

# The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

The Effect of Urea and Related Compounds on  
the Mechanical Properties of Paper

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EDITORIAL DEPARTMENT

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**THE EFFECT OF URMA AND RELATED COMPOUNDS ON  
THE MECHANICAL PROPERTIES OF PAPER**

**A thesis submitted by**

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**in partial fulfillment of the requirements  
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## INTRODUCTION

The papermaker is continually striving to better his product by designing his sheet to meet its use requirements. This has inevitably led to the introduction of many new techniques of papermaking, among which is the use of a wide variety of nonfibrous additives. When the use requirements of certain grades of paper dictate that the sheet have a certain amount of flexibility or "softness," and it is impossible or undesirable to obtain these properties by manipulation of the paper-making variables, they may be obtained by adding to the sheet one of a group of compounds spoken of as softeners or plasticizers. For example, a highly beaten greaseproof or glassine sheet may require some such additive to modify its naturally stiff, brittle characteristics so that it will not break or fracture when flexed. Various grades of food wrap must withstand folding and flexing without cracking, and thus they generally require the presence of a softening material. In certain instances a plasticizer may be used when the properties of "dead-fold" and minimum "spring-back" on folding are essential. Paper draperies are regularly treated with some type of softening agent to enhance their clothlike draping qualities, while radio program paper may contain these agents to reduce sheet rattle on folding or bending.

The terms softener, humectant, and plasticizer have all been applied to these compounds. The general adoption of the term softener may be disputed on the sound basis that the meaning of the term softness may depend on the particular paper product under discussion. To the glassine manufacturer, softness may mean flexibility; to the tissue

manufacturer, softness may connote such qualities as sheet smoothness and lack of harsh edges and corners when the sheet is crumpled. The term humectant is correctly applied to some of these compounds some of the time. However, the use of this term implies that the action of the material is wholly the result of its hygroscopicity. This is an oversimplification of the facts. The term plasticizer would seem to be the most satisfactory general term for the class of compounds under discussion. In the high-polymer field the term plasticizer generally refers to a material, often a solvent or near-solvent of low volatility, which is incorporated in a material to lower its internal cohesion and hence to enhance its toughness and flow properties and to increase its flexibility. Despite the fact that this general definition may not strictly apply to paper, there is strong reason to suspect that as more is learned of the mechanism of plasticizing paper, this definition will prove to fit the actual facts.

In this thesis the term plasticizer will be used to describe those additive compounds which reduce the rigidity of a sheet of paper and improve its flow properties. Among the many materials which have been used for this purpose, glycerin is the most important. The sugar products such as invert sugar, corn sugar, corn syrup, and dextrose have also been rather widely used. Sorbitol and ethylene glycol are also in use in the industry, and urea is rapidly becoming one of the more important of these materials.

## HISTORICAL REVIEW

In recent years increased technological advance in the paper industry has resulted in increasing interest in the actual mechanism by which certain compounds plasticize a sheet of paper. Since the literature concerning this subject has been thoroughly reviewed by both McPherson (1) and Nethercut (2), no comprehensive historical survey will be attempted in this thesis. The interested reader is referred to the works of these authors for a more complete review of the early work in the field.

Nature's softener for cellulosic materials is water. The fact that most of the plasticizers commonly used in paper are hygroscopic has led many people to assume that these compounds are effective only because of the additional moisture which they draw into the sheet of paper. The fact that a close relationship exists between hygroscopicity and plasticizing powers has been brought out by many investigators (3-12).

However, experimental evidence continues to accumulate which shows that the plasticizer molecule itself is effective in altering the mechanical properties of paper. Pike (13) first demonstrated that at relative humidities below 60%, the addition of small amounts of invert sugar or glycerin to greaseproof paper actually reduced its moisture content. Connor and Nadelmann (14) observed that below a relative humidity of 40%, plasticizers do not exert any beneficial effect on paper due to their hygroscopicity. A careful study by McPherson (1) showed that at any relative humidity the moisture content of a glycerin-treated sheet was less than the theoretical sum of the individual moisture

contents of the paper and of the glycerin. This difference between the observed and the calculated moisture contents increased with increasing glycerin content and with increasing relative humidity. At low relative humidities and low glycerin contents, the moisture content of the treated sheets was found to be lower than that of even the untreated sheets. McPherson concluded that at low glycerin contents, glycerin was effectively competing with the moisture for the reactive sorbing groups on the cellulose.

Nethercut (2) also found that the flexibilizing action of glycerin, formamide, and urea on rayon fiber could not be wholly explained on the basis of the change in moisture content of the treated fibers.

In view of the absence of any direct evidence proving that the plasticizing of paper is accomplished solely by hygroscopic moisture attracted to the sheet by a humectant, it seems logical to proceed under the assumption that other molecules, in addition to water, may have the ability to plasticize paper. If this assumption be granted, then the fundamental problem at hand is to determine how both water and other plasticizers act to alter the properties of a sheet of paper.

McPherson (1) has classified the various proposed mechanisms for the plasticizing phenomenon under the three headings: (1) the fiber lubrication concept, (2) the weakening of fiber-to-fiber bonds concept, and (3) the flexibilizing of individual fibers concept. Inasmuch as the actual basic mechanism is probably almost the same for all three of the above classifications, it is logical to consider the three categories as one.



## THE MECHANISM OF THE PLASTICIZING OF PAPER

Pike (13) and Leffingwell (2) considered that plasticizers provide lubrication between the fibers in a sheet of paper in such a way that their ability to slip over one another is enhanced. Connor and Nadelmann (14) felt that plasticizing was probably the combined result of a lubrication phenomenon and a fiber-swelling phenomenon. In considering the lubricating action of a material, they differentiated between "boundary lubrication" in which a thin, perhaps monomolecular, layer of adsorbed plasticizer reduces the unbalanced molecular attractive forces responsible for friction between contiguous faces, and "fluid lubrication" where the layer of lubricant is sufficiently thick that only the internal friction (viscosity) of the lubricant is significant. They pictured a polar plasticizing molecule whose reactive group could be firmly attached to the solid face of the fiber with its less reactive, nonpolar end at a steep angle with the face. Thus with a monomolecular layer or a partial layer of plasticizer molecules attached to the face, the attraction between molecules of lubricant would be less than either the attraction between solid faces or the attraction between the solid face and the polar end of the molecule. This would result in reduced bonding strength.

It is the feeling of the author that the concept of fluid lubrication is applicable only to extreme cases of plasticizing such as an actual wetting of the sheet. It is felt that the separation of the fibers of a sheet of paper to the point where the viscosity of an interspersed liquid could control the sheet's mechanical properties would result

in a semidispersion of the fibers and an almost complete loss of sheet strength.

Connor and Nadelmann have noted that boundary lubrication and fiber swelling are very closely related. They believed that by the same process of adsorption as that described above for boundary lubrication, a plasticizer molecule may enter the fiber and cause swelling. This swelling would result in reduced fiber stiffness.

McPherson (1) found that glycerin increased the caliper of a sheet of paper, and that a glycerin-treated pulp had less moisture-vapor sorption hysteresis than an untreated pulp. Both of these findings, he concluded, demonstrated that glycerin entered the cellulosic structure and kept it in a semiswollen state. McPherson also found that glycerin first increased and then reduced the relative internal friction of paper as measured by the damping effect of a sheet of paper on a torsion pendulum. From these data he concluded that the first increments of glycerin had swollen the fibers and the bonds in the sheet sufficiently to allow an increased movement of fibers or micelles under stress. Larger amounts of glycerin, he believed, while further increasing the relative movement of fibers, probably tended to provide some sort of boundary lubrication which reduced the frictional forces.

McPherson further found that glycerin reduces the flexural rigidity and tensile strength of an alpha sheet, but that it has no effect on the tensile strength of cotton fibers. From these data he concluded that the softening effect of glycerin on paper is the result of a weakening of the fiber-to-fiber bonds by the swelling mechanism

mentioned above.

Nethercut (2) studied the effect of various plasticizers, including water, on the dynamic stiffness of rayon filaments, ramie fibers, and ramie sheets. Although he found that the stiffness of the filaments and fibers was affected by the presence of a plasticizer, he concluded that most of the loss of stiffness occurring in a plasticized sheet was the result of changes in the fiber-to-fiber bonds rather than changes in the fibers. His work on rayon filaments indicated a close relationship between swelling ability and plasticizing ability. Formamide was found to flexibilize markedly rayon filaments while the effectiveness of alcohols seemed to be reduced by increasing the chain lengths of the alcohols.

Reed (15) studied the folding strength, tensile strength, stretch, and tearing strength of sheets treated with a series of aliphatic esters of gluconic acid. He reported that the plasticizing action appeared to increase with the size of the esterifying alcohol molecule.

Sneel (16) found that increasing the chain length of the polyalcohols decreased their plasticizing effect on paper. Thus ethylene glycol was more effective than glycerin, which, in turn, was more effective than sorbitol.

Steenberg (17)\* has published load-elongation curves which show

\*This author also presented a paper entitled "Preliminary results on the nature of the paper bond by studies of softening with amides" at the TAPPI Fundamental Research Conference in Quebec, P.Q., May 31, 1950, which was not available to the author.

that with increasing moisture content, the tensile strength and the elastic modulus of a sheet of paper are decreased. The sheet's yield point decreases with increasing moisture content, whereas flow properties and stretch increase.

#### THE PLASTICIZING OF OTHER CELLULOSIC MATERIALS

In studying the plasticizing of paper, it is desirable to bear in mind that the cellulosic raw material in paper is a high polymer. As such it may be expected to behave in the same general manner as other polymeric systems. A brief review of a portion of the literature dealing with the plasticizing of other cellulosic materials is particularly pertinent to the subject under consideration.

Ott (18) has discussed two general theories of plasticizer action for cellulosic derivatives. The first concept is one of a solvation of the polymer chains which increases the average distance between them and thus reduces the forces acting between neighboring molecules. This reduction of cross-linking forces serves to increase flexibility by increasing the amplitude of the internal movement of the chains. The second theory, attributed by Ott to Kratky, pictures a network of solvated cellulose derivatives which surround and penetrate regions in which the plasticizer content is much greater. The plasticizer-rich phase, which is a more complete solution of the derivative in the solvent, is only partially miscible with the surrounding solvated (plasticizer-poor) phase, and is held in the pores of this phase by surface tension. This prevents the collapse of the structure. The viscosity of the plasticizer-rich pockets of such a gel-type structure is said to control its flexibility.

Craver (19) agrees with the first theory of Ott in that he considers plasticizers to be high-boiling solvents which replace polymer-polymer bonds with polymer-solvent bonds. Liebhafsky, Marshall, and Verhoek (20) also considered the plasticizing of polyvinyl chloride to occur along these lines.

Meyer (21) has stated that the forces acting between the cellulose hydroxyl groups may be diminished by intermicellar swelling agents, such as water. Intramicellar swelling agents, he pointed out, would be even more effective.

The experimental work of Baker, Fuller, and Pape (22) also indicated the same mechanism as that proposed by Ott. These workers studied the effect of solvents, including water, on samples of cellulose acetate which had been heated and rapidly quenched to "freeze" the structure in a highly disordered form. They found that either solvent vapors or water caused a sufficient relaxation of the cross-linking forces by which the stresses were being frozen into the fiber to allow a considerable increase in crystallinity to take place. They concluded that a lower elastic modulus resulted when these high interchain forces, which resulted from the hydrogen bonding of residual hydroxyl groups, were turned to bonding softener.

Nickerson (23) believed that the rupturing and weakening of the -O-H...O- cross linkage in cotton was accomplished by water, and possibly by other plasticizers, first by combining with and deactivating hydroxyl groups, and secondly by increasing the molecular distances so that the residual valence forces are greatly reduced in potency.

The fact that the reduction of internal cohesive forces is sufficient to cause plasticizing has been shown by Ott (18), who "internally" plasticized some cellulosic materials by replacing hydroxyl groups with larger substituent groups. These larger chains increased the intermolecular distances and thus largely destroyed the high degree of cross bonding. The resultant effect on the material was the same as if an external plasticizer had been added.

The effect of moisture on cotton fibers and rayon filaments provides an interesting insight into the plasticizing action of water. Willkomm (24), Obermiller and Goertz (25) and Mann (26) found that the tensile strength of cotton hairs increased with increasing moisture content. On the other hand it has been reported by Peirce and his collaborators (27, 28) that a linear decrease in the modulus of rigidity of cotton hair occurs throughout most of the moisture content range as the moisture content increases. Venable (29) and Lauer (30) found that the tensile strength of rayon decreased with increasing moisture content. Nethercut (2) reported that the flexural rigidity of rayon decreased as the moisture content of the filament increased.

Both Hermans (31) and Houwink (32) have offered logical, if slightly different, explanations for this seemingly contradictory behavior of rayon and cotton. Hermans believed that the explanation lay in the distribution of tension. In the swollen natural cotton fiber, he stated, the molecules are distributed very uniformly, and as a result of the increased flexibility of the amorphous portions the chains are more evenly strained than in the more brittle, dry fiber. However, in

rayon the molecular chains are less orderly in arrangement. In the dry rayon filament the tension is therefore more evenly divided in these disordered amorphous regions than in the moist filament where the lack of uniformity comes into full play. Houwink regarded the deformation of rayon as a slippage of micelles which is facilitated by the presence of a lubricant, i.e., a swelling agent such as water. His concept of the effect of moisture on cotton fibers was similar to that just discussed in connection with Hermans' views, in that he felt that the increase in tensile strength was due to a more even distribution of stress between micelles.

Since internal cohesive forces of both rayon and cotton are reduced by water, it is to be expected that the flexibility of both materials would be increased on swelling. The effect of plasticizers other than water has been found to be similar to the effect of water. McPherson (1) found that treatment of cotton fibers with glycerin did not decrease their tensile strength, although their stiffness was adversely affected. Nethercut (2) reported that the modulus of rigidity of rayon filaments was reduced by such plasticizers as glycerin, urea, and formamide. The effect of these materials on the stiffness of ramie fiber was considerably less marked than in the case of rayon filaments.

#### UREA AND RELATED COMPOUNDS AS PLASTICIZERS FOR PAPER AND CELLOPHANE

In 1934 Herrmann (33) was granted a patent covering the use of formamide as a plasticizer for cellulosic sheets. Several years later Underwood (34) and King (35) patented the use of water-soluble amides

(including urea) and urea and glycerin mixtures, respectively, for the softening of regenerated cellulose films. Meigs (36) in 1940 patented the use of a cellulose film softener comprising a water-soluble polyhydric ester of carbamic acid. In the specifications of all of these patents the suitability of the plasticizer for paper, particularly glassine paper, was noted.

The use of unreacted urea in conjunction with hygroscopic substances such as those normally employed as paper plasticizers was patented by Roth (37) in 1942. Beecher (38) obtained a Canadian patent in 1944 which covered the use of a urea-glycerin mixture in the ratio of about 10:1 for the softening of paper. Wenberg (39) patented the use of the inorganic salts of urea, such as a double salt formed by the addition of three parts of urea to one part of sodium nitrate, for the plasticizing of glassine. He stated the preferred amount of plasticizer to be from 3 to 20%. In 1947 Feibelman (40) patented the use of a solution of urea and potassium formate as a softening agent for paper. Charles and Durgin (41) have recently been granted a patent for the use of urea as a plasticizer for creped, resin-impregnated papers.

#### THE VISCO-ELASTIC BEHAVIOR OF PAPER

In a consideration of the mechanical properties of paper, the fact cannot be overlooked that paper, like many other high polymers, exhibits both elastic and viscous properties. Elastic behavior implies that the material obeys Hooke's law so that the strain is directly pro-



portional to the applied stress and is completely and instantaneously recovered on removal of the stress. In the elastic deformation of paper no bonds are broken, but potential energy is stored up in such forms as changes in valence angles and bonding distances, and uncoiled molecules. Elastic behavior is never a time function. Viscous or flow properties, on the other hand, have a definite dependence on time. The portion of the creep which occurs when a plastic body is strained and which may be recovered with sufficient time is known as primary creep or recoverable flow. Secondary creep, on the other hand, is irreversible and results in unrecoverable deformation.

As a result of the dual nature of paper, the stress-strain behavior of the material is a function of its entire previous history (42). It is also obvious that the extent to which the elastic and viscous properties control the behavior of paper is dependent on the time required for the stressing. This has been graphically illustrated by Rance (43), who found that a paper having a tensile strength of 10 kg. broke in 11 minutes with 9 kg., in 14 hours with 8 kg., in 20 days with 6 kg., and in 220 days with 4 kg.

A number of investigators (42, 44-47) have reported and discussed the fact that when a sheet of paper is successively loaded and unloaded, the secondary creep characteristics are decreased so that the sheet becomes mechanically conditioned or work-hardened. After sufficient load-unload cycles, the stress-strain diagrams of successive cycles become almost identical.

There are strong indications that another phenomenon, similar to the extension-orientation phenomenon observed in many linear polymers, may occur in paper. Edge (48) and others (42) have found that a web of paper of random fiber orientation which is dried under unidirectional tension may have a very much higher tensile strength in the direction of the drying tension than in the cross direction. Furthermore, in highly extensible laboratory papers, Ivarsson (46) has reported finding that the slope of the load-elongation curve (the LE curve) increases as the plastic elongation continues, showing that the paper is beginning to stand up to the stress in much the same manner as do regenerated cellulose filaments. Whether these two effects are mutually related, or whether or not they bear any basic similarity to the extension-orientation of a material such as rayon is not known.

In stress-strain work on visco-elastic materials many investigators have found it convenient to describe the behavior of a material in terms of hypothetical models built up of elastic springs and viscous dashpots. This type of analysis has proven to be particularly useful as an aid in the separation of the effects of viscous and elastic behavior on the stress-strain curve. It has also made possible mathematical treatment of the data. While this method has been found to have considerable utility, its inherent limitations must be borne in mind at all times. The fact that a model satisfactorily explains the form of a stress-strain curve does not, in itself, mean that the elements of the model have submicroscopic counterparts in the structure of the material itself. Particularly is this true of a substance as complex structurally as paper. Paper is known to be made up of a vast number

of elements, each of which may exhibit visco-elastic properties and which may, therefore, be represented by a visco-elastic model. Several investigators (17, 40-51) have warned against succumbing to the urge to describe the internal structure and the mechanism of mechanical stressing in terms of tiny springs and submicroscopic dashpots.

An important discussion of the visco-elastic properties of textiles by Eyring and Halsey (40) is of interest. These authors advanced the concept of a constant interchange of "partners" in a high polymer, in which flow units are continually exchanging old neighbors for new, even when no forces are acting on the molecules. An applied stress unbalances these forces, causing a net migration of flow units in one direction. The basis of the visco-elastic model, they further state, is the concept of a fiber as a long bundle of long-chain molecules. Some of these long-chain molecules are too firmly bound to slip, hence they act as pure springs in accordance with the kinetic theory of elasticity. Other molecules are not so firmly fastened and contain loops and ends which may both stretch or slip, and hence may act as a Maxwell unit (spring and dashpot in series). These two types of units in parallel will behave in the manner of the three-element model shown in Figure 1.

Eyring and Halsey pointed out that either disentanglement or failure of the individual molecules may be the cause of failure. In order to be broken, a fiber must experience a progressive diminution in the number of chains in some cross section which sustains the force exerted on the fiber. This may occur either by (1) end slippage of the molecules, or by (2) rupture of the primary valence bonds. The actual

failure may be preceded by slippage, in which loops crossing a cross section more than once are pulled out until the number of chains in a cross section is sufficient for mechanism (1) or (2) to occur. The number of loops which can be extended and the size of these loops thus determines the extent to which fibers can lengthen without breaking. Eyring and Halsey further emphasized that the simplest visco-elastic model merely replaces all the loops with an appropriate average loop. That such a simplification is not wholly satisfactory is shown by the fact that if a wide distribution of loop sizes exists, a continuing elongation will cause successively longer loops to unfold. The net result will be a stiffening in terms of force per bond. The break results at that elongation for which the available loops in a cross section are exhausted. It does not necessarily follow, they pointed out, that this elongation is the same as the over-all fiber elongation. The mechanism which Eyring and Halsey discussed was, of course, for individual fibers. However, it seems quite possible that the general type of mechanism pictured may also be applicable to the fiber-to-fiber bonds of paper which must, ultimately, consist of intermolecular bonds similar to those in a fiber.

Ivarsson and Steenberg (52) have found that the model of Figure 1 is adequate to explain the behavior of strain-hardened papers. Other elements must be added to this model--at the very least a series dashpot--if the secondary creep properties of a virgin, unstressed paper are to be adequately explained. These authors have explained how the model of Figure 1 operates to give an LE curve of the type obtained for paper and illustrated in Figure 2. When the model and the sheet are

strained at a constant rate of elongation, they react elastically at first, the springs  $K_1$  and  $K_2$  undergoing extension. In this first region the LE curve is linear and its slope is the sum of the spring constants of springs  $K_1$  and  $K_2$ . At some point in the straining, the force exerted on the non-Newtonian dashpot causes it to start moving, and the LE curve falls away from its original straight line. As the sheet and the model are further elongated, both springs continue to be extended. The increasing force exerted by  $K_2$  on the dashpot causes its rate of movement to continue to increase. At some point the force exerted by spring  $K_2$  is just sufficient to cause the dashpot to move at the over-all rate of elongation, so that thereafter  $K_2$  ceases to extend as the sheet is strained. In this region the LE curve becomes linear again. It is evident that the slope of the LE curve in this portion of the curve is equal to the spring constant  $K_1$ .

If the jaw movement is now reversed, Ivarsson and Steenberg continued, springs  $K_1$  and  $K_2$  begin to retract. The spring  $K_2$  is still under tension so that the dashpot continues to move in the direction of original extension. Thus  $K_2$  is being shortened from both ends, and soon reaches an unstressed state. At this point dashpot movement ceases.  $K_1$  is still extended, however, so that further unloading causes  $K_2$  to be compressed, and this brings about dashpot flow in the direction of return.

When jaw movement is once again reversed so that the sample is being reloaded, the dashpot again passes through a period of zero motion before beginning to move in the direction of extension.

As an aid to visualizing the secondary creep properties of paper, Steenberg (17, 53) has introduced the concept of "microcreping" in paper. The extent of this microcreping is said to be determined by the past history of the sheet, such as the amount of tension applied to the sheet during drying. As a result of drying tension, the loops, kinks, or curls in the fibers or bonding fibrillae which may constitute this microcreping are straightened out, with a resultant orientation toward a higher state of crystallinity (46). This would account for the increase in tensile strength and modulus of elasticity observed as the result of drying under tension.

Mason (47) has described the mechanism of strain in terms of a mechanical model which consists of a series combination of a Maxwell unit (spring and dashpot in series) and a Voigt unit (spring and dashpot in parallel). The instantaneously recoverable strain may be associated with the Maxwell unit spring, and is, by implication, essentially a fiber and fiber-orientation property. Mason considered the Maxwell unit dashpot to represent the uncoiling of fibers and the slipping of unbound fibers over one another. The Voigt unit may be associated with the relative movement of bound fibers. On this basis, Mason feels that the study of instantaneous deformation should provide a measure of fiber properties, whereas the recoverable creep should be an indication of the mechanical nature of the interfiber bonding.

Gibbon (45) believed that the preliminary stressing of a sheet of paper is essentially a process in which fibers slip into positions of increased density rather than one of fiber extension. Repeated stressing

then probably acts on fibers and fiber-to-fiber bonds once this permanent set has been established. Harrison (54) stated his belief that the first loading of a sheet causes the straightening of kinks in the fibers with a resultant nonrecoverable elongation. Superimposed on this action is a smaller viscous flow caused by the gradual slippage of fibers past each other. There is also a recoverable, nonelastic deformation due to a deformation of the fiber structure. Ivarsson and Steenberg (52) believed the site of flow to be the weak cohesive forces, probably hydrogen bonds or van der Waals forces, between fiber, fibrillae, micelles, or cellulose chains.

Rance (43) believed that fibers are dried in a kinked or twisted form and that this kinking corresponds to Steenberg's micro-creping. Rance considered rupture to be the logical termination of the straining process. The irreversible flow results from the first stage of disintegration where fiber-to-fiber bonds are broken at an ever increasing rate. Rupture is caused by the concentration of stress at weakened points. Therefore, in Rance's opinion, in so far as straining involves the breaking of fiber-to-fiber bonds, it is a weakening process.

Van den Akker (55) has "listened" to rag and sulfite bond papers while they were under increasing strain. He reported that little or no noise, such as might be heard if bonds were breaking, was heard before the point of actual failure. He interpreted this to mean that in a reasonably well-beaten sheet very few bonds break before ultimate failure.

## PRESENTATION OF THE PROBLEM

Considerable headway has been made in the past few years in elucidating the mechanism by which paper is plasticized. Experimental evidence has been obtained upon which a sound concept of the phenomenon may be based. However, further work in this interesting and important field is necessary if the mechanism of plasticizing paper is to be completely understood.

The action of urea on paper has never been studied comprehensively. In addition to its increasing technological importance, urea is of considerable theoretical interest because it lacks some of the characteristics which have heretofore been associated with all paper plasticizers. First of all, urea lacks the hygroscopic characteristics common to almost all paper plasticizers. Secondly, urea probably lacks a hydroxyl group which some investigators (14) have felt is a prerequisite to plasticizing ability. It is possible, of course, that urea undergoes a tautomeric keto-enol shift which produces an enolic hydroxyl group.

The first object of the thesis, therefore, was to study the plasticizing effect of urea on paper with the hope that the investigation might shed light on the plasticizing action of other softeners as well.

A very considerable amount of work has been done on the stress-strain characteristics of high polymers, and a wealth of information on the structure of various materials has been gained from these studies. Only in the past decade, however, have the stress-strain properties of paper come into their own as an important tool for the study of the visco-



elastic properties of paper. Further study of the load-elongation (LE) curve could be expected to contribute to the understanding of this potentially highly useful tool.

The second object of the thesis was to employ the LE curve of paper as a means of evaluating the effect of urea on the mechanical properties of paper. This type of evaluation was expected to give a maximum of data which would be of value both for improving the understanding of the plasticizing phenomenon and for adding to our knowledge concerning the variation of the LE curve as changes are made in a sheet of paper.

The program outlined for the study of urea's action in paper included: (1) a study of the effect of urea and a few related compounds on the LE curve of alpha-pulp handsheets, and the effect of varying humidity conditions on the LE characteristics of the treated sheets, (2) a study of the effect of substitution on the urea molecule on its ability to change the visco-elastic properties of paper, and (3) a study of the effect of urea on other related sheet properties.

## TESTING METHODS AND ANALYTICAL PROCEDURES

### SHEET PREPARATION

A Brown Company alpha pulp was selected for use because it was felt that an alpha pulp would most nearly approach pure cellulose and yet still retain the papermaking properties typical of wood pulps in general. The relative absence of hemicelluloses in an alpha pulp was expected to simplify interpretation of the data obtained.

It is well-known that the LE curve of paper is quite sensitive to the conditions under which the paper is dried. Preliminary work showed that with increasing drying tension, the elastic moduli and the tensile strength of a sheet increased, while the stretch and work of failure fell off sharply. The fact that drying tension is of such importance to the LE curve made it necessary to employ a reproducible means of drying the test sheets. Considerable exploratory work with slow-drying techniques indicated that it was impossible to obtain a sheet completely free of cockle unless the sheet were dried with some degree of restraint. Since drying between blotters might have given the handsheet two-dimensional characteristics similar to those of the blotting paper, this method was not used. Ultimately, it was decided that the only way to produce the flat, completely reproducible test sheets necessary for the LE work was to employ the standard sheet preparation and sheet-drying method (56) in which sheet shrinkage is prevented by drying the sheets on plates and rings. It was realized that by drying under complete restraint, the sheets were made stiffer than would be the case if they were dried without restraint. This may have tended to magnify the plasticizing effect of

the various materials incorporated in the sheet. It is probably true, however, that sheets dried on plates and rings more nearly approximate machine-made papers than sheets which are dried without restraint.

Preliminary work showed that it would be extremely difficult to produce sheets having the same LE curve from one Valley beater charge to another. Consequently four beater-loads of pulp were beaten, each charge being beaten 50 minutes with a bedplate loading of 4500 grams. The beaten pulps were thoroughly mixed and made into 1.6-gram sheets on a single British sheet mold during the course of five days. The standard method of sheet preparation (56) was used. The Schopper-Riegler freeness of the mixed pulp was 640 ml. All the sheets were calipered at five points with a Schopper caliper which was graduated to 0.0001 inch and which met the specifications of the standard method (57). Each sheet was weighed on an analytical balance, and its basis weight and density were calculated. From the 550 handsheets which were prepared, about 300 standard test sheets were chosen which met visual cleanliness and formation standards, and whose basis weights and densities fell within the following limits: basis weight, 61.29-62.30 pounds per 25 x 40--500 ream; and density, 0.732-0.755 g./cc. The accepted sheets were then made up into testing groups of four sheets so that in any group the mean of the weights and the mean of the densities fell as close to the median of the limits as was possible. By this careful sheet preparation and selection procedure, as much sheet-to-sheet variability was eliminated as was practically possible.

## INTRODUCTION OF ADDITIVE COMPOUNDS INTO THE SHEETS

The majority of the compounds studied were introduced into the standard sheets by soaking the sheets in aqueous solutions of the material for a minimum of 12 hours. During this time the solution was occasionally swirled around the sheets to insure the presence of fresh solution around the soaking sheets. The wet sheets were then carefully removed from the solution, and placed on a dry blotter, glazed side up. A clean, polished drying plate was then laid on the sheet, and the blotter, sheet, and plate centered on top of the stack in the press. A fresh blotter was laid on top of the plate so that in the stack the repeated sequence from bottom to top was: fresh blotter, fresh blotter with sheet, and plate. The stack was pressed three minutes at a pressure of 50 p.s.i. after the pressure had been increased to 50 p.s.i. in 30 seconds.

The stack was then removed from the press, and the individual plate and sheet combinations were placed on drying rings in the only manner which was found to eliminate the possibility of disturbing sheet-to-plate adhesion. This method consisted of placing the stack of blotters and plates so that the plates lay sheet uppermost. After the top blotter was removed, the blotter bearing the plate was placed near the edge of a table. A ring was then carefully placed on the plate, flange downward, and pressed firmly onto the plate. By sliding the blotter partially off the table, it was possible to pick up the plate and ring without relieving the pressure of the ring against the plate. The ring and plate were then carefully placed on the bottom ring which lay rubber gasket uppermost.

This painstaking procedure was adopted when it was found that the mere handling of a plate carrying a wet, resoaked sheet was sufficient to disrupt the weak bond between the sheet and the plate. A study of the effect of drying resoaked sheets on plates and drying rings after this adhesive bond had been broken showed that sheets dried in this way had significantly different properties from sheets dried in the usual way. Peripheral restraint alone produced sheets of lower tensile strength and elastic moduli and higher extensibility than the normal peripheral restraint combined with the restraint due to the sheet-plate adhesion.

The stack of sheets was allowed to dry without benefit of artificial air circulation. Sheets which failed to dry free of all cockle or waviness were immediately discarded. The accepted sheets were generally tested within a few days after they were dry.

The same procedure was used when sheets were soaked in alcoholic solutions or in the pure compounds. In the case of sheets dried from formamide, it was sometimes found necessary to circulate air through the drying rings to speed the drying process.

#### CONDITIONING THE TEST SHEETS AT VARIOUS RELATIVE HUMIDITIES

Most of the test samples were dried and tested at the standard conditions of 50% R.H. and 73° F. Since the Baldwin tester was in a room maintained at these conditions, no special conditioning procedures were necessary for the bulk of the work.

All testing in this investigation was carried out at 73° F. However, a number of samples were tested at relative humidity conditions

other than 50%. Since it was impractical to construct a humidity cabinet around even a portion of the instrument, a method was devised in which the test samples were heat sealed inside polyethylene bags and tested inside the bags. The sample was clamped through the walls of the bag. If enough pleats were formed in the bag so that on extension they opened up without requiring appreciable load, the test could be carried out in bags without any detectable error.

The conditioning of samples prior to sealing them in the bags was done by one of the following four methods:

(1) The sheets were dried or the samples conditioned in a room or enclosure maintained at the desired relative humidity. A minimum storage time of about a week was used to insure proper conditioning.

(2) The test strips were hung in polyethylene bags over a crystallizing dish containing a saturated salt solution which was intended to give the desired relative humidity. Despite the fact that up to two weeks were allowed for conditioning, this method did not generally produce good results. This was probably due to the fact that diffusion of moisture vapor through the air space surrounding the sample was very slow. In general, static conditioning methods such as this were not found to be particularly satisfactory.

(3) A conditioning train was set up to condition the samples at 11% R.H. Compressed air from the air line was passed through a reducing valve and was then passed through a large-capacity silica gel drying tube. Enough of the air was allowed to by-pass the drying tube to bring the relative humidity of the mixed stream to the approximate humidity level

desired. The air stream was then passed over a mixture of saturated lithium chloride solution and solid lithium chloride in two conditioning trays of the type described in connection with the Neenah expansimeter (58). These trays were arranged in series. The air stream then passed through a bottle containing a thermometer and an electric hygrometer element of the type described by Van den Akker (59). From the bottle it passed through a tee to which was connected a pressure relief trap, and was then split and sent to the two conditioning sleeves. The temperature and humidity of the conditioned air could be checked at will.

The conditioning sleeves consisted of long sections of extruded polyethylene tubing which were about 12 inches in circumference. The samples were laid in the sleeves at intervals of about 10 inches, with about six or eight samples being conditioned in one sleeve. The conditioned air entered the sleeve under slight pressure at one end of the tube and passed over the samples before being exhausted from a small opening at the other end. Since the whole system was under slight pressure, any leaks in the system were outward and the humidity of the conditioning air was not affected.

When the samples had been conditioned for a week, the sleeves were heat sealed into individual testing bags, each of which contained a sample. The pressure-release trap served to relieve the air pressure which built up during the few moments it took to heat seal one end of a bag and remove it from the train. The heat sealing was done by holding the edges of the tubing together between two flat Transite sticks and sealing the protruding edges into a neat bead by passing them through a

small flame. One end of a bag could be sealed in a matter of seconds, so that probably no change in the temperature of the bag occurred during the heat-sealing process. The sealed bags were stored in a lithium chloride desiccator until needed for testing.

(4) In some instances it was desired to dry a set of sheets directly to the test humidity in such a way that after removal from the plates, they were not subjected to further changes in humidity. For this purpose a balloon about two feet in diameter and about six feet in length was constructed of 250-gage grade FF Pliofilm. This balloon was large enough to hold about eight plates on rings, a paper cutter, a conditioning tray of the type previously mentioned, and numerous smaller items such as electric hygrometer elements, polyethylene bags, and the like. Air from the balloon was sucked out by an outside blower and forced back into a conditioning tray inside the balloon. A slight amount of make-up air was necessary to keep the balloon fully inflated at all times.

Two Pliofilm sleeves were built into the balloon to permit the removal of the sheets from the plates, the test sheet cutting, and the packaging of the test strips to be accomplished within the balloon. Rubber gloves protected the atmosphere in the balloon against rapid changes due to moisture from the operator's arms. Once the conditioned sheets had been trimmed to test size and packaged in the polyethylene bags, one end of the balloon was opened up and the bags taken out and heat sealed as rapidly as possible. The sealed bags were stored at the conditioning humidity until the samples were tested.



## DETERMINATION OF THE LOAD-ELONGATION CURVE OF THE TEST SHEETS

### THE BALDWIN-SOUTHWARK UNIVERSAL TESTER

The Baldwin-Southwark universal tester is a versatile instrument capable, among other things, of measuring loads up to 60,000 pounds and loading a specimen at a constant rate of loading or a constant rate of elongation. A brief description of those portions of the instrument used in this work should suffice to acquaint the reader with the instrument.

In the low-load ranges employed in this work, load changes are detected by an air cell to which one of the two jaws is connected. A change in load on the air cell moves the diaphragm from its neutral position. This brings about an immediate increase of air pressure on one side of the diaphragm in such a way that the diaphragm is restored to its equilibrium position. This change in air pressure is communicated to the Tate-Knery load indicator of the Baldwin instrument.

One jaw of the tester is attached to a hydraulic ram which is moved by the hydraulic pressure of oil pumped into the piston cylinder by a radial piston pump. Coarse valves and needle valves are provided on the inlet and outlet side of the hydraulic cylinder to allow control of the rate of separation or the rate of closure of the jaws. Actual jaw movement is indicated on a pacer dial by a pointer which is actuated by a servomechanism consisting of a Selsyn transmitter-receiver pair.

Actual jaw movement is more sensitively measured for the recorder unit by means of a microformer deflectometer. The microformer

unit consists of an induction coil whose inductance is altered by the movement of an iron core in or out of the coil as a direct result of the deflection. The inductance of a similar microformer unit in the recorder is automatically changed by a self-balancing inductance bridge arrangement, and the movement of the iron core of this second microformer unit is used to cause rotation of the recorder drum.

In order to obtain a constant rate of jaw separation it was necessary to adjust manually the inlet needle valve on the hydraulic system so that the Selsyn-actuated pointer paced a motor-drive disk on the pacer dial. The speed of rotation of this pacer disk could be adjusted to give a wide range of jaw-movement rates. In order to obtain a constant rate of return of the jaws, it was necessary to adjust the outlet needle valve on the hydraulic system so that the rate of rotation of the Selsyn-actuated pointer was equal and opposite to that of the pacer dial. This was done by timing a half-revolution of the needle and adjusting the outlet needle valve until the proper rate of return was obtained. The inlet needle valve was not disturbed during the period of unloading. Until the machine was thoroughly warmed up, the viscosity of the hydraulic fluid in the loading system continued to change, necessitating frequent checks on the loading and unloading rates.

#### ACTUAL TESTING PROCEDURE

A pair of two-inch wide test strips was cut from the center of each test sheet. The test strips were carefully inserted into the jaws of the Baldwin universal tester and tested at a jaw span of four inches. The strip width, jaw span, and sheet weight were all arbitrarily

selected at the beginning of the work so that the maximum tensile strength obtained would be less than the 60-pound upper limit of the more sensitive range of the microformer recorder.

The rate of elongation was set at 0.05 inch per minute. This rate was slow enough to allow checks of the rate of elongation during the test. It was also slow enough that sample weighings could be made for the analytical determinations while the next test run was proceeding.

The particular LN curve desired for this work contained an unload-load loop. Consequently, the sample was extended an arbitrary 0.0625 inch (1.56%) at the constant rate of 0.05 inch per minute. When an extension of 0.0625 inch was reached, jaw movement was reversed, and the jaws were allowed to close at the same constant rate. When the sample had completely lost its load, the jaw movement was again reversed, and the sample was extended to failure at the initial constant rate of elongation.

Because the Baldwin instrument was not designed for this type of work, it was necessary to estimate the initial extension by the position of the Selsyn-driven pointer. As the result of an initial lag in this pointer, the point at which unloading was started could not be accurately reproduced from sample to sample. The actual initial extensions were generally within about 5% of each other.

It was also found difficult to judge the exact moment at which the load became zero, since the load indicator was somewhat erratic at the very bottom of the scale. For these reasons measurements which were

made of the initial extension and the extension which remained unrecovered on unloading were deemed unreliable.

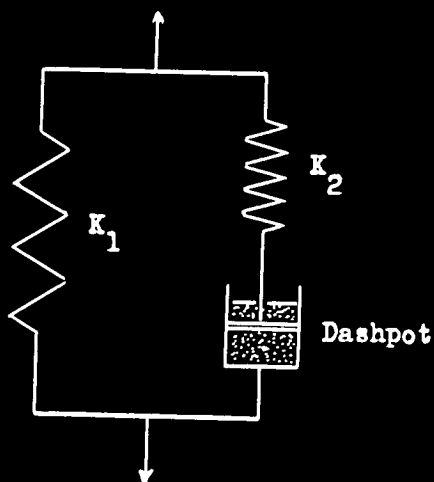
#### ANALYSIS OF THE LOAD-ELONGATION CURVES

Steenberg and his collaborators (51, 52) have found the model of Figure 1 to be very useful in describing the LE curve for paper. In this work the model of Figure 1 was used as a basis for the analysis of the LE curve. Figure 2 shows a typical LE curve of the type obtained in this investigation. A brief discussion of the various quantities measured from the LE curves and the nomenclature employed follows.

(1) The tensile strength of the two-inch test strip expressed as pounds is a in Figure 2.

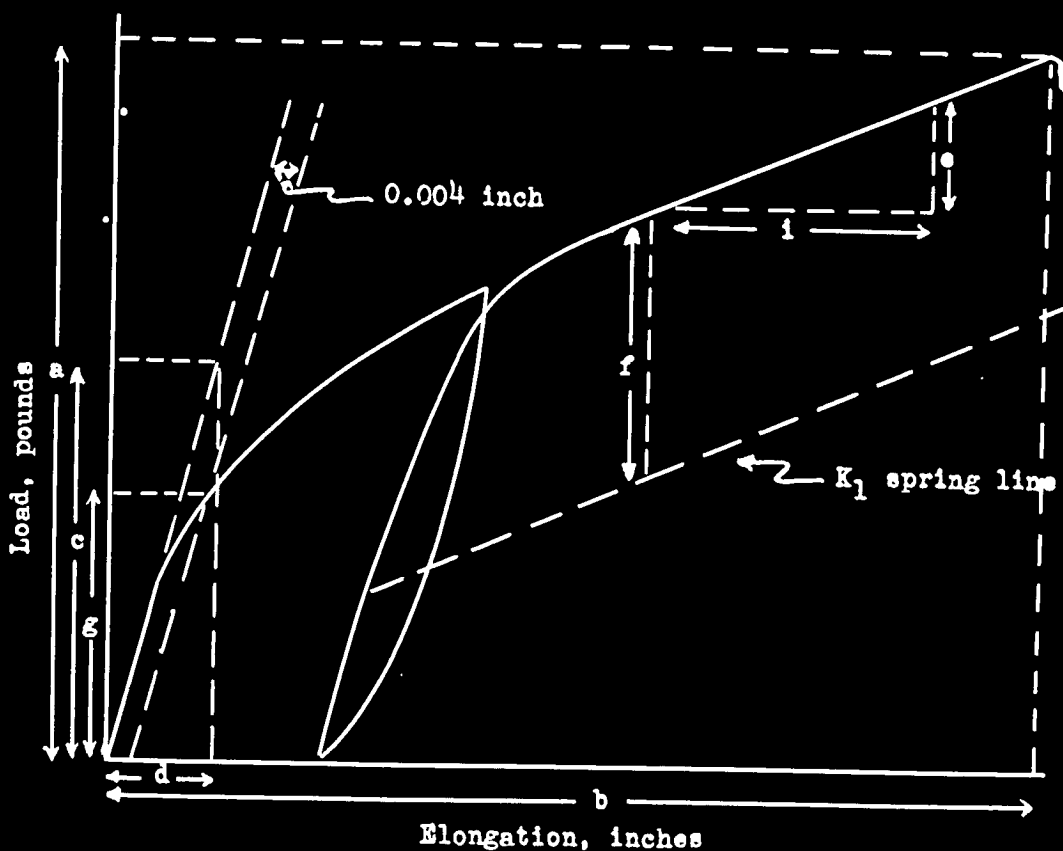
(2) The total elongation of the sample at failure, b, is expressed as a percentage of the total length and termed stretch for purposes of brevity.

(3) The initial slope of the curve, c/d, is expressed in pounds per mil, and for the constant cellulosic cross section of all the test sheets is proportional to the Young's modulus of the strip. In the model of Figure 1, the sum of the spring constants,  $K_1 + K_2$ , may be considered to be proportional to the initial slope. If the model is allowed to represent a standard two-inch test strip tested at a four-inch span and having the standard cellulose cross section, then the initial slope may be equated to  $K_1 + K_2$ .



Mechanical Model for Strain-hardened Paper

FIGURE 1



Typical Load-Elongation Curve for Paper

FIGURE 2

(4) The slope of the latter linear or near-linear portion of the curve will be termed the final slope and will be equated to the spring constant  $K_1$  of the model. The final slope is  $g/i$  in Figure 2 and has the units of pounds per mil.

(5) The "Q" value is defined as the ratio of the final slope to the initial slope and is therefore dimensionless.

(6) Since it was impossible to locate the yield point of the curve with any degree of accuracy, the method of determining the load at a given offset was adopted to give some measure of this quantity. A line of slope  $g/d$  is drawn parallel to the initial linear portion of the curve so that it intersects the elongation axis at 0.004 inch (0.1%). By then reading off the load,  $g$ , at the point of intersection of this line with the curve, the load at 0.1% offset is obtained. This will be referred to as the offset load.

(7) Andersson et al. (51) have outlined a graphical method by which the relative viscosity of a mechanically conditioned paper may be determined. Briefly, this involves the construction of a spring line of slope  $K_1$  through the unload-load loop at the point of zero dashpot movement. Graphically this point is located where the load and unload curves parallel each other. By subtracting the effect of the parallel spring,  $K_1$ , a plot of force versus elongation may be made for the Maxwell unit. This plot will have an initial linear portion in which the Maxwell unit follows Hooke's Law. This line may be extended and called the spring line for spring  $K_2$ . A plot of dashpot flow versus time may be

made from this curve if the difference between the elongation of the Maxwell unit and the elongation of the spring  $K_2$  is measured at the various loads and plotted against the appropriate time value. From this last plot the rate of dashpot flow may be determined at various loads. The value of the load on the dashpot divided by the rate of dashpot flow which it causes, is proportional to what we may term the relative viscosity of the dashpot fluid. If proper consideration is given to a shape factor, this value may be converted to units of viscosity. In this investigation the sample sizes and the cellulosic cross section remained constant for all the test strips, so that the shape factor also remained constant. Under these conditions the force required to maintain dashpot flow at the constant rate of elongation of the paper is directly proportional to the limiting relative viscosity of the dashpot fluid. This limiting relative viscosity, of course, is the effective viscosity of the dashpot fluid during the final linear portion of the LE curve.

The viscous force required to pull the dashpot at constant speed may be readily obtained from the LE curve without going through this tedious graphical analysis, by measuring the force between the properly drawn spring line of slope  $K_1$  and the final linear portion of the curve. This limiting viscous force, termed " $f$ " by Andersson and his co-workers, is  $f$  in Figure 2, and has the units of pounds. According to Andersson et al., " $f$ " is related to the limiting relative viscosity by the following relationship:

$$f = 3a\eta(dl/dt)/L$$

where:  $f$  is, as above, the limiting viscous force  
 $a$  is the cross-sectional area of the test strip  
 $\eta$  is the relative viscosity  
 $dl/dt$  is the constant rate of elongation of the strip  
 $L$  is the length of the test strip

(8) The area under the LE curve has the units of work. This work of failure is expressed as pound-inches in this investigation.

#### ANALYTICAL PROCEDURES AND METHODS

Every sample whose LE curve was determined was analysed both for additive content and moisture content. When the samples were tested at 50% R.H., the analytical samples were weighed on the pan of an analytical balance immediately after the strip had been removed from the Baldwin tester. Samples containing volatile additives were immediately placed in the Kjeldahl digestion flasks, while moisture samples were stored in weighing bottles until they could be transferred to ground glass-stoppered flasks.

In the case of samples tested in bags at relative humidities other than 50%, the test sample was torn apart inside the sealed bag and separated into two samples. One sample was then sealed in one end of the bag; the other end of the bag was opened, and the other sample very rapidly transferred to a weighing bottle of known weight. The first sample was then rapidly transferred to another weighing bottle whose weight was known, and the two sample weights were determined by difference. Since less than three seconds elapsed from the time a sample was removed



from its conditioned atmosphere in the bag until it was in a closed weighing bottle, very little error in moisture content was introduced by the transfer.

#### KJELDAHL NITROGEN PROCEDURE

The Kjeldahl nitrogen analysis used was a modification of the standard Hengar Kjeldahl determination described in Institute Method 705b. The distillation procedure was modified by combining the methods of Ma and Zuazaga (60) and Wagner (61) so that the need for a standard base solution was eliminated, and immediate titration of the distilled sample was possible. Four per cent boric acid was used as the receiving solution as suggested by Wagner and the boric acid-ammonia complex formed was titrated with acid in the presence of a mixed bromocresol green-methyl red indicator similar to that used by Ma and Zuazaga.

#### MOISTURE DETERMINATION

The fact that some of the compounds which were added to the test sheets were volatile or were subject to decomposition at high temperatures made it necessary to employ the Karl Fischer reagent for moisture determination. The usual Karl Fischer reagent is so hygroscopic that it loses its strength rapidly and within about three weeks is valueless (62). To avoid this difficulty the method of Johansson (63) was adopted in which the reagent is split into two solutions: a solution of pyridine and sulfur dioxide in methanol, and a solution of iodine in methanol. The pyridine and sulfur dioxide in methanol solution was made up according to Johansson's instructions. The iodine solution contained

about 45 grams of iodine per liter of absolute methanol. The modified titrimeter of McKinney and Hall (64), specified in Institute Method 615 (62), was used for the titration, in which an excess of iodine was back titrated with a standard methanol-water solution.

The paper samples were placed in 125-ml. ground glass-stoppered Erlenmeyer flasks which contained 25 ml. of absolute methanol of known water content. The samples were allowed to stand in the methanol for at least an hour with constant shaking. The Karl Fischer reagent at the end point was then added, and a measured excess of standard iodine added and back titrated with the aid of the titrimeter. The initial standardization of the methanol-water solution was carried out by adding a carefully weighed amount of water to a large volume of absolute methanol (M) whose iodine titer had been determined. The iodine titer of the methanol-water (MW) solution was then determined and the milligrams of water per milliliter of iodine (designated as W) was established by the formula:

$$(\underline{a}/\underline{b})/(\underline{d}-\underline{c}) = \underline{W}_0$$

where:  $\underline{a}$  is the weight of water added to  $\underline{b}$  liters of M to produce the standard MW, grams  
 $\underline{c}$  is the volume of iodine solution required to titrate 1 ml. of M, ml.  
 $\underline{d}$  is the volume of iodine solution required to titrate 1 ml. of MW, ml.  
 $\underline{W}_0$  is the W value of the iodine solution for the day of standardization.

The total water content of the standard MW was then calculated for later use as being equal to  $(\underline{W}_0 \times \underline{d})$ . On all subsequent days the iodine solution was standardized against the MW standard and its  $\underline{W}$  value calculated by

the equation:

$$\underline{W}' = (\underline{W}_0 \times \underline{d}) / \underline{E}'$$

where:  $\underline{W}'$  is the W value for the given day  
 $\underline{E}'$  is the volume of iodine required to titrate  
 1 ml. of the MW standard on the given day, ml.

The water content of any sample tested on the given day was therefore:

$$\text{Wt. of water in sample, mg.} = \underline{W}'(f - \underline{E}'g) - h$$

where:  $\underline{W}'$  is the W value for the given day  
 $\underline{f}$  is the volume of iodine added, ml.  
 $\underline{g}$  is the volume MW required for back titration, ml.  
 $\underline{E}'$  is the volume of iodine required per ml. of MW for  
 the given day, ml.  
 $h$  is the weight of water in the 25 ml. of methanol  
 in the flask, mg.

The values obtained by the Karl Fischer method were checked against the standard oven-drying moisture content determination (65) every time a series of sheets was tested. Checks of within 1% were almost always obtained between the two methods.

The standard oven-drying method (65) was sometimes used to determine the moisture contents of samples which contained no additive compounds.

#### WATER-VAPOR SORPTION MEASUREMENT

The method used for determining the moisture content of urea, dimethylurea, alpha pulp, and urea-treated alpha pulp at various relative humidities was that described by Wink (66).

## MEASUREMENT OF OTHER STRENGTH PROPERTIES

The zero-span tensile strength of a series of treated sheets was determined according to Institute Tentative Method 527. The zero-span jaws which were used embodied a number of improvements over the jaws specified in the tentative method, so that the results obtained probably are an even better measure of fiber strength than results which would have been obtained with the earlier model jaws.

The tearing strength of paper was determined on the standard Elmendorf tearing strength tester in accordance with Institute Method 512.

Sheet weight and sheet density, when determined, were obtained in accordance with the appropriate standard method in the same manner as has been described in connection with the standard test sheets.

## DETERMINATION OF ADDITIVE DISTRIBUTION THROUGH THE SHEET

A "Scotch tape" stripping method was used to obtain an estimate of the distribution of the additive compound through a treated sheet. An area four inches long by one-half inch wide on the handsheet was masked off with Scotch tape and the sheet weighed. Scotch tape was then pressed onto the masked-off area and removed with an even, longitudinal pull. Fiber pickup of each tape strip was determined by the loss in sheet weight. Depending on the amount of fiber pickup, two or more strips of tape were analysed together for nitrogen content; a blank was run to determine the very slight amount of nitrogen in the Scotch tape. In plotting the results as additive content versus distance through the

sheet, the assumption was made that fiber pick occurred in only one plane of the sheet each time a tape strip was pulled off. This obviously was not the case, but as a first approximation the assumption had some utility. The homogeneous density of the sheet was also assumed.

Since it was not possible to strip beyond 60-80% of the sheet thickness, a complete analysis included runs made from both sides of the sheet. A check on the over-all accuracy of the analysis was made by comparing the percentage nitrogen content summed from the analyses of the individual strips and the percentage nitrogen obtained on samples of the whole sheet. In general, reasonable checks were obtained.

#### THE EFFECT OF UREA AND 1,3-DIMETHYLUREA ON SHEET PROPERTIES

In the first phase of the investigation the properties of a wide range of urea and 1,3-dimethylurea content handsheets were studied. The hygroscopicity of both urea and 1,3-dimethylurea was investigated, the effect of these compounds on sheet density and caliper was determined, and their effect on the LE properties of the handsheets was compared at 11 and 50% R.H. Further work on urea included a study of urea distribution through a typical handsheet, the effect of urea on shrinkage and the development of shrinkage tension, and the effect of urea on such strength properties as internal tearing strength and zero-span tensile strength.

#### THE DISTRIBUTION OF UREA IN A HANDSHEET

The Scotch tape stripping method was employed to estimate the uniformity of urea distribution through typical handsheets. Table I

shows the results from tests made on two handsheets. Handsheet A was dried in the usual manner on a plate, and was analysed only from the side which had dried open to the air; handsheet B was dried over a period of two days while lying free on a piece of filter paper.

The data obtained for handsheet A may be regarded as typical of all the treated handsheets tested throughout the whole investigation. It should be remembered, therefore, that the additive contents reported in the data represent the average additive contents of sheets which contain an additive gradient from center to surface.

TABLE I

THE DISTRIBUTION OF UREA THROUGH HANDSHEETS

Handsheet A Quick-dried on Plate			Handsheet B Slow-dried on Filter Paper			
Analysed from Free Side			Analysed from Wire Side		Analysed from Blotter Side	
Sheet Thickness, %	Urea Content, %		Sheet Thickness, %	Urea Content, %	Sheet Thickness, %	Urea Content, %
0 - 12.7	21.3		0 - 10.2	15.8	0 - 8.3	18.8
12.7 - 29.3	30.9		10.2 - 20.7	20.1	8.3 - 18.2	17.4
29.3 - 41.4	31.9		20.7 - 33.7	15.4	18.2 - 28.7	19.6
41.4 - 51.5	37.8		33.7 - 48.0	31.2	28.7 - 39.1	25.5
51.5 - 65.8	39.7		48.0 - 100	22.3	39.1 - 49.6	28.7
65.8 - 100	24.3				49.6 - 60.5	32.2
					60.5 - 100	26.4

Table I shows that despite a considerable difference in drying rates, the same type of distribution occurred in both handsheets. Since it is logical to assume that the center of a sheet is the last portion of the sheet to give up its free water, the fact that the center of the sheet is relatively urea-rich strongly suggests that a large portion of the urea

migrates with the free water until that water leaves the sheet by evaporation. Further evidence that the urea content of any part of a sheet is determined by the amount of free water (actually, urea solution) in that portion of the sheet during drying, is the fact that uneven pressing conditions were found to produce variations in urea content from one side of a sheet to the other. A major portion of the urea, then, can not be retained by the cellulose by any kind of a selective sorption mechanism. This conclusion is further supported by the fact that urea can be quantitatively washed out of a pulp pad with a minimum of washing. Therefore, if a cellulose-urea bond does form, it probably forms at a point in the drying where the cellulose molecules are giving up their bound water to the air.

#### WATER-VAPOR SORPTION OF UREA, 1,3-DIMETHYLUREA, AND TREATED PULPS

The equilibrium moisture contents of urea, 1,3-dimethylurea, alpha pulp, and urea-treated alpha pulps were determined at various relative humidities. Urea was introduced into the pulps from an aqueous solution. The data, shown in Table II, conclusively demonstrate that neither urea nor 1,3-dimethylurea can affect the properties of paper by hygroscopic action at relative humidities below 50%. Crystalline urea takes up a negligible amount of water vapor below 65% R.H. Pure 1,3-dimethylurea also has negligible hygroscopicity below 35% R.H., and only begins to hold appreciable amounts of water at relative humidities exceeding 50%.

The treatment of alpha pulp with urea is seen from Table II to reduce the equilibrium moisture content of the pulp at relative

**TABLE II**  
**WATER-VAPOR SORPTION BY VARIOUS MATERIALS**

Relative Humidity, %	Urea	Dimethyl- urea	Alpha Pulp	Urea-treated Pulp 3.7% Urea <sup>a</sup>	Urea-treated Pulp 7.7% Urea <sup>a</sup>
	g./100 g. dry material			g./100 g. urea-free dry pulp	
Adsorption Isotherm					
0 <sup>b</sup>	0	0	0	0	0
11.1	0.01	0.03	2.64	2.03	1.78
22.9	0.01	0.11	3.94	3.25	2.97
32.9	0.01	0.22	5.00	4.28	4.05
43.9	0.01	0.59	6.12	5.44	5.28
54.1	0.02	1.78	7.23	6.71	6.73
64.8	0.02	c	8.71	8.34	8.72
75.5	1.27	---	10.64	10.79	11.80
86.5	d	---	13.66	15.12	17.64
92.9	---	---	18.08	22.49	31.44
Desorption Isotherm					
92.9	---	---	18.08	22.49	31.44
86.5	---	---	15.30	17.00	20.34
75.5	---	---	12.46	12.38	13.42
64.8	---	---	10.05	9.61	9.83
54.1	---	---	8.37	7.69	7.53
43.7	---	---	7.16	6.20	5.84
32.9	---	---	5.78	4.86	4.44
22.9	---	---	4.62	3.75	3.36
11.1	---	---	3.07	2.37	2.00
0 <sup>b</sup>	---	---	0.28	0.31	0.12

<sup>a</sup> Calculated on the basis of the dry urea-free pulp.

<sup>b</sup> Relative humidity over P<sub>2</sub>O<sub>5</sub> assumed to be zero.

<sup>c</sup> Deliquescent at 64.8% R.H.

<sup>d</sup> Deliquescent at 80.1% R.H.



humidities below about 65%. In the very low relative humidity range, more urea exerts more of a "dehydrating" action, but as the relative humidity rises to about the 40-50% level, the moisture content of the 7.7% urea content pulp begins to exceed that of the 3.7% urea content pulp. The point at which the adsorption and desorption isotherms of the urea-treated pulps cross those of the untreated pulp is seen to fall at a lower humidity the higher the urea content.

Actual measurement of the area in the hysteresis loop for each of the three pulps showed that the 3.7% urea content pulp had a hysteresis loop area which was 84.5% of that of the alpha pulp. Increasing the urea content to 7.7% reduced the area to only 73.3% of the area of the untreated alpha pulp hysteresis loop. It was also noted that the presence of the urea reduced the time required by samples to come to adsorption equilibrium at low relative humidities.

These facts may be interpreted as proof that urea in aqueous solution enters the fibrous structure of paper when it is in a state of intermicellar swelling, and remains behind when the water is evaporated to keep the cellulose in a state of partial dry swelling. The fact that urea decreases the equilibrium moisture content of the pulp at low humidities indicates that it has combined with some of the cellulosic groups which are normally active in sorbing moisture. By partially holding open the structure of the cellulose, the urea molecule prevents the formation, during desorption, of interchain cross linkages which are ordinarily broken with difficulty by the moisture during adsorption. The hysteresis effect is thereby reduced.

The rapid rise in the moisture content of the treated pulp with increasing humidity can not be due wholly to the increasing hygroscopicity of the urea, since the rise begins at a relative humidity where urea itself remains essentially nonhygroscopic. In addition to this, it is seen that the point at which the treated pulp isotherms cross the untreated pulp isotherm occurs at a lower humidity the higher the urea content. It may be that by holding open the cellulose structure, urea ultimately makes more sorbing groups available. These groups are either of lower reactivity so that they can not hold water molecules against low atmospheric water-vapor pressures, or they are unavailable, effectively, at low relative humidities in spite of the semiswollen cellulose structure. It may be that they become available only when sorbed water molecules are present to assist the urea in holding open the structure.

It should be remembered that a similar dehydrating effect has been observed for glycerin by Pike (13) and McPherson (1). McPherson's interpretation of his data was essentially the same as the discussion given above. Data which are to be presented later in this thesis on the moisture contents of sheets treated with various derivatives of urea show that this dehydration effect is general for all the ureas and formamides investigated, even when the compound in question is hygroscopic.

#### THE EFFECT OF UREA ON SHEET SHRINKAGE DURING DRYING

Preliminary tests showed that an alpha sheet dried from a 10% urea solution exhibited only about one third the shrinkage of a sheet dried from water. In order to further investigate the role of urea during the drying of a sheet, measurements were made of the shrinkage

tension developed in resoaked sheets dried at constant length from water and from a 10% urea solution. The method consisted of conditioning a set of wet-pressed strips together in a polyethylene bag so that moisture equilibrium was established between all the strips. One of the strips was then inserted in the jaws of the Baldwin tester and the other strips were hung from clamps in close proximity to the test strip. The tension developed in the test strip was read from the load indicator at one-minute intervals, and the dummy samples were taken down at varying intervals of time for moisture determination. By combining the tension versus time data obtained from the test strip with the drying curve obtained from the dummy moisture content samples, a shrinkage tension-moisture content curve was obtained. Duplicate samples were run in each instance. Surprisingly good checks between duplicate samples were obtained in spite of the relative crudity of the drying curve determination.

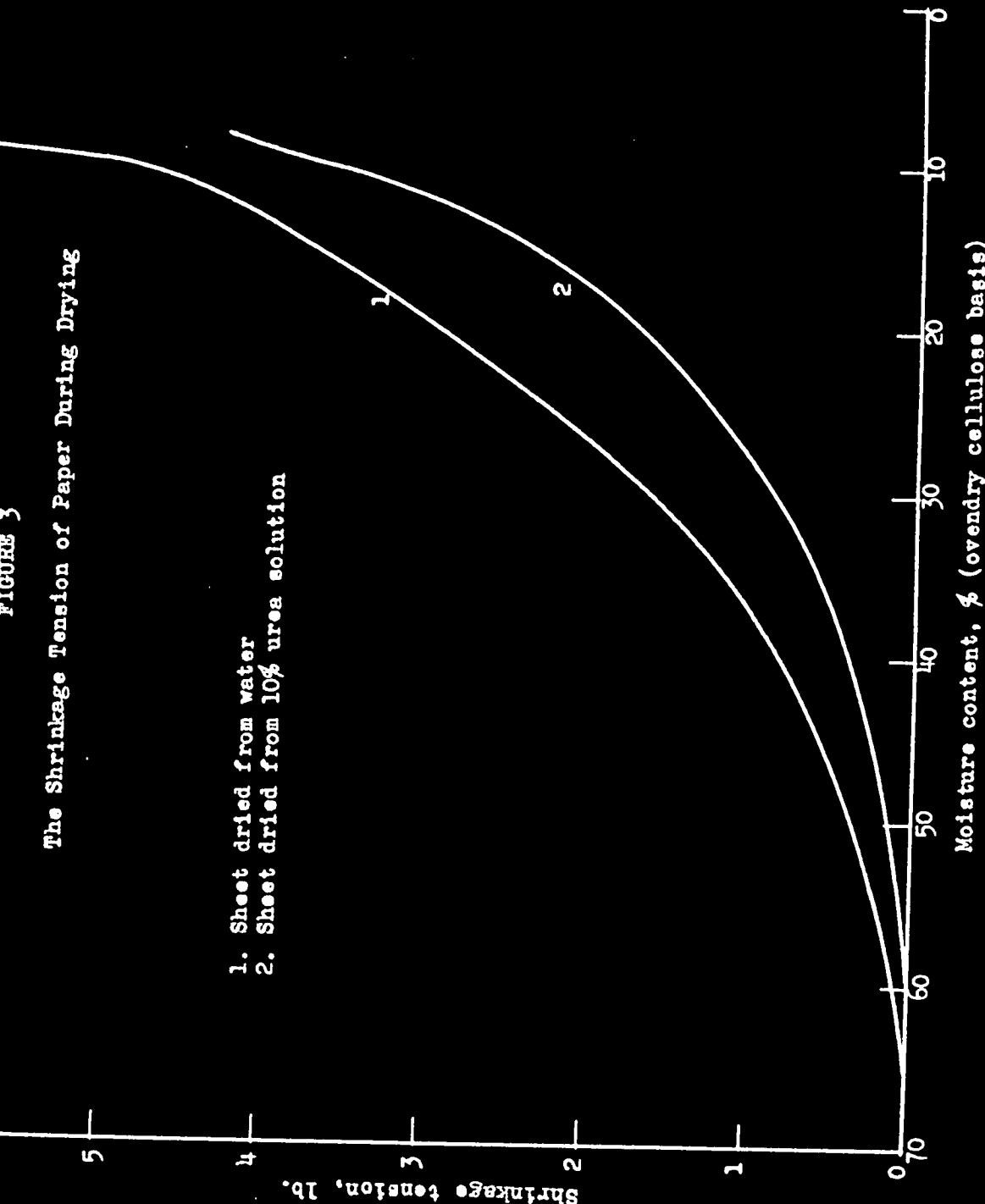
Curves showing shrinkage tension versus moisture content (based on dry cellulose) appear in Figure 3. Each curve represents the best curve through at least 25 points. These points have been omitted from Figure 3 to avoid confusion. Since all the sheets were started drying at a moisture content of about 65%, the amount of shrinkage tension developed in drying to 65% moisture was not determined. It would undoubtedly have been small. The maximum shrinkage tension value for each curve in Figure 3 was the tension at the point in the drying where the rate of stress relaxation became greater than the rate of development of shrinkage tension.

It may be seen from Figure 3 that the presence of the urea reduced both the maximum shrinkage tension attained, and the shrinkage

FIGURE 3

# The Shrinkage Tension of Paper During Drying

1. Sheet dried from water
2. Sheet dried from 10% urea solution



tension of the sheet at any given moisture content. Shrinkage started at about the same moisture content for both sets of sheets, although the initial rate of shrinkage of the urea-soaked sheet was considerably less than that of the normal sheet. In the moisture content range of about 25-45%, the two curves are seen to be roughly parallel. Thus, it was necessary for the urea-soaked sheet to dry to a moisture content about 9-10% lower than that of the normal sheet before it had a comparable shrinkage tension and rate of development of shrinkage tension. Both sets of data for the two runs on the drying of water-soaked sheets showed a nearly constant rate of shrinkage tension development in the 15-25% moisture content range. As a result, the average of these two curves, shown in Figure 3 as Curve No. 1, is linear in this region. Further investigation of the phenomenon would be necessary before it could be categorically stated that a constant rate of shrinkage tension development actually occurs in this region.

The most striking difference in the two curves of Figure 3 is noted at moisture contents below 11%. In this region the extremely rapid rise in shrinkage tension exhibited by the normal sheet does not occur in the urea-soaked sheet. Measurement of the rate of development of shrinkage tension per unit moisture content showed the final rate of shrinkage tension development for the water-soaked sheet to be about twice that of the urea-soaked sheet. Since data to be presented later in Figure 5 show that no rapid rise in tensile strength (and hence, by inference, bonding strength) characterizes this moisture content region, it must be assumed that the rapid rise in shrinkage tension of the water-soaked sheet was due to a final shrinking, twisting, or coiling tendency

of the fibers. The presence of urea either modified this final fiber shrinkage very considerably, or else so weakened the fiber-to-fiber bonds that they were unable to stand up under the resulting shrinkage stresses. The data available do not allow differentiation between the two possible actions.

Several possible actions of urea may be postulated to explain its effect on the shrinkage properties of paper. It might be suggested that the effect of urea is the result of its effect on the surface tension of the free liquid, but this seems improbable in view of the fact that 10% urea was found to reduce the surface tension of water by less than 5%. Urea may reduce internal cohesive bonds in the fibers so that local stresses set up by the deswelling mechanism are partially relieved before they can seriously distort the fiber. Molecular chains or micelles which would normally be cross-linked might thus be able to flow to relieve the internal stresses occurring during drying. Urea may also reduce the strength of fiber-to-fiber bonds and enhance their ability to flow under stress in such a way that these bonds, too, are capable of relieving some of the shrinkage stresses they are called upon to transmit. Actually probably both of these actions occur. The probability that the action of the urea in a wet sheet is basically the same as its action in a dry sheet under tensile stress will be discussed at some length in another section of this thesis.

It is interesting to note how the shrinkage tension of a water-soaked sheet develops. Figure 3 shows that one quarter of the maximum tension is developed at about 31% moisture, one half at 19%

moisture, and three quarters at 11% moisture. The final quarter of the maximum shrinkage tension is built up as the moisture content goes from 11 to 8% moisture. These data are in direct contradiction to the findings of Lyne and Gallay (62) who found that bleached sulfite and groundwood handsheets developed practically all their shrinkage tension at moisture contents above 25%.

#### THE EFFECT OF UREA AND 1,3-DIMETHYLUREA ON THICKNESS AND DENSITY

The effect of urea and 1,3-dimethylurea on the caliper and the density of the treated sheet is shown in Table III.

Both urea and 1,3-dimethylurea cause an increase in sheet thickness and a decrease in sheet density. It is probable that the reason for this is twofold: (1) the additives reduce fiber bonding strength so that the bulk of the sheet is increased, and (2) the additives increase the dry volume of the sheet by entering the cellulosic structure and preventing the collapse of the wet-swollen structure when the sheet is dried. From the data available it is impossible to judge the relative magnitudes of these two effects.

TABLE III  
THICKNESS AND DENSITY CHANGES OF SHEETS AFTER TREATMENT  
(73° F.; 50% R.H.)

Urea			1,3-Dimethylurea		
Urea in Sheet <sup>1</sup> , %	Caliper Change <sup>2</sup>	Density Change <sup>2</sup>	DMU in sheet <sup>1</sup> ,	Caliper Change <sup>2</sup>	Density Change <sup>2</sup>
0	100.0	100.0	0	100.0	100.0
2.8	101.7	99.3	2.7	114.3	88.8
5.3	104.1	99.5	5.3	116.8	88.5
9.5	106.7	101.7	9.8	123.0	88.1
15.4	123.5	92.1	15.9	127.9	89.5
18.7	127.3	93.3	23.9	136.7	90.9
23.4	129.0	95.3	28.8	141.8	91.2
34.2	135.0	96.5	35.4	149.9	89.7

<sup>1</sup>Calculated on an oven-dry pulp basis.

<sup>2</sup>Percentage of value of water-soaked sheet.

#### THE EFFECT OF UREA AND 1,3-DIMETHYLUREA ON THE LOAD-ELONGATION CURVE AT 50% RELATIVE HUMIDITY

The data obtained from the LE curves of sheets treated with varying amounts of urea and 1,3-dimethylurea and tested at 50% R.H. are given in Tables IV and V, respectively.

Both Tables IV and V show that the initial increment of additive in a sheet markedly reduces the equilibrium moisture content of the sheet. This phenomenon has already been mentioned. In the present discussion of Tables IV and V, the change in moisture content with additive content will be neglected since its effect will be considered in more detail in a later section. The effect is small enough so that neglecting it will not alter the conclusions to be drawn from the data in these tables.



TABLE IV

THE EFFECT OF UREA ON VARIOUS SHEET PROPERTIES AT 50% R.H.

Sheet Property	Urea Content, % of Oven-dry Pulp							
	0	2.8	5.3	9.5	15.4	18.7	23.4	34.2
Moisture content, % OD pulp	8.0	6.8	6.3	6.1	6.6	7.1	6.8	6.8
Tensile strength, lb.	41.7	40.1	39.6	34.7	29.4	24.7	29.8	34.5
Initial slope, lb./mil	1.47	1.41	1.32	1.07	0.83	0.55	0.76	0.89
Final slope, lb./mil	0.14	0.14	0.14	0.13	0.11	0.10	0.12	0.15
Stretch, %	2.87	2.99	3.26	3.63	4.39	4.78	4.98	4.52
Offset load, lb.	20.6	19.1	18.1	13.7	9.2	7.2	7.7	8.8
f value, lb.	17.7	16.2	14.8	11.7	8.5	6.2	7.3	7.9
Work of failure, lb.-in.	3.53	3.57	3.76	3.55	3.55	3.05	3.83	3.97

The initial effect of both urea and 1,3-dimethylurea is a reduction in the tensile strength, initial slope, final slope, offset load and f value. In the case of urea, stretch increases with increasing additive content, whereas 1,3-dimethylurea first causes a decrease and then an increase in the extensibility of the sheet. In both instances the latter increments of additive are more effective in increasing stretch than the initial portions. The work of failure is rather erratic for urea, but decreases rather steadily when 1,3-dimethylurea is added to the sheet.

TABLE V

THE EFFECT OF 1,3-DIMETHYLUREA ON VARIOUS SHEET PROPERTIES AT 50% R.H.

Sheet Property	1,3-Dimethylurea Content, % of Oven-dry Pulp							
	0	2.7	5.3	9.8	15.9	23.9	28.8	35.4
Moisture content, % OD pulp	8.0	6.4	6.2	6.1	6.7	6.9	7.4	7.9
Tensile strength, lb.	41.7	35.5	32.0	28.7	22.2	16.9	14.2	14.6
Initial slope, lb./mil	1.47	1.28	1.29	1.03	0.81	0.47	0.44	0.43
Final slope, lb./mil	0.14	0.11	0.10	0.10	0.08	0.07	0.06	0.07
Stretch, %	2.87	2.77	2.40	2.82	3.14	3.95	4.02	4.44
Offset load, lb.	20.6	19.8	17.8	14.7	10.3	6.4	4.9	4.1
$f$ value, lb.	17.7	15.3	14.1	12.1	8.4	6.0	4.7	4.2
Work of failure, lb.-in.	3.53	3.00	2.29	2.41	2.14	1.90	1.64	1.80

Since the action of these two compounds is typical of the action of all the urea-type compounds investigated, it seems justifiable to define the term plasticizer in terms of its effect on the LE curve of paper. The term plasticizer will be used henceforth in connection with the ureas to denote a compound which reduces the tensile strength and elastic moduli of a sheet, (initial and final slope), and which improves the flow properties of a sheet as evidenced by a decrease in the offset load and the limiting viscous force  $f$ . It will be noted that the effect of the compound on stretch and work of failure has been specifically omitted from this definition. The behavior of these two properties does not permit generalization.

It will be noted in Table IV that above a urea content of 18.7%, the plasticizing action of urea is reversed. Tensile strength, elastic moduli, offset load, and  $f$  all begin to increase. It is believed that at this point the urea has saturated the cellulose and that, as a result, free urea has crystallized in and around the fibers during the drying process. At high urea contents the sheet has an actual sheen such as might be obtained if a large number of small crystals were present in the sheet. Plotted curves for these data show that the point of maximum plasticizing effect occurs quite sharply in the region of 19-20% urea content. There are indications that the maximum 1,3-dimethylurea content investigated was close to the crystallization point, since the tensile strength and final slope curves had started to rise, and the initial slope curve had leveled off. If this is true, then both urea and 1,3-dimethylurea begin to crystallize at about the same molar concentration of about 350 millimoles per 100 grams of dry pulp.

Nethercut (2) observed that at 50% R.H., 11.8% urea reduced the flexural rigidity of ramie handsheets by 15.2%, and 24.8% urea reduced the flexural rigidity by 32.0%. From the change in the  $EI$  values reported by Nethercut for his urea-treated ramie handsheets, it is possible to approximate the change in the Young's modulus,  $E$ , of his sheets, if the thickness changes in his sheets are assumed to be roughly the same as those of the alpha sheets used in this work. This approximation shows that the  $E$  value of the ramie sheets was decreased 41.7% by 11.8% urea, and 65.4% by 24.8% urea. In comparison the curves for the initial slope, which, it will be remembered, is proportional to the Young's modulus of the strip, show that in this work 11.8% urea reduced the elastic modulus

of the alpha handsheets by 37.6%, and 24.8% urea reduced it by 44.8%. The agreement at the lower urea content level is excellent in view of the great difference between the sheets, the drying conditions, and the testing methods used in the two investigations. The fact that Nethercut dried his sheets at relatively high temperatures and therefore may have modified the stiffening effect of the crystallization phenomenon may account for the greater effectiveness of the 24.8% urea on his ramie handsheets than on the alpha handsheets.

The relative viscosity of the dashpot fluid in the model of Figure 1 was calculated from typical LB curves of the urea-treated sheets according to the graphical method outlined by Andersson et al. (51). The result is shown in Figure 4. The curves show that with increasing urea content, both the initial viscosity of the dashpot fluid and its final limiting viscosity are reduced. The breakdown of viscosity occurs at a lower load, the more urea present in the sheet. The over-all effect of urea on the dashpot fluid, therefore, is seen to be a reduction of viscosity at any given load, and a considerable decrease in the load required to cause a breakdown in viscosity.

#### COMPARISON OF THE LOAD-ELONGATION CURVES OF UREA AND 1,3-DIMETHYLUREA-TREATED SHEETS AT 11 AND 50% R.H.

##### METHOD OF COMPARISON

One half of each of the sheets containing urea and 1,3-dimethylurea were tested at 11% R.H. and 73° F. This made possible a comparison of the effect which the two compounds exerted on sheet properties at two levels of relative humidity. The data are presented in Tables VI-XI. The

FIGURE 4

Relative Viscosity of the Dashpot Fluid at Various Loads

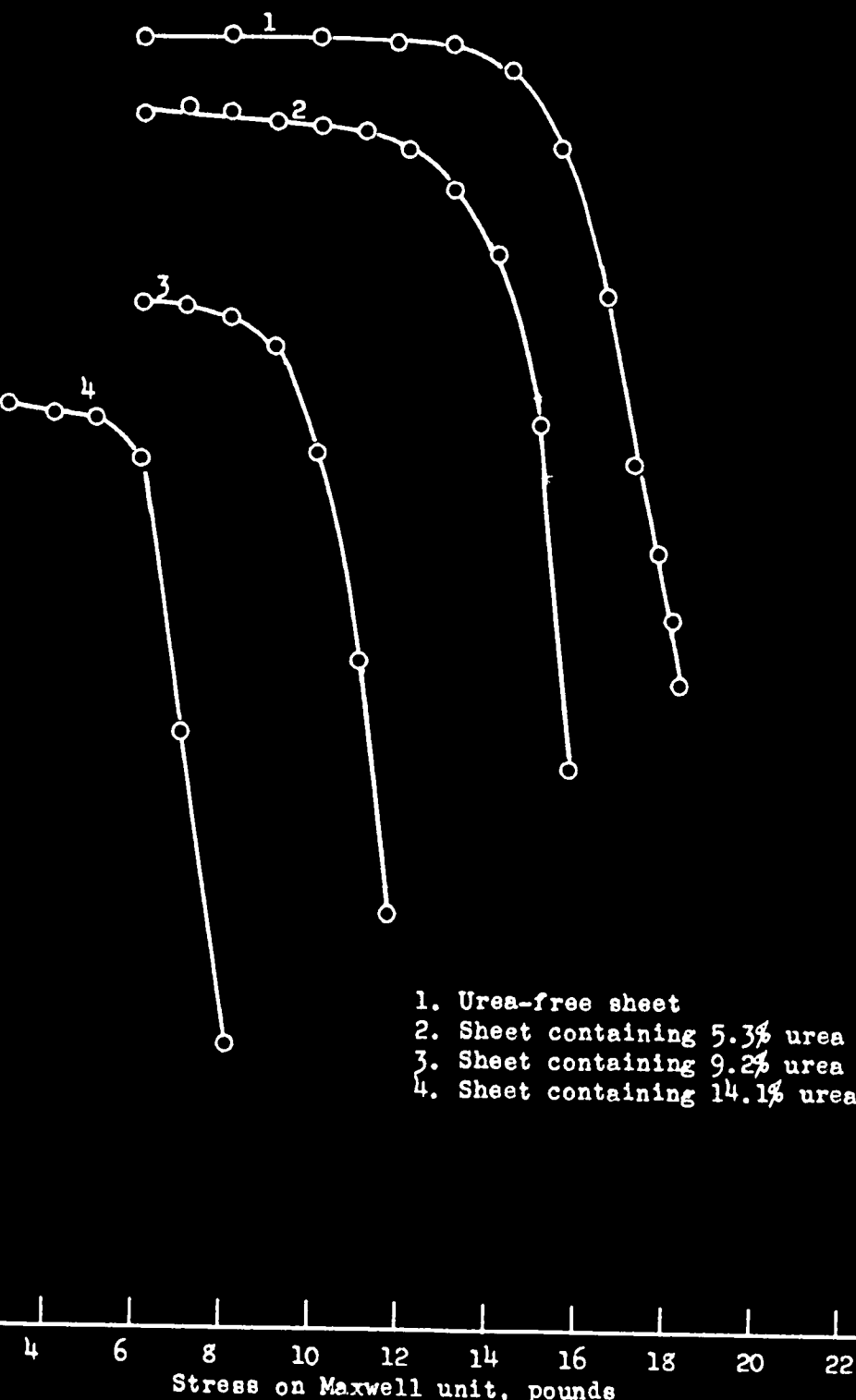


TABLE VI

COMPARISON OF CHANGE IN TENSILE STRENGTH AT 11 AND 50%  
R.H. DUE TO THE PRESENCE OF UREA AND 1,3-DIMETHYLUREA

Additive, mmoles per 100 g. dry Pulp	Urea				1,3-Dimethylurea			
	Absolute		Percentage		Absolute		Percentage	
	Loss, lb.		Loss <sup>1</sup>		Loss, lb.		Loss <sup>1</sup>	
	11% R.H.	50% R.H.	11% R.H.	50% R.H.	11% R.H.	50% R.H.	11% R.H.	50% R.H.
0	0	0	0	0	0	0	0	0
50	1.8	3.5	3.7	8.4	9.2	11.0	18.7	26.4
100	3.5	6.8	7.1	16.3	13.0	15.3	26.4	36.7
150	5.9	9.4	12.0	22.5	16.4	19.3	33.4	46.3
200	9.0	11.7	18.3	28.1	19.2	22.8	39.1	54.7
250	11.3	14.1	25.0	33.8	21.2	25.9	43.2	62.1
300	12.0	17.1	24.4	41.0	23.4	27.8	47.6	66.7
350	11.1	17.3	22.6	41.5	24.8	28.0	50.5	67.2
400	9.3	13.4	18.9	32.1	25.1	27.3	51.0	65.5

ed on additive-free value

TABLE VII

COMPARISON OF CHANGE IN STRETCH AT 11 AND 50% R.H.  
DUE TO THE PRESENCE OF UREA AND 1,3-DIMETHYLUREA

Additive, mmoles per 100 g. dry Pulp	Urea				1,3-Dimethylurea			
	Absolute		Percentage		Absolute		Percentage	
	Gain, %		Gain <sup>1</sup>		Gain, %		Gain <sup>1</sup>	
	11% R.H.	50% R.H.	11% R.H.	50% R.H.	11% R.H.	50% R.H.	11% R.H.	50% R.H.
0	0	0	0	0	0	0	0	0
50	0.06	0.41	2.8	14.3	0.26	-0.02	12.1	-0.7
100	0.02	0.81	0.9	28.2	0.60	0.18	27.9	6.3
150	0.96	1.11	44.6	38.7	1.00	0.51	46.5	17.8
200	1.31	1.47	61.0	51.2	1.29	0.74	60.0	25.8
250	1.44	1.76	67.0	61.3	1.43	0.90	66.5	31.4
300	1.50	2.03	69.7	70.7	1.55	1.12	72.1	39.0
350	1.50	2.25	69.7	78.4	1.68	1.34	78.2	46.7
400	1.50	2.39	69.7	83.2	1.80	1.56	83.8	54.4

ed on additive-free value

TABLE VIII

COMPARISON OF CHANGES IN INITIAL SLOPE AT 11 AND 50% R.H.  
DUE TO THE PRESENCE OF UREA AND 1,3-DIMETHYLUREA

Additive, Millimoles per 100 g. Ovendry Pulp	Urea				1,3-Dimethylurea			
	Absolute		Percentage		Absolute		Percentage	
	Loss, lb./mil		Loss <sup>1</sup>		Loss, lb./mil		Loss <sup>1</sup>	
	11% R.H.	50% R.H.	11% R.H.	50% R.H.	11% R.H.	50% R.H.	11% R.H.	50% R.H.
0	0	0	0	0	0	0	0	0
50	0.09	0.15	5.4	9.9	0.11	0.32	6.8	21.5
100	0.14	0.29	8.9	19.5	0.21	0.50	13.4	33.7
150	0.33	0.47	21.4	31.5	0.39	0.67	25.2	45.6
200	0.46	0.67	29.1	45.4	0.54	0.83	34.3	56.8
250	0.52	0.86	33.0	58.2	0.69	0.98	44.1	66.9
300	0.60	0.99	38.2	67.1	0.80	1.08	51.1	73.3
350	0.63	0.99	40.5	67.1	0.87	1.06	55.8	72.4
400	0.48	0.76	30.9	51.5	0.88	1.04	56.3	71.0

<sup>1</sup>Based on additive-free value

TABLE IX

COMPARISON OF CHANGES IN FINAL SLOPE AT 11 AND 50% R.H.  
DUE TO THE PRESENCE OF UREA AND 1,3-DIMETHYLUREA

Additive, Millimoles per 100 g. Ovendry Pulp	Urea				1,3-Dimethylurea			
	Absolute		Percentage		Absolute		Percentage	
	Loss, lb./mil		Loss <sup>1</sup>		Loss, lb./mil		Loss <sup>1</sup>	
	11% R.H.	50% R.H.	11% R.H.	50% R.H.	11% R.H.	50% R.H.	11% R.H.	50% R.H.
0	0	0	0	0	0	0	0	0
50	0.01	0.00	9.5	2.2	0.08	0.04	56.6	28.1
100	0.03	0.01	22.3	5.0	0.10	0.05	70.3	36.7
150	0.04	0.01	29.1	8.6	0.12	0.06	78.4	41.7
200	0.05	0.02	35.8	14.4	0.12	0.06	79.1	45.3
250	0.06	0.03	40.5	21.6	0.11	0.07	75.0	49.6
300	0.07	0.04	46.6	30.9	0.11	0.08	71.6	55.4
350	0.06	0.04	43.2	25.9	0.10	0.08	68.3	56.1
400	0.04	0.02	28.4	16.5	0.10	0.07	64.9	50.4

<sup>1</sup>Based on additive-free value

TABLE X

COMPARISON OF CHANGES IN OFFSET LOAD OF SHEETS AT 11 AND 50% R.H.  
DUE TO THE PRESENCE OF UREA AND 1,3-DIMETHYLUREA

Additive, Millimoles per 100 g. Ovendry Pulp	Urea				1,3-Dimethylurea			
	Absolute		Percentage		Absolute		Percentage	
	Loss, lb.		Loss <sup>1</sup>		Loss, lb.		Loss <sup>1</sup>	
	11% R.H.	50% R.H.	11% R.H.	50% R.H.	11% R.H.	50% R.H.	11% R.H.	50% R.H.
0	0	0	0	0	0	0	0	0
50	4.1	4.8	14.2	23.3	8.1	7.3	28.0	35.4
100	7.5	8.2	26.0	39.8	11.2	10.6	38.8	51.5
150	10.1	11.7	34.9	56.8	14.1	13.8	48.8	67.0
200	12.5	13.9	43.3	66.8	16.6	15.9	57.4	77.2
250	14.1	15.2	48.8	73.8	19.0	16.6	56.2	80.6
300	14.7	16.6	50.9	80.6	20.9	17.0	62.2	82.5
350	14.4	16.8	49.8	81.6	21.9	16.9	75.8	82.0
400	13.7	16.0	47.4	77.7	22.6	16.8	78.2	81.6

<sup>1</sup>Based on additive-free value

TABLE XI

COMPARISON OF CHANGES IN  $\alpha$  VALUE OF SHEET AT 11 AND 50% R.H.  
DUE TO THE PRESENCE OF UREA AND 1,3-DIMETHYLUREA

Additive, Millimoles per 100 g. Ovendry Pulp	Urea				1,3-Dimethylurea			
	Absolute		Percentage		Absolute		Percentage	
	Loss, lb.		Loss <sup>1</sup>		Loss, lb.		Loss <sup>1</sup>	
	11% R.H.	50% R.H.	11% R.H.	50% R.H.	11% R.H.	50% R.H.	11% R.H.	50% R.H.
0	0	0	0	0	0	0	0	0
50	2.5	4.0	10.6	22.6	6.0	6.7	25.5	37.9
100	5.1	6.8	21.7	38.4	7.5	8.9	31.9	50.3
150	7.1	8.8	30.2	49.7	9.8	10.9	41.7	61.6
200	9.0	10.2	38.3	57.6	11.9	12.2	50.6	68.9
250	10.5	11.6	44.7	65.5	14.1	13.1	60.0	74.0
300	11.6	13.6	49.4	76.8	15.4	13.9	65.5	78.5
350	11.6	13.5	49.4	76.3	16.3	14.1	69.4	79.7
400	10.0	12.5	42.6	70.6	17.0	13.7	72.3	77.4

<sup>1</sup>Based on additive-free value



data in these tables have been so calculated that the effect of the moisture content change resulting from the "dehydrating" effect of the additive has been excluded. Therefore, any changes in the properties of the sheets may be assumed to be due solely to the presence of the urea or the 1,3-dimethylurea.

The means by which the moisture effect was excluded from the data was as follows: Experimental data were obtained on the strength properties of water-soaked standard sheets which had been dried under tension to various humidities. These data will be presented at a later point in this thesis in the section dealing with the comparison of the effectiveness of various ureas in altering sheet properties. From these data a comparison could be made for sheets tested at 50% R.H. between (a) the strength of the treated sheet and (b) the strength of an untreated sheet which had the same moisture content as the sheet in (a) and which had dried to that moisture content under the same conditions of restraint as the treated sheet in (a). For reasons to be discussed later the effectiveness of the additive compound in altering a given strength property was arbitrarily taken to be the difference between the strength of these two sheets, (a) and (b).

Unfortunately, the data on the properties of treated sheets at 11% R.H. were obtained before the importance of drying under tension to the humidity conditions of test was fully realized. As a result, all the treated sheets tested at the 11% R.H. level were dried under tension to 50% R.H., and then further conditioned with no restraint to equilibrium at 11% R.H. This complicated the matter of assessing the effect of the

moisture content change due to the additive at the 11% R.H. level. Since experimental data were available on the properties of sheets dried to 50% R.H. under tension, and conditioned to lower moisture contents in a free state, the following method of approximating the moisture content change at 11% R.H. was used.

The method is best illustrated by an example. Let us assume that a sheet of urea content  $\bar{U}$  dries to an equilibrium moisture content at 50% R.H. of  $M_{50}$ . An untreated sheet at 50% R.H. has a somewhat higher moisture content,  $M$ . Now the same sheet of urea content  $\bar{U}$  when conditioned at 11% R.H., will attain a moisture content  $M_{11}$  which is lower than that attained by an untreated sheet conditioned at 11% R.H. The problem therefore is to find out what the tensile strength would be if an untreated sheet were dried to  $M_{50}$  under tension and then conditioned to  $M_{11}$  with no restraint. If this can be determined, its tensile strength can be compared with that of the treated sheet which has dried in the same manner.

Now the tensile strength of an untreated sheet dried to  $M_{50}$  under tension will exceed that of an untreated sheet dried to a higher moisture content  $M$  under tension and then to  $M_{50}$  unrestrained by an absolute amount  $x$ . The value of  $x$  can be determined from the plotted experimental data. The tensile strength  $x$  of an untreated sheet dried to  $M$  under restraint and conditioned to  $M_{11}$  without restraint can also be obtained from the plotted experimental data. The assumption must now be made that the increment in tensile strength  $x$  (due to drying from  $M$  to  $M_{50}$  under tension instead of free) is the result of additional "frozen-in" stresses. If this is true, then it is logical to assume

further that continued reduction in moisture content will further "freeze-in" these stresses. Therefore the sheet having the higher tensile strength at  $M_{50}$  will continue to have a higher tensile strength at lower moisture contents by an amount approximated by  $\underline{x}$ . By this assumption, the tensile strength of the hypothetical sheet dried to  $M_{50}$  under tension and conditioned to  $M_{11}$  without restraint exceeds the value  $\underline{x}$  by an amount equal to  $\underline{x}$ . Its tensile strength is therefore equal to  $\underline{x} + \underline{x}$ . The effect of the urea on the tensile strength of the treated sheet of urea content  $\underline{U}$  at 11% R.H. is therefore assumed to be equal to the difference between  $\underline{x} + \underline{x}$  and the actually determined tensile strength of the sheet at 11% R.H.

#### DISCUSSION OF COMPARISON

Table VI shows that a given molar concentration of urea is more effective in reducing tensile strength at 50% R.H. than at 11% R.H. On a percentage basis, urea is almost 100% more effective at 50% R.H. than at 11% R.H. 1,3-Dimethylurea is more effective than urea at both humidity levels, and like urea, is more efficient at the higher humidity level. Percentage-wise, it is almost 50% more effective at 50% R.H. than at 11% R.H. For both compounds the crystallization effect noted earlier seems to occur at about the same additive content regardless of humidity changes.

The changes in stretch values at the two relative humidities due to treatment with urea and 1,3-dimethylurea are shown in Table VII. Urea increases the absolute stretch value more at 50% R.H. than it does at 11% R.H. The difference expressed as a percentage of the initial stretch

is quite small. At 11% R.H. an initial buildup of urea seems to be necessary before the stretch is increased, and the maximum increase in stretch is produced at a much lower urea content than at 50% R.H.

In the case of the 1,3-dimethylurea, however, exactly the opposite seems to hold true. The 1,3-dimethylurea is more effective in increasing stretch at 11% R.H. on both an absolute and a percentage basis. The initial lag observed at 11% R.H. for urea is less evident when 1,3-dimethylurea is the compound added to the sheet. However, with 1,3-dimethylurea there seems to be an initial lag at the 50% R.H. level which was not evident for urea. These data represent further evidence of a trend which was noted throughout the work on the mechanical properties of treated sheets, i.e., the stretch values of a sheet do not necessarily follow the same trends as do the tensile strength, the elastic moduli, and the flow properties.

In Table VIII a comparison is made of the changes in the initial slope due to the two additive compounds at the 11 and 50% R.H. levels. At 50% R.H. the absolute decrease in initial slope values due to the additives is roughly 50% greater than at 11% R.H. On a percentage basis the two additives are about twice as effective at 50% R.H. as they are at 11% R.H. Thus the relative effect of the two compounds on initial slope values at the two humidities is very similar to their relative effect on tensile strength discussed above. 1,3-Dimethylurea, of course, surpasses urea in effectiveness in reducing the initial slope both at 11 and 50% R.H. The point at which crystallization influences the initial slope remains unchanged when the humidity of a urea sheet is

reduced. For 1,3-dimethylurea, a lowering of the humidity seems to move the point at which crystallization makes itself felt to a higher additive content.

It may be seen from Table IX that the final slope of the LE curve of the treated sheets behaves very differently from the initial slope or the tensile strength. Whereas the tensile strength- and initial slope-reducing powers of the additives were reduced by lowering the humidity, the effect of these additives on the final slope is increased by this change. At 11% R.H. both the absolute effect and the percentage effect of the initial amounts of both compounds on the final slope seem to be roughly 100% that at 50% R.H. At the higher additive contents the difference is not as great, but it is still very pronounced. Once again 1,3-dimethylurea is seen to be more effective, and very much more quickly effective than urea in reducing the final slope value.

A study of Tables X and XI in which data for the changes in the offset load and the  $f$  value are given indicates that both of these properties behave in the same manner. A reduction of these two values, it will be remembered, indicates an increase in the flow properties of the sheet. The most striking observation to be made from these tables is that, for each of the additive compounds, the absolute effect of the compound is very nearly the same at the two humidity levels. The absolute effect of the urea on these values is very slightly greater at 50% R.H. than at 11% R.H., while the reverse is generally true for 1,3-dimethylurea. Expressed on a percentage basis, both compounds are almost 50% more efficient at the higher moisture content level than they are at the lower level. /

From the above discussion of Table VI through XI the following observations and generalizations may be made:

(1) 1,3-Dimethylurea is more effective in reducing tensile strength, initial slope, final slope, offset load, and the  $f$  value than is urea at both 11 and 50% R.H. According to the definition to be employed in this thesis, 1,3-dimethylurea is therefore a better plasticizer for paper at both 11 and 50% R.H. than is urea.

(2) A lowering of the humidity seems to shift the point at which crystallization of the additive adversely affects the plasticizing action to a lower urea content and to a higher 1,3-dimethylurea content.

(3) On a percentage basis, urea and 1,3-dimethylurea are less effective in reducing tensile strength, initial slope, offset load, and  $f$  at 11% R.H. than they are at 50% R.H. On this basis, however, they are more effective in reducing final slope at 11% R.H. than at 50% R.H.

(4) On an absolute basis the two additives were less effective in reducing tensile strength and initial slope at the 11% R.H. level than at the 50% level. They were about equally effective in reducing the absolute values of offset load and  $f$  at both humidities, and they were more effective in reducing the final slope values at the lower humidity than they were at the higher humidity.

(5) 1,3-Dimethylurea retained relatively more of its plasticizing effectiveness at the low humidity level than did urea. Since 1,3-dimethylurea is known to be a better plasticizer than urea at both 11 and 50% R.H., this suggests that the better the plasticizer, the more of its

normal effectiveness it will retain at low relative humidities. The probable reason for this result will be discussed later when the theory of plasticizing with the ureas is discussed.

# THE EFFECT OF UREA ON INTERNAL TEARING STRENGTH AND ZERO-SPAN TENSILE STRENGTH

The internal tearing strength and the zero-span tensile strength of urea-treated papers were determined at 50% R.H. with the results shown in Table XII.

By applying a statistical test for the significance of the difference between two means (69), it was possible to determine whether the variations in the two strength values were actually significant or whether they could have occurred by chance.

TABLE XII

## TEARING STRENGTH AND ZERO-SPAN TENSILE STRENGTH OF UREA-TREATED HANDSHEETS

Urea Content, % of Dry Pulp	Tearing Strength, g./sheet		Zero-Span Tensile Strength, lb./in.	
	Actual Value	Standard Deviation <sup>1</sup>	Actual Value	Standard Deviation <sup>1</sup>
0	92.8	1.6	51.3	1.0
2.8	91.7	2.6	51.2	1.4
5.3	90.1	1.8	52.1	1.9
9.5	93.3	4.2	52.7	0.7
15.4	95.5	3.8	49.7	1.1
18.7	89.6	1.8	49.4	1.9
23.4	90.7	1.2	46.5	2.2
34.2	85.3	3.3	46.4	1.3

<sup>1</sup>Calculated according to Hoel (68):  $\sigma = \sqrt{\frac{\sum u_i^2 f_i}{n} - \bar{u}^2}$

The difference between the tearing strength of the control sheet and the sheet of 5.3% urea content was significant at the 95% level. In other words, a difference of this magnitude could have occurred 5% of the time by chance. The differences in tear between the sheets of urea content 5.3 and 15.4% and between the sheets of urea content 15.4 and 18.7% could have occurred by chance less than 2% of the time, and hence they are highly significant. Therefore we may state that while treatment of a sheet with urea has very little effect on its tearing strength, the addition of urea does cause a slight decrease in tear followed by a slight increase. When crystallization occurs, tearing strength drops again.

Application of simple statistics to the zero-span tensile strength data showed that the difference between the strength of the control sheet and the 5.3% urea sheet could occur by chance about 30% of the time, and hence was not statistically significant. However, the difference between the control sheet and the 9.5% urea content sheet could occur by chance less than 1% of the time and was, therefore, highly significant. In other words, zero-span tensile strength probably does increase slightly when urea is added to the sheet. The differences between the 9.5 and 15.4% urea content sheets and the 18.7 and 23.4% urea content sheets were likewise highly significant. Therefore, the initial slight rise in zero-span tensile strength is followed by a somewhat larger decrease at urea concentrations approaching the point of crystallization.



It seems probable from the zero-span tensile strength data that fiber tensile strength is not significantly reduced by plasticizing. This is probably the result of the same type of action which causes cotton fiber tensile strength to increase slightly with moisture and glycerin plasticizing (24-26, 1). The presence of the urea sufficiently reduces the internal cohesive forces of the fiber to allow a more even distribution of stress. Consequently, at a given load each chain or bundle of chains bears less actual stress, and the total load at failure may be increased.

If fiber tensile strength is relatively unchanged over the initial range of urea content, then it becomes apparent that the major cause of the decrease in actual tensile strength must be the weakening of the fiber-to-fiber bonds. This does not necessarily imply, however, that the major cause of decreased elastic moduli or increased flow properties lies in the fiber-to-fiber bonds, since in the case of cotton fibers it is known that fiber tensile strength increases under conditions which lower fiber rigidity.

#### COMPARISON OF CHANGES IN THE PROPERTIES OF UREA-TREATED SHEETS ON A UNIT BONDING STRENGTH BASIS

Zero-span tensile strength should be a measure of the ultimate tensile strength obtainable if bonding were sufficient to cause only fiber rupture. Therefore the ratio of the actual tensile strength to the zero-span tensile strength may be presumed to be an indication of the extent to which the bonds realize this ultimate tensile strength. It is, therefore, an index of bonding strength.

If the values for some of the mechanical properties of urea-treated sheets are now adjusted to a unit bonding strength by the use of this factor, it should be possible to obtain some hint as to how great a role bonding strength plays in altering these properties. It should be cautioned, however, that the fact that the changes in a property which occur with the addition of urea can be accounted for by changes in bonding strength does not, in itself, constitute proof that changes in bonding strength are actually responsible for these property changes. It is always possible that other factors, which may change to the same extent and in the same manner as bonding strength, may be responsible for the particular changes occurring in the sheet property. The adjustment has been made in Table XIII according to the following formula:

$$\text{Adjusted value} = \text{Actual value} / \text{bonding strength factor}$$

In order to eliminate data variability from the comparison, the values in Table XIII were taken off the smooth curves drawn from the strength property-urea content data. For this reason the actual values may not always correspond exactly to the values given in Table IV.

The following observations may be made on the data in Table XIII. It is seen that the bonding strength factor decreases to a minimum value of less than 65% of its original value at 18.7% urea. Thereafter, the crystallization phenomenon causes it to rise to about 90% of its original value in the untreated control sheet.

In the case of the adjusted initial alone values, bonding strength changes might account for the effect of the first small increments of urea. Thereafter, however, some factor equally as important as the

TABLE XIII

COMPARISON OF UREA-TREATED SHEET DATA ADJUSTED TO  
A COMMON UNIT BONDING STRENGTH

Urea Con- tent <sup>1</sup>	Bonding Strength Factor	Initial Slope		Final Slope		Series Spring Constant, $K_2$		Offset Load		$f$ Value	
		Actual Value <sup>2</sup>	Value/ Factor	Actual <sup>2</sup> Value	Value/ Factor	Actual <sup>2</sup> Value	Value/ Factor	Actual Value <sup>3</sup>	Value/ Factor	Actual Value <sup>3</sup>	Value/ Factor
0	0.407	1.47	3.61	0.14	0.34	1.33	3.27	20.6	50.6	17.7	43.5
2.8	0.391	1.41	3.61	0.14	0.36	1.27	3.26	19.6	50.1	16.2	41.4
5.3	0.369	1.32	3.57	0.14	0.37	1.18	3.20	18.1	49.1	14.8	40.1
9.5	0.332	1.07	3.23	0.13	0.40	0.94	2.83	13.7	41.3	12.4	37.3
15.4	0.296	0.68	2.29	0.11	0.38	0.57	1.92	9.2	31.1	8.5	28.7
18.7	0.259	0.55	2.10	0.10	0.38	0.45	1.73	7.2	27.8	6.2	23.9
23.4	0.315	0.76	2.41	0.12	0.37	0.64	2.04	7.7	24.4	7.3	23.2
34.2	0.372	0.89	2.39	0.15	0.40	0.74	1.99	8.8	23.7	7.9	21.2

<sup>1</sup>Percentage of oven-dry pulp weight

<sup>2</sup>In pounds/mil

<sup>3</sup>In pounds

change in bonding strength is operating to reduce the value of the initial slope. Presumably this factor is the flexibilizing of the individual fibers. It should be noted that this second factor also reverses its effect at the point of crystallization.

The adjusted final slope values, instead of decreasing, are found to increase with urea content. Actually the increase is so slight and so variable that it seems permissible to conclude that the adjusted final slope value remains practically constant. This means that changes in the final slope value could be explained solely on the basis of changes in fiber-to-fiber bonding strength. Further indirect evidence has also been found supporting the conclusion that the final slope value--the parallel spring constant  $K_1$ --is more sensitive to changes in bonding strength than is the series spring constant  $K_2$ . The matter is fully discussed in connection with the comparative data on the effect of substituted ureas on sheet properties.

The series spring constant,  $K_2$ , adjusted to unit bonding strength, decreases slowly at first and then more rapidly until, at the onset of crystallization, it begins to rise. The initial behavior of the adjusted  $K_2$  values makes it plain that a portion of the initial lag in the decrease of the adjusted initial slope values,  $K_1 + K_2$ , was due to the slight rise of the adjusted  $K_1$  value. In spite of the fact that  $K_2$  is independent of any such rise in  $K_1$ , the second factor, presumed to be fiber flexibilizing, does not reduce the adjusted  $K_2$  value as rapidly at small urea contents as it does at urea concentrations exceeding 5%. We may hypothesize that there must be a certain minimum amount of urea in the fiber structure before

its flexibilizing effect is comparable, percentage-wise, to the effect of the urea on the bonds. In view of the probable highly disordered nature of the cellulose units involved in a fiber-to-fiber bond, it seems logical that this region would be more immediately sensitive to small amounts of urea than would the more ordered, amorphous portions of the fiber.

The adjusted offset load and  $f$  values are seen to decrease throughout the entire urea content range investigated. Therefore the changes in bonding strength are insufficient to explain even a major part of the changes in the flow properties. It seems highly significant, however, that although bonding strength and presumably fiber stiffness increase in the region of crystallization, the factor operating to reduce the flow properties continues to effect a decrease in the offset load and  $f$  value in this region. Presumably, some other factor such as the swelling of the fibers is of equal or even greater importance to the behavior of the flow properties than is the bonding strength. If sheet flow is thought of as the result of the relative movement of individual flow units, be they chains, micelles, or fibrils, it is conceivable that the ability of these flow units to move past one another in response to an applied stress is a strong function of their relative separation. The more urea that is located in the fibers of the bonding regions, the greater will be the separation, whether the urea is bound to the cellulose or whether it is interstitial, crystalline urea. Presumably, then, flow will be facilitated even though some of the urea which is present as an excess crystallizes throughout the fibers and the sheet. The probable

reason that crystallization influences the fiber stiffness and bond stiffness but not the flow properties is that the incrusting urea in and on the fibers and fiber-to-fiber bonds has a rigidity of its own, apart from its swelling function. A fiber-to-fiber bond, for instance, if surrounded by crystalline urea, could be quite rigid under small stresses and still allow the fibers to pull apart or slide past one another quite readily.

#### SUMMARY OF THE EFFECT OF UREA AND 1,3-DIMETHYLUREA ON SHEET PROPERTIES

The observations made on the effect of urea and 1,3-dimethylurea on the mechanical properties of paper will be reviewed to emphasize the most important findings discussed in this section. It should be noted that the permanence of these effects has not been investigated. However the nature of the changes investigated was such that no fugitive effects would normally be expected.

Evidence has been found to indicate that urea migrates with the free water in a sheet of paper until a point in the drying is reached where it may successfully replace water on the sorbing groups of the cellulose. Moisture sorption data indicate that at least some of the urea actually combines with the cellulose, so that it competes with moisture for the reactive sorbing groups of the cellulose. The moisture content of a treated sheet is therefore less than that of an untreated sheet under the same conditions of temperature and humidity. The effect of urea can not, therefore, be due to any humectant action. Increasing the urea content or the relative humidity decreases the magnitude of this dehydration effect.

The fact that the urea in a sheet maintains the cellulosic structure in a state of partial dry swelling is indicated by its effect on the hysteresis loop and possibly by its effect on sheet thickness and density.

Urea reduces the magnitude of the dimensional changes of a sheet during drying. Urea was found to reduce both the maximum shrinkage tension developed in a sheet dried at constant length, and the shrinkage tension developed at any given moisture content below 65%. At low moisture contents in the neighborhood of 11%, this action seemed to be due to the ability of urea to moderate the normal intensive shrinkage of the fibers themselves.

The effect of urea and 1,3-dimethylurea on the mechanical properties of sheets at 11 and 50% R.H. was found to include a reduction in the tensile strength, the initial slope, the final slope, the offset load, and the  $f$  value. The term plasticizer was defined to denote a compound which affects these properties in this manner.

At relatively high urea or 1,3-dimethylurea contents, the plasticizing action of the compounds was found to be reversed, apparently by a crystallization of the additive in the sheet. Below 50% R.H., a change in the humidity level of test did not greatly alter the concentration of additive at which this phenomenon occurred.

The addition of urea to a sheet of paper was found to reduce the initial and final limiting relative viscosity of the sheet. The relative viscosity of the sheet at any given load was reduced by the addition of

urea, as was the load required to bring about a rapid breakdown in the viscosity.

At both 11 and 50% R.H., 1,3-dimethylurea was found to be more effective as a plasticizer than urea. The 1,3-dimethylurea was also found to retain a greater portion of its plasticizing effect at the lower humidity than urea, indicating the possibility that the relative effectiveness of a plasticizer at 50% R.H. may be an index of the extent to which it retains its effectiveness at low humidities.

Both urea and 1,3-dimethylurea were found to affect tensile strength, initial slope, offset load, and  $\frac{1}{2}$  relatively less at 11% R.H. than at 50% R.H. The final slope value, however, was more sensitive to plasticizing at 11% R.H. than at 50% R.H.

The tearing strength of paper at 50% R.H. changed only slightly over a wide range of urea contents. Zero-span tensile strength rose slightly with the first increments of urea, probably because of a more uniform stress distribution in the fibers. The bonding strength factor (actual tensile strength divided by zero-span tensile strength) decreased with increasing urea content and then increased when the plasticizing action of the urea was reversed by crystallization effects.

The changes occurring in the bonding strength factor with increasing urea content could adequately explain the changes observed in the final slope, but the initial slope and the series spring constant appeared to be decreased by an additional factor, possibly the reduction in fiber stiffness. Bonding strength alone could not account for the changes in the



flow properties of the sheet. On the basis of the fact that the factors other than bonding strength which influence these properties were relatively unaffected by the crystallization phenomenon, it was postulated that the degree of dry swelling was of primary importance in determining these properties.

#### THE EFFECT OF SOME VOLATILE MATERIALS ON SHEET PROPERTIES

Two volatile materials, formamide and dimethylformamide, were introduced into the standard handsheets, and their effect on the mechanical properties of the sheets investigated. Because of the volatility of the dimethylformamide, the compounds were introduced into the sheet by soaking them in the pure compound, and allowing them to "dry" in the usual way. In addition, sheets of various formamide contents were prepared by soaking the sheets in aqueous formamide solutions and drying in the usual way. Formamide was found to evaporate sufficiently slowly that these sheets could be dried to moisture equilibrium at 50% R.H. with the loss of only a slight amount of the formamide. Since dimethylformamide evaporated nearly as fast as the water, no treated sheets could be prepared from aqueous dimethylformamide solutions.

A comparison of the properties of sheets containing various quantities of formamide and dimethylformamide after drying from the pure compounds will be included in the next section; the discussion of these data will be deferred until that point.

## THE PROPERTIES OF SHEETS DRIED FROM VARIOUS MEDIA

The effect of drying sheets from a variety of pure materials and aqueous solutions was investigated. Table XIV presents data obtained for various additive-free sheets dried from water, 95% ethyl alcohol, formamide, dimethylformamide, and a variety of aqueous dimethylformamide solutions. Time limitations made it impossible to obtain a completely formamide-free sheet due to the extremely slow rate of evaporation of the final traces of formamide. The data for sheets dried from formamide were therefore obtained by extrapolation from the minimum formamide concentration attained, 0.6%. It may be that a certain small amount of formamide is held by the cellulose so tenaciously that it may be removed only by methods more drastic than conditioning at 50% R.H. Such methods of course would alter the sheet sufficiently to make the formamide-free sheet thus obtained useless from a comparative point of view.

It is evident from Table XIV that drying from materials other than water has reduced the equilibrium moisture content of the sheets. Presumably this is due to the fact that these materials tend to produce a state of dehydration in the cellulose so that when the softener finally leaves the sheet, moisture regain is lessened by the hysteresis effect.

In general, drying from media other than water seems to produce a sheet of lower tensile strength, elastic constants, offset load, and  $f$  value. Stretch seems to be somewhat increased. These changes generally indicate a weakening or plasticizing of the sheet which is associated with an increase, rather than a decrease, in moisture content. It is believed that the weakening of the sheet is the result of the fact that fewer

TABLE XIV

THE PROPERTIES OF SHEETS DRIED FROM DIFFERENT MEDIA

Sheet Property	Drying Medium							
	Water	95% Ethyl Alcohol	Pure Formamide	Pure DMF <sup>1</sup>	50% DMF <sup>1</sup>	30% DMF <sup>1</sup>	15% DMF <sup>1</sup>	5% DMF <sup>1</sup>
Moisture content, % OD pulp	8.01	7.84	7.21	6.74	7.71	7.58	7.69	7.90
Tensile strength, lb.	41.7	39.4	41.5	37.4	36.9	37.4	40.0	40.0
Initial slope, lb./mil	1.47	1.42	1.46	1.32	1.24	1.25	1.35	1.35
Final slope, lb./mil	0.14	0.12	0.14	0.12	0.10	0.12	0.12	0.13
Stretch, %	2.87	3.39	2.62	2.78	3.34	3.11	3.34	2.90
Offset load, lb.	20.6	16.7	23.2	17.9	18.4	17.4	18.1	18.8
f value, lb.	17.7	15.9	18.4	16.4	15.9	16.1	16.9	16.5

<sup>1</sup>Dimethylformamide

secondary bonds of an interfiber or an intrafiber nature are formed as the organic material evaporates than would normally be formed if water alone were present.

In general it was found that the scatter of results when sheets were dried from volatile materials or from aqueous solutions of volatile materials was considerably greater than was normal for sheets dried from aqueous solutions of crystalline materials. This may account for the rather frequent reversal of trends in the data of Table XIV for sheets dried from a series of aqueous dimethylformamide solutions. The data

available indicate that there might have been a maximum weakening effect when the sheets were dried from 50% dimethylformamide.

It may be seen from Table XIV that sheets dried from pure formamide have properties quite similar to those of water-dried sheets except for the fact that their flow properties are decreased. On an equalized moisture content basis, however, the formamide-dried sheets would rank somewhat weaker and more plasticized than the water-dried control sheets. The fact that formamide and water have a closely similar effect on the drying of paper was shown when sheets dried to various formamide contents from pure formamide were compared with sheets dried to the same formamide content from aqueous solutions of formamide. The comparison showed that with the single exception of stretch, all the values for the aqueous formamide-dried sheets fell within the area of uncertainty surrounding the curves for sheets dried from pure formamide. The addition of water to the formamide invariably caused a large increase in the stretch value.

From the data discussed above it is possible to conclude that a plasticizer may exert a noticeable effect on sheet properties due to its action during drying. However, in comparison to its effect on the sheet-straining mechanism during testing, the changes brought about by the plasticizer during drying are probably of secondary importance. Possibly the stretch value is one property upon which drying conditions exert a major influence.

## COMPARISON OF THE EFFECT OF ADSORBED FORMAMIDE AND RESIDUAL FORMAMIDE

A comparison was made of the effectiveness of a given amount of formamide in altering sheet properties when the given formamide concentration in the sheet was reached by (a) drying from pure formamide, or (b) adsorption of the formamide from the vapor phase. The sheets in (b) were prepared by hanging the test strips for a period of two months in an atmosphere desiccated by phosphorus pentoxide and containing formamide vapor. They were then reconditioned at 50% R.H. for four hours before being tested.

In Table XV a comparison is made of the two types of sheets with each other and with a control sheet at the same moisture content.

Several facts are immediately evident from Table IV. The first is that paper may be plasticized by the sorption of formamide from the vapor phase in the same way that it is plasticized by sorbed moisture vapor. There is, therefore, nothing unique about the capacity of water vapor to combine with the reactive cellulose groups and bring about a plasticizing action. The second rather striking point is the fact that the adsorbed formamide exerted a considerably greater effect on the sheet than did the residual formamide. This may be largely attributed to the relaxation of "frozen-in" stresses. The sheet which adsorbed formamide was under no restraint during the time it was picking up formamide and during the time it was reconditioned to 50% R.H. During this time the moisture and the plasticizer combined to relieve the stresses originally frozen into the sheet by drying under restraint.

TABLE IV

COMPARISON OF SHEETS CONTAINING ADSORBED  
AND UNDESORBED FORMAMIDE

Sheet Property	Sheet Dried from Pure Formamide			Formamide Adsorbed by Sheet		
	Sheet with Formamide A	Control Sheet B	(B-A)/A x 100	Sheet with Formamide C	Control Sheet D	(D-C)/D x 100
Formamide content <sup>1</sup>	13.8	0	—	13.8	0	—
Moisture content <sup>1</sup>	8.28	8.28	—	7.71	7.71	—
Tensile strength, lb.	22.8	41.4	45.0	20.4	42.1	51.5
Initial slope, lb./mil	0.64	1.44	55.5	0.53	1.49	64.4
Final slope, lb./mil	0.11	0.14	21.4	0.08	0.14	42.8
Offset load, lb.	7.4	20.0	63.0	5.5	21.3	74.2
f value, lb.	8.6	17.3	50.2	6.0	18.3	67.2
Stretch, %	2.75	2.98	7.7	4.34	2.82	-54.0

<sup>1</sup>On an oven-dry pulp basis

The comparison shows that the final slope value is very much more sensitive to this stress-relaxation phenomenon than are most of the other properties. This is believed to be due to the fact that the final slope is more sensitive to changes in the state of the fiber-to-fiber bond than many of the other mechanical properties.

The extensibility of a sheet dried from formamide is lower, at a given formamide content, than that of the moisture control sheet. On the other hand the same amount of formamide, introduced from the vapor phase, greatly increases the stretch value. Evidently stretch is very sensitive to the physical and chemical conditions under which a sheet is dried.

#### COMPARISON OF THE EFFECT OF VARIOUS UREAS AND FORMAMIDES ON PAPER

In order to investigate what effect alteration of the urea molecule by substitution has on its effectiveness in altering the mechanical properties of paper, a variety of methyl-, ethyl-, and butyl-substituted ureas\* were applied to the standard handsheets, and the properties of the treated sheets were evaluated. As in the case of all the work reported in this thesis, no effort was made to evaluate the permanence of the observed effects. The author believes, however, that except in cases where an additive is either volatile or subject to decomposition, the changes occurring in the sheets as a result of the addition of these compounds to the sheet are of a permanent nature.

\*These compounds were obtained through the courtesy of Sharples Chemicals, Inc.

Ideally, a comparison of the effect of various additives on the mechanical properties of paper should be carried out at a constant moisture content. If it were experimentally feasible, it would be ideal to work at zero relative humidity so that only the two-component system of cellulose and an additive would have to be considered. Lacking this ideal situation, it would be necessary to test every treated sheet at a different humidity if the work were to be carried out at a constant moisture content level. Obviously, neither of the above techniques is practicable.

All the testing which was done to compare various additives as to their effect on the properties of paper was done at the standard conditions of 73° F. and 50% R.H. Therefore the system under investigation at all times included cellulose, water, and the additive compound. Since it was found that the presence of the additive compound affected the moisture content of the cellulose, it was necessary to devise a method of subtracting the effect of moisture content changes due to the presence of the additive under investigation. Once correction had been made for the moisture content changes, the various compounds could be compared on a uniform basis.

#### DETERMINATION OF THE MOISTURE EFFECT

In order to subtract the effect of moisture content changes due to the additive from the effect of the additive itself, the following method was used. The relationship between the moisture content and the various visco-elastic properties of interest was determined. The effect of the additive on a particular sheet property was then defined as the relative difference between the value of the property in an untreated sheet



and in a treated sheet when both are at the same moisture content and the same temperature. In any one instance this moisture content was always the moisture content of the treated sheet at 50% R.H. It is obvious that according to the above definition a compound which, for example, does not alter the tensile strength of a sheet of paper, but does reduce its moisture content, is considered to have reduced the tensile strength. In the absence of the additive, the same moisture content change would have produced an increase in tensile strength, so the additive has, in effect, substituted its tensile strength-reducing powers for those of the moisture which it displaced.

It is apparent that there are several assumptions inherent in this approach to the problem. The most important of these is that a given amount of moisture per unit weight of cellulose exerts a given action on the sheet regardless of how other components may change. By this assumption the 5% of moisture contained in a sheet of paper at some low humidity exerts the same effect on its mechanical properties as does the 5% of moisture in a treated sheet at 50% R.H., assuming that the physical history of the two sheets has been similar. Since all the test sheets in this work had similar drying and conditioning treatment, it is believed that this assumption is justified.

It would also be possible to take account of the moisture effect in another manner. If the action of a material is presumed to have been a debonding action, so that a treated sheet has only a given fraction of the bonds normally present in an untreated sheet, it may be argued that the

effect of the moisture is proportionately reduced. Actually, within the confines of our present knowledge of the fiber-to-fiber bonds and the fibers themselves, it is impossible to say which of the two views conforms with the actual facts. In the absence of any definite information on either the manner in which the bonds are affected by these additives, or the relative contribution of the bonds to the mechanical properties being considered, it was felt that the adoption of the absolute moisture effect view would simplify the problem. It is important, in this connection, to remember that the effect of the additive compounds is, as a general rule, many times that of the relatively small moisture content change. Indeed, it is very probable that the conclusions to be drawn from this work would not be altered if the moisture content changes were to be neglected completely.

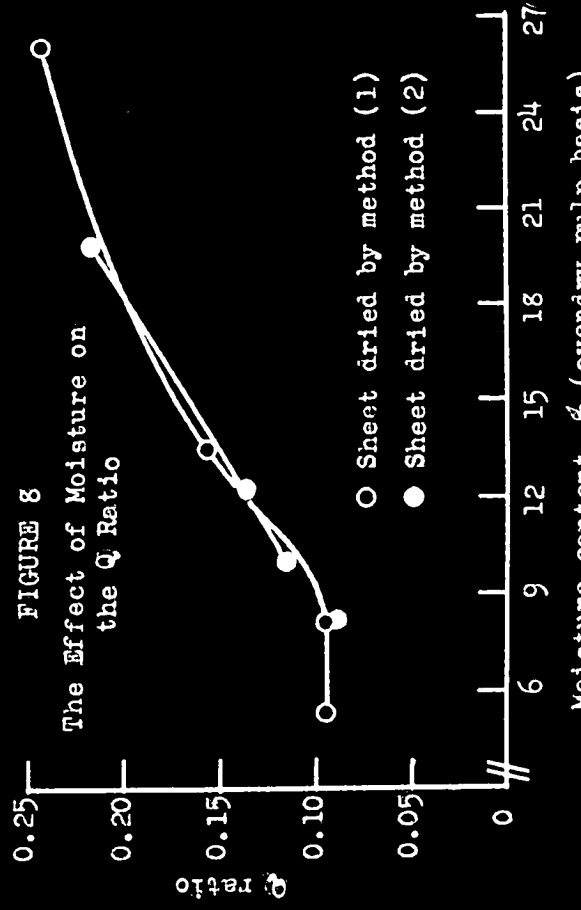
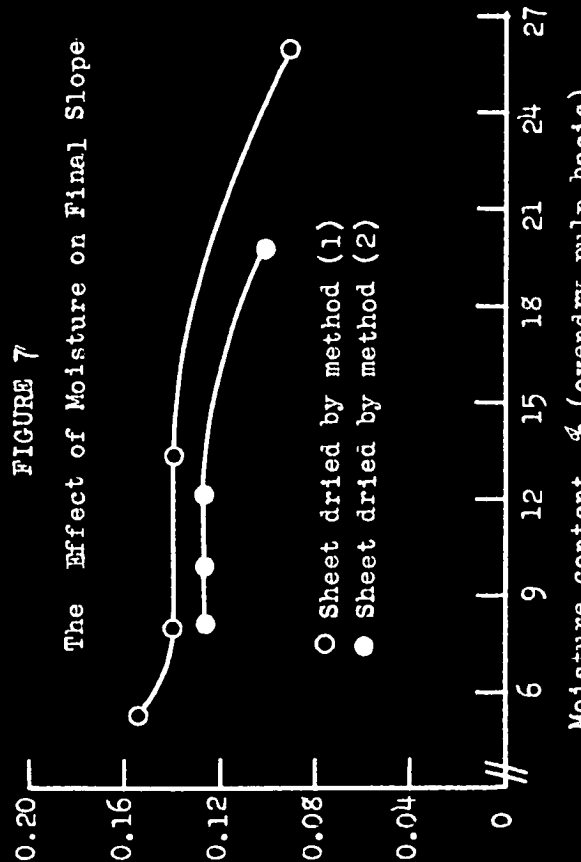
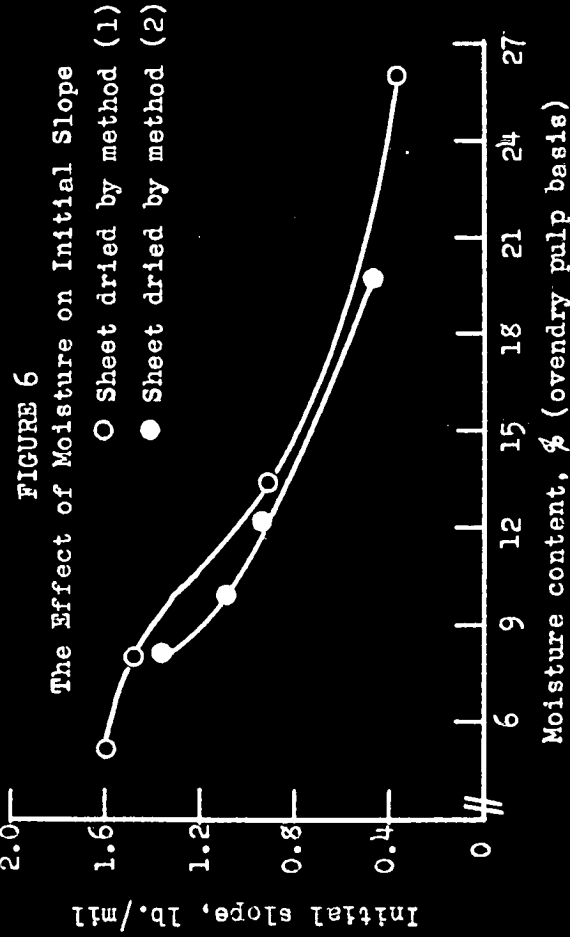
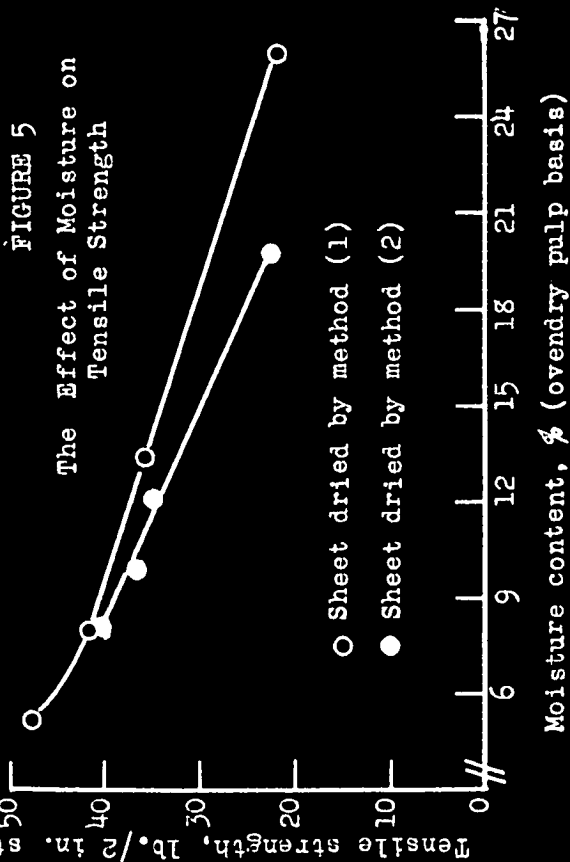
The effect of moisture content on the mechanical properties of the standard resoaked alpha sheets was determined by conditioning these sheets at various relative humidities before determining their LM curve. In the early phases of the work the resoaked sheets were dried at 50% R.H. on plates. The sheets were then removed from the plates, and the test samples were cut from the sheets. These test samples were then conditioned to the desired relative humidity and tested. A consideration of the rather unsatisfactory results obtained by this method led to the conclusion that the all-important matter of frozen-in stresses was being overlooked. It became apparent that when a free strip was subjected to humidities above 50%, some of the frozen-in stresses were relieved, and that when it was conditioned to a lower moisture content, the process of

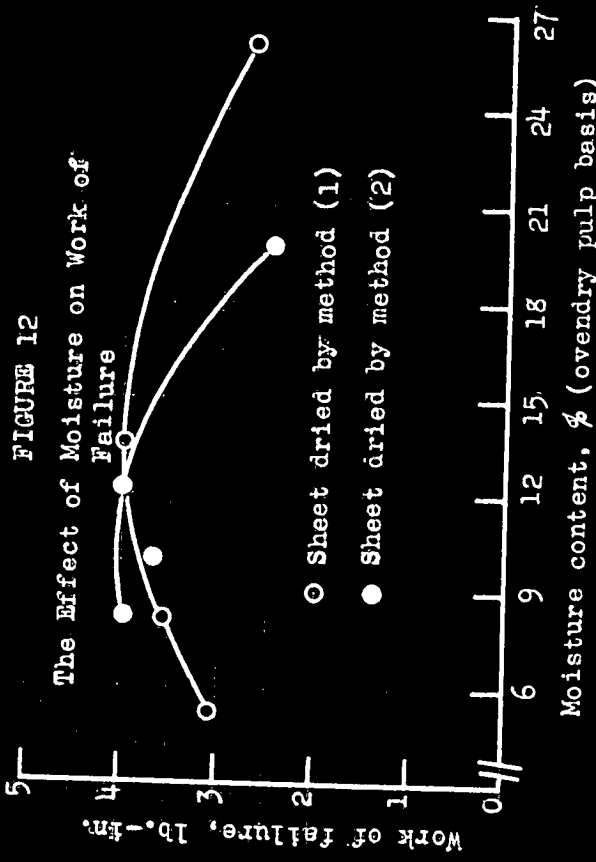
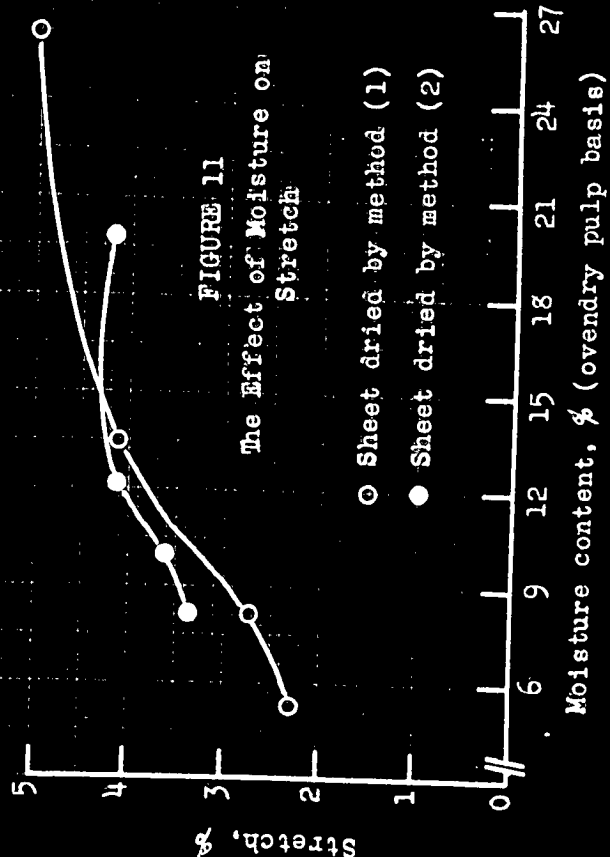
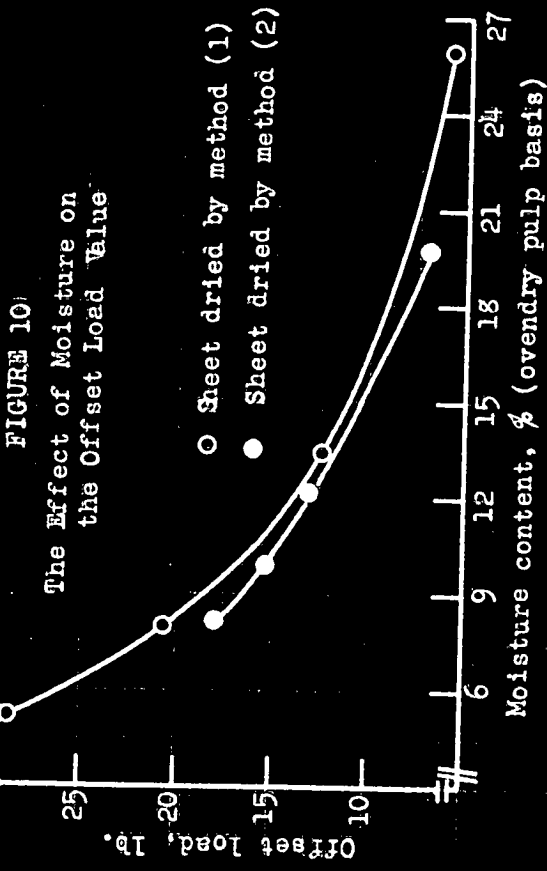
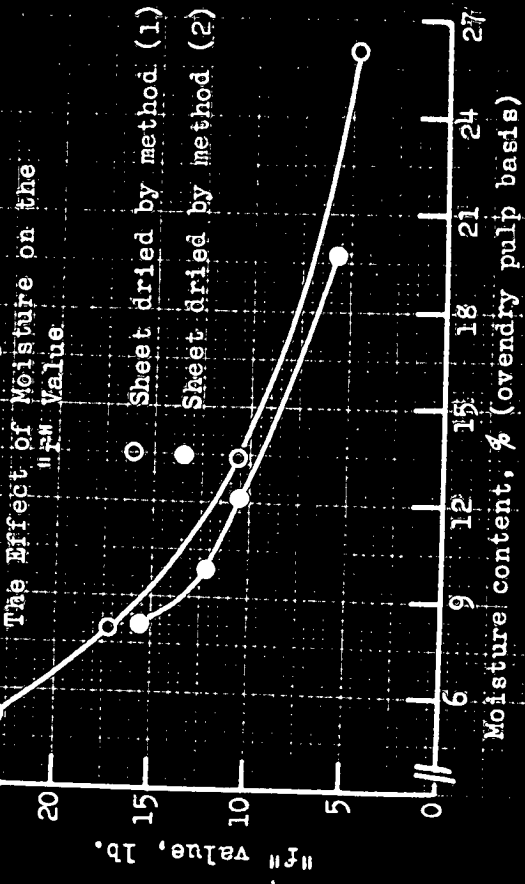
freezing in the stresses already in the sheet was continued to some undetermined extent. It was therefore decided that reliable data on the effect of the moisture present in a treated sheet could be obtained only if the fact were taken into account that the treated sheets dry to the moisture content in question under restraint. Hence, the only sound method of evaluating the effect of this moisture was to dry a water-soaked sheet to this moisture content under restraint. Thus stresses would be frozen into this sheet to the same extent as those in the unplasticized sheet. This method was adopted and all the data subsequently used for the moisture-effect subtraction process were obtained in this way. The method is described below as Method 1, together with a second method, Method 2, which was used to obtain an indication of the effect of relieving some of the frozen-in stresses before conditioning the sample:

Method 1: The wet sheets were dried on plates to the humidity at which they were tested. They were then cut and tested without a variation of the humidity conditions.

Method 2: The sheets were dried on plates to 50% R.H., and the samples were cut. The strips were then preconditioned at 92% R.H. with no restraint before being conditioned at the desired humidity. All samples therefore approached equilibrium by desorption.

The properties of sheets conditioned by Methods 1 and 2 at various moisture contents are shown in Figures 5-12. In general the curves for the sheets conditioned by Method 2 closely parallel those of the sheets dried by Method 1. As theory would predict, the Method 2 sheets,





in which stresses were partially relieved by preconditioning, have lower tensile strengths, lower elastic constants, and greater flow properties at any moisture content than do the sheets dried under restraint.

It may be seen from Figure 5 that the tensile strength increases almost linearly as moisture content decreases. The data of Figure 5 are not in agreement with the findings of Lyne and Gallay (62), who reported that at a moisture content of 25% the rate of development of tensile strength with decreasing moisture content fell off. These authors also found indications of a maximum tensile strength at about 10% moisture content.

In Figure 6 it is indicated that the initial slope value has its greatest increase in the region from 9-18% moisture. The rate of increase of initial slope with decreasing moisture content is lower both above and below this region.

In this moisture content range of from 9-18%, the final slope in Figure 7 is seen to be almost unchanged. The relief of stresses seems to have affected this quantity somewhat more than the other properties. It will be remembered that the same was true when formamide was the stress-relieving agent.

The  $Q$  ratio in Figure 8 decreases rather rapidly during drying to a moisture content of about 9%, indicating that the initial slope is increasing at a considerably greater rate in this region than is the final slope.

Figures 9 and 10 for the  $f$  value and the offset load show the same trends for both properties. Flow properties of a sheet are increasingly reduced as moisture content is diminished. It may be seen that the flow properties are nearly at a maximum ( $f$  value and offset load at a minimum) at a moisture content of 21%, so that further large increases in moisture content contribute only slightly to the ease with which the sheet exhibits flow.

Figure 11 establishes that increasing the moisture content increases the extensibility of the sheet. It may be seen in Figure 12 that the work of failure seems to be at a maximum in the 10-15% moisture content region.

In the sense of the term defined earlier in this thesis, water is a plasticizer for paper. It reduces tensile strength and elastic moduli and enhances the flow properties of a sheet of paper.

#### METHOD OF COMPARING EFFECTIVENESS OF VARIOUS PLASTICIZERS

Data on the properties of urea- and 1,3-dimethylurea-treated sheets over a wide range of additive contents have been given in Tables IV and V. In order to study more fully the effect of substitution, twelve other ureas were used to treat sheets, and their effect on sheet properties determined at two or more concentrations. The urea and 1,3-dimethylurea tests were run on four samples, each from a different sheet. These data indicated that the variability between sheets was of a lower magnitude than the over-all experimental variability. In later work, therefore, four samples cut from only two sheets were tested to reduce the rate of consumption of the limited number of standard handsheets.

The number of concentrations of additive compound studied in each case was as follows: urea, 1,3-dimethylurea formamide and dimethylformamide, at least eight points each; 1,1-dimethylurea, six points; 1,3-diethylurea and methylurea, four points each; ethylurea and 1,1-diethylurea, three points each; thiourea, butylurea, 1,1-dibutylurea, 1,3-dibutylurea, tetrabutylurea, tetramethylurea, and 1,3-diethylthiourea, two points each. In each case the mechanical properties determined were plotted against additive content, and the tabulated values were taken from these curves at certain molar additive concentrations. All the treated sheets were compared at additive concentration intervals of 25 millimoles per 100 grams of oven-dry pulp. By utilizing the additive content-moisture content curves determined for each additive and the data of Figures 5-12, it was possible to determine the properties of an untreated sheet at the same moisture content as that of any given set of treated sheets. For any one property the difference between the untreated sheet values and those of the treated sheet, expressed as a percentage of the untreated, the value of the control sheet was taken to be a measure of the effectiveness of the additive in altering the property. It will be noted in the tables and figures which follow that the data have been calculated and plotted from the baseline additive content-sheet property curves rather than from the raw data. The points on the figures serve only to indicate the number of experimentally determined points; the shape of the curve has been determined by calculation from the baseline curves. In some instances only a portion of the additive content range studied has been included.



## THE VARIOUS MEANS OF INTRODUCING THE ADDITIVES INTO THE SHEET

Since some of the higher substituted ureas were not water-soluble, it was necessary to apply them to the sheet from a less polar solvent. Ninety-five per cent ethyl alcohol was selected, since it met the requirements that it be a solvent with poor swelling properties for cellulose, and one which would not evaporate so fast as to make conventional pressing and drying procedures impractical. It is unfortunately true that the use of more than one solvent undoubtedly prevents a completely accurate comparison of all the results obtained.

The subtraction of the moisture content effect for the alcohol-dried sheets was complicated by the fact that the additive-free, alcohol-dried control sheet had properties which were slightly different from those of a water-dried sheet of the same moisture content. This was shown in Table XIV. It was therefore necessary to make a correction for this discrepancy if the moisture content-mechanical property data of Figures 5-12 were to be used. For any given sheet property a factor could be calculated which would equalize the strength property value of the alcohol-dried control sheet and that of the water-dried control sheet of the same moisture content. This factor was then used in all the calculations for this property of alcohol-dried sheets. The method will be clarified by an example in which tensile strength is used. Let the symbol  $X$  denote the tensile strengths of water-dried sheets such as those in Figures 5-12, and let  $Y$  denote the tensile strengths of all alcohol-dried sheets:

If  $M_0$  = the moisture content of an additive-free, alcohol-dried sheet at 50% R.H.

$M_1$  = the moisture content of an alcohol-dried sheet of given additive content at 50% R.H.

$X_{M_0}$  = the tensile strength of untreated, water-dried sheet at moisture content,  $M_0$ .

$X_{M_1}$  = the tensile strength of an untreated, water-dried sheet at moisture content  $M_1$ .

$Y_{M_0}$  = the tensile strength of an additive-free, alcohol-dried sheet whose moisture content is  $M_0$ .

and  $Y_{M_1}$  = the tensile strength of a treated alcohol-dried sheet whose additive content gives it a moisture content of  $M_1$ .

Then

$$\text{Reduction in tensile strength due to additive content (\%)} = \frac{X_{M_1}(Y_{M_0}/X_{M_0}) - Y_{M_1}}{Y_{M_0}} \times 100$$

To check the degree of validity of this method, one concentration of urea was applied to a set of sheets from an alcoholic solution. A comparison of the effect of the aqueous urea and the alcoholic urea on the various sheet properties appears in Table XVI. On the whole it is felt that Table XVI indicates that a semiquantitative comparison may be made between the effects of additives, even though they may not have been applied to the sheet from the same solvent. A further check in which 1,3-diethylthiourea was applied to the sheets from both aqueous and alcoholic solutions over the very small range of 0-5% additive gave less satisfactory agreement than did the urea check shown above. It was found that the alcoholic 1,3-diethylthiourea showed a lower effect than did the aqueous compound. Therefore, it may be that in a comparison

TABLE XVI

COMPARISON OF THE EFFECT OF UREA ON SHEET PROPERTIES WHEN  
APPLIED FROM WATER AND FROM ALCOHOL

Sheet Property	Percentage Change in Property Due to the Presence of 11.8% Urea (Moisture Effect Subtracted)	
	Aqueous Urea	Alcoholic Urea
Tensile strength	27.7	30.5
Initial slope	44.3	45.1
Final slope	13.9	5.7
Offset load	66.0	64.1
$f$ value	57.0	62.9
Stretch	50.2	48.0

of alcohol-applied and water-applied softeners, the efficiency figures for the additives applied from alcohol would be spuriously low. Since the error is in this direction, the major conclusions to be drawn from the comparative data will not be changed.

The data for formamide and dimethylformamide were obtained on sheets dried from the pure material. The same type of calculation was used to determine their effectiveness as was used for the alcohol-applied additives. It will be remembered that a comparison of sheets dried from pure formamide and aqueous formamide showed that, with the exception of stretch, sheet properties at any given formamide content were very nearly the same. This was probably due to the similar effect of formamide and water on the drying mechanism. Although no such check could be made for dimethylformamide because of its volatility, a considerable difference between the mechanical properties of sheets dried from pure dimethylformamide and aqueous dimethylformamide might be expected on the basis of the data in Table XIV. We may conclude that although the comparison of

sheets dried from formamide with sheets dried from aqueous solutions would be justifiable, comparisons drawn between sheets dried from dimethylformamide and aqueous solutions of other additive materials may be less accurate. Only the fact that the additives are to be compared on a percentage basis makes a comparison of dimethylformamide with the other compounds justifiable. There can be no objection, however, to comparing the dimethylformamide data with the formamide data, since they were both obtained in the same manner.

#### PRESENTATION OF COMPARATIVE DATA

##### THE EFFECT OF THE ADDITIVES ON THE MOISTURE CONTENT OF THE SHEET

Table XVII shows the equilibrium moisture contents at 50% R.H. of sheets containing varying amounts of the compounds studied. It will be noted that the moisture content of all the sheets decreased with the addition of small amounts of additive. Even when the compound was hygroscopic, as in the cases of formamide and dimethylformamide, there was an initial competition between the water and the additive for the sorbing groups of the cellulose, with the result that the moisture content of the cellulose was reduced. This dehydration effect was also shown by the moisture-vapor sorption data reported in Table II.

The data of Table XVII indicated that a minimum moisture content was reached within the additive concentration range of about 75 to 150 millimoles per 100 grams of dry pulp. This minimum point varied with the compound. The subsequent increase in moisture content with further increases in additive content was probably due to the higher degree of dry

TABLE XVII

MOISTURE CONTENT OF VARIOUS TREATED SHEETS AT 50% R.H. AND 73° F.  
(Percentage of oven-dry pulp)

Additive Compound	Additive Content of Sheet, millimoles per 100 grams of oven-dry pulp						
	0	25	50	75	100	125	150
Compounds applied from aqueous solution							
Water	8.01	8.46	8.91	9.36	9.81	10.26	10.71
Urea	8.01	7.26	6.73	6.37	6.19	6.12	6.10
Thiourea	8.01	7.04	6.42	6.05	5.87	5.77	5.72
Methylurea	8.01	7.33	6.87	6.56	6.37	6.27	6.22
1,1-Dimethylurea	8.01	7.46	6.90	6.55	6.50	6.56	6.70
1,3-Dimethylurea	8.01	6.77	6.20	6.11	6.07	6.06	6.10
Tetramethylurea <sup>a</sup>	8.01	7.71	7.33	--	--	--	--
Ethylurea	8.01	7.73	7.14	6.66	6.36	--	--
1,1-Diethylurea <sup>b</sup>	8.01	6.98	6.41	5.98	--	--	--
1,3-Diethylurea	8.01	7.40	6.95	6.58	6.25	5.98	5.76
1,3-Diethylthiourea <sup>c</sup>	8.01	7.42	--	--	--	--	--
Compounds applied from 95% ethyl alcohol solutions							
Butylurea <sup>d</sup>	7.84	6.84	5.89	--	--	--	--
1,1-Dibutylurea <sup>e</sup>	7.84	6.82	5.99	5.33	--	--	--
1,3-Dibutylurea <sup>f</sup>	7.84	6.53	--	--	--	--	--
Tetrabutylurea <sup>g</sup>	7.84	7.41	--	--	--	--	--
Sheets dried from pure compound							
Formamide	7.21 <sup>h</sup>	6.78	6.63	6.57	6.56	6.59	6.66
Dimethylformamide	6.74	6.88	6.51	6.61	7.07	7.64	8.20

<sup>a</sup>7.19 at 59 millimoles

<sup>b</sup>5.65 at 97 millimoles

<sup>c</sup>7.18 at 34 millimoles

<sup>d</sup>5.15 at 73 millimoles

<sup>e</sup>4.95 at 92 millimoles

<sup>f</sup>5.98 at 44 millimoles

<sup>g</sup>7.41 at 33 millimoles

<sup>h</sup>This value by extrapolation from 16 millimoles

swelling maintained by the large amount of additive. This may have prevented some of the sorbing groups from forming cellulose-cellulose bonds and thus left them available for moisture sorption. Presumably, these groups are satisfied by water molecules rather than other additive molecules, since at the higher additive concentrations at which this rise in moisture content occurred, there was a large amount of additive in the sheet. A similar moisture content rise, relative to the untreated sheet, was found in Table II when the humidity of a treated sheet was raised. It is possible that the two phenomena are caused by the same type of action.

It is widely believed that the sorbed water on cellulose is held by reactive hydroxyl groups, probably through hydrogen bonding. If the presence of the urea additives decreases moisture content, it is reasonable to conclude that the additives are bonding to the hydroxyl groups in the cellulose. In view of the structure of the ureas, it is not unlikely that they, like water, are also hydrogen-bonded to the cellulose. It is known that the bonding forces between urea and cellulose are not true chemical bonds since they are readily broken in the presence of water. The fact that complete substitution of the amide nitrogen atoms does not affect the moisture-reduction phenomenon strongly indicates that the bonding group on the urea molecule is the carbonyl group. It seems probable, therefore, that the polar, carbonyl oxygen atom is the electron-donor and the hydroxyl hydrogen atom is the electron acceptor. No active hydrogen atoms on the urea molecule appear to be necessary for the formation of cellulose-urea bonds.

## THE EFFECT OF THE ADDITIVES ON TENSILE STRENGTH

The actual tensile strength values of the test sheets containing the various additives are given in Table XVIII. Table XIX shows the percentage reduction in tensile strength due only to the additive; the moisture effect has been subtracted. The data of Table XIX are plotted in Figures 13-16.

In connection with Figures 13-16 and all subsequent figures, it should be recalled that the curves were plotted from values calculated from the baseline additive content-mechanical property curves. In some cases the curves shown in the figures represent only the initial portions of the complete curves, so that the shape of the curves is influenced by values for additive concentrations not included in the plot, e.g., Curve 3 of Figure 15. In the case of a curve such as Curve 4 of Figure 16, the additive content-tensile strength baseline curve passed through a minimum point between the two experimentally determined points, and consequently the calculated curve of Figure 16 passes through a corresponding maximum between the two points. It should be remembered, therefore, that the shape of the curves is determined by the shape of the baseline curves, and the points are plotted merely to indicate the number of experimentally determined values.

TABLE XVIII

ACTUAL TENSILE STRENGTH OF THE TREATED SHEETS  
(Pounds per two-inch strip)

Additive Compound	Additive Content of Sheet, millimoles per 100 grams of oven-dry pulp						
	0	25	50	75	100	125	150
Compounds applied from aqueous solution							
Water	41.7	41.2	40.7	40.2	39.7	39.1	38.6
Urea	41.7	40.9	40.0	38.9	37.8	36.6	35.4
Thiourea	41.7	40.6	39.8	39.2	38.9	38.7	38.6
Methylurea	41.7	41.0	39.3	36.0	32.4	30.0	28.5
1,1-Dimethylurea	41.7	39.7	35.7	32.2	32.0	33.6	37.3
1,3-Dimethylurea	41.7	36.0	33.6	31.5	29.6	27.5	25.5
Tetramethylurea <sup>a</sup>	41.7	31.8	28.2	--	--	--	--
Ethylurea	41.7	33.0	30.3	27.8	25.1	--	--
1,1-Diethylurea <sup>b</sup>	41.7	35.4	30.1	25.5	--	--	--
1,3-Diethylurea	41.7	33.3	27.8	22.7	18.2	16.1	17.1
1,3-Diethylthiourea <sup>c</sup>	41.7	33.8	--	--	--	--	--
Compounds applied from 95% ethyl alcohol solutions							
Butylurea <sup>d</sup>	39.4	34.3	30.2	--	--	--	--
1,1-Dibutylurea <sup>e</sup>	39.4	34.1	29.0	23.7	--	--	--
1,3-Dibutylurea <sup>f</sup>	39.4	30.7	--	--	--	--	--
Tetrabutylurea <sup>g</sup>	39.4	17.6	--	--	--	--	--
Sheets dried from pure compound							
Formamide	41.5 <sup>h</sup>	40.0	38.4	37.0	35.3	33.8	32.3
Dimethylformamide	37.4	32.3	28.7	25.8	23.1	20.5	18.0

<sup>a</sup>27.6 at 59 millimoles

<sup>b</sup>21.4 at 97 millimoles

<sup>c</sup>30.9 at 34 millimoles

<sup>d</sup>27.6 at 73 millimoles

<sup>e</sup>20.1 at 92 millimoles

<sup>f</sup>28.2 at 44 millimoles

<sup>g</sup>17.5 at 33 millimoles

<sup>h</sup>This value by extrapolation from 16 millimoles



TABLE XIX

RELATIVE EFFICIENCIES OF VARIOUS COMPOUNDS  
IN REDUCING TENSILE STRENGTH  
(Percentage of tensile strength of untreated sheet at 50% R.H.)

Additive Compound	Additive Content of Sheet, millimoles per 100 grams of oven-dry pulp						
	0	25	50	75	100	125	150
Compounds applied from aqueous solution							
Water	0	1.2	2.4	3.6	4.8	6.2	7.4
Urea	0	4.3	8.4	12.7	16.3	19.7	22.5
Thiourea	0	5.8	10.6	13.7	16.1	17.0	17.8
Methylurea	0	3.8	9.8	18.9	28.3	34.8	38.6
1,1-Dimethylurea	0	6.7	18.2	28.0	28.8	24.7	14.9
1,3-Dimethylurea	0	18.0	26.4	31.9	36.7	41.7	46.3
Tetramethylurea <sup>a</sup>	0	24.7	34.5	--	--	--	--
Ethylurea	0	21.6	30.2	38.1	46.0	--	--
1,1-Diethylurea <sup>b</sup>	0	18.7	33.8	47.5	--	--	--
1,3-Diethylurea	0	22.1	36.9	51.3	63.1	70.0	69.1
1,3-Diethylthiourea <sup>c</sup>	0	20.9	--	--	--	--	--
Compounds applied from 95% ethyl alcohol solutions							
Butylurea <sup>d</sup>	0	16.8	32.5	--	--	--	--
1,1-Dibutylurea <sup>e</sup>	0	17.5	34.5	52.8	--	--	--
1,3-Dibutylurea <sup>f</sup>	0	27.4	--	--	--	--	--
Tetrabutylurea <sup>g</sup>	0	56.6	--	--	--	--	--
Sheets dried from pure compound							
Formamide	0	5.3	9.9	13.5	17.6	21.2	24.3
Dimethylformamide	0	13.1	24.1	31.6	36.9	42.0	46.8

<sup>a</sup>36.5 at 59 millimoles

<sup>b</sup>59.2 at 97 millimoles

<sup>c</sup>28.5 at 34 millimoles

<sup>d</sup>44.7 at 73 millimoles

<sup>e</sup>65.5 at 92 millimoles

<sup>f</sup>36.8 at 44 millimoles

<sup>g</sup>57.1 at 33 millimoles

FIGURE 13

The Efficiency of the Lower-Molecular Weight Compounds in  
Reducing Tensile Strength

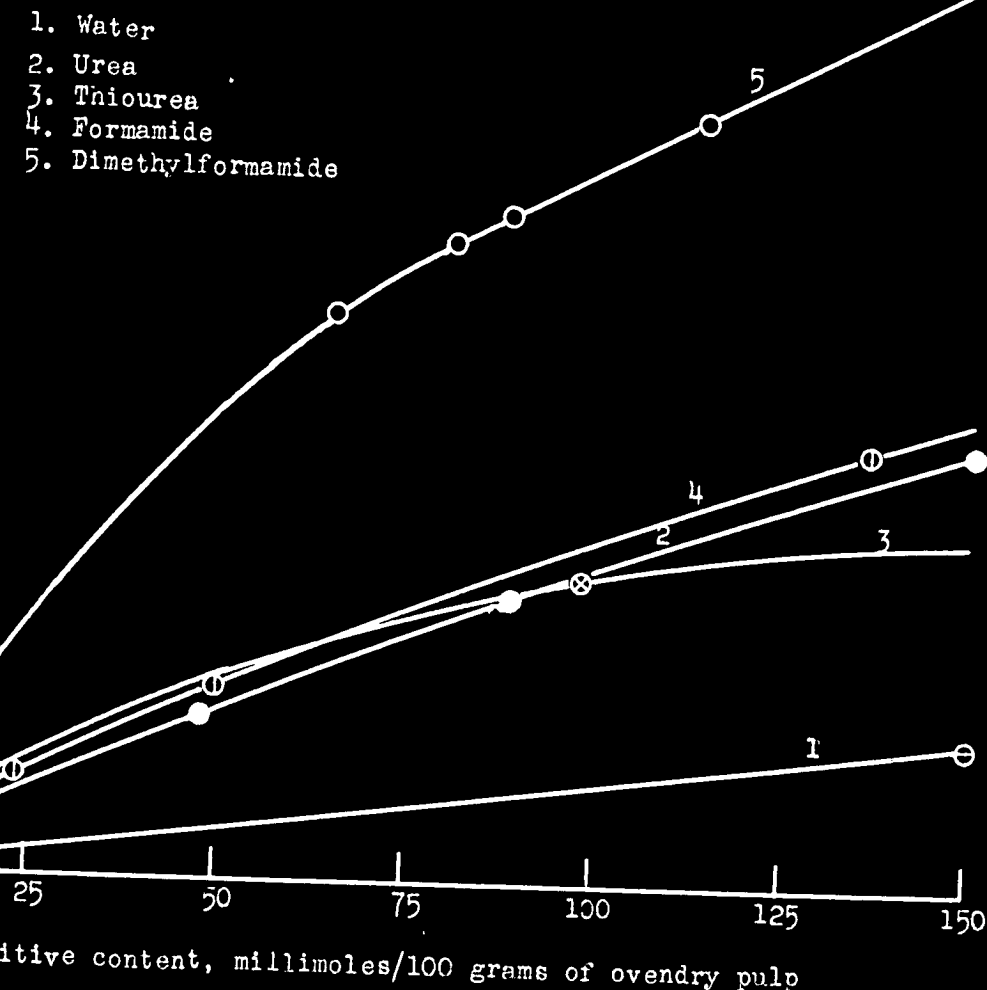


FIGURE 14

The Efficiency of the Methyl-substituted Ureas in Reducing Tensile Strength

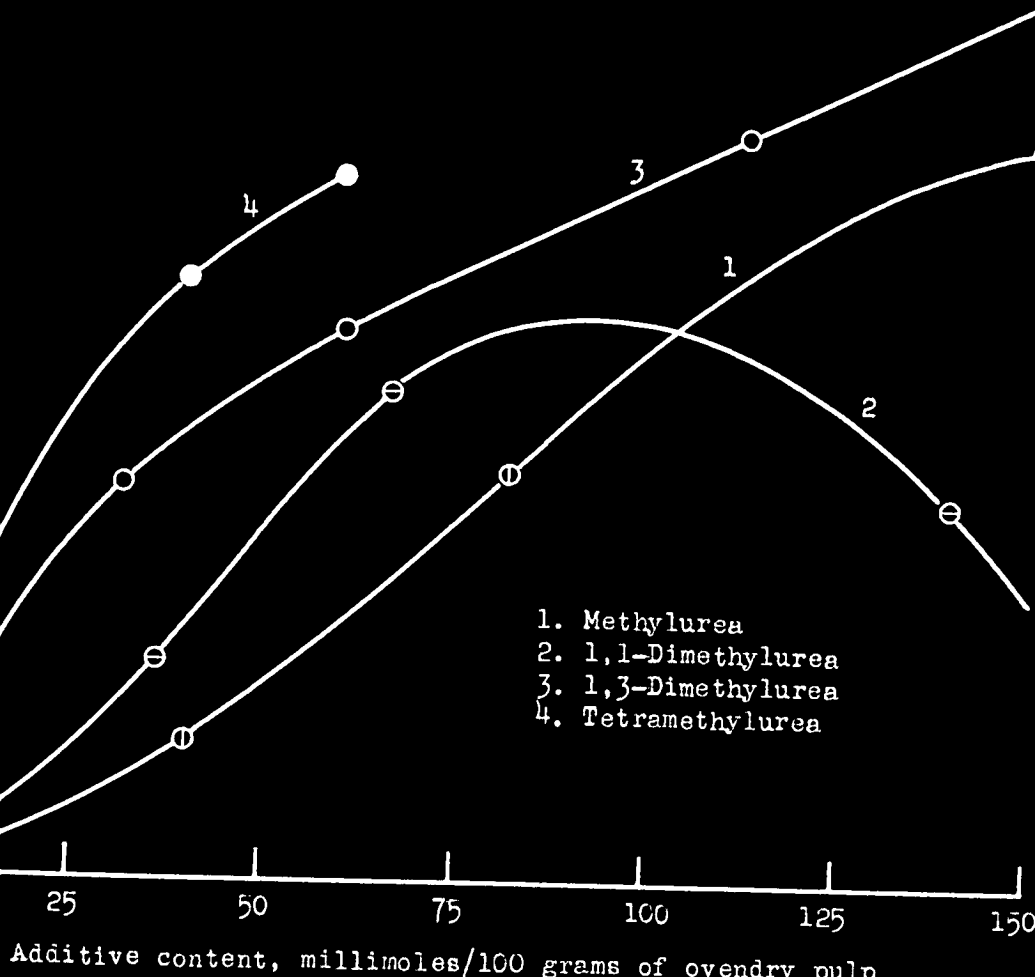


FIGURE 15

The Efficiency of the Ethyl-substituted Ureas in Reducing  
Tensile Strength

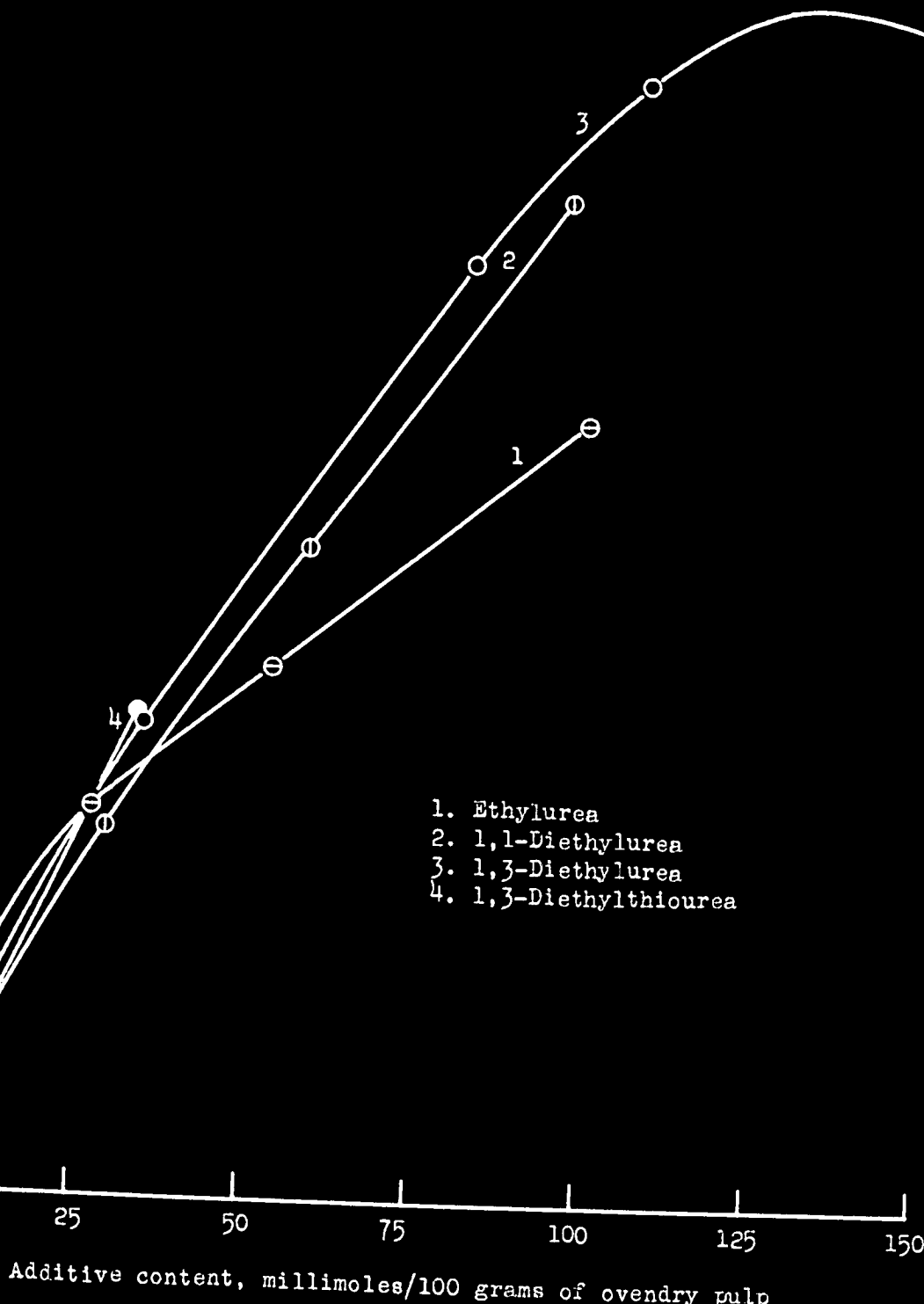
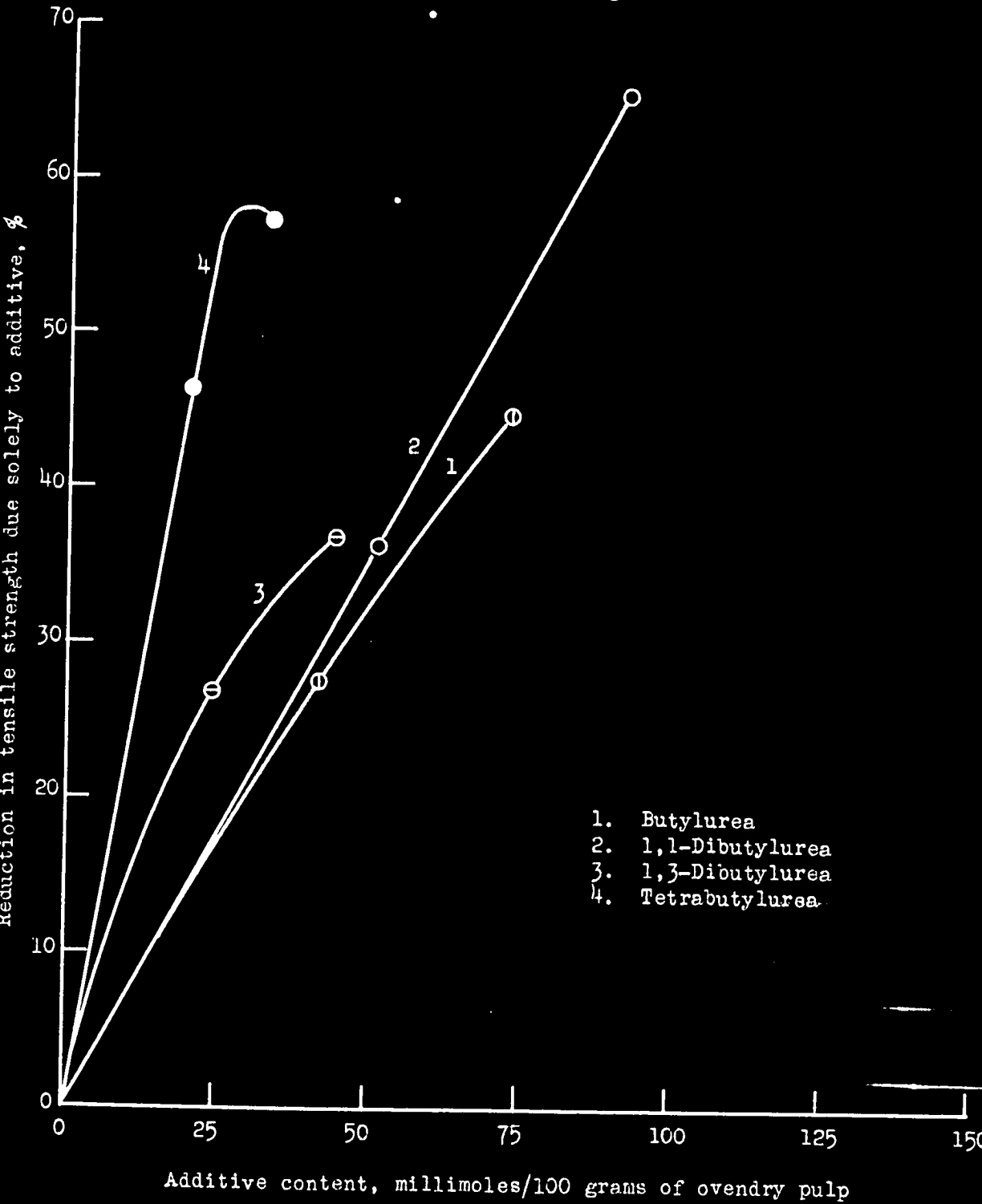


FIGURE 16

The Efficiency of the Butyl-substituted Ureas in Reducing Tensile Strength



Water has been included in these tables for comparative purposes. It was seen in Figures 5-12 that the effect of a given increment in the moisture content of a sheet may depend on the baseline moisture content which is selected. Table XVII showed that the moisture content of most of the treated sheets was in the 6-8% range. Since the moisture content value changes with the particular additive as well as with the additive content of the sheet, no one baseline moisture content would be wholly satisfactory for all conditions. Figures 5-12 indicated that the effect of adding additional water to a sheet at 6% moisture content was not widely different from that of adding the same amount of moisture to a sheet at 8% moisture content. It was therefore decided to use the 50% R.H. equilibrium value of 8% moisture as the arbitrary baseline from which to assess the effect of water on sheet properties.

The following points should be noted in the data presented in Table XIX and plotted in Figures 13-16:

(1) Water, at least at the baseline chosen, had comparatively little effect on tensile strength. The fact that on a molar basis water has a relatively small effect on sheet properties, amply borne out by the data to follow, is in direct contradiction to the widespread concept of water as the perfect softener or the perfect plasticizer for paper. On a weight basis, of course, the effectiveness of water may compare more favorably with that of other materials.

(2) Substitution increased the efficiency of urea and formamide in reducing tensile strength. In general the higher the degree of substitution in a mono-, di-, or tetrasubstituted series, the greater the

effectiveness of the material in lowering tensile strength. Symmetrical substitution appeared to have a slightly greater effect on strength-reducing powers than unsymmetrical substitution, although the effect of symmetry was very much less than the effect of substitution.

(3) Tensile strength reduction was the greatest when the molecular weight of the additive was the greatest. Increasing the size of the substituent groups increased the weakening action of the material.

(4) The replacement of carbonyl oxygen of urea with a sulfur atom reduced the maximum plasticizing effect of the compound. Although the data shown in Table XIX and Figure 13 do not clearly indicate it, at higher additive concentrations urea continued to exert a weakening effect, whereas thiourea soon began to strengthen the sheet, presumably by crystallization. Thiourea is very much less soluble than urea, probably because the sulfur atom reduces the polarity of the material. It may be suggested that for the same reason thiourea has less tendency to bond to the cellulose than does urea. Since sulfur compounds are known to be poorer hydrogen-bond formers than the corresponding oxygen compounds, this may be considered to be indirect evidence that urea is hydrogen-bonded to cellulose through the carbonyl oxygen.

In the case of 1,3-diethylthiourea, the effect of the sulfur in the molecule seems to have been greatly overshadowed by the important effect of increased molecular size.

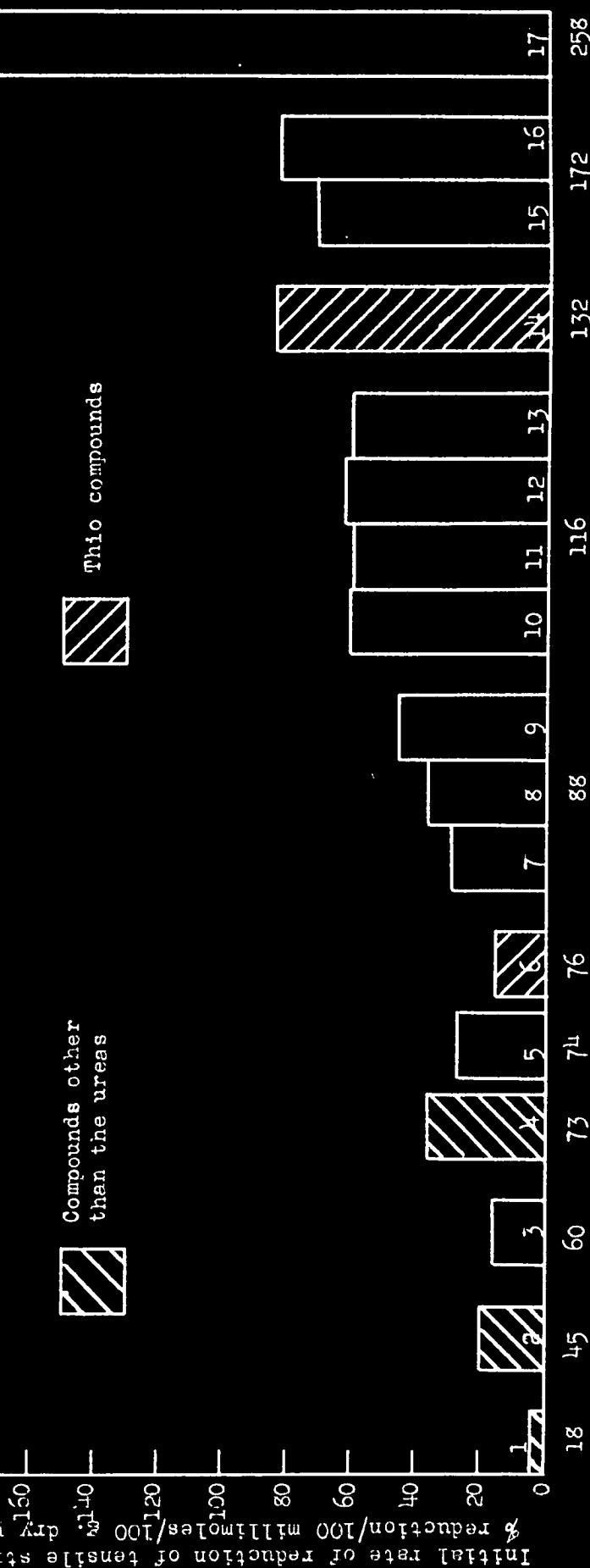
Complete substitution of the amide nitrogen atoms, in itself, had no deleterious effect on the initial effectiveness of the molecule in

reducing tensile strength. This excludes the amide hydrogen atoms (and with them any enolic hydroxyl group) from consideration in the cellulose-urea bonding mechanism, and points again to the carbonyl group as the reactive group.

(5) The rapid decrease in the 1,1-dimethylurea curve after an early maximum is characteristic of the rather anomalous behavior of this compound in many of the plasticizing efficiency curves to follow for the other mechanical properties. Check samples verified the existence of this maximum. It may be that the relatively low solubility of 1,1-dimethylurea is responsible for this behavior, or it may be that the single sample of the material used in this work was not completely pure.

Figure 17 shows the efficiency of the various compounds in reducing tensile strength against their respective molecular weights. It is difficult to assign an average tensile strength-reducing efficiency to the various additives since the slopes of their curves in Figures 13-16 change with increasing additive concentration. In order to compare tensile strength-reducing efficiencies on a uniform basis, the percentage reduction of tensile strength at 100 millimoles per 100 grams of pulp was taken as the measure of this property. Where the study did not include concentrations as high as 100 millimoles, or where the effect of the additive dropped off before this additive content was reached, the initial curve was extrapolated to 100 millimoles and the extrapolated value taken. The molar efficiency figures, therefore, are a measure of the average rate of reduction of the property over the first 100 millimoles additive content range. As such, this efficiency is distinctly





Molecular weight

- |                      |                         |
|----------------------|-------------------------|
| 1. Water             | 12. 1,3-Diethylurea     |
| 2. Formamide         | 13. Butylurea           |
| 3. Urea              | 14. 1,3-Diethylthiourea |
| 4. Dimethylformamide | 15. 1,1-Dibutylurea     |
| 5. Methylurea        | 16. 1,3-Dibutylurea     |
| 6. Thiourea          | 17. Tetrabutylurea      |

separate from the maximum reduction effect which may occur at any additive content.

Figure 17 illustrates the importance of molecular weight, or more fundamentally, molecular size, on the tensile strength-reducing powers of the additives. The trend is even more pronounced if the formamides and the thioureas are excluded from the comparison. A possible illustration of a trend within a trend is the fact that the symmetrically substituted ureas are uniformly more effective than their unsymmetrically substituted analogs. Crystalline density data for the dimethylureas (20) indicate that the unsymmetrically disubstituted ureas have a higher density and hence a lower molecular volume than do the symmetrically disubstituted ureas. Hence, again the effect of molecular volume is evident.

We may conclude from the data discussed that the extent to which a material is capable of maintaining the dry swelling of cellulose plays a direct part in determining the molar rate of tensile strength reduction of that compound.

#### THE EFFECT OF THE ADDITIVES ON INITIAL SLOPE

The uncorrected values of initial slope for the variously treated sheets are given in Table XX. Table XXI shows the percentage reduction in initial slope due only to the additive compound. The data of Table XXI are plotted in Figures 18-21 to facilitate comparison. The following observations may be made from the data:

TABLE XI

ACTUAL INITIAL SLOPE ( $K_1 + K_2$ ) VALUES FOR SHEETS  
CONTAINING VARIOUS COMPOUNDS  
(Pounds per mil)

Additive Compound	Additive Content of Sheet, millimoles per 100 grams of oven-dry pulp						
	0	25	50	75	100	125	150
Compounds applied from aqueous solution							
Water	1.47	1.43	1.37	1.32	1.27	1.22	1.15
Urea	1.47	1.44	1.40	1.35	1.28	1.20	1.11
Thiourea	1.47	1.48	1.48	1.48	1.48	1.46	1.44
Methylurea	1.47	1.42	1.35	1.28	1.18	1.04	0.84
1,1-Dimethylurea	1.47	1.38	1.27	1.14	1.08	1.13	1.24
1,3-Dimethylurea	1.47	1.35	1.25	1.16	1.08	0.99	0.90
Tetramethylurea <sup>a</sup>	1.47	1.15	0.96	--	--	--	--
Ethylurea	1.47	1.34	1.20	1.06	0.93	--	--
1,1-Diethylurea <sup>b</sup>	1.47	1.44	1.31	1.12	--	--	--
1,3-Diethylurea	1.47	1.39	1.31	1.19	0.96	0.82	0.85
1,3-Diethylthiourea <sup>c</sup>	1.47	1.40	--	--	--	--	--
Compounds applied from 95% ethyl alcohol solutions							
Butylurea <sup>d</sup>	1.42	1.40	1.34	--	--	--	--
1,1-Dibutylurea <sup>e</sup>	1.42	1.30	1.20	1.12	--	--	--
1,3-Dibutylurea <sup>f</sup>	1.42	1.32	--	--	--	--	--
Tetrabutylurea <sup>g</sup>	1.42	1.04	--	--	--	--	--
Sheets dried from pure compound							
Formamide	1.46 <sup>h</sup>	1.40	1.33	1.26	1.19	1.13	1.06
Dimethylformamide	1.32	1.06	0.95	0.85	0.75	0.65	0.55

<sup>a</sup>0.92 at 50 millimoles

<sup>b</sup>0.92 at 97 millimoles

<sup>c</sup>1.37 at 34 millimoles

<sup>d</sup>1.20 at 73 millimoles

<sup>e</sup>1.09 at 92 millimoles

<sup>f</sup>1.26 at 44 millimoles

<sup>g</sup>1.12 at 33 millimoles

<sup>h</sup>This value by extrapolation from 16 millimoles

TABLE XXI

RELATIVE EFFICIENCIES OF VARIOUS COMPOUNDS  
IN REDUCING INITIAL SLOPE ( $K_1 + K_2$ )  
(Percentage of initial slope of untreated sheet at 50% R.H.)

Additive Compound	Additive Content of Sheet, millimoles per 100 grams of oven-dry pulp						
	0	25	50	75	100	125	150
Compounds applied from aqueous solution							
Water	0	2.8	6.5	9.9	13.8	16.7	21.4
Urea	0	5.5	9.9	14.4	19.5	25.0	31.5
Thiourea	0	3.7	5.5	6.3	6.9	8.0	9.7
Methylurea	0	6.9	12.9	18.4	25.9	35.5	49.7
1,1-Dimethylurea	0	8.6	18.5	28.1	32.3	29.2	21.2
1,3-Dimethylurea	0	13.7	21.5	27.7	33.7	39.8	45.6
Tetramethylurea <sup>a</sup>	0	23.6	39.5	--	--	--	--
Ethylurea	0	10.4	22.3	33.2	43.1	--	--
1,1-Diethylurea <sup>b</sup>	0	6.5	16.9	30.7	--	--	--
1,3-Diethylurea	0	8.4	15.7	24.6	41.2	51.5	49.8
1,3-Diethylthiourea <sup>c</sup>	0	8.0	--	--	--	--	--
Compounds applied from 95% ethyl alcohol solutions							
Butylurea <sup>d</sup>	0	5.1	12.4	--	--	--	--
1,1-Dibutylurea <sup>e</sup>	0	12.6	21.5	28.3	--	--	--
1,3-Dibutylurea <sup>f</sup>	0	11.8	--	--	--	--	--
Tetrabutylurea <sup>g</sup>	0	28.8	--	--	--	--	--
Sheets dried from pure compound							
Formamide	0	5.9	11.0	15.5	20.2	24.7	29.3
Dimethylformamide	0	19.5	28.6	35.5	42.4	47.9	52.3

<sup>a</sup>43.3 at 59 millimoles

<sup>b</sup>45.2 at 97 millimoles

<sup>c</sup>11.1 at 34 millimoles

<sup>d</sup>23.0 at 73 millimoles

<sup>e</sup>30.4 at 92 millimoles

<sup>f</sup>17.4 at 44 millimoles

<sup>g</sup>22.9 at 33 millimoles

FIGURE 18

The Efficiency of the Lower-Molecular Weight Compounds in Reducing Initial Slope.

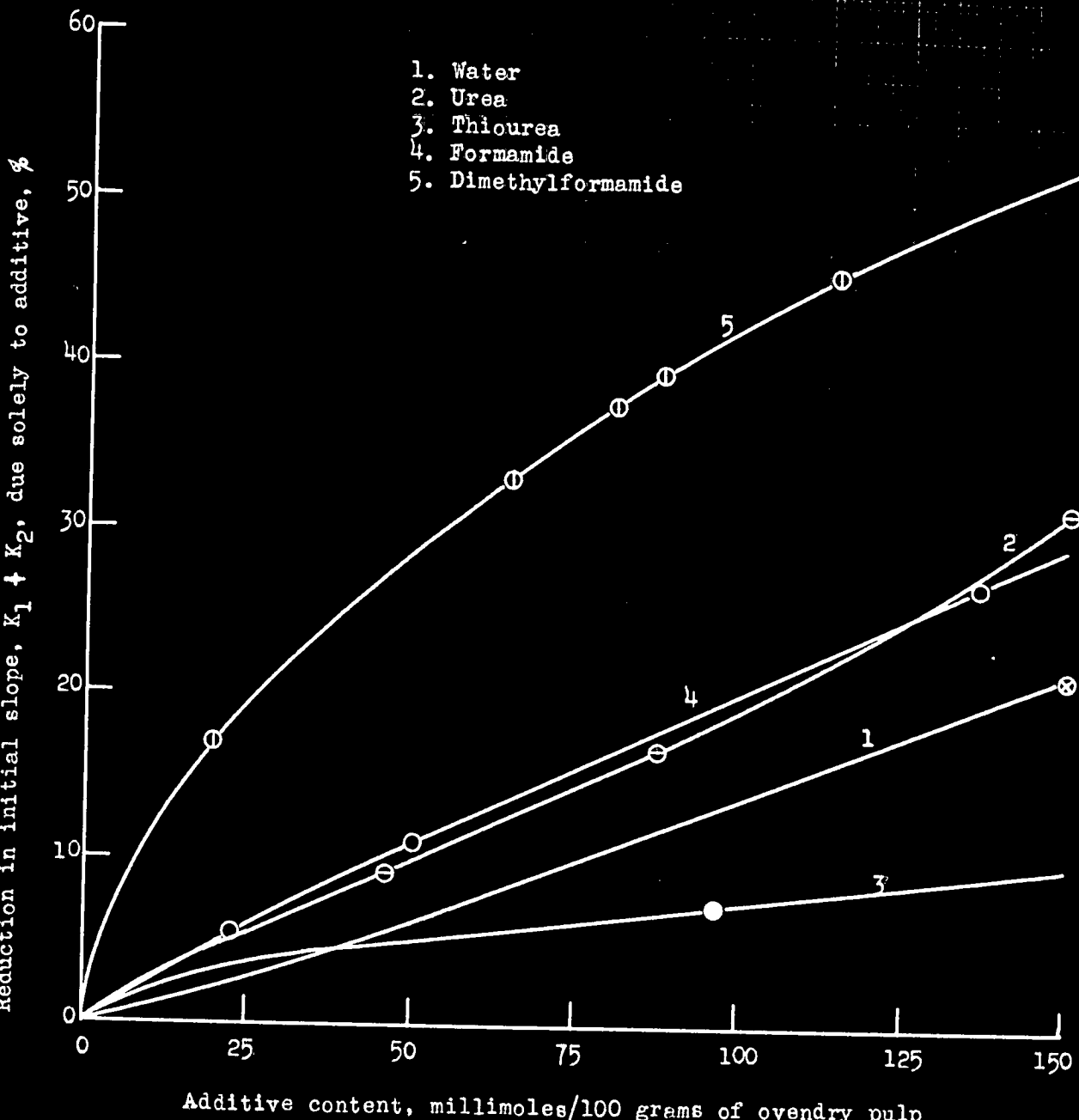


FIGURE 19

The Efficiency of the Methyl-substituted Ureas in Reducing Initial Slope

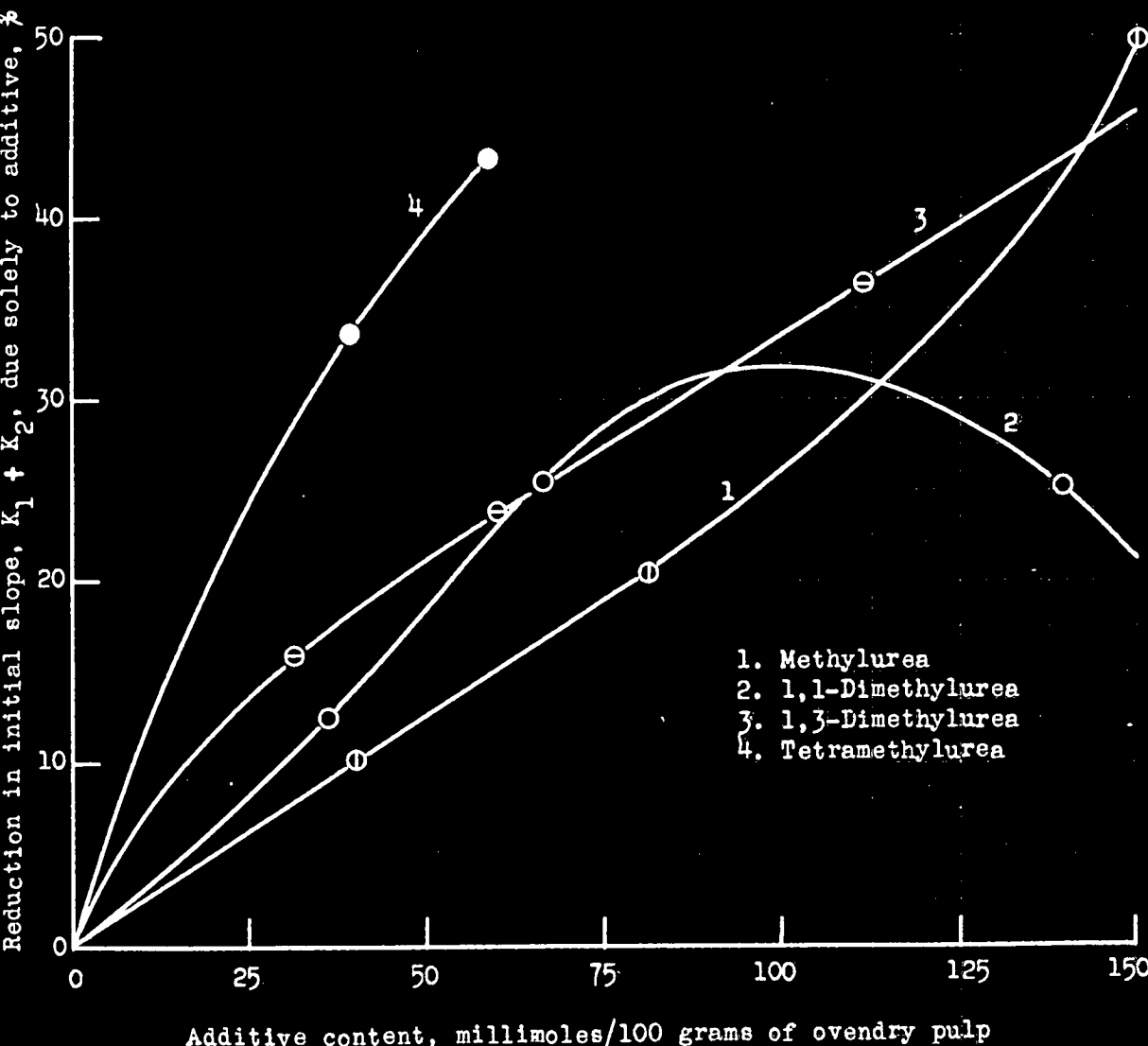


FIGURE 20

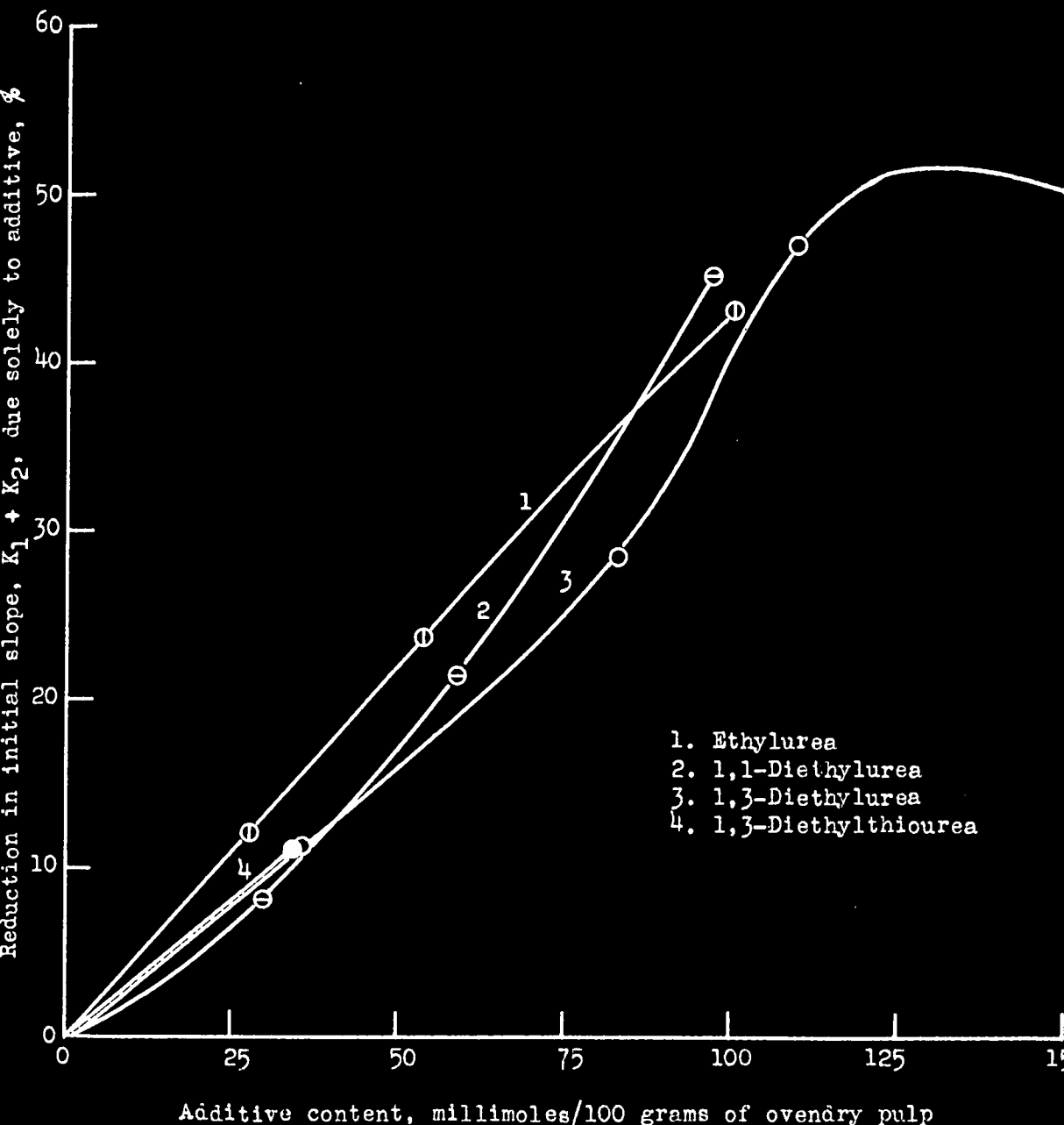
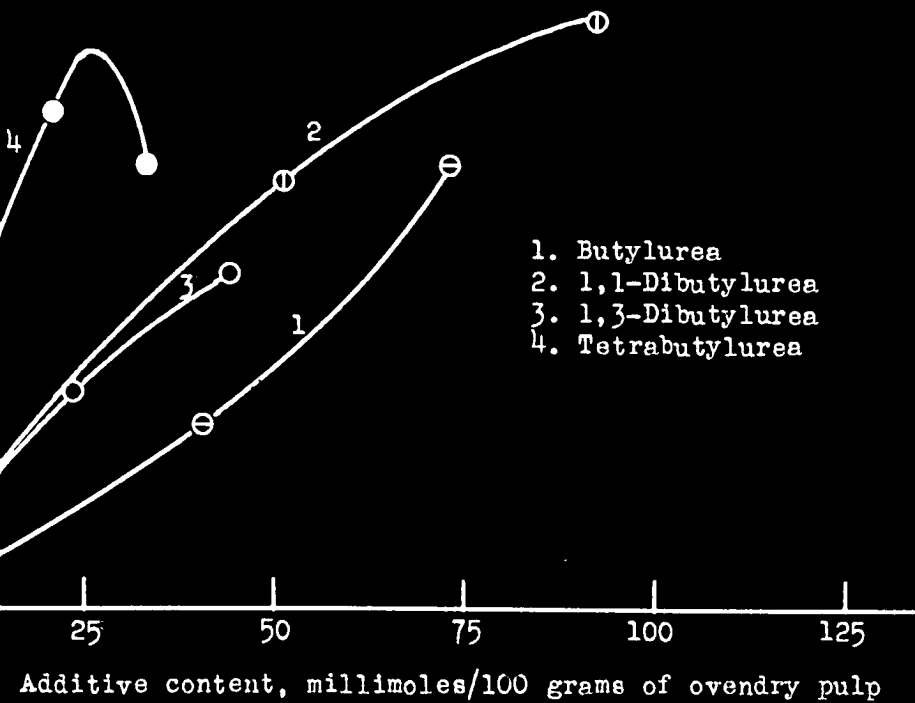
The Efficiency of the Ethyl-substituted Ureas in Reducing  
Initial Slope

FIGURE 21

The Efficiency of the Butyl-substituted Ureas in Reducing Initial Slope





(1) In general, the higher the degree of substitution and the larger the substituent group, the more immediately effective was the material in reducing the initial slope. The tetrasubstituted ureas far surpassed the mono- and the disubstituted ureas with the same substituent group in the reduction of initial slope. The mono- and disubstituted butylureas showed no increase in initial slope-reducing properties over the corresponding ethyl-substituted compounds. This, of course, may have been due to the fact that additives applied from alcoholic solutions may show relatively less effect than additives applied from aqueous solutions. It will be remembered that this was found to be true for 1,3-diethylthiourea.

(2) The differences between the symmetrically disubstituted ureas and their unsymmetrically substituted isomers were slight. While symmetrically substituted dimethylurea exceeded the unsymmetrically substituted dimethylurea in the reduction of the initial slope, the reverse seemed to hold true for the diethyl- and the dibutylureas.

(3) Increasing the molecular size of the additive, either by increasing the degree of substitution or by increasing the substituent chain length, produced an increase in the rate of reduction of initial slope per molar unit of additive. However, it also tended to limit the maximum initial slope reduction of which the material was capable. The tetrasubstituted amides, for instance, showed an immediate high reduction in initial slope, but they also showed a tendency to reach an early, and fairly low, maximum reduction of initial slope. There were other indications that the maximum initial slope-reducing action of some of the

most efficient materials would have been less than that of the less efficient mono- or disubstituted compounds. Therefore, initial rate of reduction of initial slope increased with molecular size, whereas it appeared that the maximum effect would have been attained by compounds in the molecular weight range of 70-90 such as methylurea and dimethylurea.

(4) Water was second only to thiourea as the least effective compound in reducing initial slope. As compared with urea, thiourea was even less effective in reducing initial slope than in reducing tensile strength. Again, the effect of substitution of sulfur for oxygen on the 1,3-diethylurea was not apparent.

Because the initial slope value is largely determined by the value of the series spring constant  $K_2$ , the changes in the two properties are very similar at all times. To avoid unnecessary repetition, therefore, a graphical comparison of the initial slope-reducing efficiencies of the compounds has not been made. In order to obtain a good indication of the effect of molecular size on the initial slope-reducing powers of the ureas, the reader is referred to Figure 31, which shows the  $K_2$ -reducing efficiencies of the various compounds.

#### THE EFFECT OF THE ADDITIVES ON FINAL SLOPE ( $K_1$ )

In Table XXII actual values of the final slope taken from the final slope-additive content curves are presented. Table XXIII gives data on the percentage reduction in final slope due to the additives alone. These data are graphically presented in Figures 22-25.

TABLE XXII

ACTUAL FINAL SLOPE ( $K_2$ ) VALUES FOR SHEETS  
CONTAINING VARIOUS COMPOUNDS  
(Pounds per mil)

Additive Compound	Additive Content of Sheet, millimoles per 100 grams of oven-dry pulp						
	0	25	50	75	100	125	150
Compounds applied from aqueous solution							
Water	0.139	0.139	0.139	0.139	0.139	0.138	0.138
Urea	0.139	0.139	0.138	0.138	0.137	0.136	0.133
Thiourea	0.139	0.134	0.131	0.129	0.129	0.130	0.134
Methylurea	0.139	0.136	0.132	0.128	0.124	0.119	0.114
1,1-Dimethylurea	0.139	0.124	0.111	0.105	0.107	0.119	0.138
1,3-Dimethylurea	0.139	0.115	0.105	0.099	0.094	0.090	0.087
Tetramethylurea <sup>a</sup>	0.139	0.113	0.106	--	--	--	--
Ethylurea	0.139	0.099	0.095	0.095	0.097	--	--
1,1-Diethylurea <sup>b</sup>	0.139	0.111	0.098	0.090	--	--	--
1,3-Diethylurea	0.139	0.127	0.089	0.070	0.065	0.064	0.064
1,3-Diethylthiourea <sup>c</sup>	0.139	0.100	--	--	--	--	--
Compounds applied from 95% ethyl alcohol solutions							
Butylurea <sup>d</sup>	0.122	0.100	0.086	--	--	--	--
1,1-Dibutylurea <sup>e</sup>	0.122	0.099	0.078	0.058	--	--	--
1,3-Dibutylurea <sup>f</sup>	0.122	0.087	--	--	--	--	--
Tetrabutylurea <sup>g</sup>	0.122	0.060	--	--	--	--	--
Sheets dried from pure compound							
Formamide	0.140 <sup>h</sup>	0.139	0.138	0.138	0.137	0.136	0.135
Dimethylformamide	0.123	0.115	0.112	0.111	0.110	0.110	0.108

<sup>a</sup>0.108 at 59 millimoles

<sup>b</sup>0.088 at 97 millimoles

<sup>c</sup>0.084 at 34 millimoles

<sup>d</sup>0.084 at 73 millimoles

<sup>e</sup>0.048 at 92 millimoles

<sup>f</sup>0.071 at 44 millimoles

<sup>g</sup>0.060 at 33 millimoles

<sup>h</sup>This value by extrapolation from 16 millimoles

TABLE XXIII

RELATIVE EFFICIENCIES OF VARIOUS COMPOUNDS  
IN REDUCING FINAL SLOPE ( $K_1$ )  
(Percentage of final slope of untreated sheet at 50% R.H.)

Additive Compound	Additive Content of Sheet, millimoles per 100 grams of oven-dry pulp						
	0	25	50	75	100	125	150
Compounds applied from aqueous solution							
Water	0	0	0	0	0	0.7	0.7
Urea	0	0.7	2.2	3.6	5.0	6.5	8.6
Thiourea	0	4.3	8.6	11.5	12.2	12.9	10.1
Methylurea	0	2.9	6.5	10.1	13.7	18.0	21.6
1,1-Dimethylurea	0	10.8	20.8	26.6	25.2	16.5	2.8
1,3-Dimethylurea	0	18.7	28.1	33.1	36.7	39.6	41.7
Tetramethylurea <sup>a</sup>	0	18.7	24.5	—	—	—	—
Ethylurea	0	28.8	32.4	33.8	33.1	—	—
1,1-Diethylurea <sup>b</sup>	0	20.9	32.4	40.3	—	—	—
1,3-Diethylurea	0	8.6	36.7	51.8	56.8	59.0	60.5
1,3-Diethylthiourea <sup>c</sup>	0	28.1	—	—	—	—	—
Compounds applied from 95% ethyl alcohol solutions							
Butylurea <sup>d</sup>	0	19.7	34.4	—	—	—	—
1,1-Dibutylurea <sup>e</sup>	0	34.4	55.7	72.6	—	—	—
1,3-Dibutylurea <sup>f</sup>	0	45.1	—	—	—	—	—
Tetrabutylurea <sup>g</sup>	0	50.8	—	—	—	—	—
Sheets dried from pure compound							
Formamide	0	1.4	2.1	2.9	3.6	4.3	5.0
Dimethylformamide	0	6.5	9.8	10.6	9.8	8.9	10.6

<sup>a</sup>23.0 at 59 millimoles

<sup>b</sup>43.9 at 97 millimoles

<sup>c</sup>40.3 at 34 millimoles

<sup>d</sup>41.8 at 73 millimoles

<sup>e</sup>89.3 at 92 millimoles

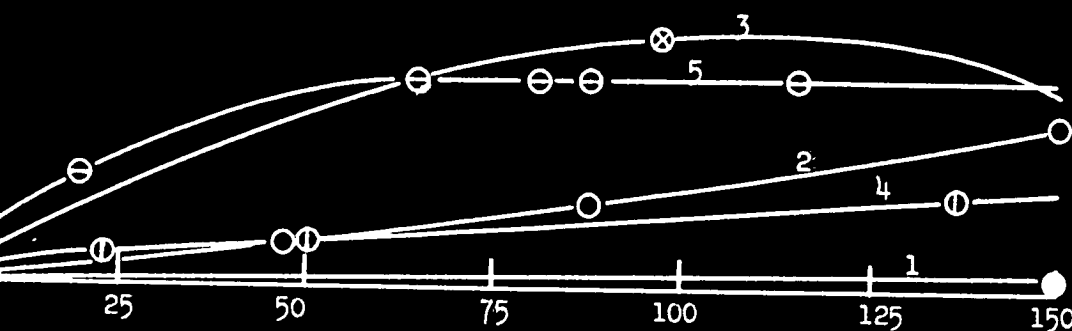
<sup>f</sup>61.5 at 44 millimoles

<sup>g</sup>50.8 at 33 millimoles

FIGURE 22

The Efficiency of the Lower-Molecular Weight Compounds in Reducing Final Slope

1. Water
2. Urea
3. Thiourea
4. Formamide
5. Dimethylformamide

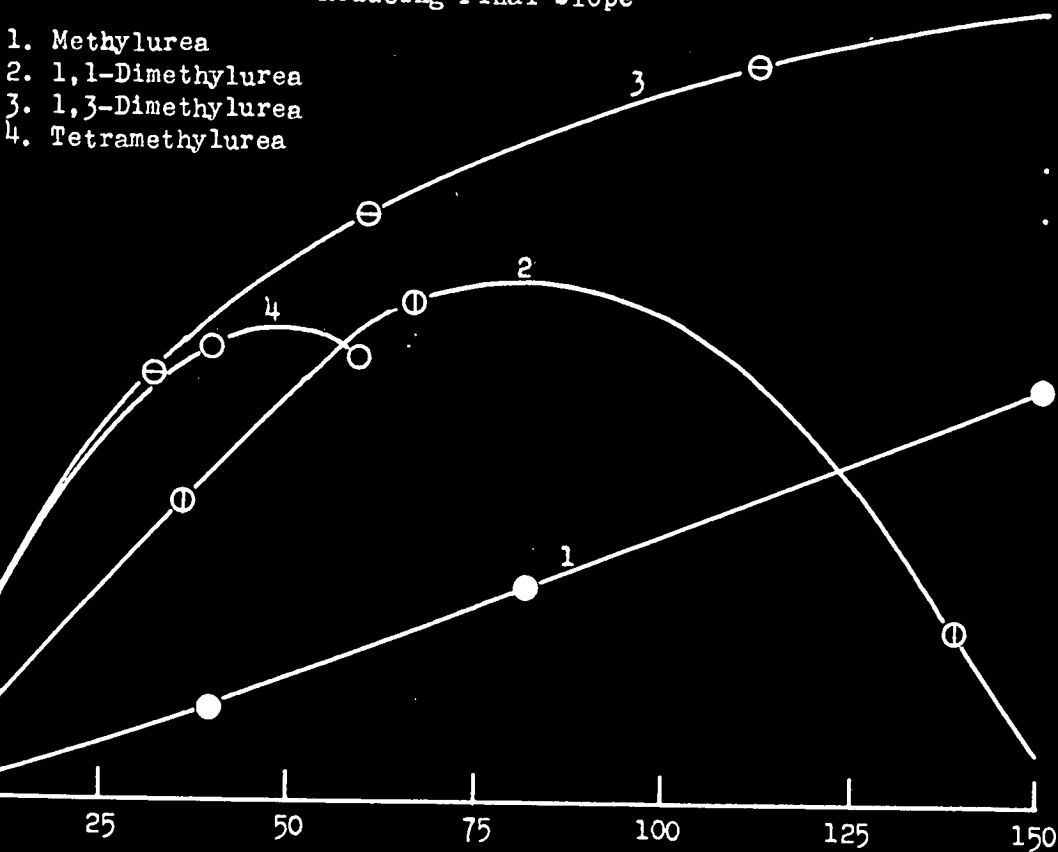


Additive content, millimoles/100 grams of oven-dry pulp

FIGURE 23

The Efficiency of the Methyl-substituted Compounds in Reducing Final Slope

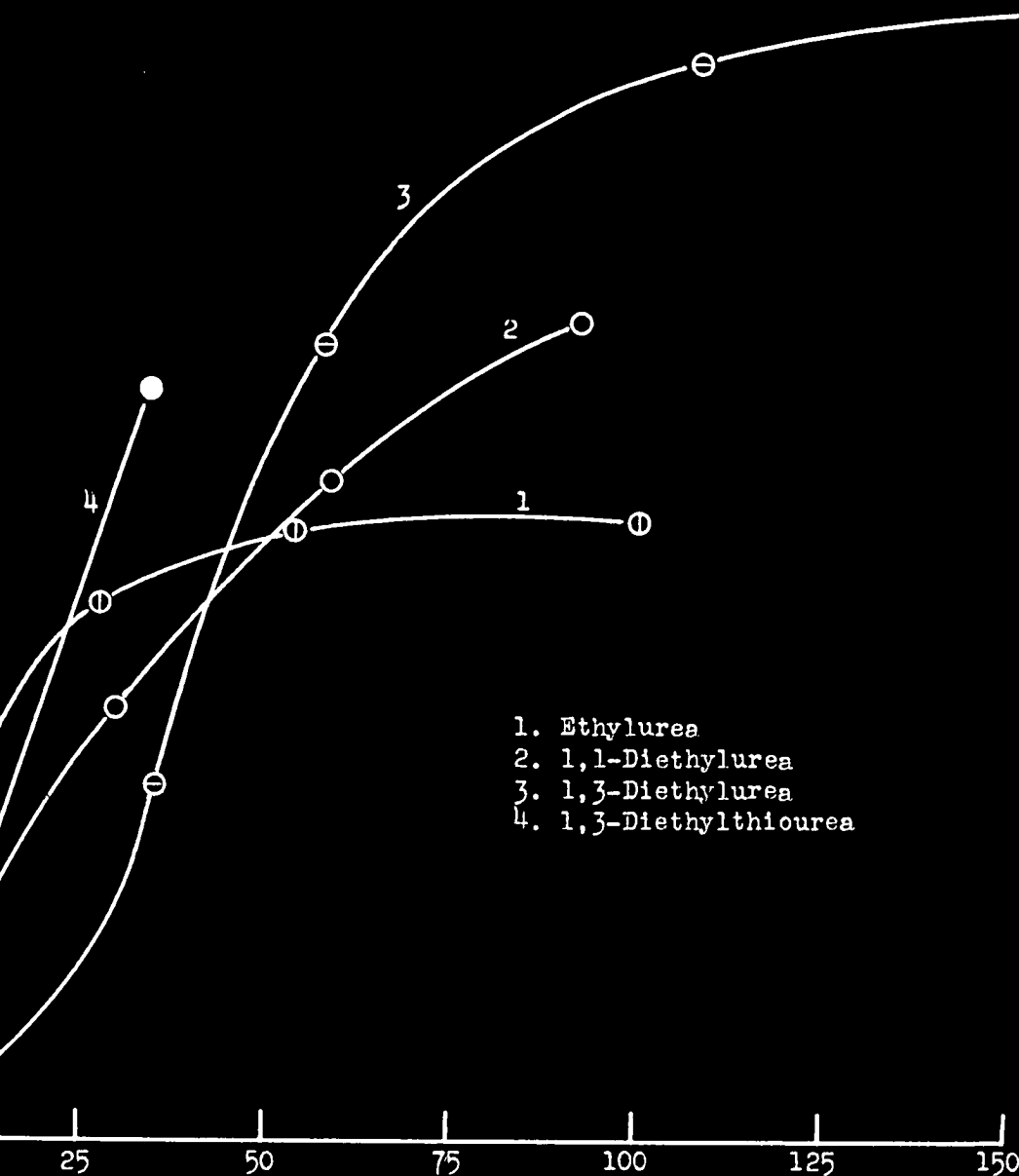
1. Methylurea
2. 1,1-Dimethylurea
3. 1,3-Dimethylurea
4. Tetramethylurea



Additive content, millimoles/100 grams of oven-dry pulp

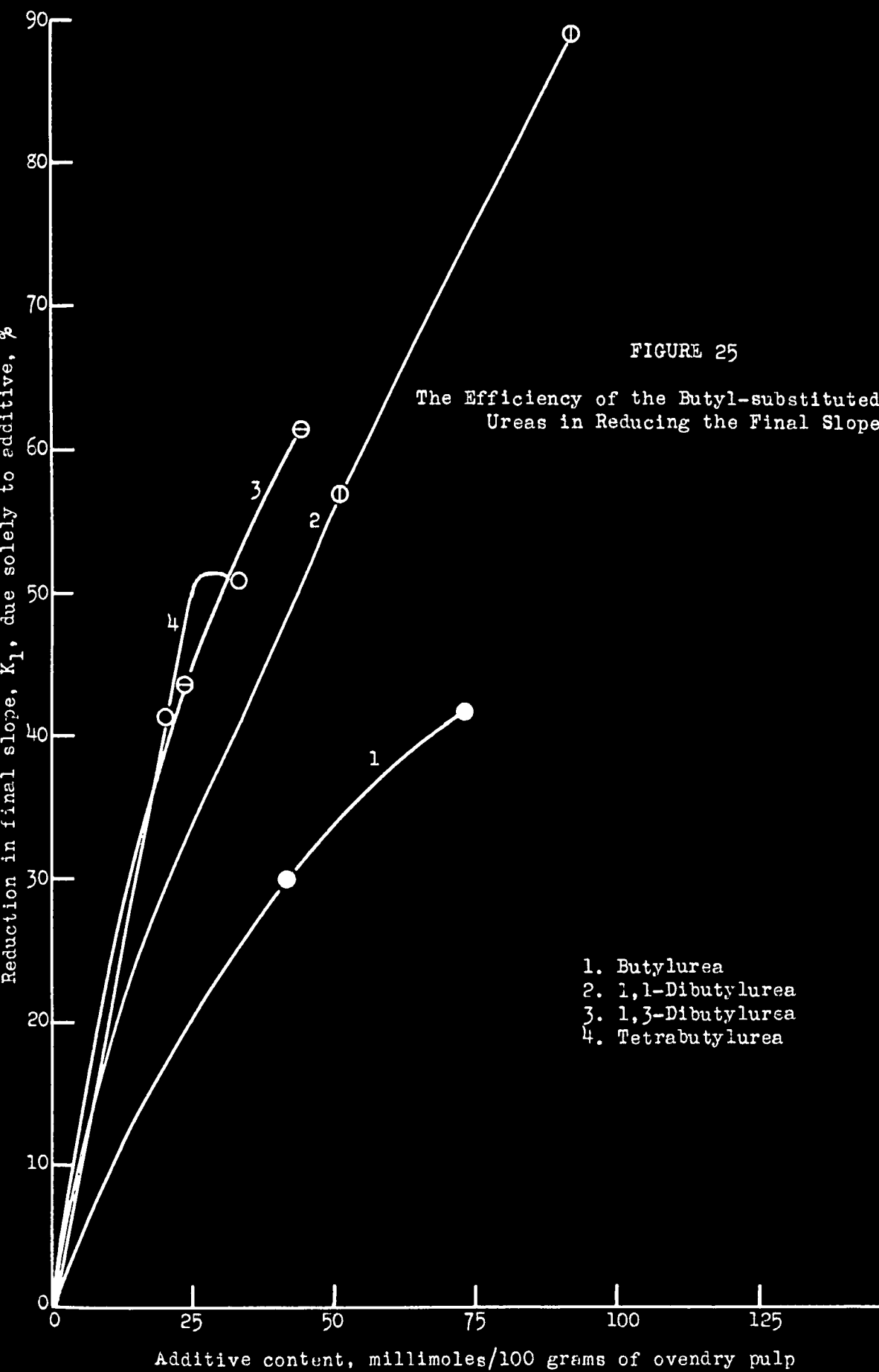
FIGURE 24

The Efficiency of the Ethyl-substituted Ureas in Reducing Final Slope



1. Ethylurea
2. 1,1-Diethylurea
3. 1,3-Diethylurea
4. 1,3-Diethylthiourea

Additive content, millimoles/100 grams of oven-dry pulp



The following points should be noted in connection with these data:

(1) Water had almost no effect on the final slope value when the baseline moisture content was taken to be 8%. The other small molecule additives are also seen from Figure 22 to have had little effect on this property. Among this group thiourea is surprisingly effective in view of its poor performance in reducing initial slope and tensile strength.

(2) The final slope value was even more sensitive to the effect of increasing substitution and increasing substituent size than were initial slope and tensile strength. The lower substituted ureas such as ethyl- and butylurea had fairly high final slope-reducing efficiencies at low concentrations, but an early maximum effect was indicated with increasing concentration. Likewise, the tetrasubstituted ureas, although they showed an initial high rate of reduction of final slope, lacked staying power as concentration increased and soon dropped off in effectiveness. The disubstituted ureas, on the other hand, although they exhibited somewhat less immediate effectiveness than the tetrasubstituted compounds, continued to reduce final slope as plasticizer concentration increased. The maximum reduction of final slope was attained by the dibutylureas.

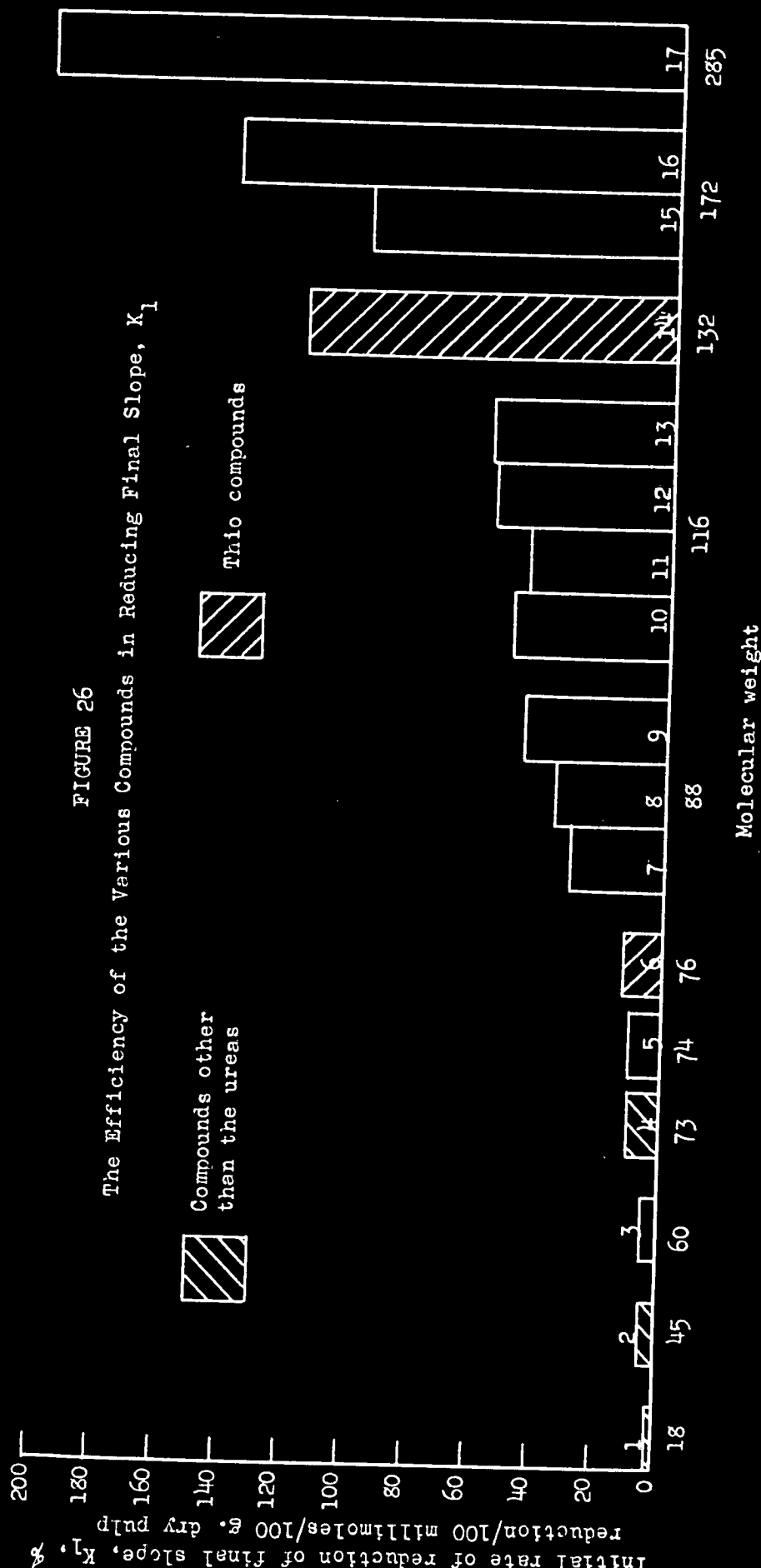
(3) Symmetrically substituted compounds clearly excelled the unsymmetrically substituted compounds in reducing final slope.

Figure 26 presents a comparison of the final slope-reducing efficiencies of the various compounds. It is immediately evident that the effect of molecular size on the final slope is very much greater than



FIGURE 26

The Efficiency of the Various Compounds in Reducing Final Slope,  $K_1$



- 1. Water
- 2. Formamide
- 3. Urea
- 4. Dimethylformamide
- 5. Methylurea
- 6. Thiourea
- 7. 1,1-Dimethylurea
- 8. 1,3-Dimethylurea
- 9. Ethylurea
- 10. Tetramethylurea
- 11. 1,1-Diethylurea
- 12. 1,3-Diethylurea
- 13. Butylurea
- 14. 1,3-Diethylthiourea
- 15. 1,1-Dibutylurea
- 16. 1,3-Dibutylurea
- 17. Tetramethylurea

it is on either the tensile strength or the initial slope. An approximate fortyfold increase in initial rate of reduction of final slope was shown when the urea molecule was completely substituted with butyl groups. The effect of the larger molecular volume of the symmetrically substituted compounds as compared to the unsymmetrically substituted compounds is clearly shown by the differences in the efficiencies of these compounds in reducing final slope. It may be concluded, therefore, that the final slope value is extremely sensitive to the molecular size of the additive. It is seemingly less dependent on the swelling or penetrating powers of the additive molecule than are the initial slope or  $K_2$ , since increasing the molecular size increases both the initial effectiveness of an additive and its maximum attainable effectiveness in reducing  $K_1$ .

#### THE EFFECT OF THE ADDITIVES ON THE SERIES SPRING CONSTANT, $K_2$

The value of the series spring constant,  $K_2$ , is the difference between the initial slope and the final slope. Since the absolute value of the final slope is generally about one tenth that of the initial slope, changes in the  $K_2$  value largely control the behavior of the initial slope. The values for  $K_2$  of the various treated sheets are tabulated in Table XXIV. The percentage reduction in  $K_2$  at various additive contents corrected for the moisture effect appears in Table XXV and is graphically presented in Figures 27-30. The same trends were found to hold for  $K_2$  that were observed in the initial slope data:

(1) The smaller molecular weight compounds had a relatively slow rate of  $K_2$  reduction. As the molecule was increasingly substituted, the rate of decrease of  $K_2$  per mole of additive increased. A high degree of substitution or the substitution of several large groups on the additive molecule markedly increased this initial rate of  $K_2$  reduction per molar unit of additive.

(2) At the same time this increase in molecular size definitely lowered the maximum reduction of  $K_2$  of which the compound was capable, and caused this maximum to occur at a lower molar additive content. Molecules of the molecular-weight range of 70-90, such as dimethylformamide, methylurea, and 1,3-dimethylurea seemed to have a maximum  $K_2$ -reducing ability.

Figure 31 compares the efficiency of the various compounds in reducing  $K_2$ . Very nearly the same figure could be drawn for the initial slope-reducing efficiencies of the compounds. The effect of increasing molecular size, although still evident, is very much less striking than was the case with the final slope,  $K_1$ . If the tetrasubstituted ureas are excluded, it seems that the efficiency of  $K_2$ -reduction is the greatest at an intermediate molecular weight. Strong indications were found that the maximum  $K_2$  reduction of which the material was capable also would be the greatest for these medium-molecular weight materials.

A study of Figure 31 leads to the conclusion that the swelling power or penetrating ability of the compound is of importance to its  $K_2$ -reducing ability. The formamides, for example, are known to excel in swelling ability and are found to be more active in reducing  $K_2$  than would

TABLE XXIV

SERIES SPRING CONSTANT ( $K_2$ ) VALUES OF THE TREATED SHEETS  
(Pounds per mil)

Additive Compound	Additive Content of Sheet, millimoles per 100 grams of oven-dry pulp						
	0	25	50	75	100	125	150
Compounds applied from aqueous solution							
Water	1.33	1.29	1.24	1.19	1.13	1.09	1.02
Urea	1.33	1.30	1.27	1.21	1.15	1.07	0.98
Thiourea	1.33	1.34	1.35	1.35	1.35	1.33	1.30
Methylurea	1.33	1.28	1.22	1.16	1.06	0.92	0.72
1,1-Dimethylurea	1.33	1.26	1.16	1.04	0.98	1.01	1.10
1,3-Dimethylurea	1.33	1.23	1.15	1.06	0.98	0.88	0.81
Tetramethylurea <sup>a</sup>	1.33	1.03	0.85	--	--	--	--
Ethylurea	1.33	1.24	1.11	0.97	0.83	--	--
1,1-Diethylurea <sup>b</sup>	1.33	1.33	1.21	1.03	--	--	--
1,3-Diethylurea	1.33	1.27	1.22	1.12	0.90	0.75	0.78
1,3-Diethylthiourea <sup>c</sup>	1.33	1.30	--	--	--	--	--
Compounds applied from 95% ethyl alcohol solutions							
Butylurea <sup>d</sup>	1.29	1.30	1.25	--	--	--	--
1,1-Dibutylurea <sup>e</sup>	1.29	1.20	1.12	1.06	--	--	--
1,3-Dibutylurea <sup>f</sup>	1.29	1.24	--	--	--	--	--
Tetrabutylurea <sup>g</sup>	1.29	0.98	--	--	--	--	--
Sheets dried from pure compound							
Formamide	1.32 <sup>h</sup>	1.26	1.19	1.12	1.06	0.99	0.92
Dimethylformamide	1.20	0.94	0.84	0.74	0.64	0.54	0.44

<sup>a</sup>0.81 at 59 millimoles

<sup>b</sup>0.83 at 97 millimoles

<sup>c</sup>1.28 at 34 millimoles

<sup>d</sup>1.11 at 73 millimoles

<sup>e</sup>1.05 at 92 millimoles

<sup>f</sup>1.19 at 44 millimoles

<sup>g</sup>1.06 at 33 millimoles

<sup>h</sup>This value by extrapolation from 16 millimoles

TABLE XXV

RELATIVE EFFICIENCIES OF VARIOUS COMPOUNDS IN REDUCING  
THE SERIES SPRING CONSTANT ( $K_2$ )  
(Percentage of  $K_2$  of untreated sheet at 50% R.H.)

Additive Compound	Additive Content of Sheet, millimoles per 100 grams of oven-dry pulp						
	0	25	50	75	100	125	150
Compounds applied from aqueous solution							
Water	0	3.1	7.1	10.9	15.3	18.4	23.6
Urea	0	5.9	10.8	15.5	21.1	26.9	33.9
Thiourea	0	3.7	5.1	5.7	6.4	7.5	9.7
Methylurea	0	7.3	13.5	19.3	27.2	37.4	52.6
1,1-Dimethylurea	0	8.4	18.3	18.3	33.1	30.5	23.2
1,3-Dimethylurea	0	13.2	20.8	27.1	33.4	41.3	46.0
Tetramethylurea <sup>a</sup>	0	24.1	41.1	--	--	--	--
Ethylurea	0	8.4	21.3	33.2	44.1	--	--
1,1-Diethylurea <sup>b</sup>	0	5.0	15.3	29.7	--	--	--
1,3-Diethylurea	0	8.3	13.5	21.8	39.5	50.7	48.7
1,3-Diethylthiourea <sup>c</sup>	0	5.9	--	--	--	--	--
Compounds applied from 95% ethyl alcohol solutions							
Butylurea <sup>d</sup>	0	3.7	9.8	--	--	--	--
1,1-Dibutylurea <sup>e</sup>	0	11.8	19.4	24.7	--	--	--
1,3-Dibutylurea <sup>f</sup>	0	9.8	--	--	--	--	--
Tetrabutylurea <sup>g</sup>	0	26.7	--	--	--	--	--
Sheets dried from pure compound							
Formamide	0	6.4	11.8	16.8	21.9	26.9	31.9
Dimethylformamide	0	20.8	30.5	38.1	45.7	51.9	56.6

<sup>a</sup>45.4 at 59 millimoles

<sup>b</sup>45.3 at 97 millimoles

<sup>c</sup>8.0 at 34 millimoles

<sup>d</sup>20.8 at 73 millimoles

<sup>e</sup>26.0 at 92 millimoles

<sup>f</sup>14.3 at 44 millimoles

<sup>g</sup>20.2 at 33 millimoles

FIGURE 27

The Efficiency of the Lower-Molecular Weight Compounds in Reducing the Series Spring Constant,  $K_2$

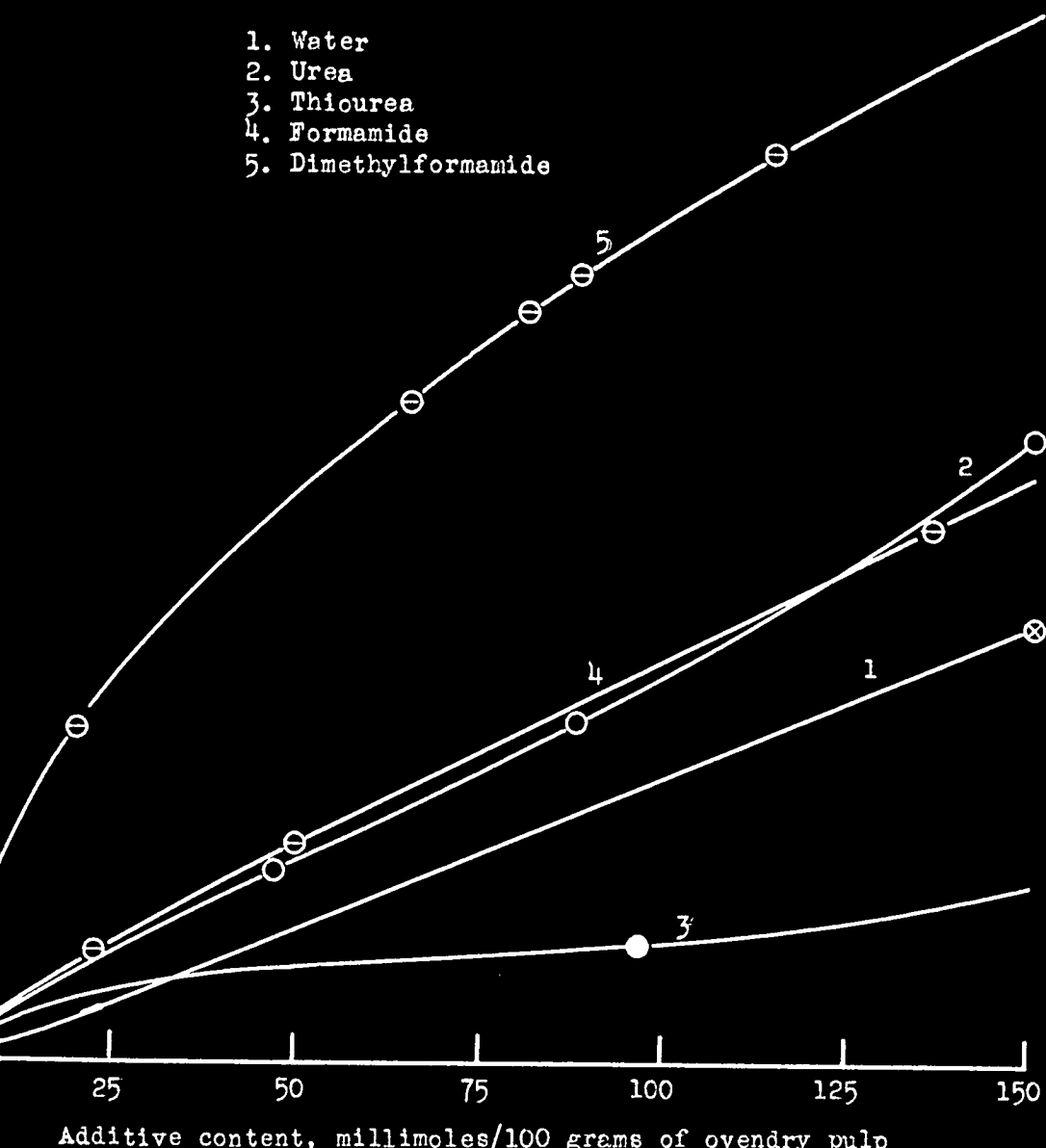


FIGURE 28

The Efficiency of the Methyl-substituted Urees in Reducing  
the Series Spring Constant,  $K_2$

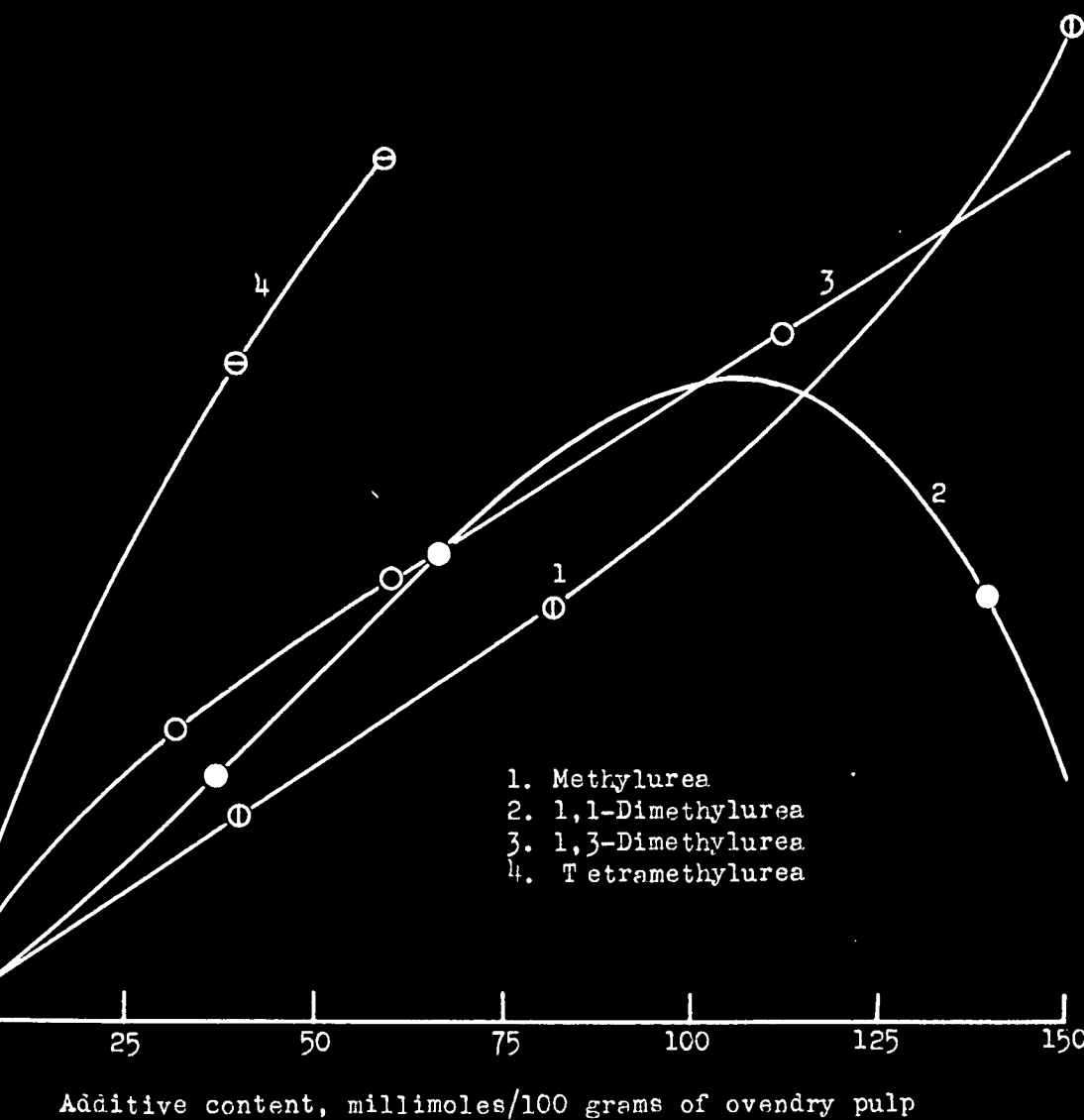


FIGURE 29

The Efficiency of the Ethyl-substituted Ureas in Reducing the Series Spring Constant,  $K_2$

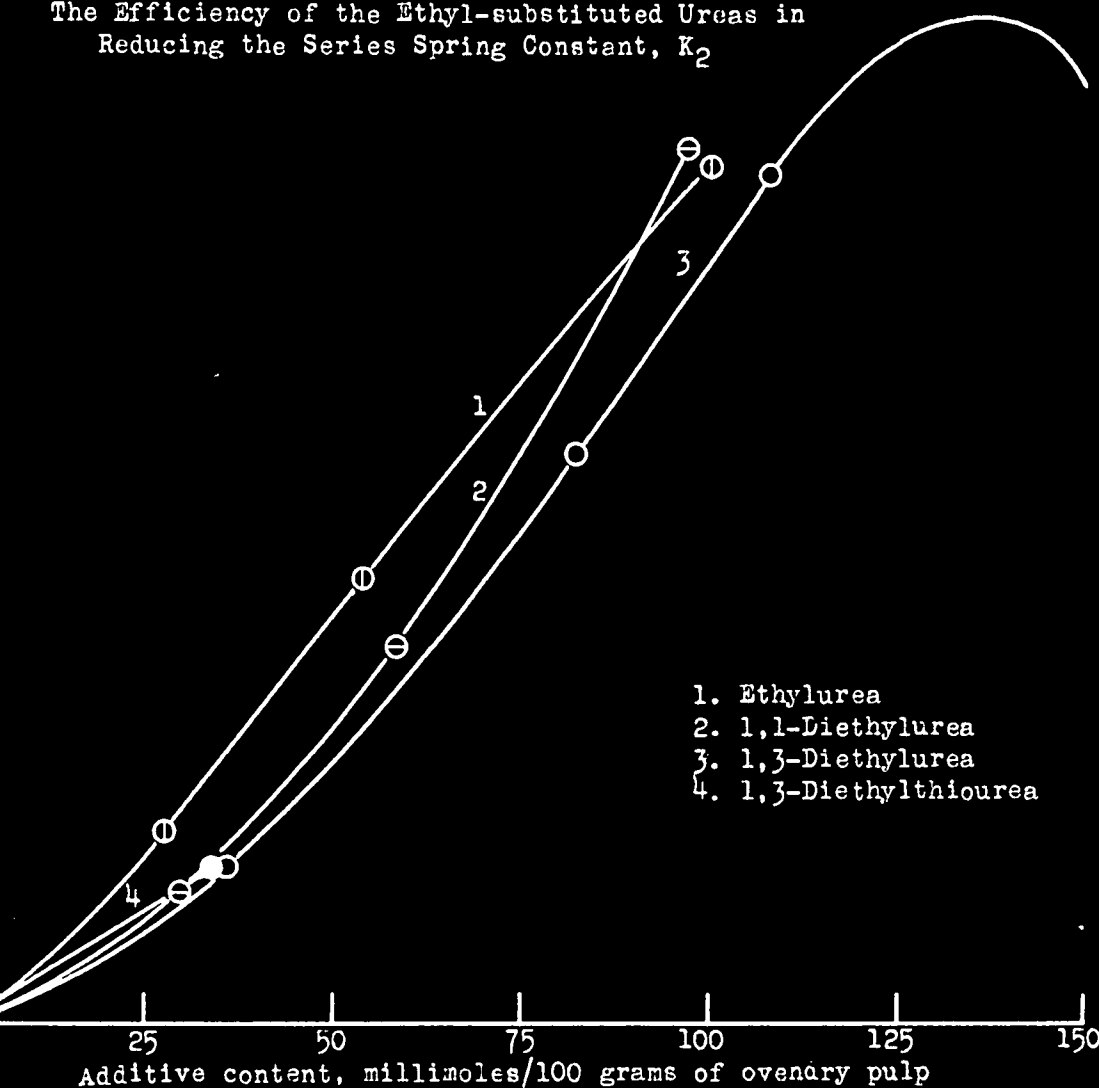


FIGURE 30

The Efficiency of the Butyl-substituted Ureas in Reducing the Series Spring Constant,  $K_2$

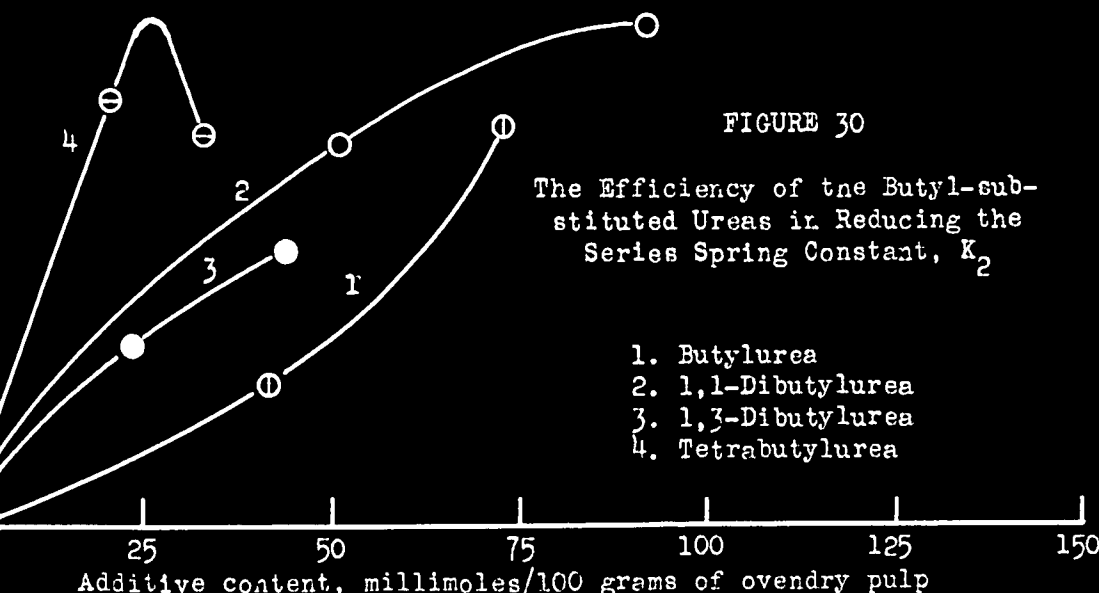
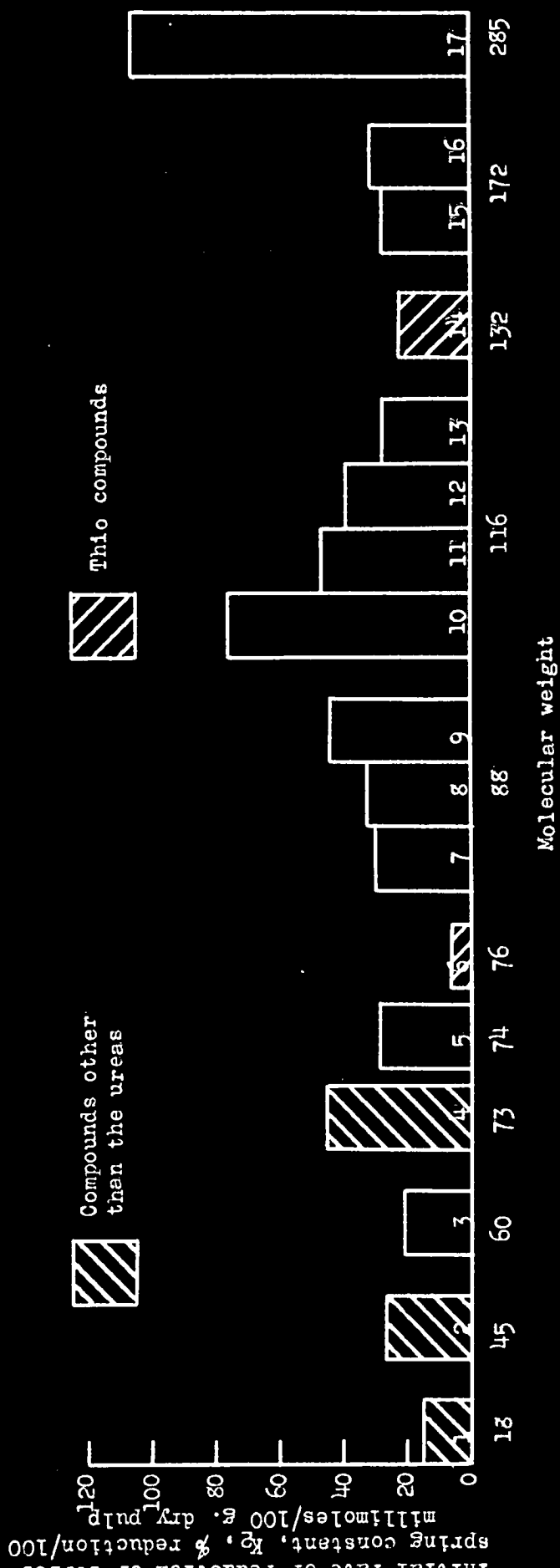




FIGURE 31

The Efficiency of the Various Compounds in Reducing the Series Spring Constant,  $K_2$



- |                      |                     |                         |
|----------------------|---------------------|-------------------------|
| 1. Water             | 7. 1,1-Dimethylurea | 12. 1,3-Diethylurea     |
| 2. Formamide         | 8. 1,3-Dimethylurea | 13. Butylurea           |
| 3. Urea              | 9. Ethylurea        | 14. 1,3-Diethylthiourea |
| 4. Dimethylformamide | 10. Tetramethylurea | 15. 1,1-Dibutylurea     |
| 5. Methylurea        | 11. 1,1-Diethylurea | 16. 1,3-Dibutylurea     |
| 6. Thiourea          |                     | 17. Tetrabutylurea      |

be expected on the basis of their molecular size alone. The thioureas, on the other hand, are probably less effective cellulose-swelling agents than their corresponding oxygen compounds. Their poor  $K_2$ -reducing powers may stem from this fact. The inability of the larger molecules to increase the swelling of the cellulose, or to penetrate into a pre-swollen cellulose structure may account for the fact that beyond a point, increasing molecular weight has little effect on the  $K_2$ -reducing efficiency of the molecule. It is not difficult to conceive of an optimum molecular weight at which the best balance is obtained between the ability of a molecule to enter the cellulose structure, and its effectiveness in maintaining dry-swelling once it has been able to enter. Molecular size would reduce penetrating ability of the material, but it would be important to its effectiveness once penetration had been accomplished.

#### THE EFFECT OF THE ADDITIVES ON THE $Q$ RATIO

The  $Q$  ratio is defined as the ratio of the final slope to the initial slope. Eyring and Halsey (49) found that the  $Q$  value for rayon was an excellent index of orientation. Highly oriented rayon was found to have a  $Q$  value of about 0.5, whereas high extensibility rayons had  $Q$  values approaching zero. In speaking of paper, Ivarsson and Steenberg (52) have noted, " $Q$  is a measure of the orientation in the material. A large value of  $Q$  will mean a high degree of orientation." Table XXVI shows the  $Q$  values of the various treated sheets. It seems obvious from the wide variation in  $Q$  that  $Q$  bears no direct relationship to the degree of plasticizing of a sheet. In view of the complexity of paper, it seems very dubious whether  $Q$  has any actual significance as a measure of orientation for paper.

TABLE XXVI

Q VALUES OF THE TREATED SHEETS

Additive Compound	Additive Content of Sheet, millimoles per 100 grams of oven-dry pulp						
	0	25	50	75	100	125	150
Compounds applied from aqueous solution							
Water	0.095	0.097	0.101	0.105	0.110	0.114	0.120
Urea	0.095	0.096	0.098	0.102	0.107	0.113	0.120
Thiourea	0.095	0.091	0.089	0.087	0.087	0.089	0.093
Methylurea	0.095	0.096	0.098	0.100	0.105	0.114	0.136
1,1-Dimethylurea	0.095	0.090	0.087	0.092	0.099	0.106	0.112
1,3-Dimethylurea	0.095	0.085	0.084	0.085	0.087	0.091	0.097
Tetramethylurea <sup>a</sup>	0.095	0.099	0.111	--	--	--	--
Ethylurea	0.095	0.074	0.079	0.089	0.104	--	--
1,1-Diethylurea <sup>b</sup>	0.095	0.077	0.075	0.080	--	--	--
1,3-Diethylurea	0.095	0.091	0.068	0.059	0.068	0.078	0.076
1,3-Diethylthiourea <sup>c</sup>	0.095	0.072	--	--	--	--	--
Compounds applied from 95% ethyl alcohol solutions							
Butylurea <sup>d</sup>	0.086	0.071	0.064	--	--	--	--
1,1-Dibutylurea <sup>e</sup>	0.086	0.076	0.065	0.052	--	--	--
1,3-Dibutylurea <sup>f</sup>	0.086	0.066	--	--	--	--	--
Tetrabutylurea <sup>g</sup>	0.086	0.058	--	--	--	--	--
Sheets dried from pure compound							
Formamide	0.096 <sup>h</sup>	0.100	0.104	0.109	0.115	0.121	0.128
Dimethylformamide	0.093	0.109	0.118	0.130	0.147	0.171	0.198

<sup>a</sup>0.117 at 59 millimoles

<sup>b</sup>0.096 at 97 millimoles

<sup>c</sup>0.062 at 34 millimoles

<sup>d</sup>0.070 at 73 millimoles

<sup>e</sup>0.044 at 92 millimoles

<sup>f</sup>0.056 at 44 millimoles

<sup>g</sup>0.054 at 33 millimoles

<sup>h</sup>This value by extrapolation from 16 millimoles

However, it is possible that the behavior of  $Q$ , shown in Table XXVI, may shed some light on the fundamental significance of the spring constants,  $K_1$  and  $K_2$ . In this connection the ratio  $K_1/K_2$  was calculated for the data represented in Table XXVI, and it was found that this ratio increases and decreases with  $Q$  at all times.

The behavior pattern for  $Q$  has been analysed in Table XXVII. In this table the molar additive content range during which a particular behavior obtained has been noted in each column. Some additional data for additive concentrations above the 150 millimoles per 100 grams of pulp limit of the other tables have been included in this table.

As a result of study of Table XXVII and a general consideration of the results of the whole investigation, it seems reasonable to advance a hypothesis concerning the nature of spring constants  $K_1$  and  $K_2$ .  $K_1$  and  $K_2$  are closely related to the elasticity of both the fiber-to-fiber bonds and fibers themselves. Although any changes in the sheet which affect the elastic characteristics of either the bonded zones or the fibers will undoubtedly be reflected in both  $K_1$  and  $K_2$ , it is reasonable to assume that one of the spring constants will be relatively more sensitive to changes in bonding strength than the other. Bearing in mind the fact that both constants are probably affected by any changes in the sheet, let us advance the hypothesis that the spring constant  $K_1$  is affected relatively more by changes in the elastic properties of the bonded zone than is  $K_2$ , and that, conversely,  $K_2$  is more sensitive to changes in fiber elasticity than is  $K_1$ .

TABLE XXVII

THE BEHAVIOR OF  $Q$   
(Values indicate range in which behavior occurred  
in millimoles/100 g. dry pulp)

	1	2	3	4	5	6	7	8
	$K_1$ Con- stant, $K_2$ In- creases	$Q$ Value In- creases faster than $K_1$	$Q$ Value Decreases $K_1$ De- creases faster than $K_2$	$K_1$ De- creases $K_2$ In- creases	$K_1$ Con- stant $K_2$ De- creases	$Q$ Value In- creases faster than $K_2$	$Q$ Value Increases $K_2$ De- creases faster than $K_1$	$K_2$ De- creases $K_1$ In- creases
Water								
Urea		350-400				320-350 400-450	0-400 0-320	
Formamide							0-400 0-400	
Dimethylformamide								100-200
Thiourea				0-100				
Methylurea							0-150	
1,3-Dimethylurea			0-50 300-350				50-300	350-400
1,1-Dimethylurea			0-50			100-174	50-75	75-100
Tetramethylurea							0-50	50-59

[Continued on next page]

TABLE XXVII (Cont.)

THE BEHAVIOR OF  $Q$   
(Values indicate range in which behavior occurred  
in millimoles/100 g. dry pulp)

	1	2	3	4	5	6	7	8
	$K_1$ Con- stant, $K_2$ In- creases	$Q$ Value In- creases faster than $K_1$	$Q$ Value Decreases $K_1$ De- creases faster than $K_2$	$K_1$ De- creases $K_2$ In- creases	$K_1$ Con- stant $K_2$ De- creases	$Q$ Value In- creases faster than $K_2$	$Q$ Value In- creases faster than $K_1$	$K_2$ De- creases $K_1$ In- creases
Ethylurea								
1,1-Diethylurea			0-25				25-75	75-100
1,3-Diethylurea	125-172		0-75				50-97	
1,3-Diethylthiourea			0-34				75-125	
Butylurea			0-50					
1,1-Dibutylurea			0-92					
1,3-Dibutylurea			0-44					
Tetrabutylurea	25-33		0-25				50-73	

The following shreds of indirect evidence tend to support this hypothesis:

(1) Table XXVII shows that the lower-molecular weight, more polar, more hydrophilic compounds tend to reduce  $K_2$  faster than  $K_1$  when they are incorporated in a sheet of paper ( $Q$  value in Column 7). On the other hand, as the molecule becomes less polar, more hydrophobic, and water-insoluble, it tends to reduce  $K_1$  very much faster than  $K_2$  ( $Q$  value falls in Column 3). This change in the relative effect on the two spring constants with increasing molecular size and decreasing polarity is believed to be of considerable significance. The large butyl-substituted ureas were, of necessity, applied to the sheet from alcohol since their nonpolar nature rendered them insoluble in water. Since alcohol itself is known to have poor cellulose-swelling powers, and since in view of their size and their largely hydrocarbon nature, these butyl-substituted ureas could hardly be expected to have cellulose swelling properties of their own, it is reasonable to assume that they were largely held on the surface of the cellulose fibers. Consequently, they must have exerted a disproportionately large effect on the bonding zones relative to the fibers. Since  $K_1$  decreases much faster than  $K_2$  when these compounds are incorporated in a sheet, it seems logical to conclude that  $K_1$  is more sensitive than  $K_2$  to changes in the fiber-to-fiber bonds.

(2) In contrast, the lower-molecular weight additives such as water, formamide, and the like have swelling properties which readily enable them to penetrate the fibers and to keep them in a state of dry swelling.

If, therefore, these compounds decrease  $K_2$  at a greater rate than  $K_1$ , it may be inferred that  $K_2$  is somewhat more sensitive to changes in fiber flexibility than  $K_1$ . That, of course, is not to say that the known effect of these compounds on the fiber-to-fiber bonds does not account for a large part of the reduction in  $K_2$ .

(3) The medium-molecular weight compounds in the middle of Table XXVII were applied from aqueous solutions. These compounds show an initial tendency to reduce  $K_1$  more than  $K_2$ . At higher concentrations they tend to reverse this order and reduce  $K_2$  more than  $K_1$ . It may be presumed that these compounds initially reduce fiber-to-fiber bonding strength more than intrafiber bonding strength. As the molecular concentration increases, a greater number of molecules penetrate the fibrous structure to reduce intrafiber secondary bonding forces. In this second phase the effect on fiber stiffness is more pronounced than the effect on fiber-to-fiber bonding strength. If this line of reasoning is correct, it supports the hypothesis advanced above.

(4) The accessibility of the bonded zone to additive molecules must be considerably higher than the accessibility of the amorphous portions of the fiber. The swelling ability of a molecule or its ability to penetrate a cellulosic structure would therefore be of less importance in altering the elastic properties of the bonded zone than in altering the elastic properties of the fiber. Hence, the fact that a continued increase in molecular size did not limit the ability of a material to reduce  $K_1$  more rapidly and more completely, constitutes indirect evidence that  $K_1$  is sensitive to the changes in fiber-to-fiber bonds. Molecular



size, however, did prove to limit both the efficiency and the maximum effectiveness which a compound had in reducing  $K_2$ . It may be supposed that fiber penetration difficulties at high molecular weights caused this limitation, and therefore that  $K_2$  is somewhat more sensitive to the flexibilizing of the fibers.

Furthermore, the formamides proved to be more effective in reducing  $K_2$  than would have been predicted from their molecular weight alone. This was explained as being due to their greater swelling powers-- and again may be interpreted to mean that penetration or swelling of the fibers is essential to a high rate of  $K_2$  reduction. This can only mean that  $K_2$  is affected by changes in fiber stiffness to a greater extent than  $K_1$ .

Both of the thioureas had a greater  $K_1$ -reducing efficiency than was normal for their oxygen analogs. The introduction of sulfur into the urea molecule has been presumed to decrease its swelling powers in the same way that it decreases its solubility. Therefore, at a given concentration of additive, probably more of the thio compounds was concentrated on the fiber surfaces than would normally have been the case with the ureas. Hence they might be expected to exhibit an extraordinary effect on bonding strength. The fact that  $K_1$  reflected this state of affairs constitutes evidence in support of the hypothesis.

(5) When excess additive in a sheet tends to crystallize, tensile strength and elastic moduli tend to increase. In order to increase the tensile strength of a sheet that is relatively weak due to plasticizer

action, this crystallization must occur in such a way as to reinforce the fiber-to-fiber bonds. At the point where the sheet tensile strength and elastic moduli start to increase, the behavior of  $Q$  in Table XXVII is found to shift from Column 7 to Column 8 or Column 6. This shift either means that  $K_1$  starts to increase before  $K_2$  stops decreasing (Column 8), or it means that  $K_1$  increases at a more rapid rate than  $K_2$  (Column 6). If the effect of crystallization is the greatest on the fiber-to-fiber bonds, then this relationship between the behavior of  $K_1$  and the strengthening of the bonds again suggests the greater sensitivity of  $K_1$  to changes in bonding strength.

(6) At low relative humidities the structure of a sheet of paper must be rather well-frozen. Fibers are held rigid by strong intermolecular secondary forces, and tend to resist flexure of any kind. Likewise the bonds are strong and rigid. When such a sheet is strained, there will be a rapid rise in stress as the structure is elastically strained, followed by the onset of plastic flow at a relatively high stress. Failure occurs soon after the start of plastic flow, indicating that the rigidity of the fiber-to-fiber bonds eliminates the possibility of much extension. The LE curve for such a sheet shows an almost complete lack of a final linear portion because of the inability of the sheet to flow. Under these conditions it would seem that, as a result of their greater accessibility, the fiber-to-fiber bonds would be more affected by small amounts of a plasticizer than would the fibers. If this is true, then the fact that at low humidities the  $K_1$  value is more sensitive to the effect of moisture content changes than  $K_2$  indicates the closer relationship of  $K_1$  to bonding strength. Likewise, the fact that  $K_1$  was very much more affected by plasti-

cizing at 11% R.H. than at 50% R.H. would further support the hypothesis that  $K_1$  is sensitive to changes in bonding strength.

(7) The differences in the mechanical properties of sheets dried from water, alcohol, and dimethylformamide must be largely due to differences in the fiber-to-fiber bonding. Fiber stiffness would not be expected to be influenced nearly as much as bonding strength by the media from which a sheet is dried. The fact that  $K_1$  is more affected by a change of the liquid from which a sheet is dried than is  $K_2$  is further evidence in support of the hypothesis.

The results of relieving frozen-in stresses are probably largely attributable to changes which have occurred in the fiber-to-fiber bonds, since a mere humidification-dehumidification process would not be expected to change greatly fiber properties. The hypothesis advanced above would therefore predict that stress relief would bring about a greater change in  $K_1$  than in  $K_2$ . This was found to be the case when both formamide (Table XV) and water (Figures 7 and 8) were used as the stress-relieving agents.

(8) It was found in Table XIII that the changes in the bonding strength factor could adequately explain changes in  $K_1$ , but that they were insufficient to account for changes in  $K_2$ . In other words, there were strong indications that some factor other than bonding strength was of equal or greater importance in causing changes in  $K_2$ , whereas there were no indications that this was true for  $K_1$ . This is another point of evidence in support of the hypothesis.

On the other hand there is some evidence from which it could be inferred that the opposite of the hypothesis is true. Figure 7 showed that  $K_1$  was highly insensitive to moisture content changes in the general moisture content range of 7-13%. Since one would logically expect the elastic characteristics of the fibers to be less affected by moisture content changes than the elastic properties of the bonds, this evidence tends to contradict the hypothesis advanced above.

#### THE EFFECT OF THE ADDITIVES ON THE LIMITING VISCOUS LOAD VALUE, $\bar{f}$

The  $\bar{f}$  values for the various treated sheets are tabulated in Table XXVIII, and the percentage reduction in  $\bar{f}$  data, with the moisture effect excluded, are presented in Table XXIX. The data of Table XXIX are graphically presented in Figures 32-35.

The following should be noted from these data:

(1) The trends established in the previous discussions of tensile strength and the elastic constants continue to hold true for the  $\bar{f}$  value. Water was the least effective compound in reducing  $\bar{f}$ . The thioureas were slightly less effective than the corresponding ureas.

(2) As before, the higher the degree of substitution, the more effective was the material in reducing  $\bar{f}$ . In general, an increase in the molecular size increased the effectiveness of the material. However, the dibutylureas were quite similar to the diethylureas in their efficiency. Except in the case of the diethylureas, symmetrical substitution was more effective than unsymmetrical substitution.

TABLE XXVIII

1 VALUE OF THE TREATED SHEETS  
(Pounds)

Additive Compound	Additive Content of Sheet, millimoles per 100 grams of oven-dry pulp						
	0	25	50	75	100	125	150
Compounds applied from aqueous solution							
Water	17.7	17.0	16.2	15.6	14.8	14.2	13.5
Urea	17.7	16.8	16.1	15.3	14.4	13.5	12.6
Thiourea	17.7	17.4	17.1	16.8	16.6	16.3	16.0
Methylurea	17.7	17.4	16.7	15.6	14.2	12.3	10.0
1,1-Dimethylurea	17.7	15.6	14.2	13.5	13.3	13.4	13.7
1,3-Dimethylurea	17.7	15.7	14.5	13.6	12.5	11.6	10.5
Tetramethylurea <sup>a</sup>	17.7	13.5	11.4	--	--	--	--
Ethylurea	17.7	16.2	14.7	13.2	11.7	--	--
1,1-Diethylurea <sup>b</sup>	17.7	16.9	14.4	11.8	--	--	--
1,3-Diethylurea	17.7	15.0	13.4	12.0	10.9	10.0	9.3
1,3-Diethylthiourea <sup>c</sup>	17.7	16.2	--	--	--	--	--
Compounds applied from 95% ethyl alcohol solutions							
Butylurea <sup>d</sup>	15.9	15.6	14.6	--	--	--	--
1,1-Dibutylurea <sup>e</sup>	15.9	15.6	14.8	12.9	--	--	--
1,3-Dibutylurea <sup>f</sup>	15.9	15.8	--	--	--	--	--
Tetrabutylurea <sup>g</sup>	15.9	10.0	--	--	--	--	--
Sheets dried from pure compound							
Formamide	18.4 <sup>h</sup>	17.6	16.8	16.0	15.2	14.4	13.6
Dimethylformamide	16.4	12.7	11.5	10.2	9.0	7.8	6.6

<sup>a</sup>10.9 at 59 millimoles

<sup>b</sup>9.5 at 97 millimoles

<sup>c</sup>15.6 at 34 millimoles

<sup>d</sup>12.7 at 73 millimoles

<sup>e</sup>11.0 at 92 millimoles

<sup>f</sup>14.3 at 44 millimoles

<sup>g</sup>10.2 at 33 millimoles

<sup>h</sup>This value by extrapolation from 16 millimoles

TABLE XXIX

RELATIVE EFFICIENCIES OF VARIOUS COMPOUNDS  
IN REDUCING THE  $\zeta$  VALUE  
(Percentage of  $\zeta$  value of untreated sheets at 50% R.H.)

Additive Compound	Additive Content of Sheet, millimoles per 100 grams of oven-dry pulp						
	0	25	50	75	100	125	150
Compounds applied from aqueous solution							
Water	0	4.0	8.5	11.9	16.4	19.8	23.7
Urea	0	13.0	22.6	31.6	38.4	44.6	49.7
Thiourea	0	11.9	20.9	26.6	29.9	33.3	35.6
Methylurea	0	9.0	17.5	27.7	37.8	49.1	63.3
1,1-Dimethylurea	0	17.5	31.6	39.5	41.2	40.1	36.7
1,3-Dimethylurea	0	24.3	37.9	44.1	50.3	55.9	61.6
Tetramethylurea <sup>a</sup>	0	27.1	42.9	--	--	--	--
Ethylurea	0	11.9	26.0	40.1	52.0	--	--
1,1-Diethylurea <sup>b</sup>	0	15.3	36.2	55.9	--	--	--
1,3-Diethylurea	0	21.5	35.6	47.5	57.6	66.1	72.9
1,3-Diethylthiourea <sup>c</sup>	0	14.7	--	--	--	--	--
Compounds applied from 95% ethyl alcohol solutions							
Butylurea <sup>d</sup>	0	12.6	30.2	--	--	--	--
1,1-Dibutylurea <sup>e</sup>	0	12.6	27.7	47.2	--	--	--
1,3-Dibutylurea <sup>f</sup>	0	14.5	--	--	--	--	--
Tetrabutylurea <sup>g</sup>	0	41.5	--	--	--	--	--
Sheets dried from pure compound							
Formamide	0	8.7	14.7	19.6	23.9	27.7	31.5
Dimethylformamide	0	21.3	32.3	39.0	42.1	43.9	46.3

<sup>a</sup>46.9 at 59 millimoles

<sup>b</sup>72.9 at 97 millimoles

<sup>c</sup>20.3 at 34 millimoles

<sup>d</sup>50.9 at 73 millimoles

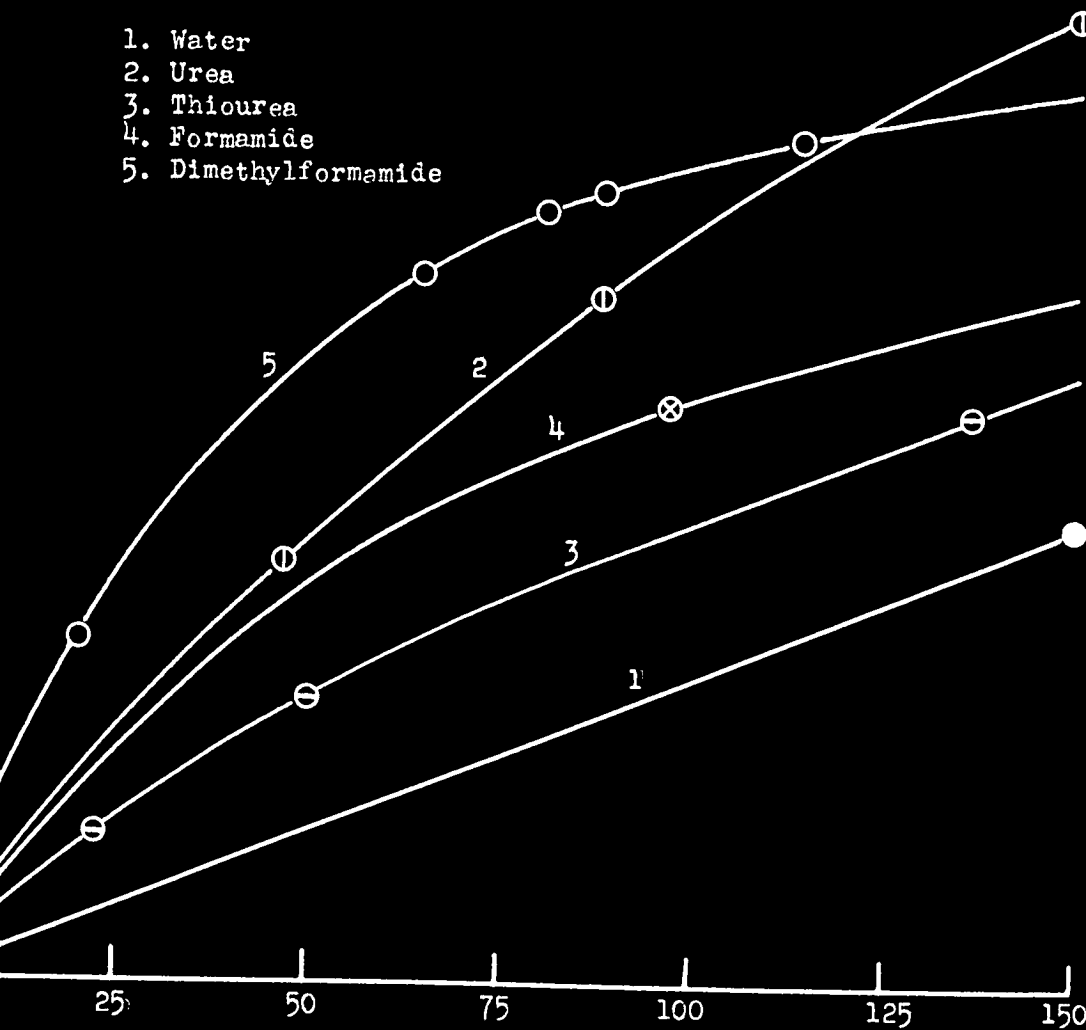
<sup>e</sup>63.5 at 92 millimoles

<sup>f</sup>30.8 at 44 millimoles

<sup>g</sup>40.3 at 33 millimoles

The Efficiency of the Lower-Molecular Weight Compounds in  
Reducing the Limiting Viscous Load, "f"

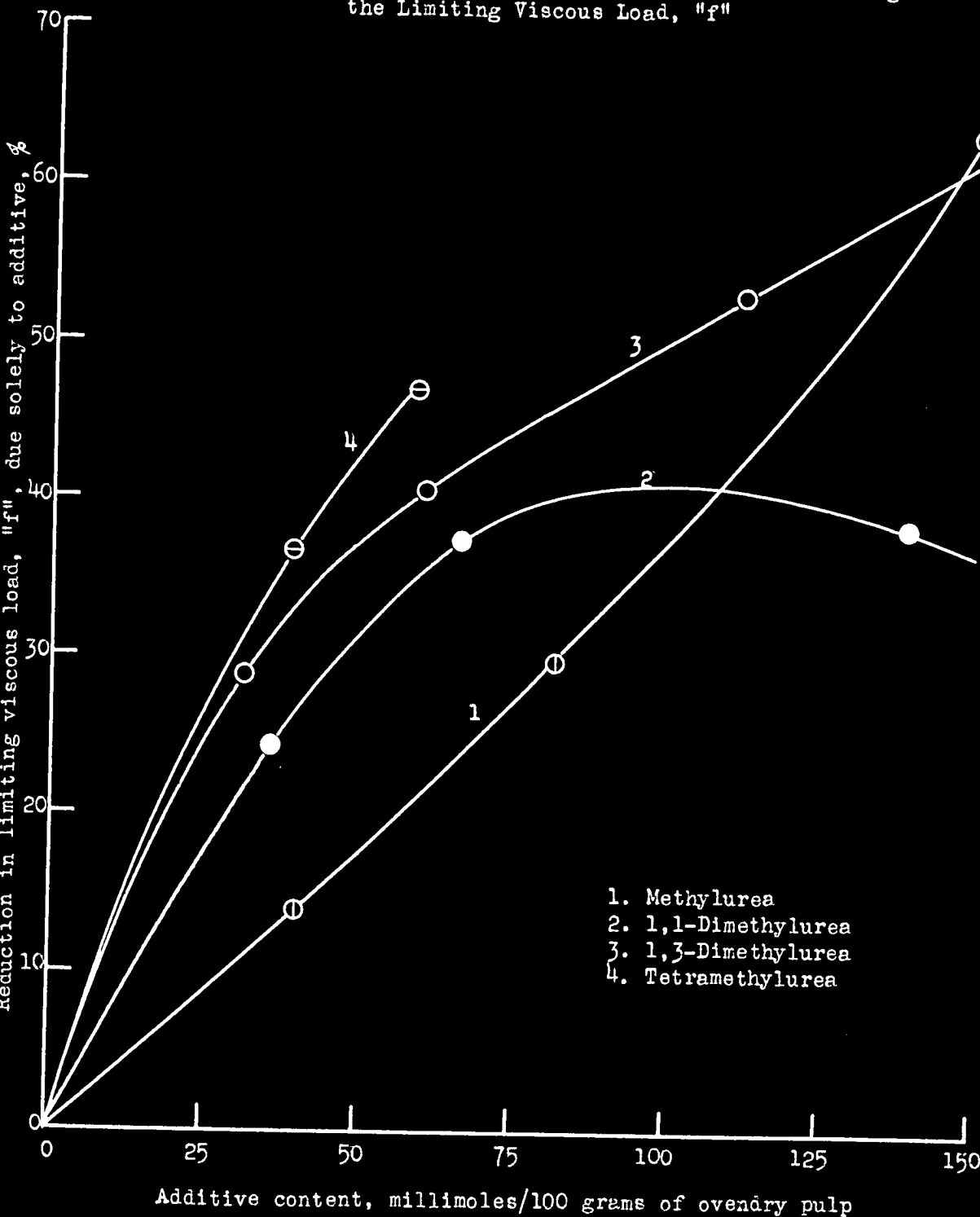
1. Water
2. Urea
3. Thiourea
4. Formamide
5. Dimethylformamide



Additive content, millimoles/100 grams of oven-dry pulp

FIGURE 33

The Efficiency of the Methyl-substituted Ureas in Reducing the Limiting Viscous Load, "f"





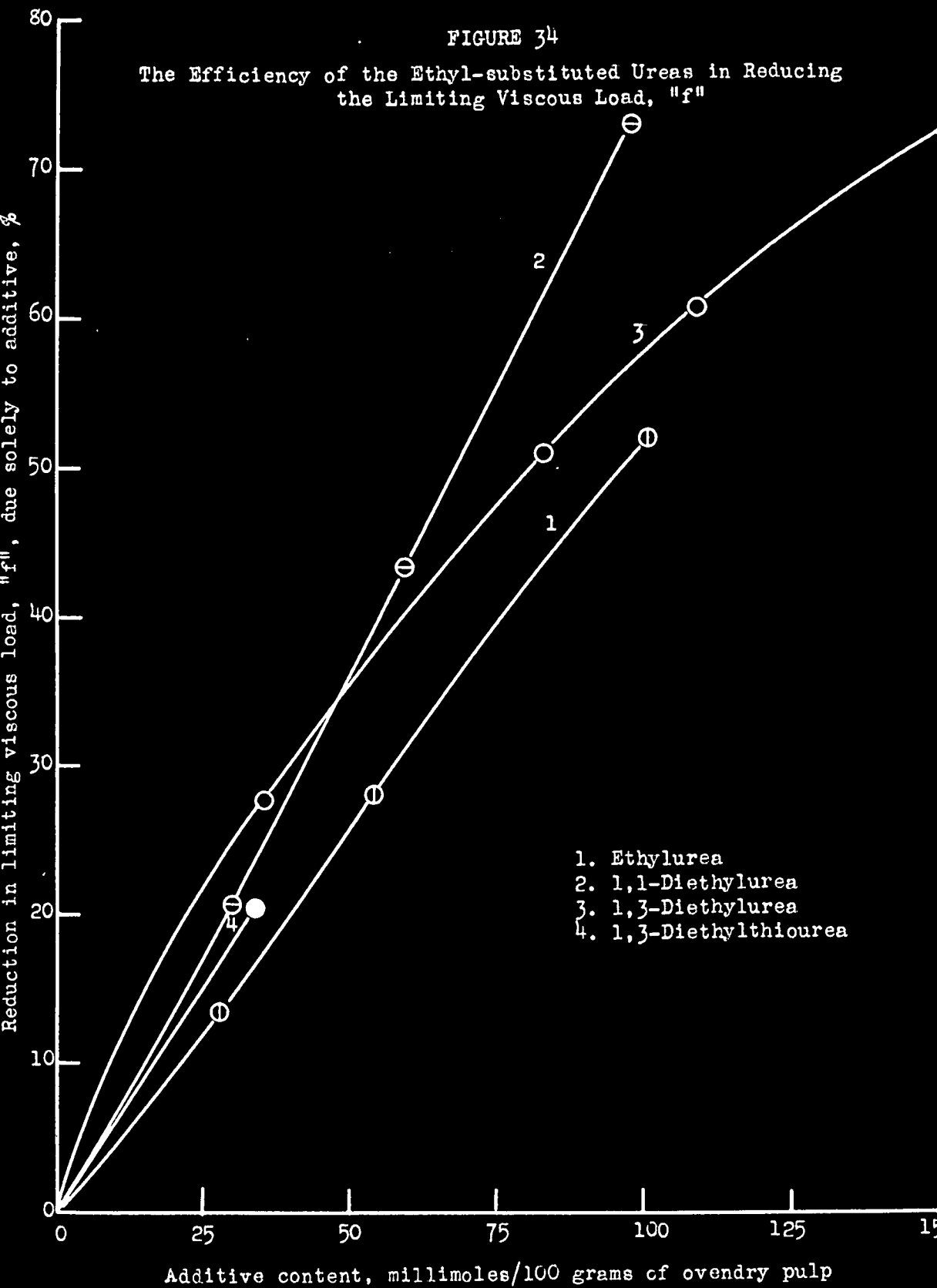
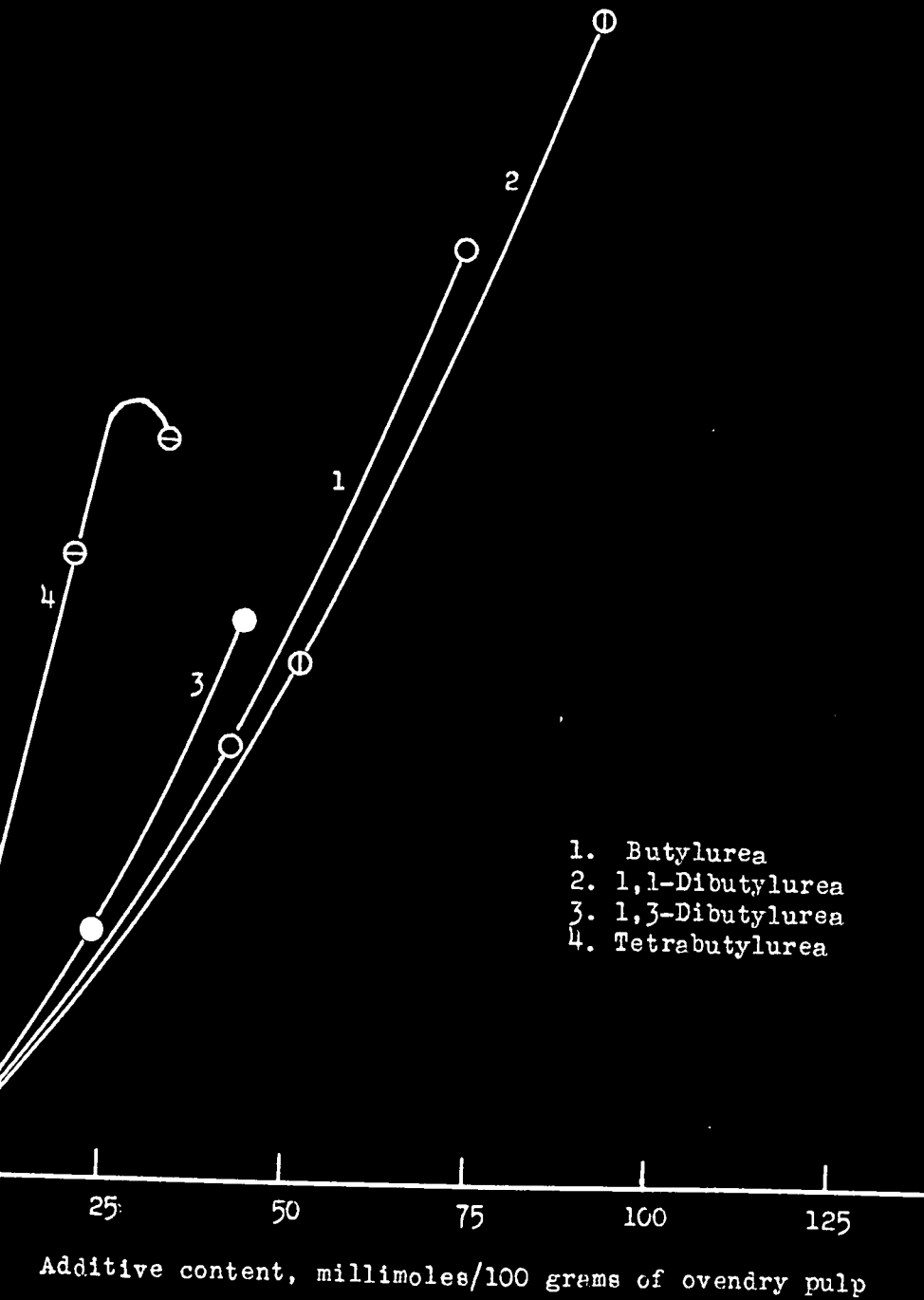


FIGURE 35

The Efficiency of the Butyl-substituted Ureas in Reducing the Limiting Viscous Load, "f"



(3) Although the tetrasubstituted compounds typically lacked staying power, there were no indications that the other high-molecular weight compounds would be any less effective in ultimate maximum reduction of  $f$  than the smaller-molecular weight materials.

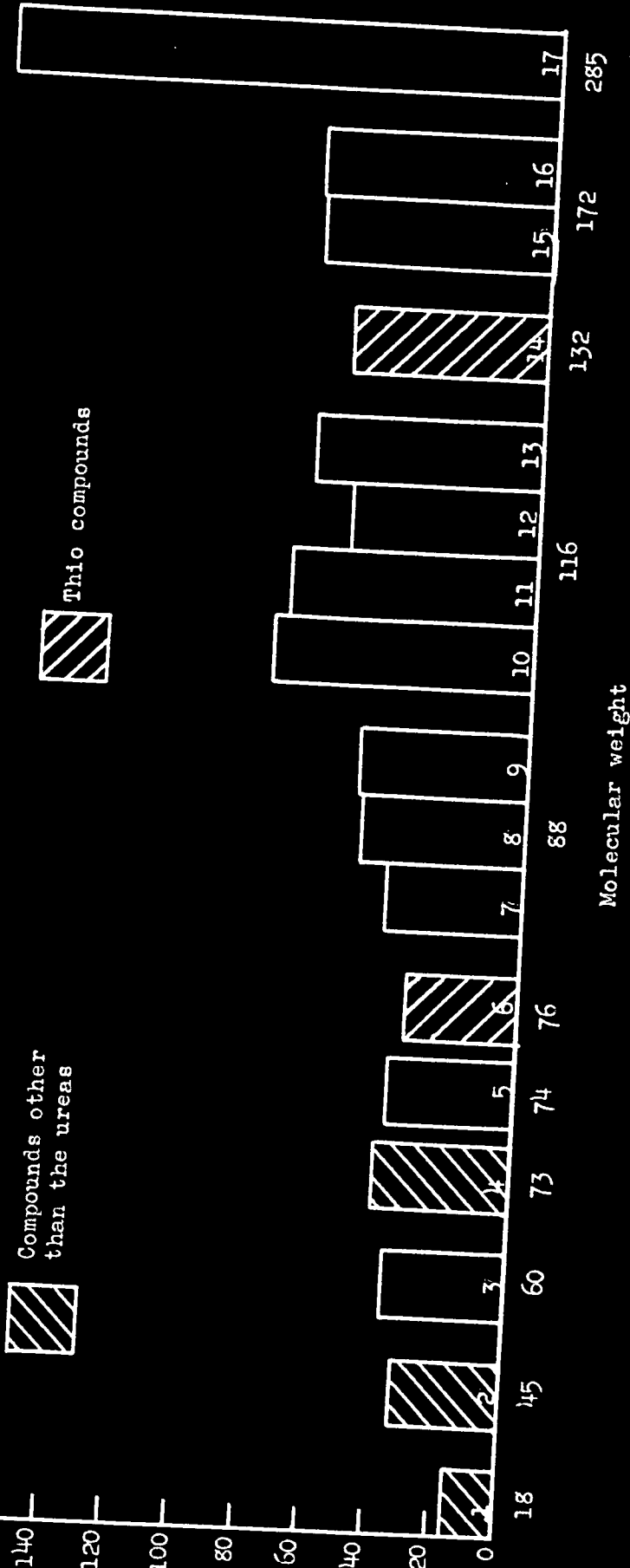
Figure 36 compares the average  $f$ -reducing efficiencies of the various compounds. The increasing effectiveness of the additive in reducing  $f$  with increasing molecular size is very evident in Figure 36. If the tetrabutylurea value is neglected, there would seem to be a leveling off of the  $f$ -reducing efficiency at the higher molecular weights. Whether this is a bona fide effect, or whether it is the result of applying these materials to the sheet from alcoholic solutions is not known.

#### THE EFFECT OF THE ADDITIVES ON THE OFFSET LOAD

The values for offset load for the various treated sheets are given in Table XXX. Table XXXI presents the percentage reduction in offset-load figures for the data with the moisture effect excluded. The data of Table XXXI are plotted in Figures 37-40. These data show the same general trends as did the  $f$  data, and hence no additional comment is necessary. From Figure 41, where the offset load-reducing efficiencies of the compounds are compared, it seems that the dibutyl compounds are slightly less effective, relative to the diethylureas, than they were in the case of the  $f$  value. This indication, in addition to the fact that the formamides seem to be slightly more efficient than might be predicted on the basis of molecular size, prompts the observation that offset load may be more sensitive to the ability of a material to swell the fibers than

FIGURE 36

The Efficiencies of the Various Compounds in Reducing the Limiting Viscous Load, "f"



- |                      |                         |
|----------------------|-------------------------|
| 1. Water             | 12. 1,3-Diethylurea     |
| 2. Formamide         | 13. Butylurea           |
| 3. Urea              | 14. 1,3-Diethylthiourea |
| 4. Dimethylformamide | 15. 1,1-Dibutylurea     |
| 5. Methylurea        | 16. 1,3-Dibutylurea     |
| 6. Thiourea          | 17. Tetrabutylurea      |

TABLE XXX

VALUES FOR LOAD AT 0.1% OFFSET FOR TREATED SHEETS  
(Pounds)

Additive Compound	Additive Content of Sheet, millimoles per 100 grams of oven-dry pulp						
	0	25	50	75	100	125	150
Compounds applied from aqueous solution							
Water	20.6	19.5	18.5	17.6	16.8	16.1	15.4
Urea	20.6	20.1	19.4	18.6	17.5	16.0	14.3
Thiourea	20.6	19.5	18.6	17.8	17.4	17.3	17.4
Methylurea	20.6	19.7	18.6	17.6	16.2	14.6	12.4
1,1-Dimethylurea	20.6	19.5	17.5	15.5	14.7	14.7	15.2
1,3-Dimethylurea	20.6	19.6	18.4	17.0	15.4	13.8	12.2
Tetramethylurea <sup>a</sup>	20.6	16.3	12.0	--	--	--	--
Ethylurea	20.6	18.4	16.6	15.0	13.2	--	--
1,1-Diethylurea <sup>b</sup>	20.6	18.8	16.2	13.4	--	--	--
1,3-Diethylurea	20.6	16.5	14.4	12.8	10.2	8.6	8.9
1,3-Diethylthiourea <sup>c</sup>	20.6	17.6	--	--	--	--	--
Compounds applied from 95% ethyl alcohol solutions							
Butylurea <sup>d</sup>	16.7	16.4	15.3	--	--	--	--
1,1-Dibutylurea <sup>e</sup>	16.7	17.2	16.6	14.6	--	--	--
1,3-Dibutylurea <sup>f</sup>	16.7	17.9	--	--	--	--	--
Tetrabutylurea <sup>g</sup>	16.7	10.6	--	--	--	--	--
Sheets dried from pure compound							
Formamide	23.2 <sup>h</sup>	21.6	19.9	18.2	16.6	15.3	13.9
Dimethylformamide	17.9	12.4	10.4	9.1	7.8	6.7	5.6

<sup>a</sup>10.6 at 59 millimoles

<sup>b</sup>10.8 at 97 millimoles

<sup>c</sup>16.3 at 34 millimoles

<sup>d</sup>13.3 at 73 millimoles

<sup>e</sup>12.2 at 92 millimoles

<sup>f</sup>16.4 at 44 millimoles

<sup>g</sup>11.1 at 33 millimoles

<sup>h</sup>This value by extrapolation from 16 millimoles

TABLE XXXI

THE RELATIVE EFFICIENCIES OF VARIOUS COMPOUNDS  
IN REDUCING OFFSET LOAD  
(Percentage of offset load of untreated sheets at 50% R.H.)

Additive Compound	Additive Content of Sheet, millimoles per 100 grams of oven-dry pulp						
	0	25	50	75	100	125	150
Compounds applied from aqueous solution							
Water	0	5.3	9.8	14.6	18.5	21.8	25.2
Urea	0	12.1	23.3	32.1	39.8	48.1	56.8
Thiourea	0	18.0	31.1	40.3	45.1	47.1	47.6
Methylurea	0	13.1	24.8	34.0	43.7	52.9	64.1
1,1-Dimethylurea	0	12.6	29.6	44.7	49.0	48.1	43.7
1,3-Dimethylurea	0	21.4	35.4	43.7	51.5	59.7	67.0
Tetramethylurea <sup>a</sup>	0	24.3	50.5	--	--	--	--
Ethylurea	0	14.1	30.6	45.6	58.3	--	--
1,1-Diethylurea <sup>b</sup>	0	22.3	42.7	63.1	--	--	--
1,3-Diethylurea	0	27.7	44.2	57.3	74.3	86.4	87.9
1,3-Diethylthiourea <sup>c</sup>	0	22.3	--	--	--	--	--
Compounds applied from 95% ethyl alcohol solutions							
Butylurea <sup>d</sup>	0	15.0	35.3	--	--	--	--
1,1-Dibutylurea <sup>e</sup>	0	10.8	26.3	47.3	--	--	--
1,3-Dibutylurea <sup>f</sup>	0	10.2	--	--	--	--	--
Tetrabutylurea <sup>g</sup>	0	42.5	--	--	--	--	--
Sheets dried from pure compound							
Formamide	0	12.5	22.0	29.7	36.6	42.2	47.4
Dimethylformamide	0	28.5	44.1	50.3	52.5	51.4	52.0

<sup>a</sup>59.2 at 59 millimoles

<sup>b</sup>80.6 at 97 millimoles

<sup>c</sup>31.6 at 34 millimoles

<sup>d</sup>58.1 at 73 millimoles

<sup>e</sup>67.7 at 92 millimoles

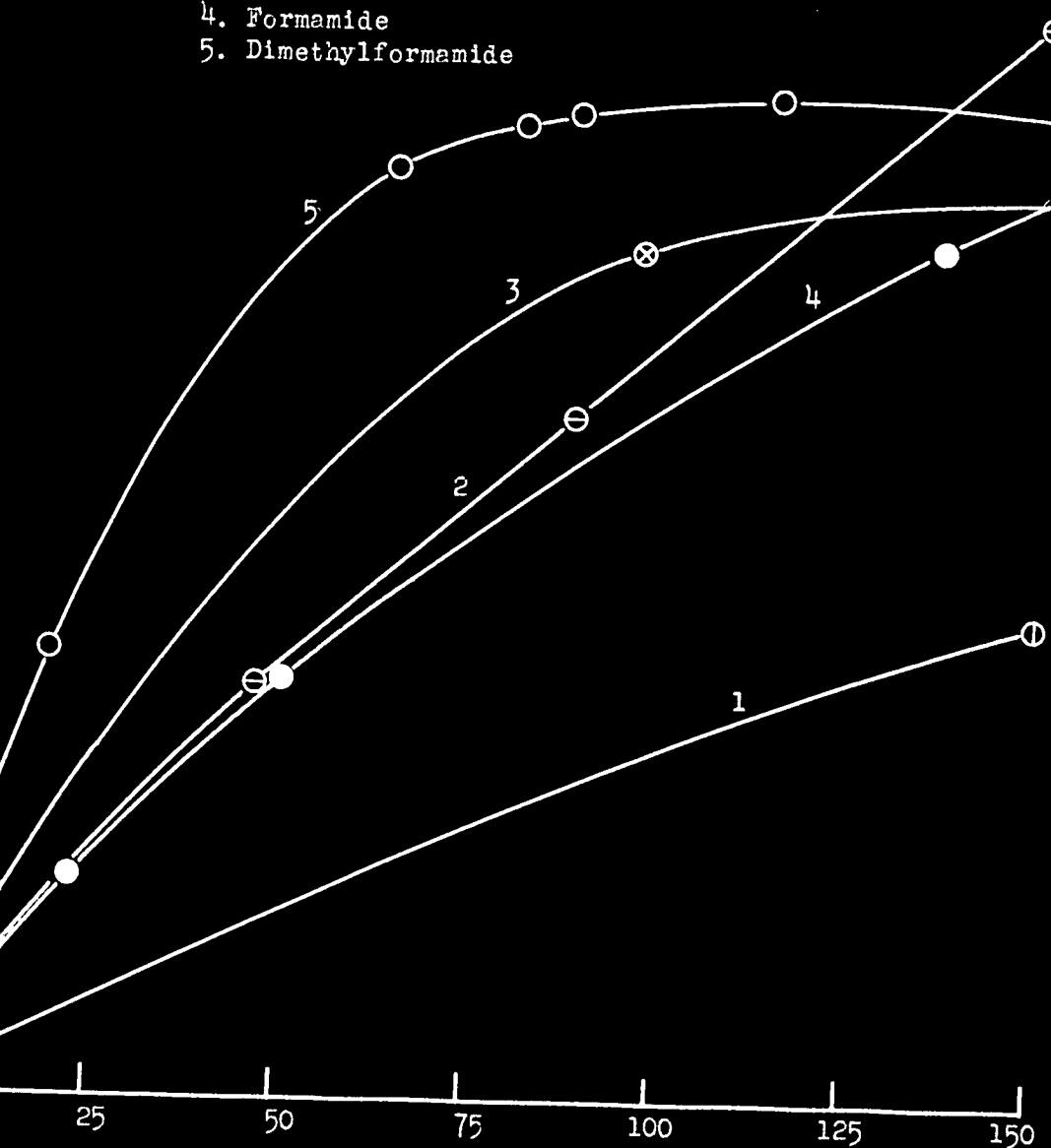
<sup>f</sup>29.3 at 44 millimoles

<sup>g</sup>39.5 at 33 millimoles

FIGURE 37

The Efficiency of the Lower-Molecular Weight Compounds in Reducing Offset Load

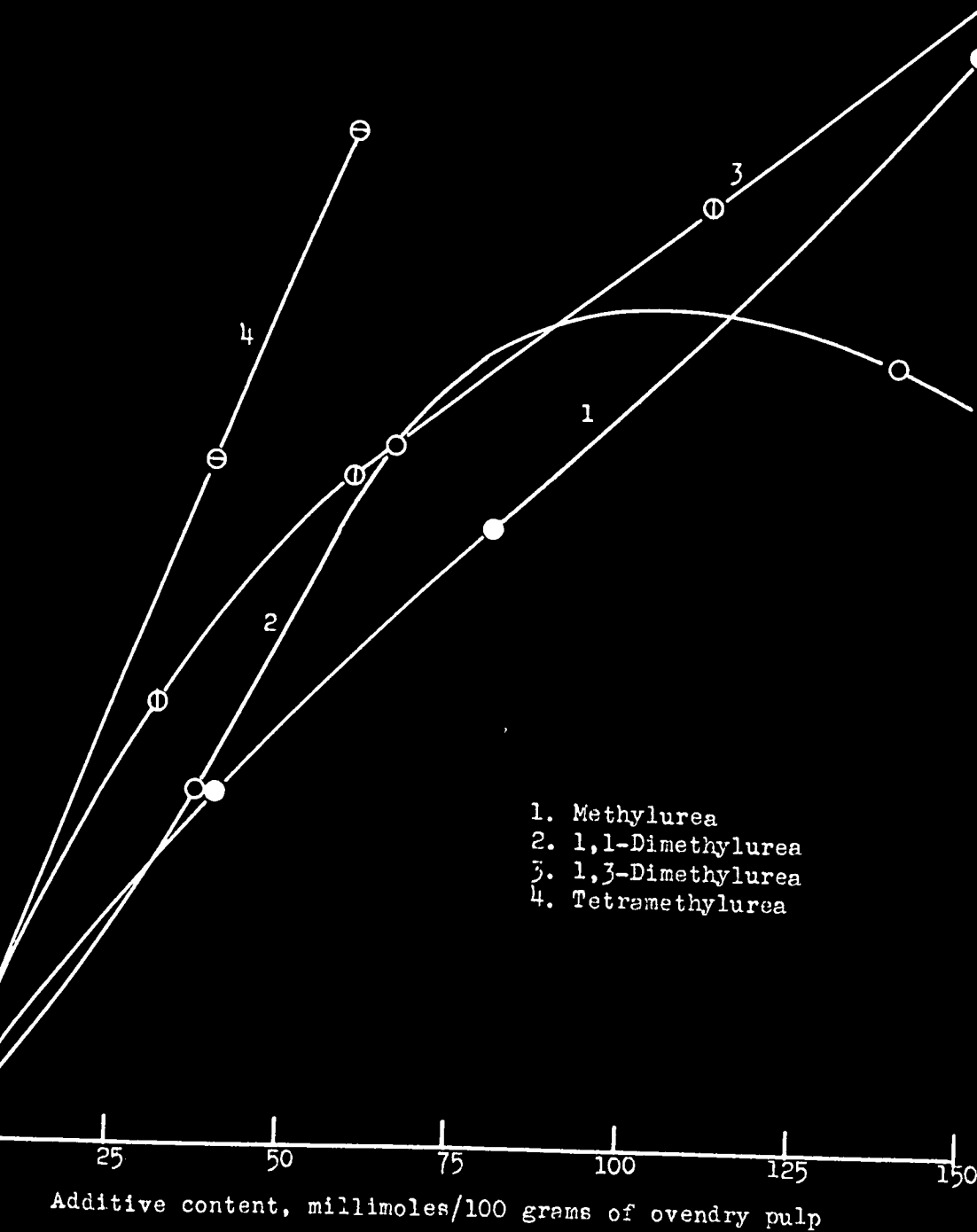
1. Water
2. Urea
3. Thiourea
4. Formamide
5. Dimethylformamide



Additive content, millimoles/100 grams of oven-dry pulp

FIGURE 38

The Efficiency of the Methyl-substituted Ureas in Reducing Offset Load





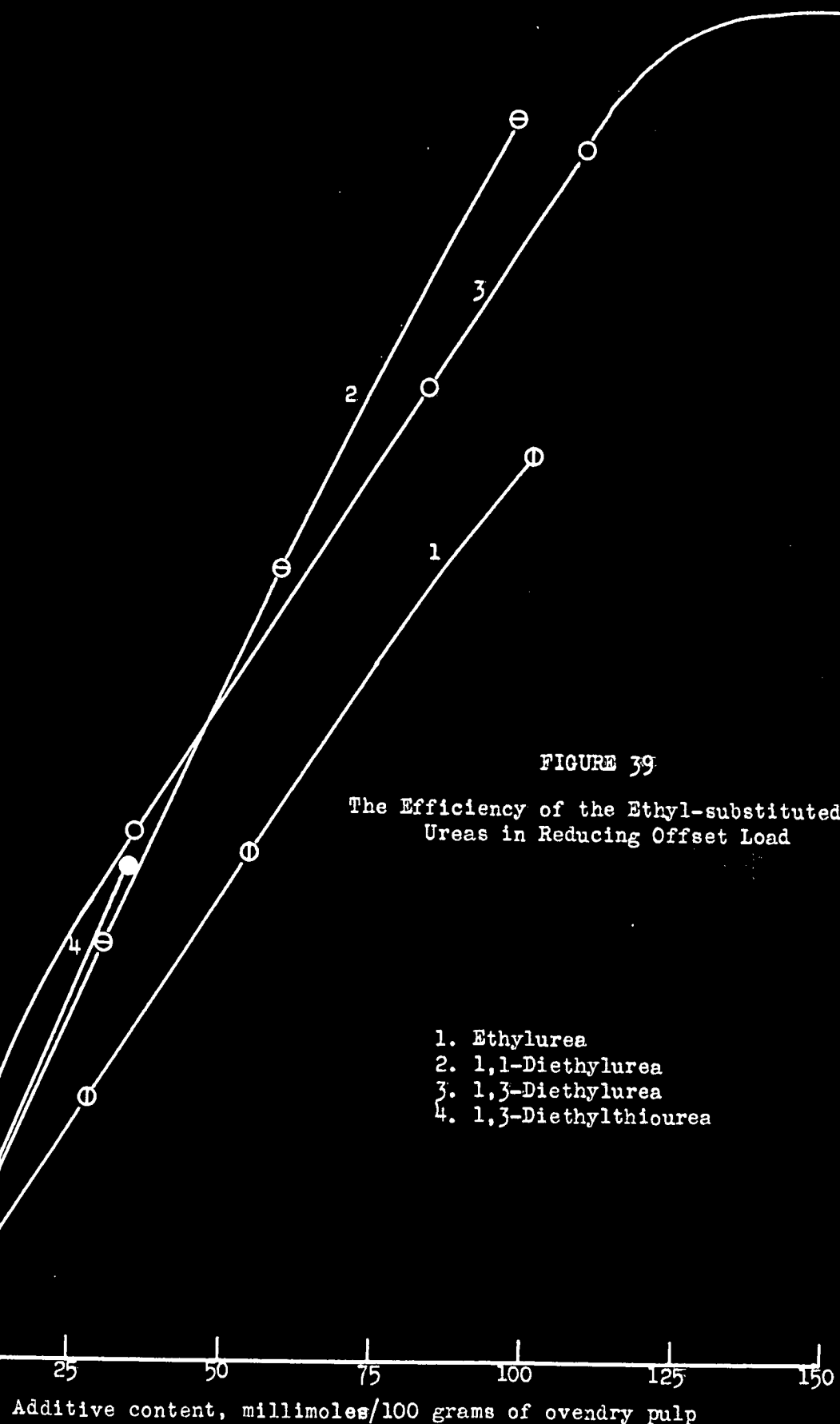
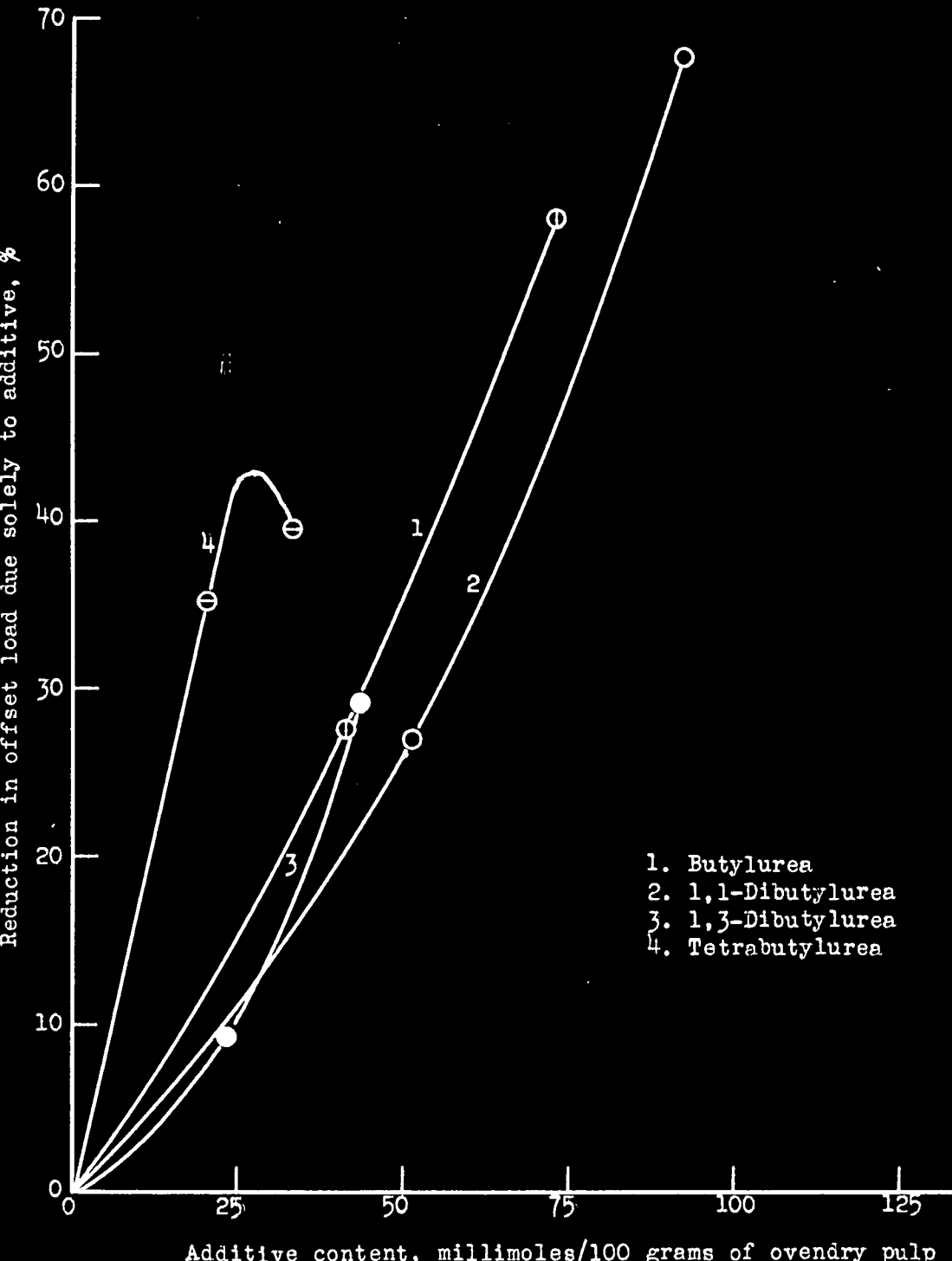
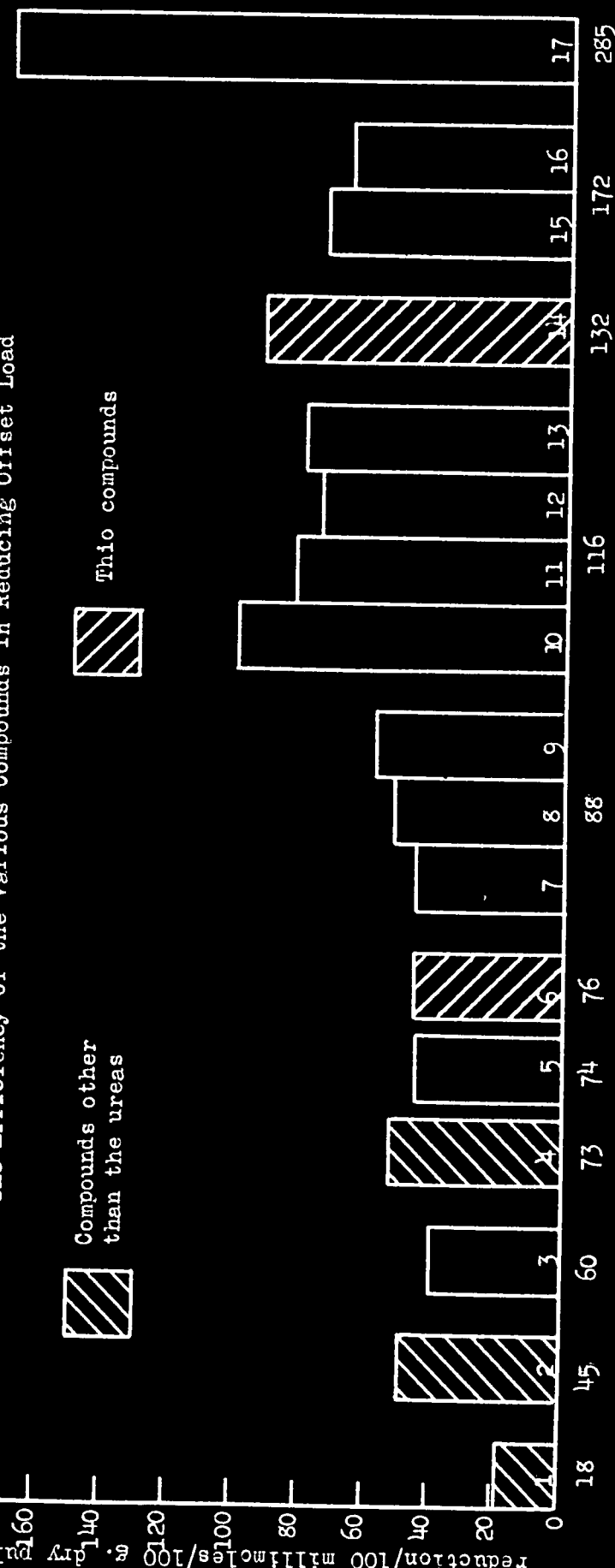


FIGURE 40

The Efficiency of the Butyl-substituted Ureas in Reducing Offset Load





1. Water
2. Formamide
3. Urea
4. Dimethylformamide
5. Methylurea
6. Thiourea
7. 1,1-Dimethylurea
8. 1,3-Dimethylurea
9. Ethylurea
10. Tetramethylurea
11. 1,1-Diethylurea
12. 1,3-Diethylthiourea
13. Butylurea
14. 1,3-Diethylthiourea
15. 1,1-Dibutylurea
16. 1,3-Dibutylurea
17. Tetra butylurea

is the  $f$  value. The stress at which plastic flow is first apparent--the quantity of which offset load is an indirect measure--may be lowered if a greater swelling of the fibers takes place.

#### THE EFFECT OF THE ADDITIVES ON STRETCH

The stretch values for the variously treated sheets are compiled in Table XXXII. The percentage increase in stretch, moisture effect excluded, for the various materials is tabulated in Table XXXIII and plotted in Figures 42-45. It should be noted here that the stretch values obtained in this work were characterized by a considerably higher variability than was the case in the quantities heretofore discussed. Therefore the average values reported in Table XXXII and used in the calculation of Table XXXIII and Figures 42-45 are subject to a greater degree of uncertainty than those for the other mechanical properties.

A comparison of the figures for stretch indicates that only the relatively low-molecular weight additives bring about an appreciable increase in the extensibility of the sheet. Water, which the previous discussions have shown to be comparatively ineffective in altering sheet properties, is seen to rank quite high in ability to increase stretch. Urea and the methyl-substituted ureas showed considerable effectiveness. As substituent size and total molecular weight increased, however, the additives became more prone to reduce significantly the stretch value before increasing it. Indeed, tetrabutylurea gave no indication of anything but a precipitous decrease in stretch.

TABLE XXXII

PERCENTAGE STRETCH VALUES FOR TREATED SHEETS

Additive Compound	Additive Content of Sheet, millimoles per 100 grams of oven-dry pulp						
	0	25	50	75	100	125	150
Compounds applied from aqueous solution							
Water	2.87	2.99	3.10	3.20	3.30	3.41	3.52
Urea	2.87	2.92	3.01	3.14	3.29	3.45	3.58
Thiourea	2.87	2.98	3.05	3.10	3.12	3.09	3.04
Methylurea	2.87	2.86	2.85	2.84	2.90	3.10	3.47
1,1-Dimethylurea	2.87	2.88	2.90	2.93	2.97	3.07	3.28
1,3-Dimethylurea	2.87	2.81	2.46	2.45	2.64	2.80	2.98
Tetramethylurea <sup>a</sup>	2.87	3.12	3.16	--	--	--	--
Ethylurea	2.87	2.65	2.55	2.55	2.61	--	--
1,1-Diethylurea <sup>b</sup>	2.87	2.35	2.28	2.42	--	--	--
1,3-Diethylurea	2.87	2.36	2.13	2.10	2.22	2.42	2.70
1,3-Diethylthiourea <sup>c</sup>	2.87	2.62	--	--	--	--	--
Compounds applied from 95% ethyl alcohol solutions							
Butylurea <sup>d</sup>	3.39	2.95	2.98	--	--	--	--
1,1-Dibutylurea <sup>e</sup>	3.39	2.80	2.50	2.37	--	--	--
1,3-Dibutylurea <sup>f</sup>	3.39	2.57	--	--	--	--	--
Tetrabutylurea <sup>g</sup>	3.39	2.17	--	--	--	--	--
Sheets dried from pure compound							
Formamide	2.62 <sup>h</sup>	2.63	2.65	2.65	2.66	2.67	2.68
Dimethylformamide	2.78	2.85	2.89	2.90	2.87	2.82	2.73

<sup>a</sup>3.14 at 59 millimoles

<sup>b</sup>2.65 at 97 millimoles

<sup>c</sup>2.52 at 34 millimoles

<sup>d</sup>3.33 at 73 millimoles

<sup>e</sup>2.37 at 92 millimoles

<sup>f</sup>2.69 at 44 millimoles

<sup>g</sup>2.10 at 33 millimoles

<sup>h</sup>This value by extrapolation from 16 millimoles

TABLE XXXIII

RELATIVE EFFICIENCIES OF VARIOUS COMPOUNDS  
IN INCREASING PERCENTAGE STRETCH  
(Percentage of stretch of untreated sheet at 50% R.H.)

Additive Compound	Additive Content of Sheet, millimoles per 100 grams of oven-dry pulp						
	0	25	50	75	100	125	150
Compounds applied from aqueous solution							
Water	0	4.2	8.0	11.5	15.0	18.8	22.6
Urea	0	7.0	14.3	21.6	28.2	34.1	38.7
Thiourea	0	10.8	18.1	22.6	24.7	24.4	23.0
Methylurea	0	4.5	7.3	9.8	13.2	20.9	34.2
1,1-Dimethylurea	0	3.8	9.1	12.9	14.3	17.8	23.7
1,3-Dimethylurea	0	7.0	-0.7	-0.7	6.3	12.1	17.8
Tetramethylurea <sup>a</sup>	0	10.5	15.0	--	--	--	--
Ethylurea	0	-6.3	-4.9	-1.4	3.1	--	--
1,1-Diethylurea <sup>b</sup>	0	-10.8	-8.7	-0.3	--	--	--
1,3-Diethylurea	0	-13.6	-18.1	-16.4	-9.8	-0.3	10.8
1,3-Diethylthiourea <sup>c</sup>	0	-4.9	--	--	--	--	--
Compounds applied from 95% ethyl alcohol solutions							
Butylurea <sup>d</sup>	0	-5.3	3.2	--	--	--	--
1,1-Dibutylurea <sup>e</sup>	0	-9.4	-9.7	-10.9	--	--	--
1,3-Dibutylurea <sup>f</sup>	0	-13.9	--	--	--	--	--
Tetrabutylurea <sup>g</sup>	0	-26.5	--	--	--	--	--
Sheets dried from pure compound							
Formamide	0	4.2	6.1	6.9	7.3	7.3	6.9
Dimethylformamide	0	1.4	5.8	5.4	0.7	-5.8	-14.4

<sup>a</sup> 15.3 at 59 millimoles

<sup>b</sup> 9.8 at 97 millimoles

<sup>c</sup> -6.3 at 34 millimoles

<sup>d</sup> 18.6 at 73 millimoles

<sup>e</sup> -8.0 at 92 millimoles

<sup>f</sup> -5.9 at 44 millimoles

<sup>g</sup> -34.5 at 33 millimoles

FIGURE 42

The Efficiency of the Lower-Molecular Weight Compounds in Increasing Stretch

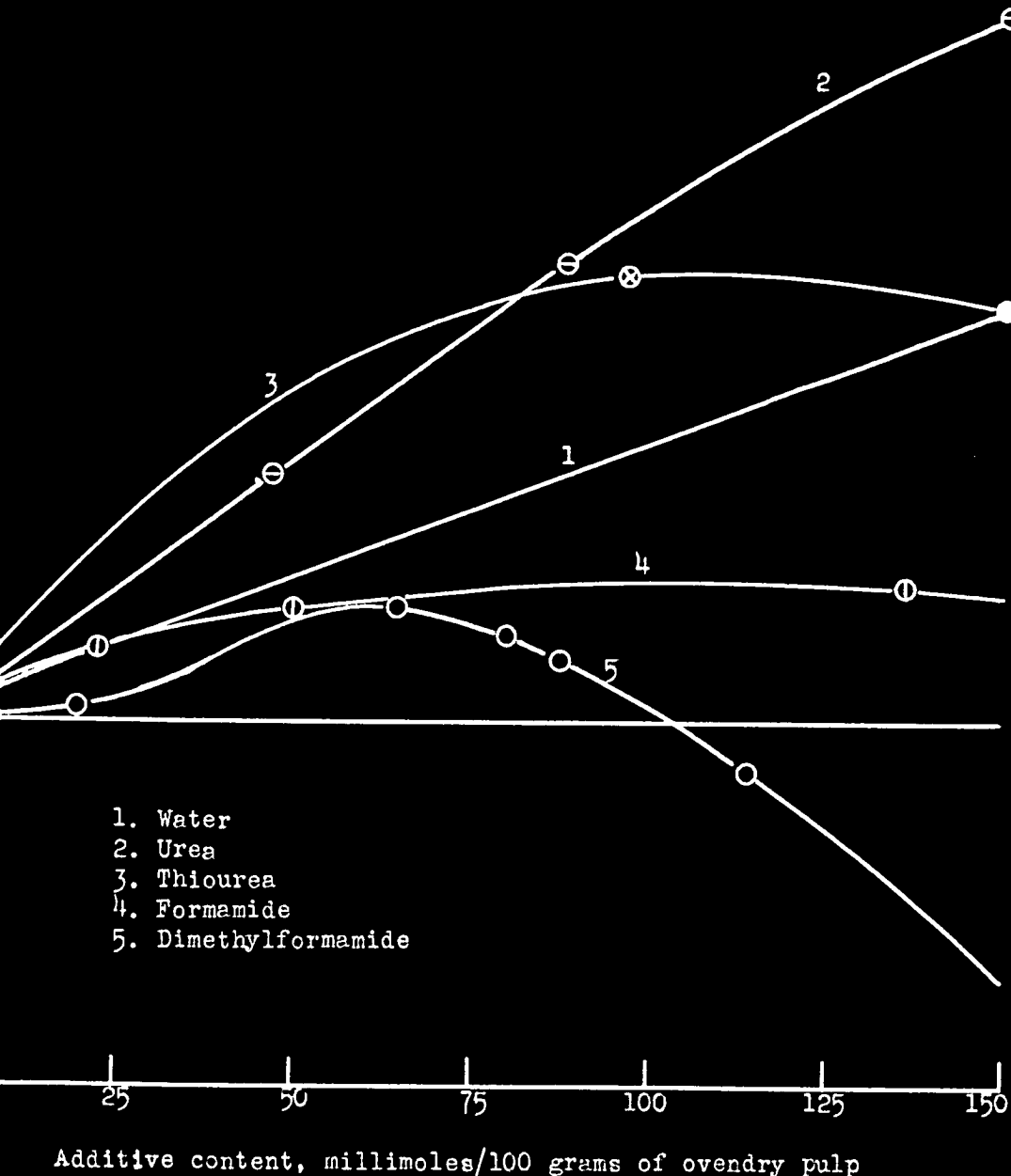


FIGURE 43

The Efficiency of the Methyl-substituted Ureas in Increasing Stretch

1. Methylurea
2. 1,1-Dimethylurea
3. 1,3-Dimethylurea
4. Tetramethylurea

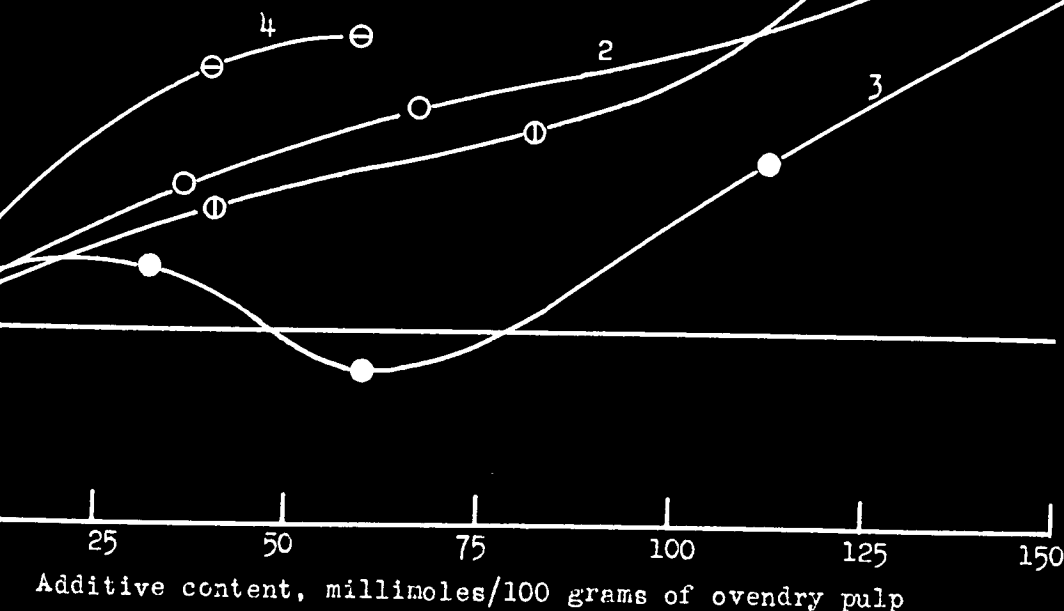




FIGURE 44

The Efficiency of the Ethyl-substituted Ureas in Increasing Stretch

1. Ethylurea
2. 1,1-Diethylurea
3. 1,3-Diethylurea
4. 1,3-Diethylthiourea

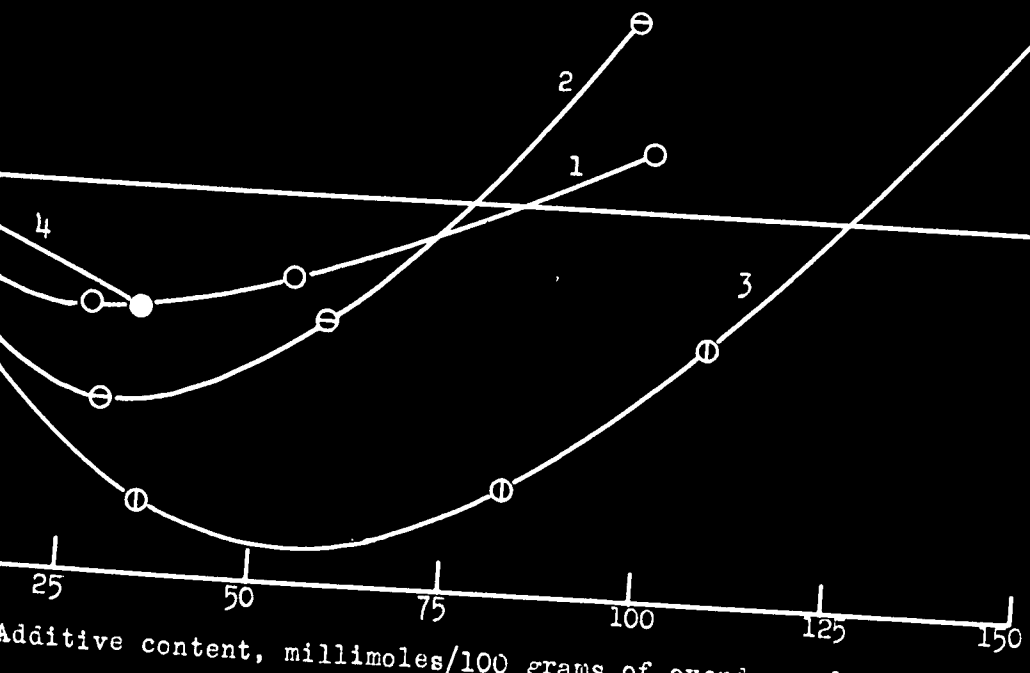
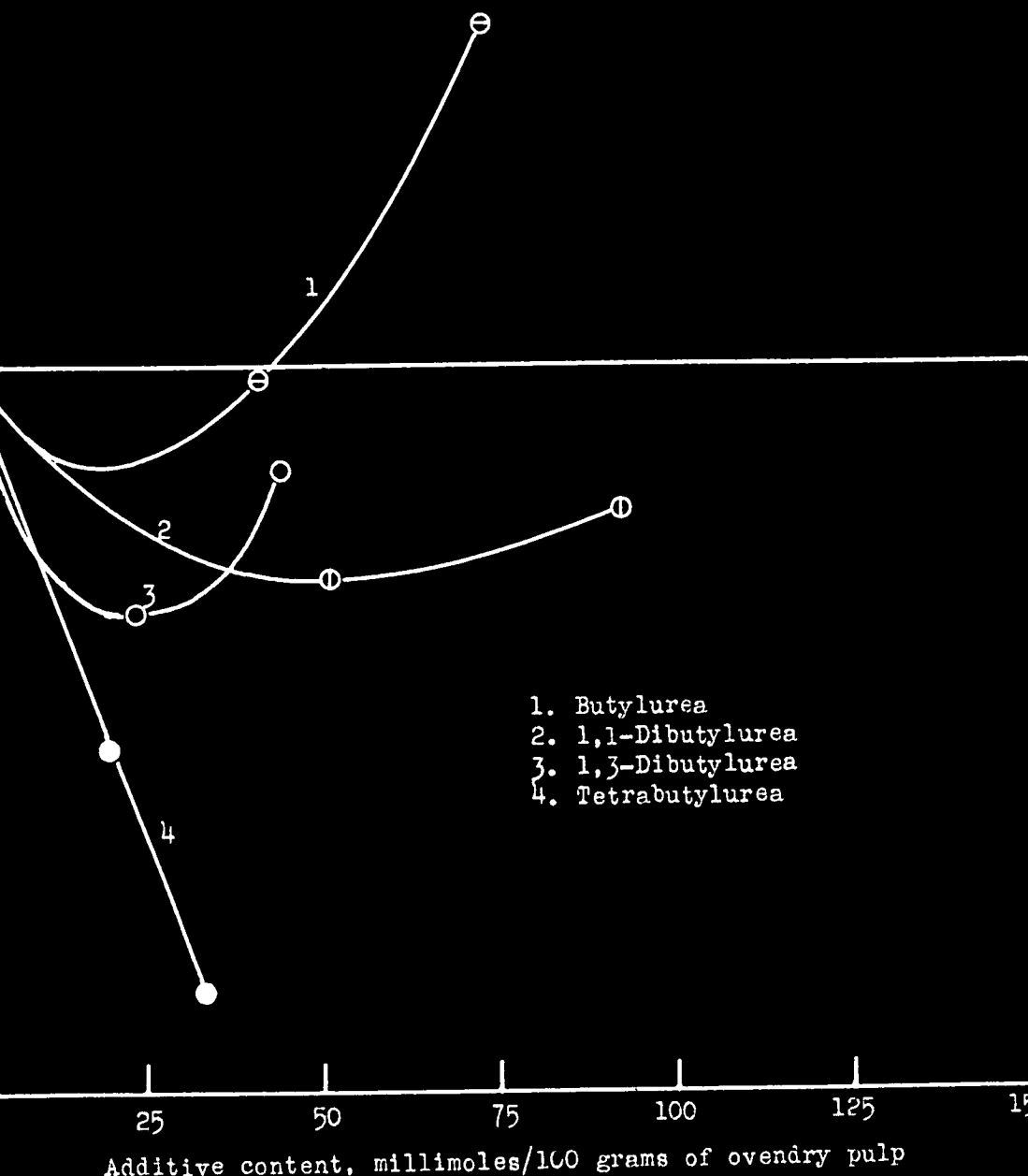


FIGURE 45

The Efficiency of the Butyl-substituted Ureas in Increasing Stretch



To explain these results it is necessary to consider the fact that a sheet of paper will continue to extend only as long as bonding strength is adequate to resist the applied stress. As long as bonding strength is sufficient to prevent failure, extension may take place by elastic or viscous deformation of the fiber, the fiber-to-fiber bonds, or those portions of the fibers immediately adjoining the bonded zone.

In the case of the higher-molecular weight compounds, which, on the basis of the data discussed previously, are believed to cause an early and abrupt decrease in bonding strength with relatively little effect on fiber properties, this weakening effect is evidently sufficient to cause failure at a relatively low extension. The molecules of lower molecular weight undoubtedly have greater swelling and penetrating powers than the large hydrophobic molecules. As has already been pointed out in the discussion of the  $Q$  value, this undoubtedly allows them to exert a greater effect on the fibers themselves. It is probably this fact which accounts for their ability to increase stretch. Presumably if an additive molecule is to increase the extensibility of a sheet, it must plasticize the fibers and fibrils enough so that they will strain before the weakened fiber-to-fiber bonds fail.

Decreasing molecular size past a point may also decrease the ability of the molecule to increase stretch, as in the case of water and formamide. It may be supposed that water is unable to increase stretch to the same extent as urea because of its relative inability to maintain a state of dry swelling in a fiber. Therefore, in a moisture-treated sheet, the less-swollen fibers will resist extension and cause failure in the

fiber-to-fiber bonds before much additional stretch has taken place.

#### THE EFFECT OF THE ADDITIVES ON THE WORK OF FAILURE

Table XXXIV shows the variation in the work of failure for the sheets treated with the various compounds. From these data it will be seen that the additives such as water, urea, and thiourea which were able to increase stretch without greatly affecting tensile strength caused a slight increase in the work of failure, or maintained it at about the same level. Most of the compounds, however, either reduced both tensile strength and stretch, or they reduced tensile strength without significantly increasing stretch, with the result that the work required to cause failure fell off.

#### SUMMARY OF COMPARISON OF VARIOUS COMPOUNDS

The observations made from the data presented in this section will be briefly summarized and discussed.

All the substituted ureas and formamides investigated reduced the moisture content of the sheet when they were added in small quantities. Sheet moisture content was found to rise again in cases where a sufficiently high additive content was investigated, but it was found to exceed the value of the untreated sheet only when the additive was hygroscopic. It was obvious from the moisture content data that none of the ureas investigated affected the sheet properties as the result of any hygroscopic action.

TABLE XXXIV

WORK OF FAILURE FOR SHEETS CONTAINING VARIOUS COMPOUNDS  
(Pound-inches)

Additive Compound	Additive Content of Sheet, millimoles per 100 grams of oven-dry pulp						
	0	25	50	75	100	125	150
Compounds applied from aqueous solution							
Water	3.53	3.59	3.64	3.69	3.73	3.77	3.80
Urea	3.53	3.55	3.58	3.70	3.72	3.65	3.58
Thiourea	3.53	3.54	3.55	3.56	3.55	3.50	3.44
Methylurea	3.53	3.48	3.12	2.78	2.71	2.74	2.77
1,1-Dimethylurea	3.53	3.17	2.96	2.93	3.05	3.17	3.58
1,3-Dimethylurea	3.53	3.11	2.53	2.32	2.38	2.35	2.26
Tetramethylurea <sup>a</sup>	3.53	2.97	2.54	--	--	--	--
Ethylurea	3.53	2.77	2.32	2.11	1.92	--	--
1,1-Diethylurea <sup>b</sup>	3.53	2.48	2.41	2.15	--	--	--
1,3-Diethylurea	3.53	2.41	2.02	1.95	1.27	1.18	1.53
1,3-Diethylthiourea <sup>c</sup>	3.53	2.67	--	--	--	--	--
Compounds applied from 95% ethyl alcohol solutions							
Butylurea <sup>d</sup>	3.85	3.22	3.81	--	--	--	--
1,1-Dibutylurea <sup>e</sup>	3.85	3.01	2.25	1.80	--	--	--
1,3-Dibutylurea <sup>f</sup>	3.85	2.45	--	--	--	--	--
Tetrabutylurea <sup>g</sup>	3.85	1.26	--	--	--	--	--
Sheets dried from pure compound							
Formamide	2.95 <sup>h</sup>	2.91	2.86	2.79	2.69	2.57	2.44
Dimethylformamide	3.05	2.71	2.37	2.03	1.70	1.41	1.15

<sup>a</sup>2.43 at 59 millimoles

<sup>b</sup>1.69 at 97 millimoles

<sup>c</sup>2.33 at 34 millimoles

<sup>d</sup>3.81 at 73 millimoles

<sup>e</sup>1.52 at 92 millimoles

<sup>f</sup>2.39 at 44 millimoles

<sup>g</sup>1.15 at 33 millimoles

<sup>h</sup>This value by extrapolation from 16 millimoles

The ability of the various ureas and formamides to plasticize a sheet of paper was found to be a relatively strong function of their molecular size. The term plasticize is here used to signify the ability to reduce tensile strength, elastic constants, offset load and  $f$ . Increasing the molecular weight of the ureas increased the molar efficiency of the compound in reducing tensile strength and final slope. No limitation to this trend was found; hence, the larger the molecule the greater was its efficiency in reducing tensile strength and final slope.

Over a large portion of the molecular weight range investigated, the molar efficiency of the ureas in reducing initial slope ( $K_2$ ), offset load, and  $f$  increased with increasing molecular weight. However, there were indications that the efficiency of the compounds in reducing initial slope and  $K_2$ , and possibly also offset load and  $f$ , was at a maximum in the molecular weight range from 100-120. It was believed that these particular properties are more sensitive to the state of dry swelling in the fibers than are tensile strength and final slope. Therefore the molecular weight at which maximum efficiency was obtained probably corresponded to the molecular size which was small enough to penetrate the fiber and yet large enough to be effective in maintaining dry swelling.

There were indications that the greatest reduction in tensile strength, final slope, offset load, and  $f$ , would have been accomplished by the largest urea molecules. In the case of the initial slope and  $K_2$ , however, the maximum reduction would probably have been attained by urea molecules having a molecular weight in the range of 70-90. The inability of the large molecules to produce a large over-all decrease in the initial

slope or  $K_2$  was attributed to their relative inability to penetrate the fiber structure. The fact that no such trend was evident for the flow properties, offset load, and  $f$ , indicated that these properties were less dependent on fiber swelling than initial slope and  $K_2$ .

The mechanical properties under discussion, therefore, seem to fall into three general categories. The properties in the first group, including tensile strength and final slope, are relatively insensitive to changes in the fiber, but are quite dependent on the strength of the fiber-to-fiber bonds. Therefore they are less affected by the relative swelling and penetrating abilities of the various additives in a series of increasing molecular weight. The second group, including the flow properties, offset load and  $f$ , seems to be intermediate in its dependence on inter- and intra-fiber bonding. There were slight indications that the  $f$  value might be closer to the first group than offset load, because of the appreciably greater sensitivity of offset load to swelling powers. The third group, comprising initial slope and  $K_2$ , seems to be more responsive to changes in fiber flexibility than the other properties. Therefore, the limitations imposed on the fiber-swelling and fiber-penetrating powers of an additive by increased molecular weight are reflected by these two properties.

It should be recalled at this point that the data in Table XIII for the values of urea-treated sheet properties, adjusted to a unit bending strength, showed that bonding strength could account for the changes in tensile strength and final slope. Initial slope and  $K_2$  were found to change more than could be accounted for by bonding strength, and it was concluded that fiber stiffness was of importance to these properties.

The flow properties, likewise, seemed to be influenced by some factor or factors other than bonding strength, which were believed to be related to the degree of fiber swelling. Thus the speculations made on the basis of the data in Table XIII led to the same general conclusions as did the comparative data on the substituted ureas.

Considerable other evidence was gathered to support the hypothesis that  $K_1$  was more sensitive to fiber-to-fiber bonding strength than  $K_2$ , and that, conversely,  $K_2$  was more sensitive to the state of internal bonding in a fiber than was  $K_1$ .

A subsidiary indication of the effect of molecular volume on the plasticizing efficiency of an additive molecule was observed in a comparison of the symmetrically and unsymmetrically disubstituted ureas. The changes in the properties of tensile strength and final slope, which, it was pointed out, are the properties most responsive to changes in molecular size, showed that the  $N,N'$ -disubstituted ureas were more effective than the  $N, N$ -disubstituted compounds. The meager density data available indicate that the  $N, N'$ -compounds also have a larger molecular volume than the  $N, N$ -compounds.

The introduction of sulfur into the urea atom in place of the carbonyl oxygen reduced the plasticizing efficiency of the molecule. At a higher molecular weight level, 1,3-diethylthiourea was generally no less active than 1,3-diethylurea. It is believed that in this case the effect of molecular weight overshadowed the effect of reduced hydrogen-bonding ability.



A complete substitution of the amide groups of formamide and urea was found to enhance rather than decrease the plasticizing efficiency of the molecule. It was concluded that the amide hydrogen atoms can not be responsible for the additive-cellulose bond. Rather, it would seem that the ureas and the formamides bond to the cellulose by forming hydrogen bridges between the carbonyl groups of the additive and the hydroxyl groups of the cellulose.

The  $Q$  value was not found to have any particular significance for paper except as an aid in following the relative changes in the elastic constants  $K_1$  and  $K_2$ , as changes are made in the sheet.

The low-molecular weight ureas were found to excel in increasing stretch. The more efficient plasticizers of high molecular weight decreased stretch, probably because of their marked weakening action on the fiber-to-fiber bonds. Work of failure, likewise, decreased with plasticizing except where the material was capable of increasing stretch without causing an excessive decline in tensile strength.

#### THE MECHANISM OF PLASTICIZING WITH THE UREAS

From the data which have been presented and discussed in this thesis, it is possible to present a reasonable theory covering the mechanism of plasticizing paper with the ureas. Although it is believed that the phenomena involved in plasticizing with the ureas are common to many of the other paper plasticizers, no experimental evidence has been obtained on materials other than the formamides and the ureas. Therefore any extension of the theory to other plasticizers must be purely speculative.

Chronologically, the action of a urea-type plasticizer may be divided into its effect during the drying of a sheet of paper, and its effect during the later mechanical stressing of the sheet. Actually, the role of the plasticizer is probably much the same in both instances so that one may be considered to be a logical extension of the other.

When a sheet of paper is soaked in water or an aqueous solution of a plasticizer, the fiber-to-fiber bonds are swollen in the same way as the amorphous regions of the fibers. This swelling action must disrupt some of the intermolecular bonds which are responsible for fiber strength and bending strength, so that when a water-soaked sheet is redried, some of the bonds fail to re-form. The extent to which this soaking process disrupts bonds is probably related to the swelling power of the solvent or the additive solution. If, as is probably the case, the bonded zones are more readily swollen than the amorphous regions in the fibers, then it is probable that the strength of the fiber-to-fiber bonds is more seriously impaired by soaking in a swelling agent than that of the intra-fiber bonding forces.

In the presence of a large excess of water the plasticizer molecules are probably not strongly adsorbed by the cellulosic hydroxyl groups. However, as water is removed from the sheet during drying, molecules of the plasticizer tend to form hydrogen bonds with the cellulosic hydroxyl groups, thereby anchoring themselves throughout the amorphous portions of the fiber structure and the bonded areas, and effectively satisfying some of the residual valence forces of the cellulose so that they no longer attract hygroscopic moisture. It is believed that the ureas and formamides form this hydrogen bond through

their carbonyl oxygen atom.

By thus fixing themselves throughout the amorphous regions of the cellulosic structure, the plasticizer molecules force the cellulose to retain a higher degree of swelling at any given water content than would normally be the case. This reduces the extent to which the secondary bonding forces between adjacent cellulose molecules, believed to be hydrogen bonds, are able to set up. This action of the plasticizer not only reduces the tendency of the individual fibers to shrink, and in shrinking to twist and coil, but it also reduces the ability of the individual fiber-to-fiber bonds to transmit the stresses resulting from fiber shrinkage.

The effect of drying tension on the mechanical properties of paper is well known. The effect of a plasticizer in effectively reducing drying tension, however, has thus far received almost no attention. It is obvious that if, in drying, a plasticizer has relieved some of the drying tension and reduced the extent of frozen-in stresses, the resulting sheet will have different mechanical properties than an untreated sheet. This effect will be over and above whatever effect the plasticizer molecule exerts on the straining mechanism when the sheet is subjected to tensile stress. The work has indicated, however, that the effect of the plasticizer during drying probably is of minor importance compared to the action of the plasticizer molecules during actual mechanical stressing.

In summary, a dry, plasticized sheet is different from a dry, unplasticized sheet in at least three respects: (a) The fiber structure and the bonded areas of the plasticized sheet are forced to retain some

greater measure of dry swelling than would normally be the case, with the result that their internal bonding strength is reduced and the rigidity of the whole structure is lessened; (b) the extent to which drying tension and frozen-in stresses have stiffened and strengthened the sheet is less in the plasticized sheet; and (c) some of the residual secondary forces of the cellulose have been satisfied by bonding with the plasticizer, so that they no longer seek to attract and hold moisture.

When a dry plasticized sheet is strained, the load-elongation properties of the sheet are markedly affected by the state of dry swelling which exists in the sheet. It may be supposed that the presence of the plasticizer molecules in the zone of fiber-to-fiber bonding reduces the total strength of any given fiber-to-fiber bond in three ways: (1) Reactive hydroxyl groups which would normally have formed bonds with hydroxyl groups of neighboring cellulose chains are prevented from doing so, because they are covered by a plasticizer molecule which has satisfied their residual bonding forces; (2) the number of intermolecular bonds formed in the immediate neighborhood of a plasticizer molecule is reduced because the mechanical separation of the cellulose chains by the large plasticizer molecule prevents groups which would normally cross link from approaching within the necessary bonding distance; and (3) the bonds which form in spite of the presence of plasticizer molecules are weakened because of the greater bonding distances. Since the molar plasticizing effect on the bonds was found to be a strong function of the molecular size of the plasticizer, it must be concluded that the bonded zone is weakened primarily by (2) and (3) rather than (1).

The action of a plasticizer molecule in the amorphous portions of a fiber must be the same as that just postulated for the fiber-to-fiber bonds. In the case of the fibers, however, the effect of plasticizing is probably lessened by penetration difficulties and by the limitations placed on swelling by the crystalline regions. The greater disorder in the bonded zones undoubtedly makes them more easily accessible to plasticizer molecules. This accounts for the fact that a large portion of the plasticizing effect may be explained by the changes in the bonding strength.

The reduction of fiber-to-fiber bonding strength and internal bonding strength of the fibers naturally brings about a reduction in tensile strength and elastic properties. The reduction in secondary bonding forces resulting from the state of dry swelling also frees the molecular or macromolecular flow units of some of their restrictions, and enhances their ability to flow past one another. If the effect of the reduction of fiber-to-fiber bonding strength does not exceed the effect of freeing these flow units, the extensibility of the paper will probably be increased.

If two plasticizers are compared at 50% R.H. on a molar basis, the plasticizer which is capable of maintaining the highest degree of dry swelling will probably be found to be the better plasticizer. Other factors being equal, this will probably be the material having the higher molecular volume. If these same two plasticizers are compared at 11% R.H., the material which can best resist the increased attractive forces between cellulose chains will retain relatively more of its plasticizing effectiveness. The larger molecule will probably be able to do this better than the small molecule, because it will not require the assistance of the water molecules to hold the structure open as will the smaller molecule.

With the above discussion as a background, it seems possible to list some of the properties which are instrumental in determining the relative effectiveness of a material as a plasticizer for paper. These are:

(1) The ability to permeate the amorphous regions of the cellulose structure, including the bonded areas. In order to exert an effect on the fibers and the fiber-to-fiber bonds, a material must be able to penetrate these portions of the sheet. Since water has swelling properties, a plasticizer which is applied from aqueous solution probably does not require swelling properties of its own, although it must be able to take advantage of the water-swollen state to enter into the vital regions of the sheet.

The swelling and penetrating powers of the small, highly polar molecules are probably very much greater than those of the large, heavily substituted ureas, so that these small molecules are more effective in the reduction of intrafiber secondary bonding than the large molecules. The large molecules probably penetrate the fibrous structure only with difficulty, especially if they are applied from alcoholic solution. In this case, their penetration is probably largely restricted to the more disordered, amorphous cellulosic areas such as the bonded zones.

The relative ability or inability of the plasticizer to permeate the fiber structure tends to affect its ability to reduce initial slope and  $K_2$  more than it influences its effect on tensile strength and  $K_1$ . The ability to reduce intrafiber bonding strength is also of importance to the flow properties and extensibility of the sheet.

(2) The ability to bond to the cellulose. Some functional group capable of forming a bond with the cellulose is necessary in order to anchor the molecule in the cellulose structure. Reduction of the ability of the molecule to bond to cellulose places it in a poor competitive position with water and probably hampers its ability to hold the cellulose structure open. Complete elimination of any cellulose-bonding powers leaves the molecules of the additive free to form bonds between themselves and thus to crystallize where they may be left in the sheet. It is probable that the polar group which is responsible for the cellulose-bonding ability of the plasticizer molecule is also important to the ability of the compound to penetrate the fibrous structure.

(3) The ability to maintain a state of dry swelling by mechanical separation of the cellulose molecules. If the molecule has adequate penetrating ability and cellulose-bonding powers, this third factor determines its efficiency in plasticizing a sheet. Increasing molecular volume by higher substitution or by the substitution of larger groups greatly enhances plasticizing ability due to the increased ability of the molecule to keep the cellulose molecules from cross linking.

Plasticizing then is essentially a weakening action in which the number and the strength of the secondary bonding forces--those forces which are largely responsible for the mechanical characteristics of the fibers and the bonds--are reduced. This concept of the plasticizing of paper is fundamentally the same as the accepted concept of the plasticizing of other high polymeric systems.

## CONCLUSIONS

1. Crystalline urea is effectively nonhygroscopic at relative humidities below 65%, since below this humidity it sorbs less than 0.03% moisture. 1,3-Dimethylurea holds less than 1% moisture at relative humidities below 50%. Since both of these materials reduce sheet moisture content when they are incorporated in a sheet of paper, it is inconceivable that, at relative humidities below 50%, their plasticizing action on paper is due to any hygroscopic action.

2. All the ureas and the formamides investigated reduce the moisture content of the paper by competing with the moisture for the reactive sorbing groups of the cellulose. Their action on a sheet, therefore, would class them not as humectants but as dehydrating agents.

3. The formamides and the ureas are bonded to the cellulose through their carbonyl groups. The bond probably takes the form of a hydrogen bridge in which the hydrogen atom from the cellulosic hydroxyl is the link between the hydroxyl oxygen atom and the carbonyl oxygen atom of the amide. This bond is easily broken by the action of a stronger hydrogen bonding agent such as water.

4. The effect of urea on the moisture-vapor sorption loop indicates that the urea-type compounds maintain a sheet in a state of dry swelling. The action of these compounds in preventing deswelling of the cellulose structure and the fiber-to-fiber bonds reduces in number and in strength the secondary bonding forces which are largely responsible for the mechanical strength of paper.



5. In order to accomplish this reduction of secondary bonding forces which is fundamental to plasticizing, a material must be able (a) to penetrate the fiber-to-fiber bonds and/or the fiber structure by its own swelling properties or by utilization of the swelling powers of the solvent; (b) to bond to the cellulose, once penetration has been accomplished and the solvent removed; and (c) to reduce the secondary bonding forces of the cellulose by mechanical separation of the cellulose chains. Properties (a) and (b) require the presence of a polar group to give the molecule swelling powers or solubility in a solvent with swelling powers and to give it the ability to bond to cellulose. Property (c) is a strong function of the molecular size of the material.

6. Urea and its related compounds exert an effect on sheet properties by their presence during the drying of the sheet. The shrinkage tension developed by a urea-treated sheet is lower, at any given moisture content, than that of a normal sheet. The effect of the plasticizer during drying, however, is secondary in importance to its effect during the straining of the sheet.

7. Plasticizers such as water, the ureas, and the formamides reduce the tensile strength, the initial slope, the final slope, the offset load, and the limiting viscous load ( $f$ ) of a sheet of paper. The extensibility of a sheet is generally increased by a mild plasticizing action, but may drop off sharply if the plasticizing action is too great. In some instances, the presence of an excess of a crystalline plasticizer in a sheet may result in crystallization of the material in and around the fibers, which reverses the plasticizing action of the material.

8. Changes in the fiber-to-fiber bonding strength of a sheet have the greatest effect on tensile strength and final slope. Indeed, the changes occurring in these properties with the first increments of urea in the sheet may be wholly explained on the basis of changes in the strength of the fiber-to-fiber bonds. Since tensile strength and final slope are strongly influenced by changes in bonding strength, they reflect the effect of the molecular size of a plasticizer the most strongly. Fiber-to-fiber bonds are accessible to large molecules of plasticizer where the fiber structure may not be, so that those properties which are closely related to bonding strength tend to show an increasing change as plasticizer molecular weight continues to increase.

9. The initial slope and the series spring constant ( $K_2$ ) appear to be relatively more sensitive to changes in the mechanical properties of the fibers than are tensile strength and final slope. The flow properties, offset load and  $f$ , also seem to be influenced by the state of the intrafiber bonds. Since penetration of the fiber becomes more difficult as plasticizer molecular size increases, these properties tend to exhibit a maximum change when plasticizer molecular size is at an intermediate value which permits both penetration of the fibers and the maintenance of a high degree of dry swelling.

10. The efficiency of urea and 1,3-dimethylurea in reducing tensile strength, initial slope, offset load, and  $f$  is decreased at 11% R.H. relative to 50% R.H. Their effect on final slope, however, is increased at the lower humidity level. In effect, the removal of moisture from the sheet leaves the plasticizer with a more difficult task of prevent-

ing the formation of secondary bonds. In a comparison of two plasticizers, the one which is better able to reduce internal bonding at the higher humidity level will probably be the one which will lose relatively less of its plasticizing effectiveness at the lower humidity levels.

11. The internal tearing strength of paper is relatively insensitive to the changes brought about by plasticizing the sheet with urea.

12. The zero-span tensile strength of a urea-treated sheet increases slightly with increasing urea content before dropping off. This increase is attributed to an increase in fiber strength due to the action of the urea in improving stress distribution in the fibers.

13. The properties of a sheet of paper at a given moisture content may be significantly altered by the degree of restraint exerted on the sheet during its drying or conditioning.

14. Water is a relatively inefficient plasticizer of paper when compared to the ureas and the formamides on a molar basis.

15. There is nothing unique about the water molecule which enables it to be adsorbed from the vapor phase by the cellulose in such a way that it exerts a plasticizing action on paper. Other molecules, such as formamide, which are small enough to be volatile and which have the capacity to bond to the reactive sorbing groups of the cellulose, may do the same thing in an anhydrous atmosphere.

16. The plasticizing of paper is fundamentally a matter of the reduction of the number and the strength of intermolecular and inter-fiber secondary bonding forces. As such, it is primarily a weakening action. This concept of the plasticizing of paper is basically the same as the accepted concept of the plasticizing of other high polymers.

17. The load-elongation curve is an excellent tool for use in studying the effect of plasticizers on the properties of paper, both because of its sensitivity to changes in the sheet, and because of the large amount of information it yields relative to other strength tests.

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