 | 81.6 | 83.8 | 82.8 | 82.7 | 86.3 |
| 1.25 % strain | 71.4 | 74.5 | 77.3 | 77.6 | 77.6 | 81.3 |
| 1.50 % strain | 61.6 | 65.6 | 69.1 | 69.8 | 70.7 | 74.1 |

Table XXV

Physical Properties of Paper Containing Intra-Fibre Cross-Links.

Samples conditioned at 50 % r.h. and 20°C.

| Pulp: | Softwood Sulphate | | Cotton Linters | | Esparto | |
|-------------------------------------|----------------------|-------|-------------------|-------|---------|-------|
| Freeness | 32.0 | | 34.5 | | 33.0 | |
| Reagent (%) | 0 | 3.26 | 0 | 2.61 | 0 | 3.70 |
| Drainage Time (sec.) | 7.40 | 6.24 | 6.86 | 6.93 | 6.13 | 6.58 |
| Basis Weight (g.m. ⁻²) | 72.3 | 60.5 | 62.3 | 62.3 | 58.3 | 61.3 |
| Sheet Density (g.cm ⁻³) | 0.674 | 0.605 | 0.555 | 0.443 | 0.471 | 0.411 |
| Air Permeability (ml/min) | 243 | 442 | 1180 | 1651 | 6011 | 7105 |
| Tear Factor | 141.1 | 120.9 | 94.8 | 80.8 | 68.1 | 67.0 |

Table XXVI

Mechanical Properties of Paper Containing Intra-Fibre Cross-Links.
Samples conditioned at 50 % r.h. and 20°C.

| Pulp: | Softwood Sulphate | | Cotton Linters | | Esparto | |
|--|-------------------|-------|----------------|------|---------|------|
| Reagent (%) | 0 | 3.26 | 0 | 2.61 | 0 | 3.70 |
| Breaking Length (m) | 13100 | 12310 | 4492 | 4399 | 7496 | 6867 |
| Breaking Extension (%) | 3.90 | 3.46 | 2.76 | 2.29 | 2.46 | 2.10 |
| Initial Modulus (g x 10 ⁻⁵) | 7.12 | 7.15 | 3.86 | 3.75 | 5.33 | 4.97 |
| Rupture Energy (g.cm.cm ⁻¹) | 197.5 | 168.1 | 56.0 | 45.2 | 75.8 | 59.3 |

CHAPTER V

D i s c u s s i o n

1. Introduction

This chapter covers the reactions of cyanuric chloride with certain nucleophilic reagents and the reactions of these derivatives with paper. Finally, the effects of these derivatives on the physical properties of paper are discussed.

The preparation of aminochlorotriazines have utilised methods described for similar compounds and the desired products have been obtained with little difficulty. The reactions of cyanuric chloride with dihydroxy compounds to produce derivatives containing two dichlorotriazine molecules linked by an aliphatic chain have been unsuccessful. Sulphonation of the triazine rings in some aliphatic aminochlorotriazines has been carried out on the hypothesis that this would render them water soluble but this has not been found to be so.

The amount of reagent present in the paper has been determined by measuring its nitrogen content. Although this is only an arbitrary measure of the degree of cross-linking, it is felt that, in view of the complexity of the system, it is satisfactory for comparing the effects of the compounds used.

Testing of air-dry paper was originally carried out at 20°C and 65 % r.h. but in later work the humidity was changed to 50 % r.h. The conditions for testing are noted above each

table of results. The comparative tests between the three main compounds used, however, have been carried out under the same conditions.

The three aminochlorotriazines described in Chapter III, (2,i,a,b and c) were used in the majority of experiments involving the surface sizing of paper. The mean values of breaking lengths, breaking extensions, initial moduli, and rupture energies of air dry paper treated with these compounds are given in Tables III to VIII. The mean values of breaking lengths, breaking extensions, initial moduli and rupture energies of wet paper treated in the same manner are recorded in Tables XI to XVI. The dry and wet values for paper treated with the stilbene diamine derivative and rewetted before conditioning at 20°C and 65 % r.h. are recorded in Tables XVII to XX.

The treatment of paper by the surface sizing process resulted in a fall in tensile strength, rupture energy and initial modulus after one treatment, due to the effect of wetting with alkali and redrying the paper. The extent of these strength losses were determined by impregnating the paper with alkali alone followed by squeezing and drying in the usual manner. The results obtained from wet and dry tests on the Instron Tester are shown in Tables I, II, IX and X.

When the first results from the surface sizing technique were obtained, they showed poor reproducibility in the results for the tests carried out. This was blamed on the unequal

distribution of pressure along the bowls of the 'Acme' wringer used for the process. Several prints of the bowls were taken, using 'Cariboni' Red Box' carbon paper, at the different pressures used. Even at the highest pressure involved, the prints were ill-defined, but no obvious variations in pressure along the bowl could be detected. The expression of the mangle at different nip pressures was also measured and found to have values lying between a maximum of 115 % and a minimum of 100 %.

When the question of intra-fibre cross-links capable of imparting wet strength to paper arose, experiments were carried out attempting to determine which type of cross-link would affect the physical properties of the paper in this manner. No conclusive results were obtained, but work involving the introduction of intra-fibre cross-links into the fibres before sheet formation led to a more detailed investigation of the effect of intra-fibre cross-links on conformability.

In the sections 4 to 14 the changes in the physical properties of the paper due to the treatment received are discussed. The experimental scatter obtained in the determination of the results is recorded for each set of results and, although high in many cases, is always less than the change in the property examined.

2. Reactions of Cyanuric Chloride with Alcohols and Polyethylene oxides.

The progress of these reactions has been followed by continuous titration of the hydrochloric acid produced with alkali. In the cases where reaction was carried out without alkali addition the extent of reaction has been determined by titration after a predetermined time. For continuous titration, reaction curves similar to Fig. 4 were obtained where 100 % reaction indicates that 1 Cl atom/triazine ring has been substituted. The same extents of reaction were obtained when mixtures were titrated at the end of the reaction only. It would appear from these results that the first two Cl atoms in the ring have similar reactivities in these reactions. The variation of the reaction temperature between 10°C and 20°C and the variation or non-addition of alkali made no difference to the extent of reaction obtained.

The reactions of cyanuric chloride with aliphatic alcohols does not proceed in as simple a manner as the corresponding amines. The reactivity of the remaining chlorine atoms in the triazine ring is much lower for alkoxy substituents than the corresponding amino substituents. Matsui et al.⁽⁴⁶⁾ have investigated the reactivity of some alcohols to cyanuric chloride and found that various substituents deactivated the chlorine atoms in the following order:

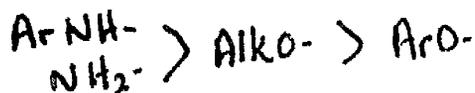
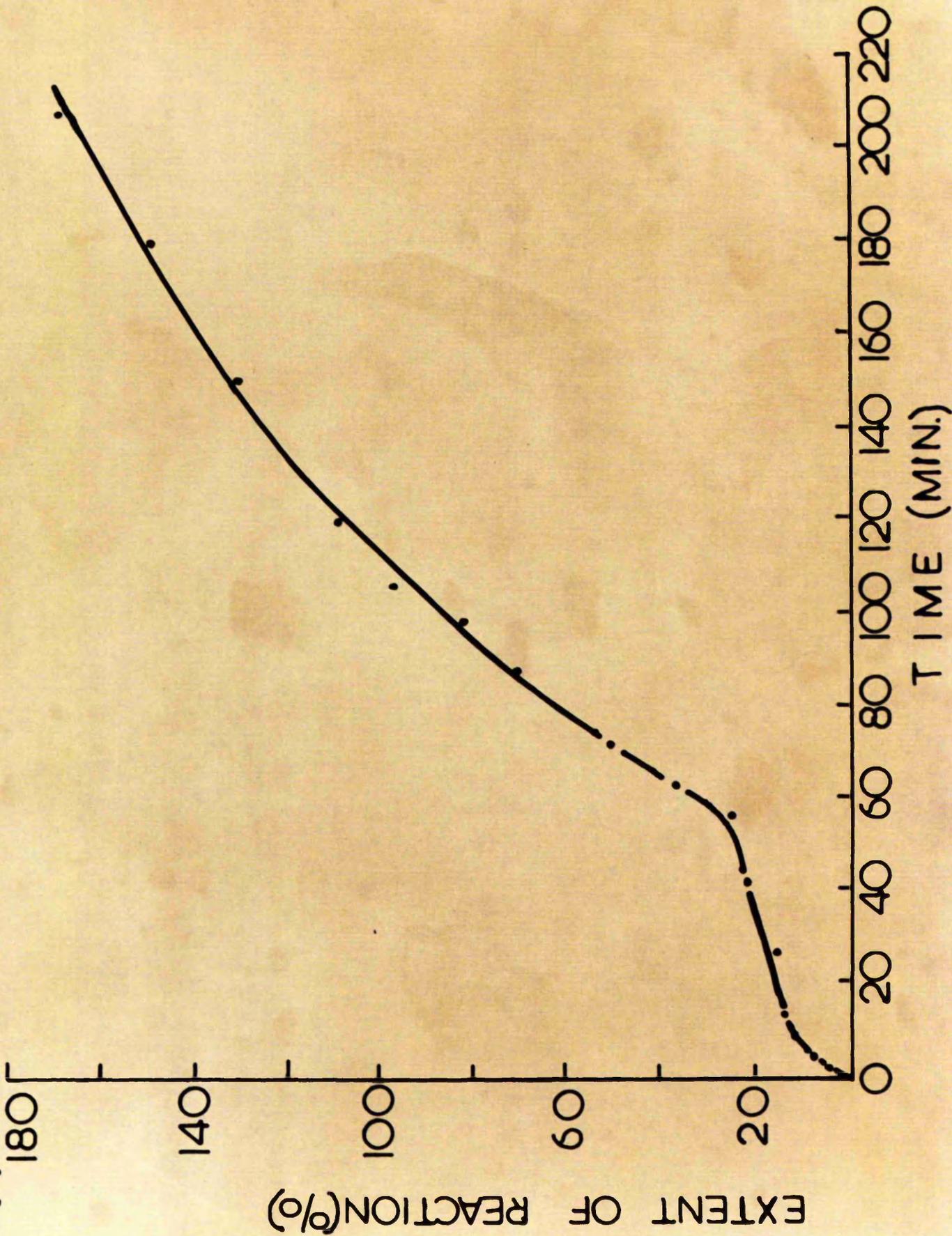


FIG. 4. REACTION OF CYANURIC CHLORIDE WITH CARBOWAX 400



They also found that methanol and cyanuric chloride reacted at low temperatures, without the presence of alkali, yielded 2,4,6-trimethoxy-s.triazine and that the addition of acid accelerated the reaction. They suggested that the removal of acid with sodium bicarbonate or calcium carbonate would enable stepwise reaction to take place. This has been confirmed by Thurston et al.⁽⁴³⁾ who treated cyanuric chloride with sodium bicarbonate in methanol to obtain 2-methoxy-4,6-dichloro-s.triazine. Matuszka and Chang⁽⁴⁷⁾ found that the reaction of cyanuric chloride with 1,4-butane diol or 1,5-pentane diol yielded tetrahydrofuran or tetrahydropyran respectively together with cyanuric acid.

Although the substitution of cyanuric chloride is harder to control with alcohols than amines, there is no satisfactory explanation why two chlorine atoms in the same ring should be consistently replaced when cyanuric chloride is reacted with polyethylene oxides.

3. The Reactions of Chlorotriazine Derivatives with Paper

The cross-linking agent was originally applied by dyeing either the pulp or the paper and the resultant sheets were air-dried. It was found that no signs of inter-fibre cross-linking had taken place although the paper was insoluble in cuprammonium hydroxide suggesting that some intra-fibre

cross-links were present. It was concluded that this was due to: -

i) The time lapse between adding the reagent to the stock or the sheets and drying the sheets would allow most of the reagent to penetrate the fibres making it unavailable for inter-fibre cross-linking.

ii) The drying time was such that much of the reagent in a suitable position for inter-fibre cross-linking would have been hydrolysed before the fibres were sufficiently close for cross-linking to take place.

It was believed that by using a shorter ^edrying period and by drying the sheets in a plastics press at 110°C and 200 lb/sq.in. this problem could be solved. The high pressure used, however, prevented the removal of water vapour from the press and the finished paper showed similar properties to that which had been air dried. Several arrangements by which the temperature of both platens were altered and various combinations of felts and blotters were used to facilitate the removal of water from the sheet, without success.

A Palmer Drier was found to provide the most efficient drying conditions for the treated paper. The large drying area of the cylinder enabled the water to be removed quickly bringing about bonding at the same time as reaction between the reagent and the cellulose was taking place. The main disadvantage in this means of drying lay in the fact that the

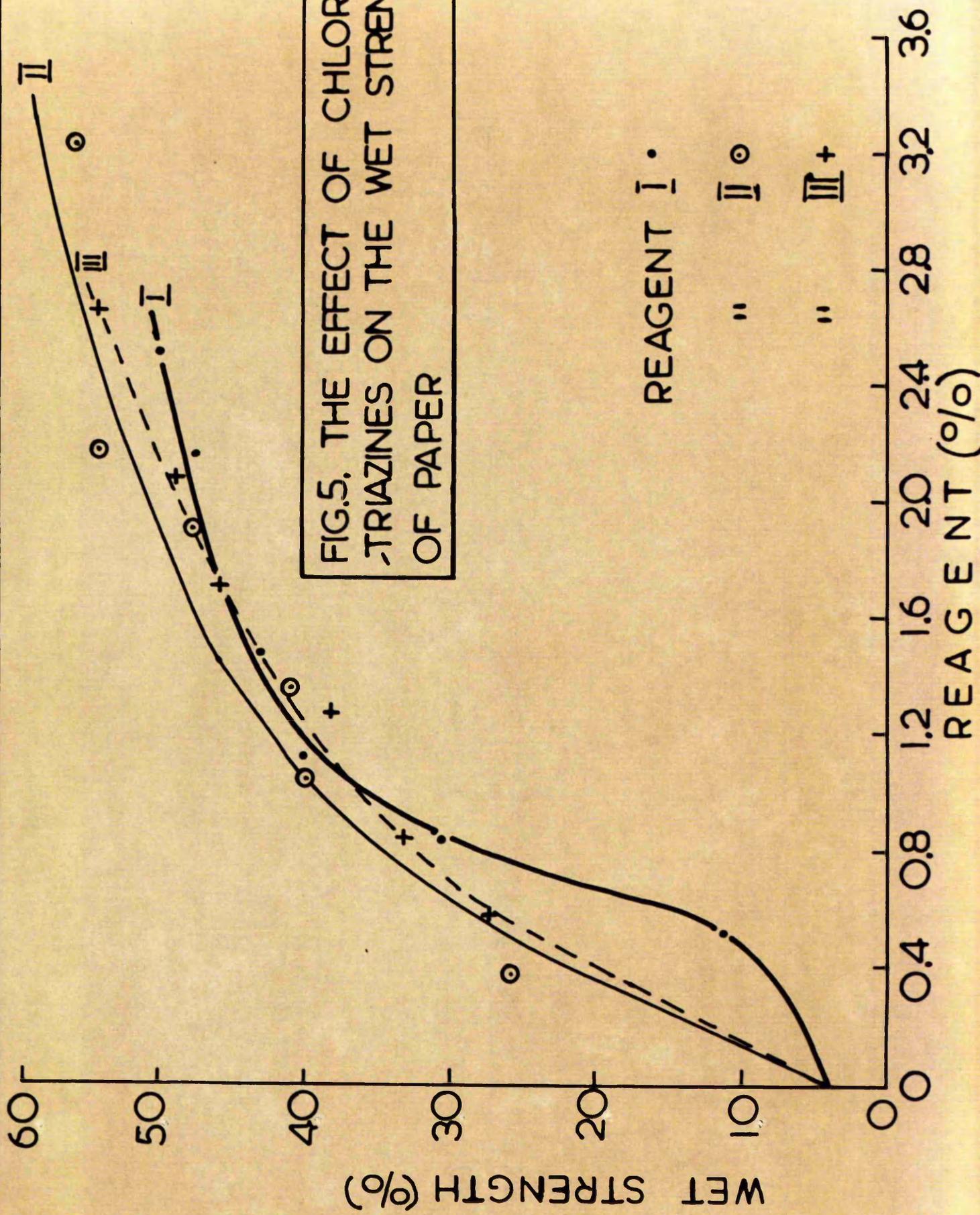


FIG.5. THE EFFECT OF CHLORO-
 TRIAZINES ON THE WET STRENGTH
 OF PAPER

REAGENT I •
 " II ○
 " III +

tension in the drying felt could not be measured and consequently it was impossible to duplicate drying conditions for each set of experiments. The variability introduced here, together with differences in the purity of the three compounds used, could contribute more to the differences in the physical properties of the paper than the differences in the chemical structure of the reagents themselves.

4. Evidence for Cross-Link Formation

The evidence for the presence of either intra- or inter-fibre cross-links has been taken to be the insolubility of the fibres in cuprammonium hydroxide. It was believed that the presence of inter-fibre cross-links could be shown by an increase in the wet tensile strength of the paper. Fig. 5 shows the relation between wet-strength and the amount of reagent added to the paper. It can be seen that for the three compounds used the wet tensile strength rises to a maximum lying between 50 and 55 % for 2.5-3.0 % of the reagent in the paper. For the reasons stated in section 1 of this chapter, no real comparisons could be made upon the effect of size and structure of the compounds on the degree of cross-linking. There is probably very little difference in the degree of cross-linking for each of the compounds used, the cross-links probably being formed across the same triazine ring in each case.

The effect of intra-fibre cross-links on the wet strength of a treated paper has also been considered. It has been suggested that intra fibre cross-links formed after the maximum degree of bonding had occurred would make the fibre network so rigid that the penetration of water and the consequent disruption of hydrogen bonds would be prevented. Some experimental work has been carried out in order to determine the cross-links formed but no conclusive evidence has been obtained.

To obtain minimum penetration, the sheets were impregnated with cyanuric chloride in xylene first, dried, impregnated with solution of 1 % sodium carbonate and dried again at 140°C. This method produced a wet strength of 20 % compared to 5 % for a paper treated in a similar manner but without the addition of cyanuric chloride. Although, at the temperature used for drying, the diffusion within the fibre would be increased, the majority of the cyanuric chloride would react on, or near, the surface of the fibre forming a majority of inter-fibre cross-links.

For intra-fibre cross-linking to be effective in producing wet strength it is necessary to introduce the cross-links after the maximum degree of bonding has taken place. The only method of ensuring that only intra-fibre cross-links are present in paper requires that the fibres are separated before reaction occurs. When this happens the conformability of the

fibres is reduced and no comparison of the properties of the resultant paper and the original paper can be made.

Although there is no direct evidence for inter-fibre cross-links being produced by the methods used, the evidence obtained does indicate that the wet strength is caused by inter-fibre cross-links. That such cross-linking is feasible is illustrated by the fact that the distances involved in hydrogen bond formation are small compared with the size of the molecules used for cross-linking. If the reaction between the reagent and the cellulose occurs before fibre bonding takes place, the conformability of the fibres would be reduced and the dry tensile strength of the paper would fall. The dry tensile strength does, in fact, fall but this is shown in section 3 of this chapter to be due to the wetting of the paper with alkali during the treatment and not due to intra-fibre cross links. If reaction takes place during the period of maximum bonding, neighbouring fibres must be close enough for some inter-fibre cross-links to be formed. As the period between impregnation of the paper and drying is short (80-100 sec.), there will be little penetration of the fibre and most of the reagent will be on the surface during reaction. Specimens of treated paper left for several days in cuprammonium hydroxide formed a gelatinous mass but showed no signs of disintegrating, which would be expected if there were only intra-fibre cross-links present. Early experiments involving dyeing the pulp followed by sheet formation in an alkaline medium

did not produce any wet strength although the reactions were probably taking place during the period of maximum bonding.

From the information available it is probable that the majority of the cross links lie between the fibres, the few within the fibres having very little effect on the wet strength of the paper.

5. Tensile Strengths (Air Dry) of Treated Paper

Fig. 6 shows the relationship between the tensile strength of the treated paper and the amount of reagent added to the paper. Fig. 7 shows the relationship between the tensile strength of alkali treated paper and the number of treatments received. It will be remembered that, in order to obtain relatively high extents of reaction it was necessary to repeat the treatments until the required amount of reagent had been applied. The 2nd point on the curve represents one treatment and the final point represents ten successive treatments. It can be seen that the effect of the first treatment does not appear to produce any real cross-linking on comparison with the graph illustrating treatment with alkali alone. The initial fall in tensile strength of the paper can be seen to be due to the physical effect of the treatment and not to any intra-fibre cross-linking.

It has been found in cross-linking studies on cotton

FIG. 6. THE EFFECT OF CHLOROTRIAZINES ON THE BREAKING LENGTH OF DRY PAPER

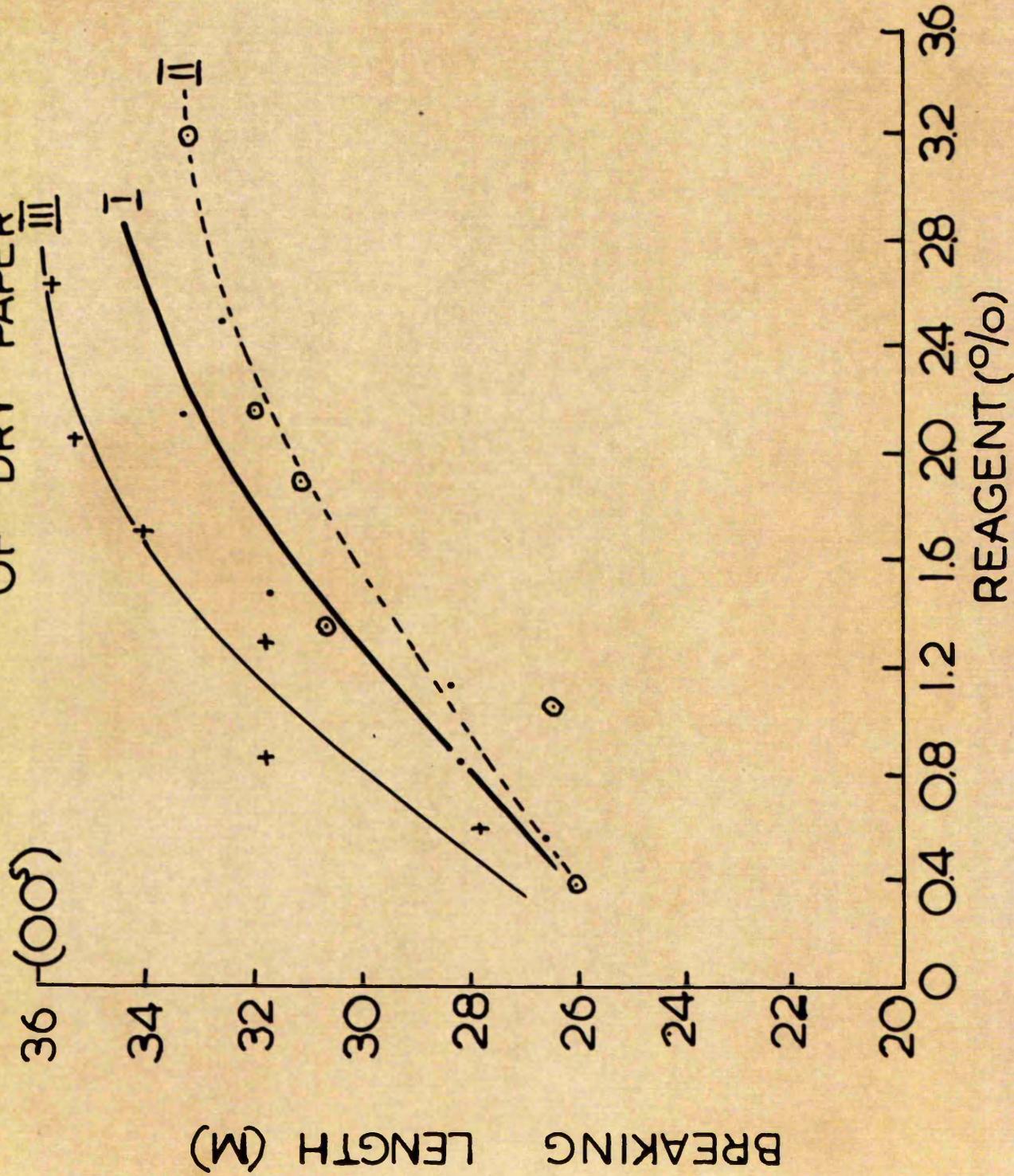
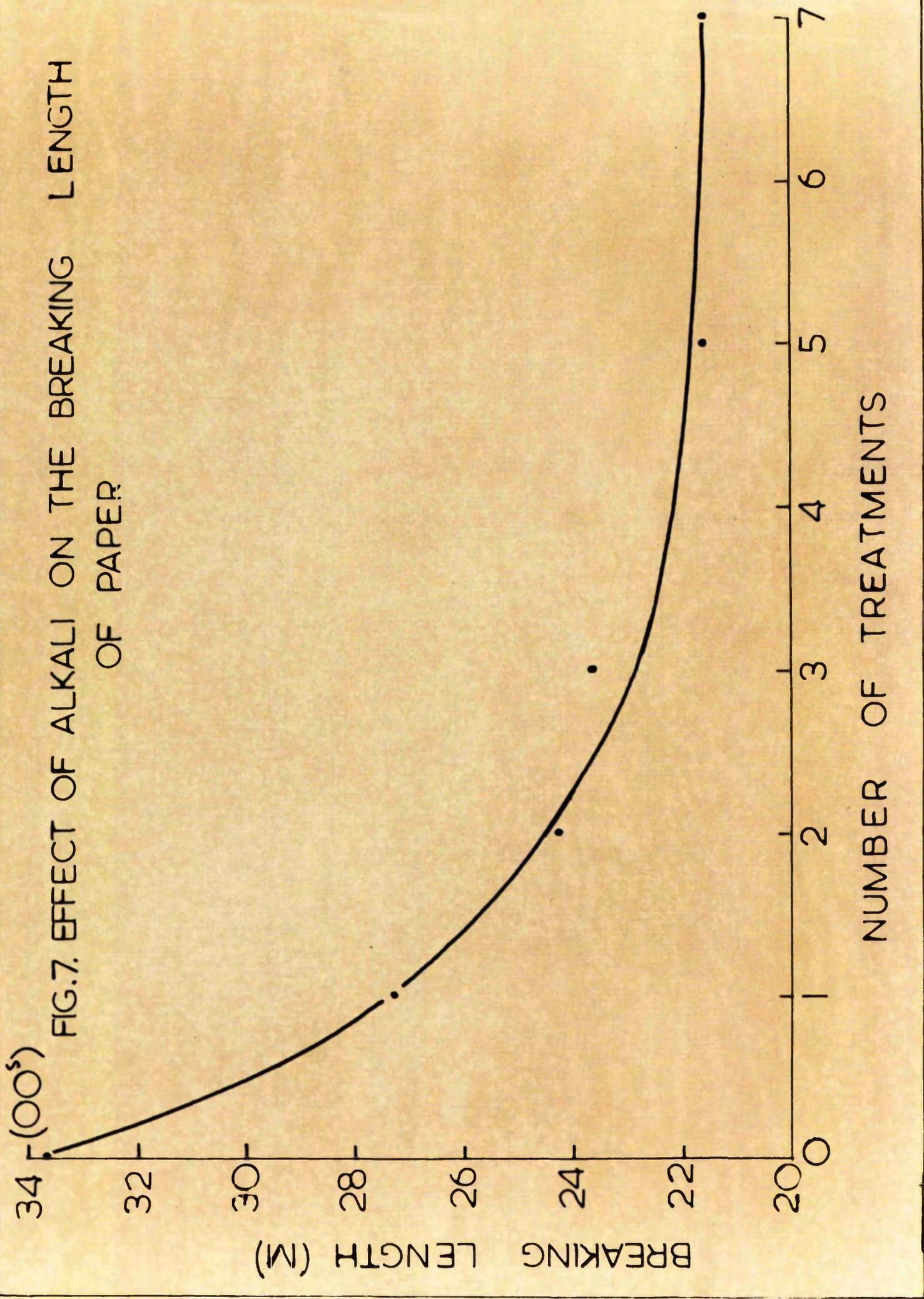


FIG.7. EFFECT OF ALKALI ON THE BREAKING LENGTH OF PAPER



fibres that one of the effects of inter-molecular cross-linking is to reduce the tensile strength of the fibre. As the degree of cross-linking increases, the tendency for molecular slippage along the fibre decreases and the distribution of stress along the individual chains is not equalised. Consequently high local stress concentrations occur, leading to increased probability of chain ruptures.

The effect of heavy intra-fibre cross-linking could be to eventually lower the dry tensile strength of the paper. As the paper begins to rupture the number of fibres spanning the rupture zone decrease. The stress in individual fibres in the rupture area may be increased sufficiently for fibre rupture to occur. If intra-fibre cross-links were the only type of covalent cross link present in the paper the air-dry tensile strength of the paper would be expected either to fall or be unaffected. The tensile strength in fact rises after the first treatment and this can only be explained by either increasing the number of hydrogen bonds or Van den Waals forces or by the introduction of inter-fibre cross-links into the paper. As the reaction of cellulose with chlorotriazines should not increase the number of hydrogen bonds or Van den Waals forces between the fibres, the increase in dry tensile strength must be due to inter-fibre cross-links. The tendency for the dry tensile strength to fall at high extents of reaction could be due to increasing numbers of intra-fibre cross-links being formed.

Normally, increased bonding between the fibres would be expected to increase the density of the resultant paper. The sheet density measurements in the present work did not give consistent results and tended to decrease as the amount of cross-linking agent in the paper increased. The chlorotriazine cross-links which are large compared with hydrogen bonds or the hemiacetal cross-links used by Zeronian⁽⁶⁾ would, in sufficient quantity, tend to decrease the density of the paper.

Fig. 8 shows that the rewetting of the paper after treatment has no significant effect on the dry tensile strength of the paper, compared with the effect of wetting untreated paper.

6. Tensile Strengths (WET) of the Treated Paper.

Fig. 9 shows the relationship between the wet ^{tensile} strength of the treated paper, ~~as a percentage of its dry tensile strength,~~ and the extent of reaction. The wet strengths of the papers are in units of grams for specimens of basis weight 70 gm^{-2} and width 1.5 cm. Therefore, for the purpose of calculating the percentage wet strengths, the dry strengths were converted to this unit from the unit of metres. For clarity, only the curves for tests in the machine direction of the paper are shown. The curves for the cross direction of the paper overlap those for the machine direction. It can be seen that the three compounds used show little difference in the wet strength achieved

FIG. 8 THE EFFECT OF REWETTING ON THE TENSILE STRENGTH OF PAPER

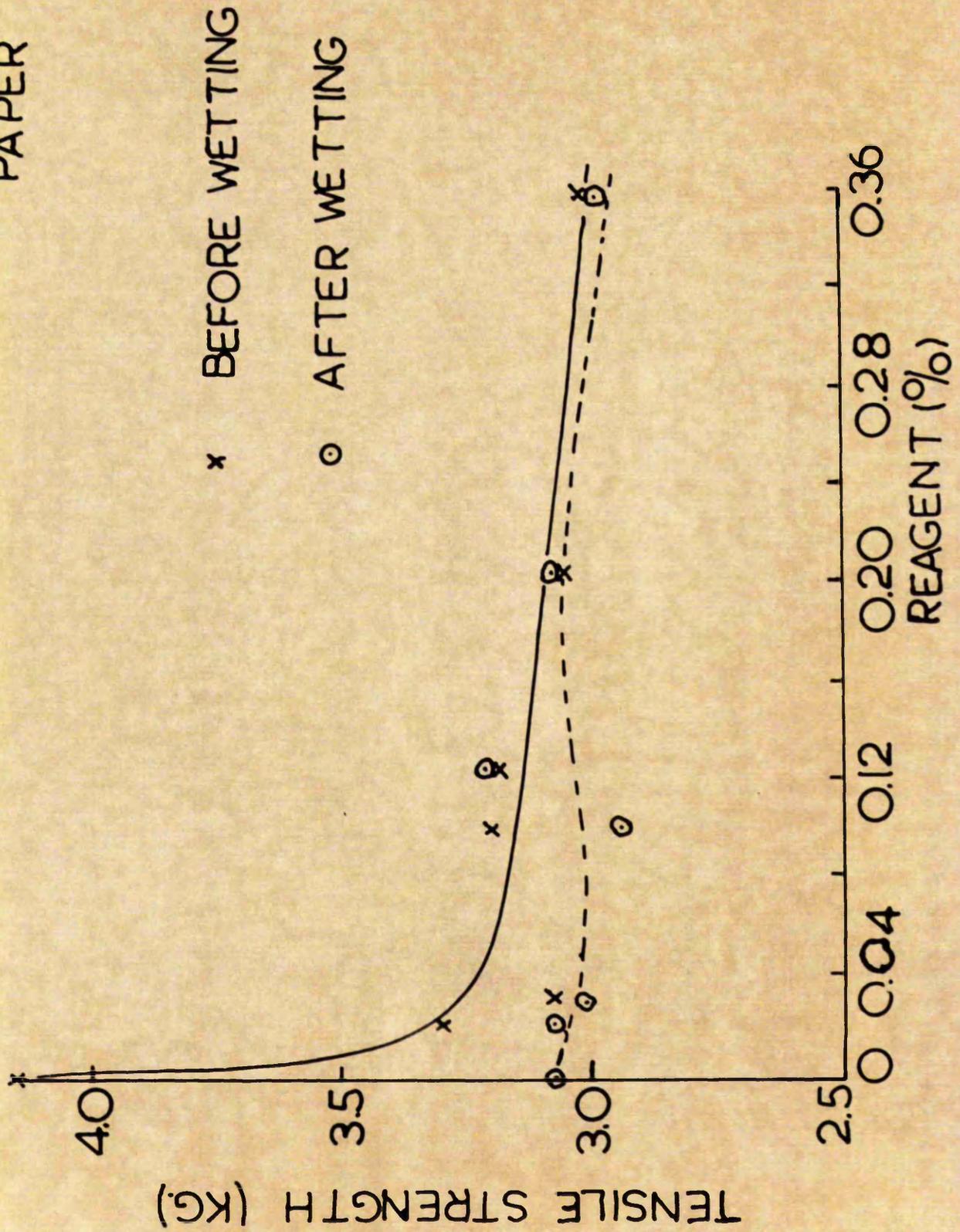
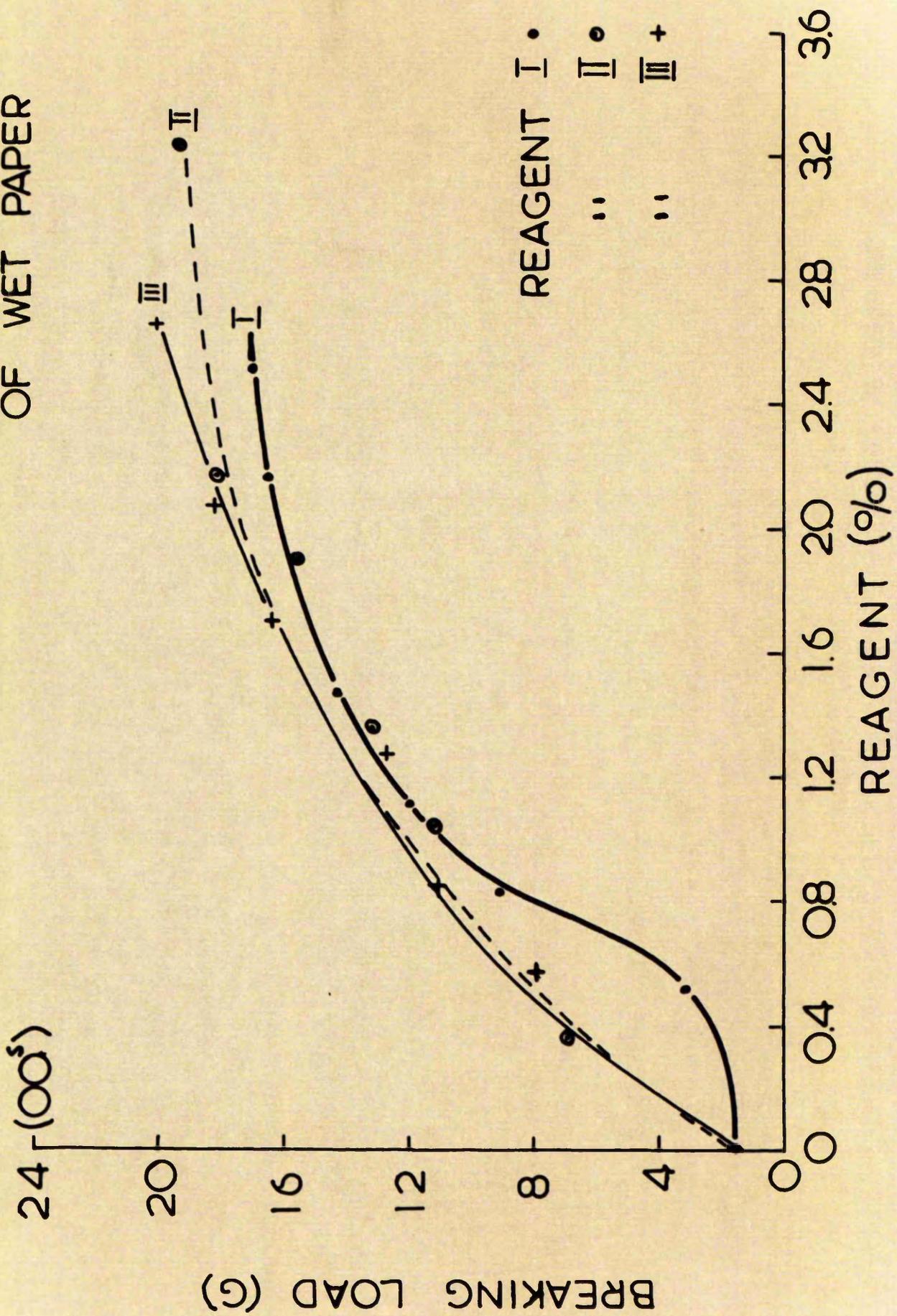


FIG.9. EFFECT OF CHLOROTRIAZINES ON THE TENSILE STRENGTH OF WET PAPER



suggesting that the reaction takes place between the two chlorine atoms in the same triazine ring. The arguments for wet strength as a criterion for inter-fibre cross-links have already been put forward in section 2 of this chapter and will not be discussed any further. The shape of the curves with their rapid initial rise with gradual falling off of the rate of increase of wet strength would be expected from additives which did not degrade or reduce the strength of the fibres in any way.

The highest wet strength obtained by the methods used was about 55 per cent. This compares favourably with a wet strength of 53 per cent obtained by Jurecic et al. on impregnation of a cotton paper with 5 per cent of unmodified U-F resin and curing for 12 hours at 120°C.

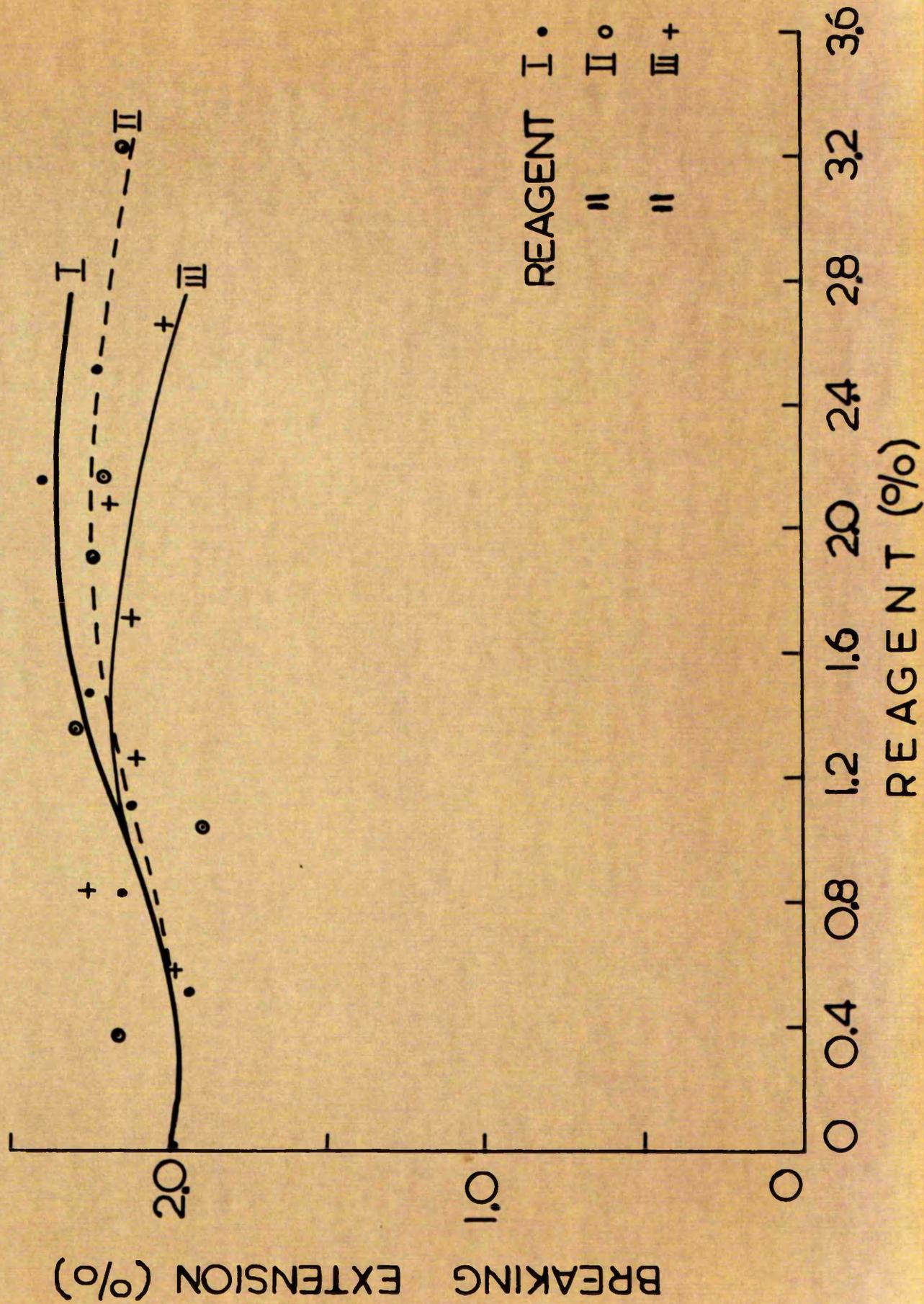
Several specimens have been immersed in water for several days without any loss of wet strength. This would not be expected if the wet strength were due to intra-fibre cross-links.

7. Breaking Extensions (Air Dry) of Treated Paper.

Fig. 10 shows the relationship between the breaking extension of the air dry paper and the amount of reagent added. It can be seen that for each of the three compounds used there is very little consistent change in breaking extension.

Page and Tydeman⁽²⁶⁾ have suggested that the extensibility

FIG.10. EFFECT OF CHLOROTRIAZINES ON THE BREAKING EXTENSION OF PAPER



of paper is related to the microcompressions in the fibres at bonded areas and further microcompressions and kinks in the fibre segments between bond sites. When the paper is stretched the applied force tends to pull out the kinks and microcompressions in and between the bond areas. On the introduction of cross links into the paper it would be expected that the state of microcompression of the fibres as they formed bonds would be reinforced and the extension of the paper for a given load would be smaller.

Fig. 11 shows the relationship between the extension, at loads of 2.5 kg ~~and 2.0 kg~~ for the machine ^{direction} ~~and cross directions~~ of the paper ~~respectively~~, and the amount of reagent present. It can be seen that, as the amount of reagent present increases, the extension at given load decreases. This would indicate that cross-links are present although it would not distinguish between inter- and intra-fibre cross-links.

8. Breaking Extensions (Wet) of Treated Paper.

Fig. 12 shows the relationship between the breaking extension of wet treated papers and the amount of reagent added. For clarity, only the curves for the machine direction of the paper are shown. The cross direction curves are of similar shape but have slightly higher values for breaking extension.

The maximum breaking extension in the machine direction

FIG.11. EXTENSION AT LOAD 2500G OF
PAPER TREATED WITH REAGENT II

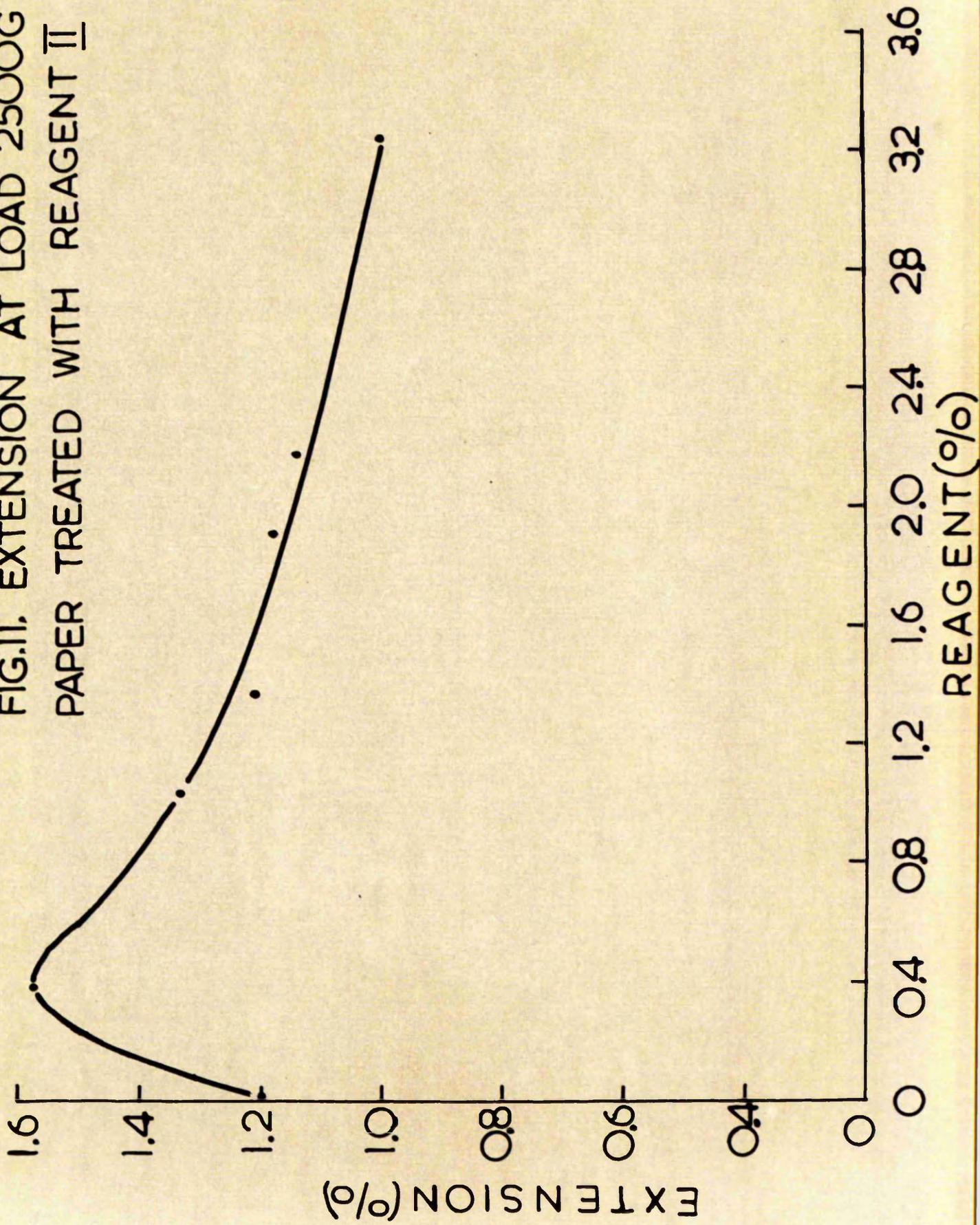
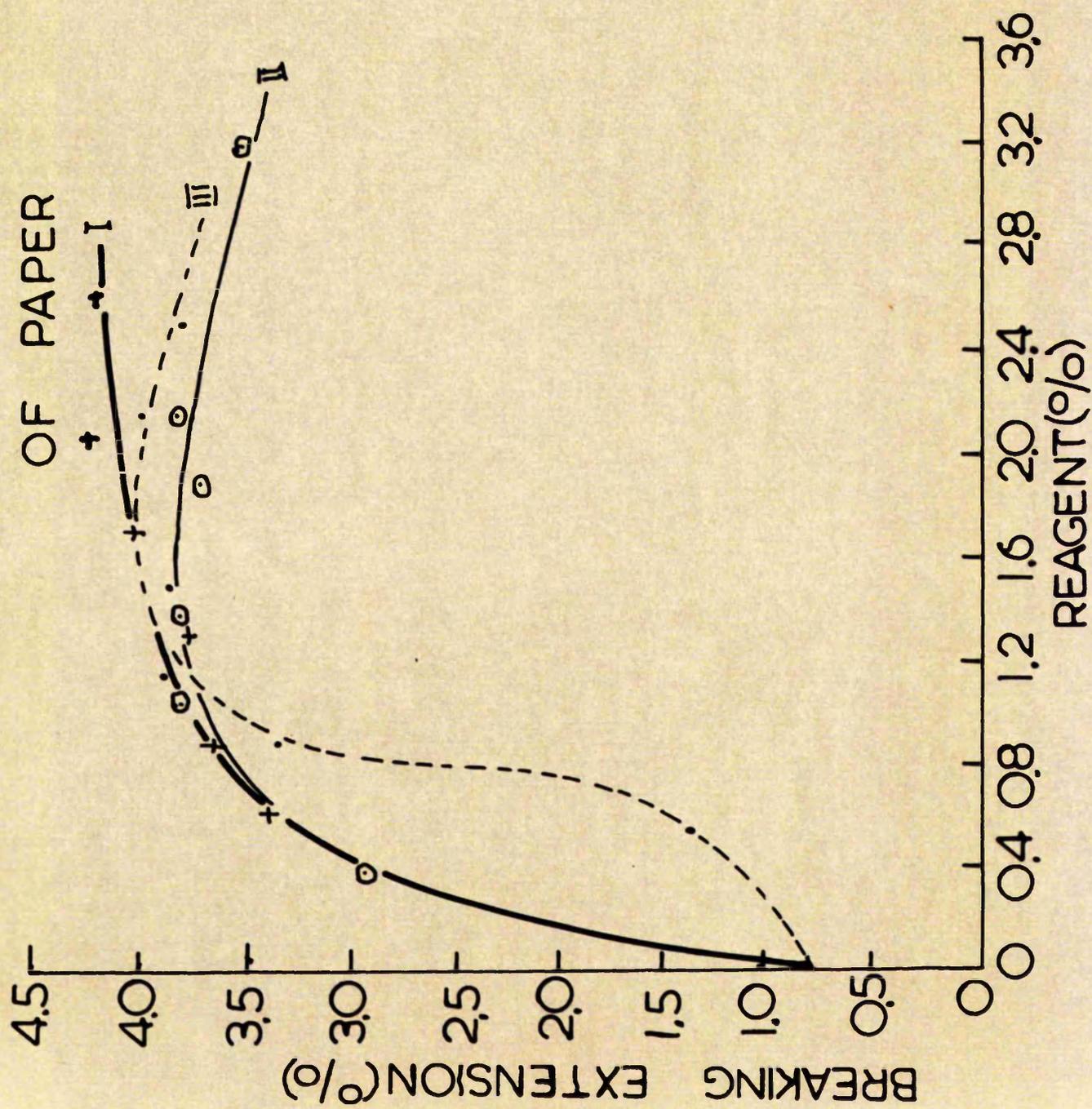


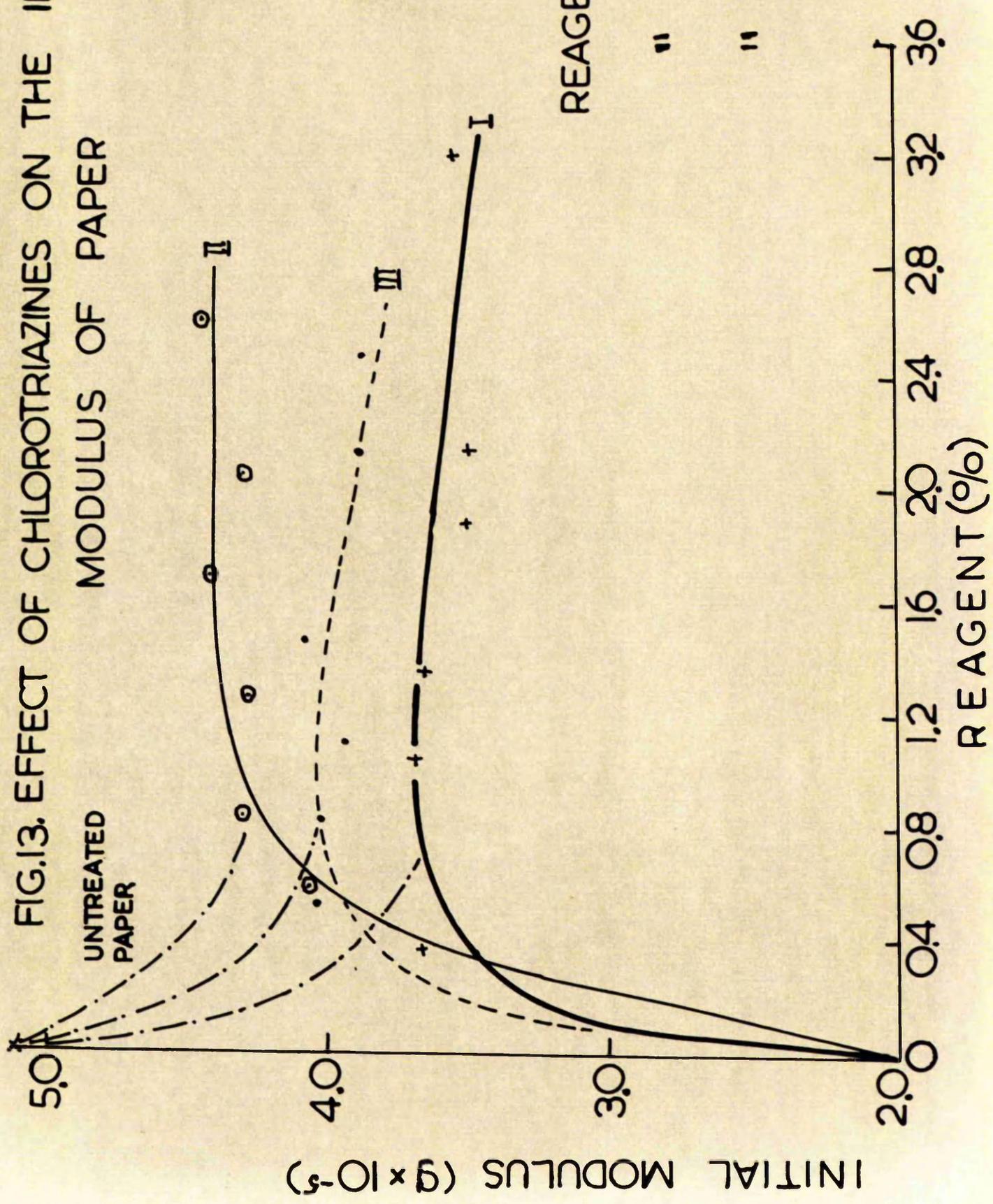
FIG.12. EFFECT OF CHLOROTRIAZINES ON THE WET BREAKING EXTENSION OF PAPER



REAGENT I +
 " II o
 " III x

FIG.13. EFFECT OF CHLOROTRIAZINES ON THE INITIAL MODULUS OF PAPER

UNTREATED PAPER



REAGENT I +
 " II o
 " III x

for the wet paper can be seen to reach about 4.25 %, after which the breaking extension tends to fall. The corresponding value for air dry paper is approximately 65 % of the value for wet paper. As there is no marked increase in the extensibility of the fibres on wetting, the increase must be obtained from the network structure of the paper. The microcompressed structure of paper suggested by Page and Tydeman, described in the previous section, could be used to explain the increased extensibility of the wet paper. On wetting the paper the hydrogen bonds and Van der Waals forces will be broken leaving only the covalent bonds between the fibres. Although the size of the bonded areas should remain approximately the same, the forces maintaining the micro compressions in the bond areas would be reduced. Thus the force required to stretch the paper would be reduced and the extensibility of the paper would be increased. If, however, only intra-fibre cross-links were present, allowing very little penetration of the bond areas, the number of bonds in the bond areas would remain almost the same and wetting of the paper would have little or no effect on the extensibility.

9. Initial Moduli (Air-Dry) of Treated Paper.

Fig. 15 shows the relationship between the initial modulus of air dry treated papers and the amount of reagent present

for the machine direction of the paper only. It can be seen that the initial modulus of the paper never reaches that of the original paper, although it attains a considerably higher value than the value for paper treated with alkali alone.

Several workers⁽⁴⁸⁾, using resins as cross-linking agents in fibres, have found that, as the degree of crystallinity of the fibres is increased, the effect of interchain cross-links on the initial moduli of the fibres is diminished. They have shown that the initial moduli of dry cotton fibres are not significantly increased by the introduction of interchain cross-links. There is a significant increase in the initial modulus of the treated paper compared with that treated with alkali alone. The alkali, however, will reduce the crystallinity of the fibres with a corresponding fall in their initial modulus. Therefore, if intra-fibre cross-links are formed, there would be an increase in the initial modulus of the fibres. It would not be possible to say, in these circumstances, which type of cross-link would be responsible for the increase in the initial modulus of the paper. However, it is believed that the inter-fibre bonds are the main factor influencing the initial modulus of the paper, and the fall in the initial modulus on treatment with alkali is due to a reduction in the numbers of inter-fibre bonds rather than a decrease in the crystallinity of the fibres. If this is true, the increase in the initial modulus of the paper can be attributed to covalent crosslinks between the

fibres. The low crystallinity of the fibres will prevent the initial modulus from attaining the value for paper which has not been treated in any manner.

10. Initial Modulus (Wet) of Treated Paper.

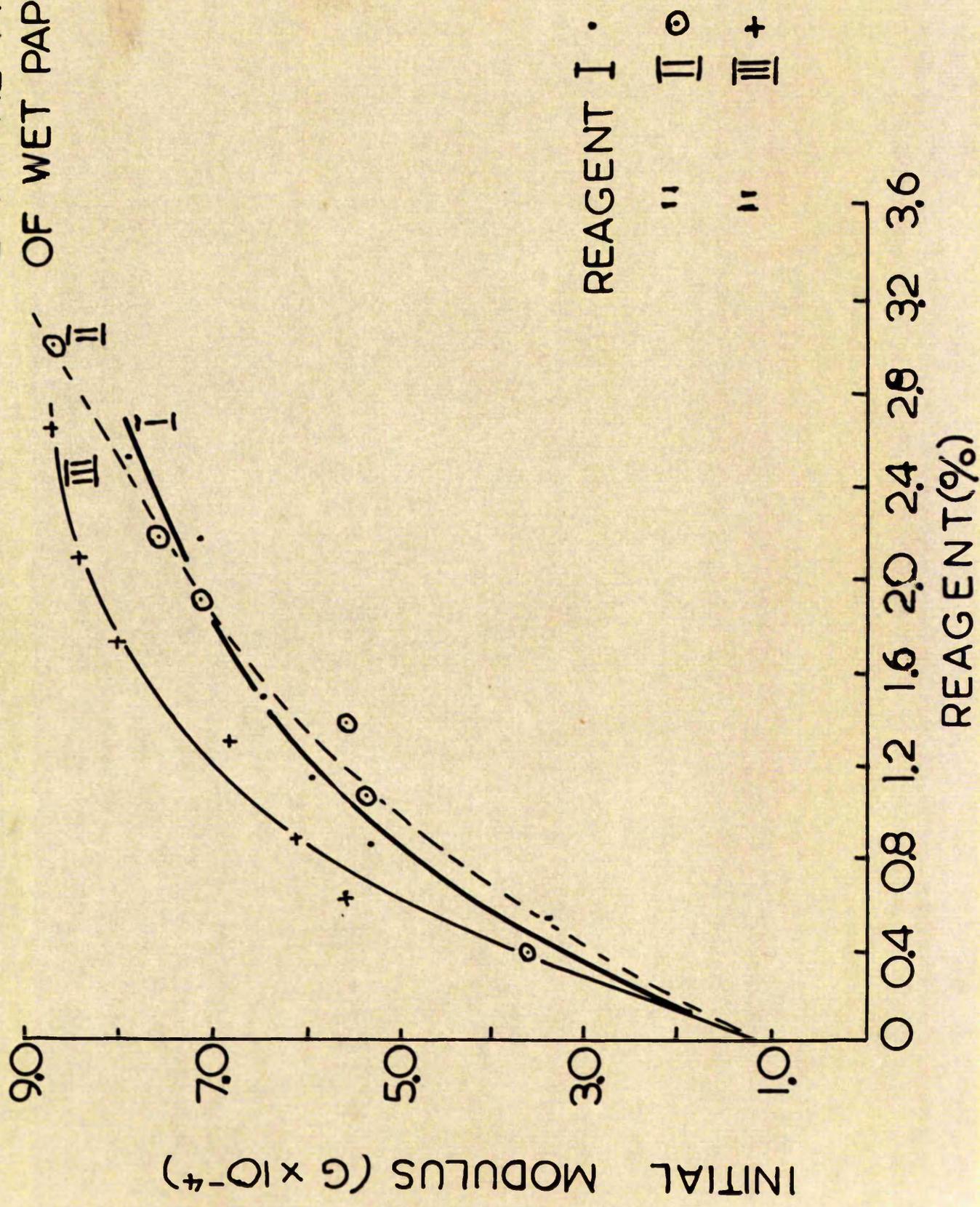
Fig. 14 shows the relationship between the initial modulus of wet treated papers and the amount of reagent present for the machine direction of the paper only. The initial moduli of the paper treated with the three compounds can be seen to rise to similar values in each case.

The fact that there is a considerable increase in the initial modulus of the wet paper does not furnish much information about the location of cross-links, several alternative explanations being possible. The presence of inter-fibre cross-links would increase the number of inter-fibre bonds and then increase the initial modulus of the paper. However, intra-fibre cross-links, capable of preventing the penetration of water between the fibres, would retain many of the original inter fibre bonds as well as improving the initial modulus of the fibres themselves.

11. Rupture Energies (Air Dry) of Treated Paper.

The measurements of rupture energy from the load extension

FIG.14. THE EFFECTS OF CHLOROTRIAZINES ON THE INITIAL MODULUS OF WET PAPER



curves have shown the greatest variability in the values obtained. Fig. 15 shows the relationship between the rupture energies of the air dry treated papers and the amount of reagent present for the machine direction of the paper. Although the scatter in the experimental points is large, it can be seen that there is an increase in the rupture energy of the paper with the introduction of covalent cross-links. This contrasts with Zeronian⁽⁶⁾ who found that the introduction of inter-fibre cross-links into paper, by periodate oxidation of the pulp, although increasing the tensile strength of the paper initially caused the rupture energy to fall because of a decrease in breaking extension.

12. Rupture Energies (Wet) of Treated Paper.

Fig. 16 shows the relationship between the rupture energies for the wet treated papers and the amount of reagent present for the machine direction of the paper only. The high variability present in the figures for air dry paper are found here, but the greater effect of the cross-links on the rupture energy of the wet paper has produced smoother curves. It is interesting to note that the rupture energy of the wet paper tends to approach that of the dry paper as the amount of cross-linking reagent present in the fibre increases.

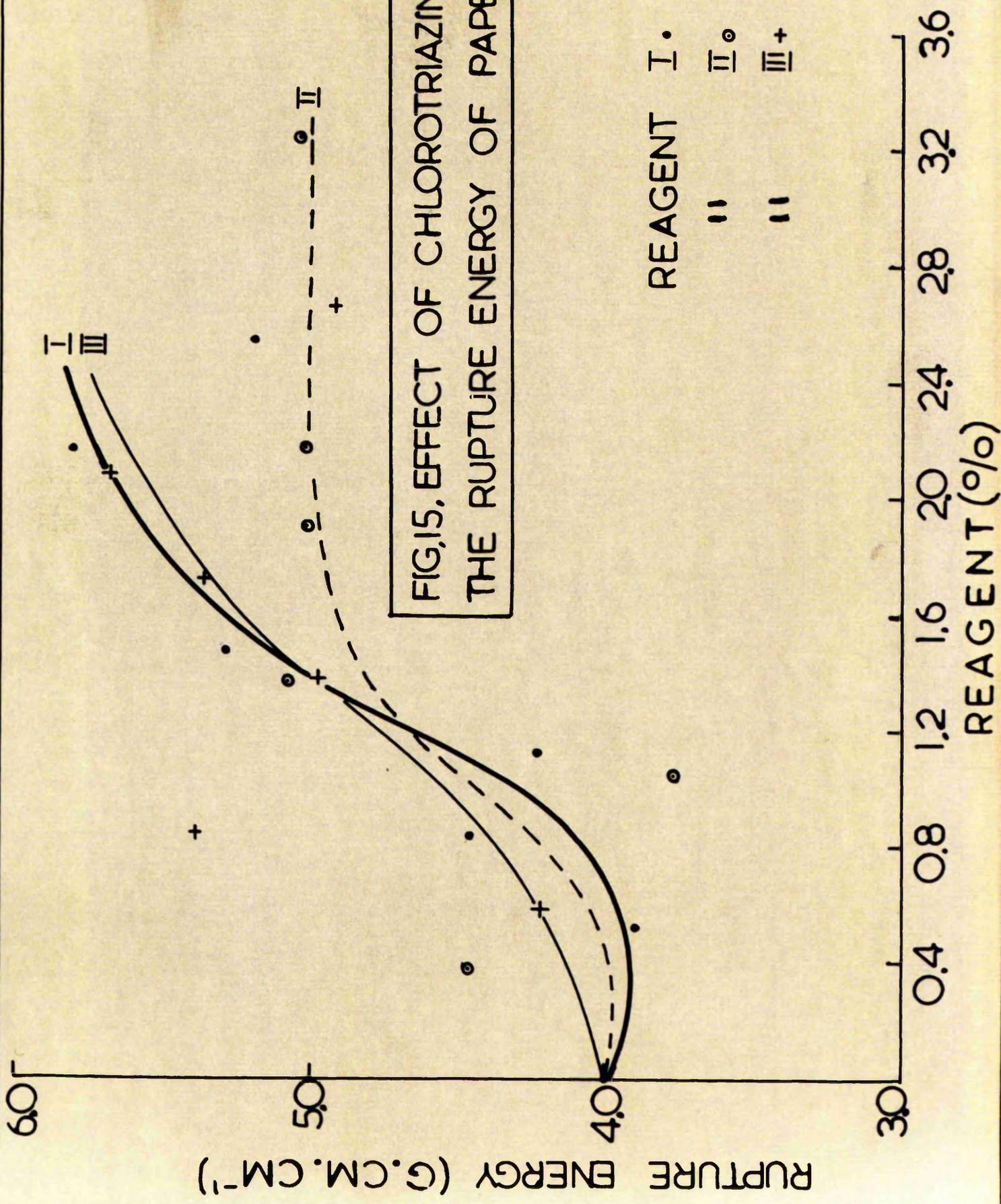


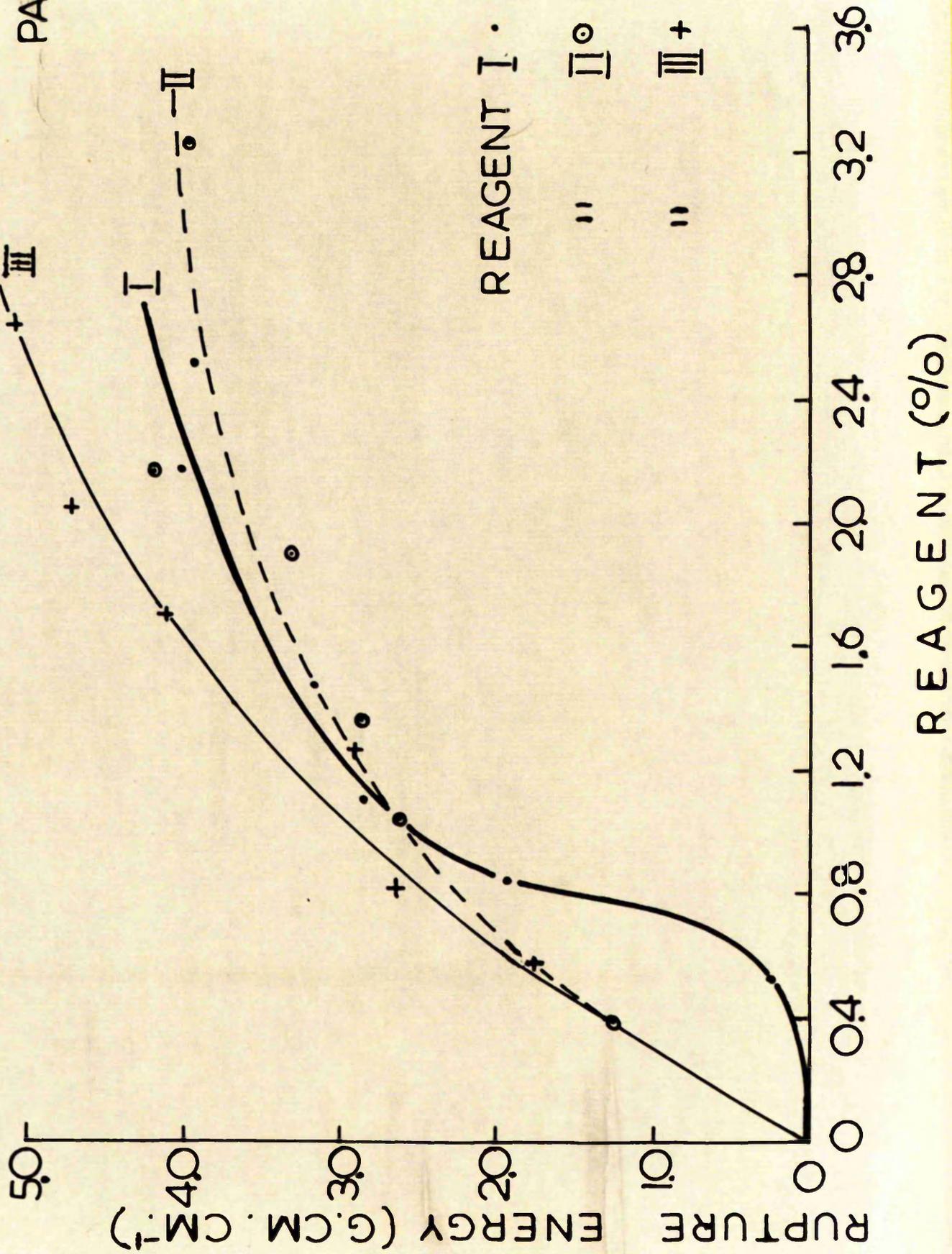
FIG.15, EFFECT OF CHLOROTRIAZINES ON THE RUPTURE ENERGY OF PAPER

REAGENT I.
 " II.
 " III.

RUPTURE ENERGY (G.C.M. CM⁻¹)

REAGENT (%)

FIG.16. EFFECT OF CHLOROTRIAZINES ON THE RUPTURE ENERGY OF WET PAPER



There has been a tendency in all the physical properties of the wet paper measured, for the first addition of cross-linking agent to have very little effect on the property in question. After the first impregnation the values for the property being measured have tended to rise sharply. This has not been so evident in paper treated with the stilbene diamine derivative as with the other two compounds, but, in view of the errors in measurement of the low values obtained, it is doubted whether any significant conclusions can be drawn from this.

13. Recovery Capacities (Air Dry) of Treated Paper.

Recovery measurements on untreated and treated paper are recorded in Table XXI and XXIV. The figures given are a combination of immediate and delayed recoveries. It can be seen from Fig. 17 that up to a strain of 0.6 % the scatter in results is large. This is due to the small extensions and permanent sets of the paper over this range and the values derived depend to a great extent on the sensitivity of the instrument. Consequently the recovery capacities at 0.75, 1.00, 1.25 and 1.50 % strain have been measured, the specimens usually breaking at higher strains.

Figs. 18 to 21 show the relationship between the recovery capacities of the paper and the amount of reagent present together

FIG.17. PAPER TREATED WITH REAGENT I (1.11%)

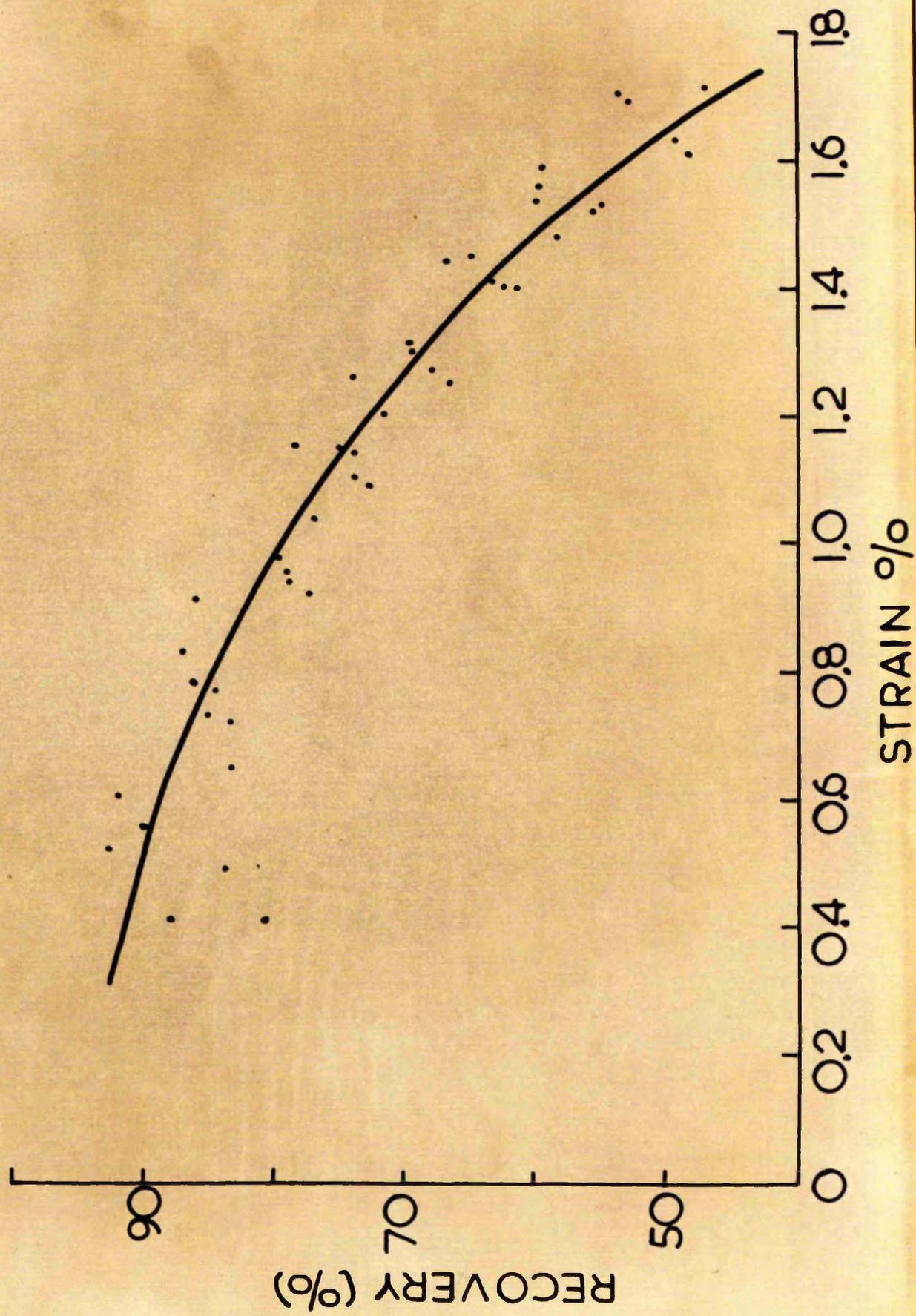


FIG.18, EFFECT OF ALKALI ON THE RECOVERY OF PAPER

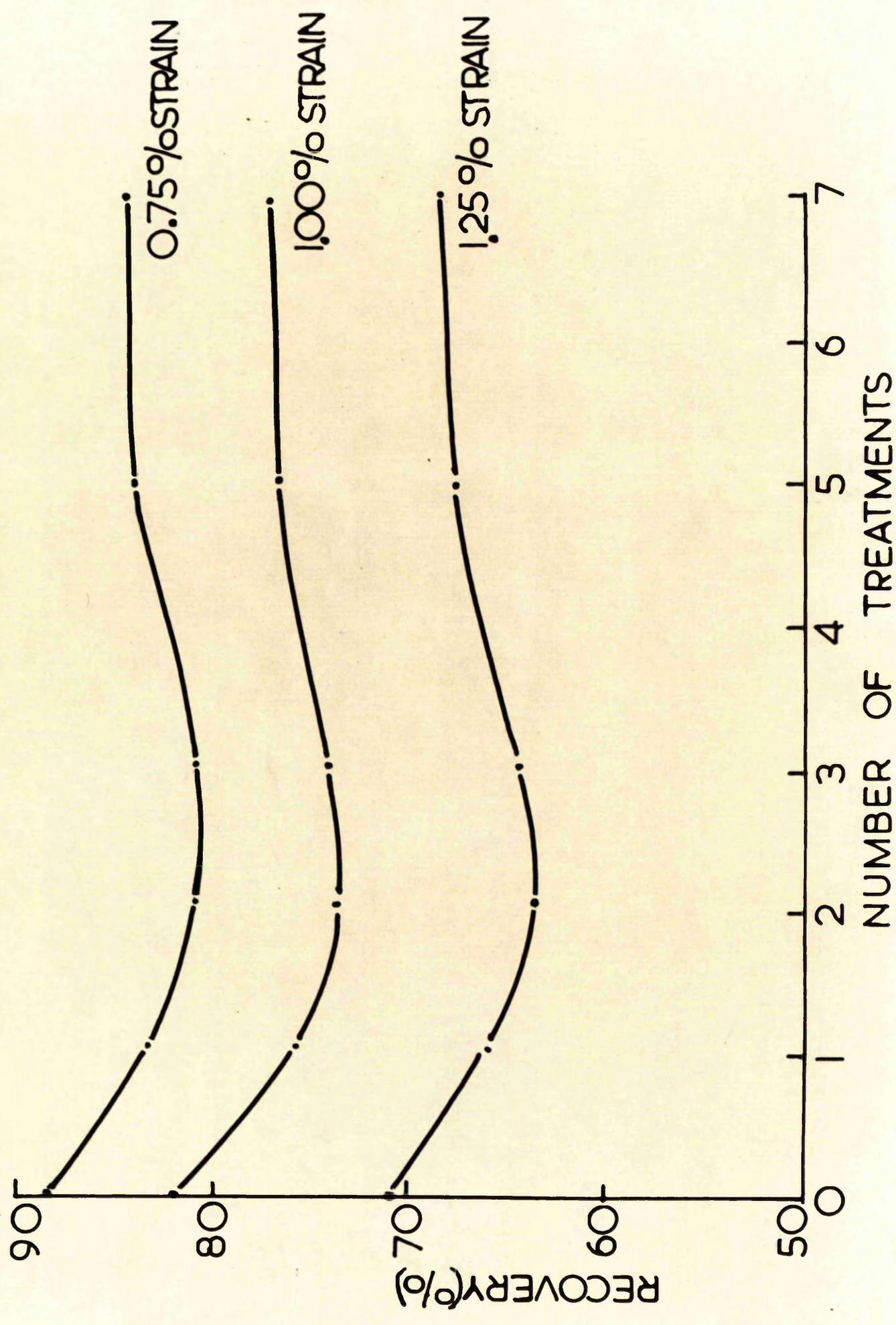


FIG.19. RECOVERY OF PAPER TREATED WITH REAGENT I

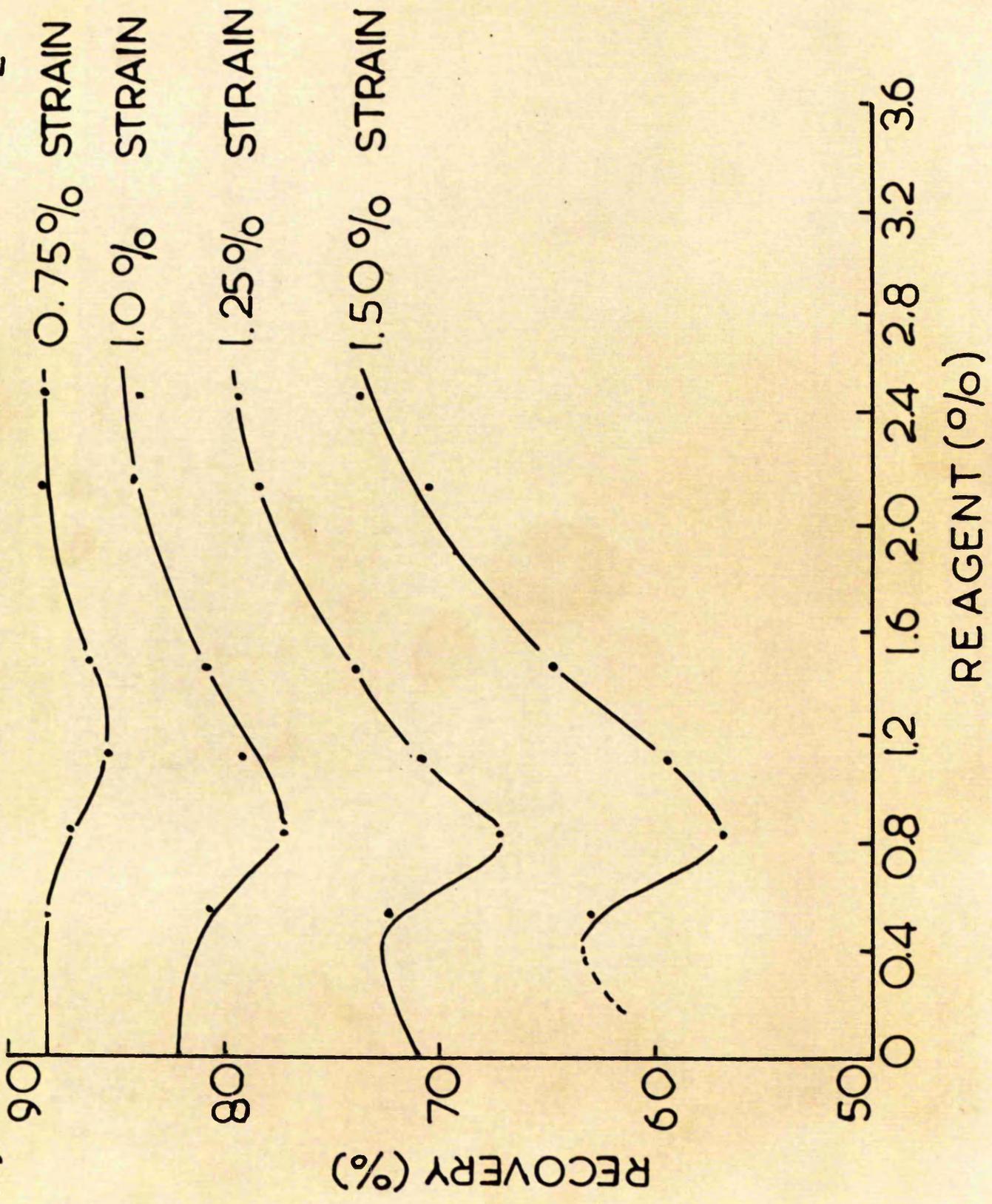


FIG. 20. RECOVERY OF PAPER TREATED WITH REAGENT II

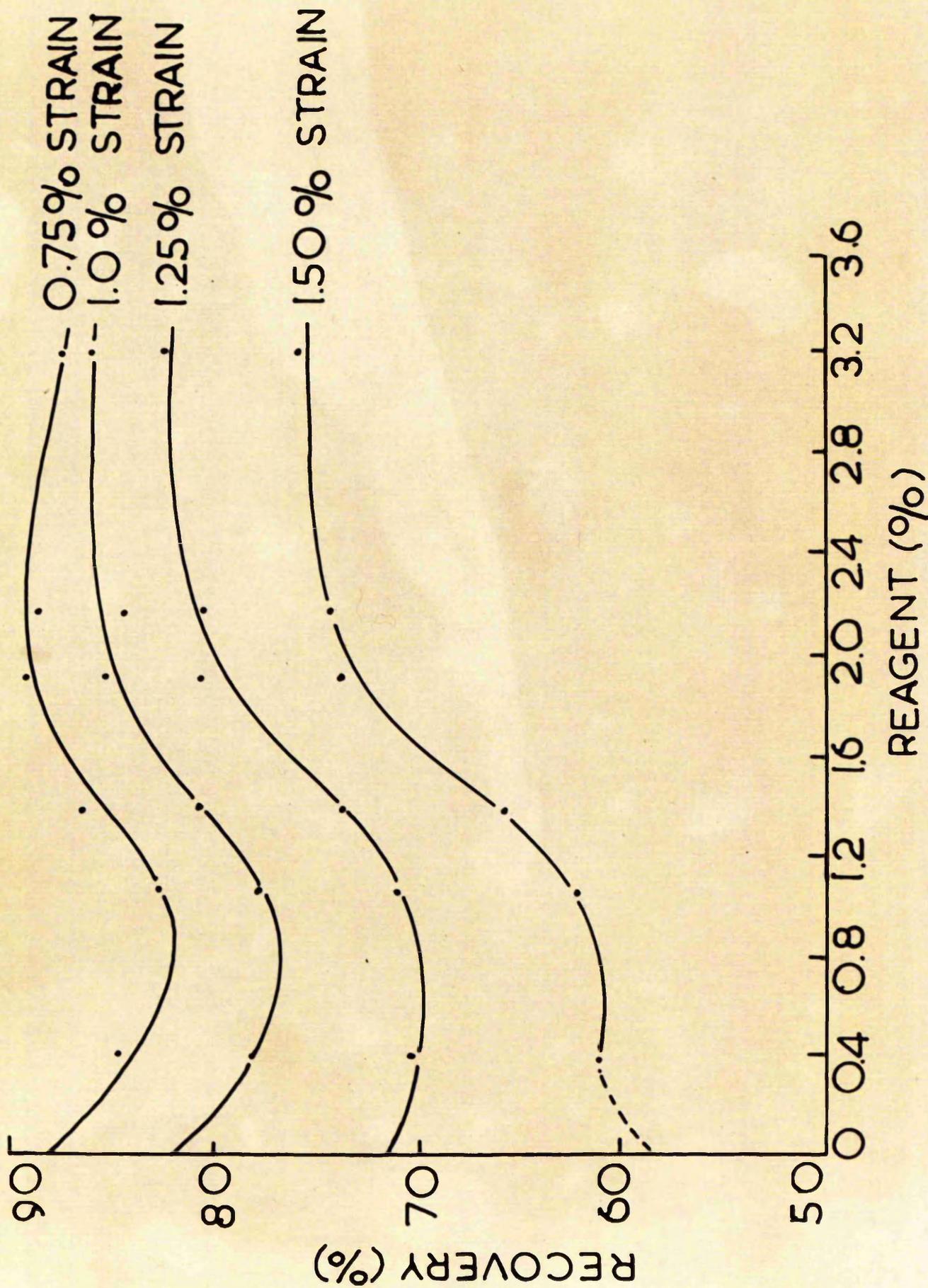
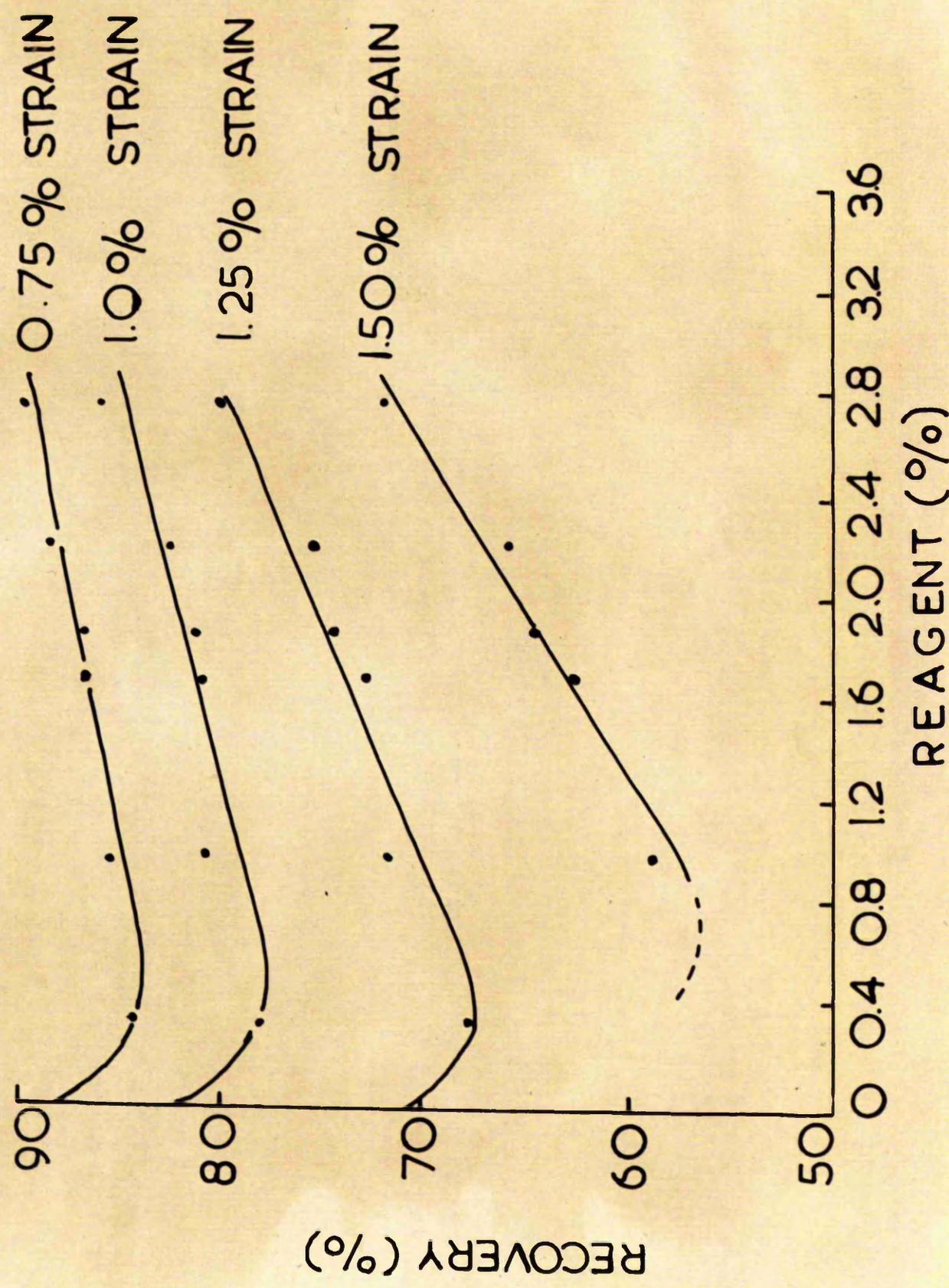


FIG.21. RECOVERY OF PAPER TREATED WITH REAGENT III



with that for paper treated with alkali alone. It can be seen that, although there is an overall increase in the recovery capacity of the paper with the introduction of covalent cross-links, the curves tend to dip in the middle regions. These regions, however, correspond to the lowest points on the curves for paper treated with alkali alone. Thus although the recovery capacity of the paper is increasing, the effect of the treatment is decreasing the effect of the cross-links in this region. As the number of treatments the paper has received increases, the recovery capacity for both the reagent treated and alkali treated paper increases emphasizing the relatively low values obtained in the previous treatments.

The decrease in recovery of the paper on increasing the stress or strain will result in a corresponding increase in permanent set. Most workers in this field agree that permanent set is a result of bond breakage. Page and Tydeman have suggested that as the bond slowly breaks, the microcompressions in the bond area are released, allowing a greater extension and a greater permanent set. Delayed recovery by this theory is considered to be a purely intra fibre phenomenon. Although it would appear that the decrease in permanent set in paper with the addition of chlorotriazine derivatives is caused by covalent inter-fibre cross-links, it is possible that intra-fibre cross-links, by reinforcing micro compressions, could produce a similar effect.

14. The Effect of Intra-Fibre Cross-Links on Conformability.

It was realised, when formulating experiments to determine whether inter- or intra-fibre cross-links were increasing the wet strength of the paper, that all methods for introducing intra-fibre cross-links alone into the paper would decrease the conformability of the fibres. Some work has been done to investigate the effect of intra-fibre cross-linking on the lateral conformability of the fibres and the properties of the resultant paper. The fibres chosen differ in wall thickness and crystallinity and the effects of the intra-fibre cross-links are expected to increase in the order:

pine > cotton linters > exparto grass.

In a recent paper, McKenzie and Higgins⁽⁴⁹⁾ have examined the relative effects of plasticity and external fibrillation upon the bonding capacity of fibres. From earlier work they had found that the addition of cationic starch to wet pulp was sufficient to preserve the external characteristics of the fibre on drying. They used this information to compare, by physical tests and optical examination, paper made from pulp which had been (a) not dried, (b) air dried after starch addition, and (c) air dried alone. By this means pulps (a) and (b) had different conformabilities but a similar degree of external fibrillation, whereas (b) and (c) had different degrees of external fibrillation but similar conformabilities. The starch was removed by enzyme hydrolysis before sheet preparation.

The paper produced shows similarities between the properties for both of the air-dried pulps with differences from the wet pulp, suggesting that the lateral conformability of the fibres rather than external fibrillation is the dominant factor in hydrogen bond formation.

The work described in the following pages considers the effect of intra-fibre cross-linking before sheet formation on drainage rate, air porosity, tear strength and sheet density, and relating these properties to conformability. Three fibre types of differing rigidity (cotton linters, esparto, and bleached sulphate pulp) were used for comparative purposes. The period spent on this work was fairly short, and in one case (bleached sulphate pulp), there was a considerable difference between the basis weights of the treated and untreated papers. Sheet density, however, which is independent of basis weight shows that there is a real difference between the treated and untreated paper. Measurements of tensile properties on the Instron Tester have also been carried out.

1) Drainage Rates of Untreated and Cross-linked Pulps.

The values for drainage time, together with the other physical properties measured in connection with intra-fibre cross-linking are recorded in Table XXV.

It would be expected that the formation of intra-fibre

cross-links would increase the rigidity of the fibres and thus increase the drainage rate during sheet formation. This is not found to be so, the drainage rate for the cotton linters and esparto pulps being slightly less when cross-linked than the untreated pulps. The bleached sulphate pulp does show an increase in drainage rate on cross-linking, but, in view of the difference in basis weight between the two pulps, no real conclusions can be drawn from this fact.

The unexpected rise in drainage time for cross-linked fibres can probably be best explained by the experimental error in time measurement. The uncertainty of determining the point at which drainage is complete could mean an error of 0.2 sec. in 7 sec., an error which, coupled with the variations in basis weight and temperature, could reverse the result for accurate measurements. No conclusive explanations can be drawn from these results about the effect of intra-fibre cross-links on conformability.

ii) Densities of Sheets

It can be seen that for each type of fibre examined, there is a decrease in sheet density on treating the pulp with cross-linking agent. This is due to increasing rigidity of the fibres and a corresponding decrease in conformability. The expected differences in the effect of cross-linking on rigid

and flexible fibres are not shown but this is probably due to variations in the effect of beating on the different fibres and the amount of reagent present. These variations have occurred in all the properties measured and no comparisons between fibre types has been made.

iii) Tear Strengths

Tearing strength, the product of the force required to continue a tear and the distance over which the force operates, is known to vary inversely with the density of the sheet. This is generally accepted to be due to increased fibre bonding causing more fibre rupture and less removal of intact fibres from the web. As the work required for fibre rupture is less than that for fibre removal the tearing strength of the paper falls. It would be expected that the introduction of intra-fibre cross-links with a corresponding decrease in conformability and fibre bonding would increase the tearing strength of the sheets. The reverse can be seen to be true for each pulp used. Page and Tydeman have shown that, on drying, kinks and micro-compressions are formed between and in the bond areas of the paper. The kinks will distribute the applied force over a wider area and the work of tear will be increased. In rigid fibres there will be a lower degree of kinking and the tearing forces will be concentrated over smaller areas. Comparison of the three

types of paper show that the more rigid the fibre the lower the tearing strength. Thus although cross-linking reduces the bonding between the fibres, the rigidity of the fibres cause an overall reduction in tearing strength.

iv) Air Permeabilities.

The air permeability of paper increases markedly with decreasing sheet density. Thus a reduction in conformability with a corresponding decrease in sheet density would be expected to show an increase in air permeability. The flow rate values have been corrected for a basis weight of 60 g.m.⁻² by multiplying by a factor given by dividing the basis weight of the paper by 60. It can be seen from the values given in Table XXV that there is an increase in air permeability with intra-fibre cross-linking, the extent of which decreases with an increase in the original rigidity of the fibres.

v) Tensile Properties

The tensile properties are also a function of inter-fibre bonding and Table XXVI shows the effect of the introduction of intra-fibre cross-links on these properties. The values for breaking length and rupture energy fall, on decreasing the

conformability of the fibres, as predicted, but not in the order expected for the different fibres. This is most obvious in the values of initial moduli, the expected order for the fall in initial modulus being reversed. In view of the scatter in the experimental results these values are not significant and further work would have to be carried out before any definite conclusions could be drawn. The change in tensile properties of the fibres would also have to be taken into account before the effects of intra-fibre cross-linking on bonding capacity could be examined.

15. Conclusions

i). It has been shown that either intra-fibre, inter-fibre, or a mixture of both types of cross-links are introduced into paper on treatment with certain chlorotriazine derivatives under suitable conditions. Reaction probably takes place through the two chlorine atoms in the same triazine ring.

ii). No experimental method, capable of absolute determination of the type of cross-links present, has been found, but the evidence available indicates that there is a mixture of both types with the inter-fibre cross-links being the dominant factor in changing the physical properties of the paper.

iii) The introduction of covalent cross-links into paper has a similar effect to increasing the amount of beating given to a pulp in that the tensile strength, initial modulus and rupture energy of dry paper are increased. The density of the paper, however, is not increased, probably because the triazine cross-links are bulky compared with the hydrogen bonds and other secondary valence forces. No evidence has been found to show that the reduction in tensile strength of the fibres, due to interchain cross-linking, is sufficient for the strength of the fibres to influence that of the paper.

iv) The hypothesis that paper treated with chlorotriazine derivatives would attain high wet strength has been confirmed. The usefulness of this system is limited by the low water solubility of the compounds used, several treatments being necessary before high wet strengths are obtained.

v) It has been shown that, by reducing the lateral conformability of the fibres by cross-linking before sheet formation, the bonding capacity of the fibres is reduced.

vi) It has been shown that rewetting of the paper, after cross-linking has occurred, has no significant effect on the physical properties of the paper.

Suggestions for Further Work

The major factors in reducing the accuracy of the results in work described have been:

- i) The necessity for several treatments to be applied before a high degree of covalent bonding is achieved,
- ii) The lack of control of the temperature and paper tension during drying.

These situations may be improved by:

- i) Increasing the water solubility of the reagents by further study of the sulphonation of chloro triazines.
- ii) Changing the drying technique so that the same drying conditions are achieved with more positive control.

The study of other systems may provide more information about the effects of covalent inter-fibre bonds on the physical properties of paper. Diacid chlorides applied from non-polar solvents could not penetrate the fibres and only inter-fibre cross-links would be formed.

The effect of intra-fibre cross-links on conformability should be studied more comprehensively. The amount of reagent present and the degree of beating should be varied.

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Acknowledgments

I would like to express my gratitude to my supervisors Prof. R.H. Peters and Dr. F.L. Hudson for their advice and support during the course of this work, to Mr. W. Bolton for making the paper used, and to my colleagues in the Department of Polymer and Fibre Science for many helpful discussions.

APPENDIX

The paper used in this work was a white wove, unsized, absorbent paper made on the old College machine which was scrapped in 1963.

| | |
|---------------------------------------|----------------------------------|
| <u>Run Number</u> | 63/4 (14.1.1963) |
| <u>Furnish</u> | Bleached, 1st cut cotton linters |
| <u>Freeness</u> | 29 ^o S.R. |
| <u>Substance</u> | 70 g.m. ⁻² |
| <u>App. Sp. Gr.</u> | 0.59 |
| <u>Air Permeability</u> (See p.53) | 2170 ml. min ⁻¹ |
| <u>Burst Factor (a)</u> | 1.35 |

| | <u>Machine</u> <u>Direction</u> | <u>Cross</u> <u>Direction</u> |
|---|------------------------------------|----------------------------------|
| Breaking Length (m) | 3683 | 3051 |
| <u>Breaking Extension (%)</u> | 1.57 | 2.31 |
| Initial Modulus ^(b) (g x 10 ⁻⁵) | 4.98 | 3.77 |
| Rupture Energy (g.cm.cm. ⁻¹) ^(c) | 54.1 | 42.4 |
| <u>Tear Factor</u> | 88.2 | 81.0 |

$$(a) \text{ Burst Factor} = \frac{\text{Bursting Strength (g.cm}^{-2}\text{)} \times 100}{\text{Basis Weight (g.m}^{-2}\text{)}}$$

(b) The initial slope of the stress/strain curve

(c) Rupture energy has been expressed in units of stress x strain, i.e. g. x cm.cm⁻¹.