

TENSILE STRENGTH STUDIES OF AN
ADHESIVE POLYMER FROM ZEIN
AND DIALDEHYDE STARCH

by

William Morton Swift

A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
MASTER OF SCIENCE

Major Subject: Chemical Engineering

Signatures have been redacted for privacy

Iowa State University
Of Science and Technology
Ames, Iowa

1967

TABLE OF CONTENTS

	Page
ABSTRACT	111
INTRODUCTION	1
LITERATURE REVIEW	4
EXPERIMENTAL PROCEDURE	15
Preparation of the Dialdehyde Starch Solutions	15
Preparation of the Zein Solution	16
Preparation of the Reaction Products	16
Testing the Reaction Products for Tensile Strength	19
RESULTS AND DISCUSSION	28
Preliminary Investigations	28
Effects of Concentration and Pressure on Tensile Strength	29
Effect of Reaction Time on Tensile Strength	37
Effects of Curing Time and Temperature on Tensile Strength	40
CONCLUSIONS AND RECOMMENDATIONS	47
LITERATURE CITED	50
ACKNOWLEDGEMENTS	54

ABSTRACT

Previous work has shown that a good adhesive of moderate tensile strength could be made from a reaction product of zein and dialdehyde starch. The purpose of this work was to further study the tensile strength characteristics of the zein-dialdehyde starch adhesive and to analyze its potential as an adhesive. To accomplish this the variables of adhesive concentration at application, curing pressure, reaction time, curing time, and curing temperature were investigated to determine their effects on tensile strength.

The results seem to indicate that the ultimate tensile strength of the adhesive is limited by the force of adhesion between the glue and the wood rather than the internal cohesive force of the glue. It is also apparent that the cross-linking effect of the dialdehyde starch on the zein molecule has a very small and perhaps even negative effect on the adhesive forces. It was also found that the zein-dialdehyde starch adhesive was considerably weaker than the adhesives prepared from wheat gluten and dialdehyde starch. Nevertheless, due to the fact that zein, an adhesive used in making high grade veneers, has been made waterproof by combining it with formaldehyde, leaves hope that the zein-dialdehyde starch adhesive may be industrially desirable for this same type of application.

INTRODUCTION

Over the past several years, the American farmer has been faced with the problem of over-production, especially in the commodities of corn and wheat. This has resulted in the building up of large surpluses of these commodities and an undesirably low economic return to the farmer for his products. The United States government has tried to help the farmer economically through price support programs and other programs designed to reduce existing surpluses by restricting land use and production. These programs are, however, costly to administer and often quite unpopular. They tend, at best, to deal with the symptoms of the problem and not its cause; that is, the ability of the American farmer to produce corn and wheat in abundance.

Looking to the future, we can see even more clearly the need for additional ways of handling this problem. An ever increasing technology promises an ever increasing yield from the same amount of land, both in this country and around the world. Thus it would seem quite likely that while our own capacity for production of corn and wheat will continue to increase, our exports to foreign markets may in fact decrease as more and more countries become self-sufficient. Hence if the problem of surpluses is to be solved, it seems essential that new answers be found.

An obvious alternative or aid to government controls is

to find new non-food uses for the commodities of corn and wheat. The low cost of corn and wheat as raw materials for industrial use makes them attractive as such, and has stimulated the United States government to investigate the possibilities of developing commercial products from them. This work is an investigation of one such possibility.

Dialdehyde starch and zein are two principal raw materials obtainable from corn and wheat. Dialdehyde starch is an aldehyde polymer produced by the chemical modification of pure starch with periodic acid (17). Zein, on the other hand, is a member of the class of proteins which are called protamines. Zein can be obtained quite readily from corn gluten, the protein fraction of corn, by extraction with aqueous isopropyl alcohol (10). The fact that aldehydes are good tanning agents led to the idea that perhaps dialdehyde starch, a polymer of high molecular weight, could be reacted with a high molecular weight protein such as zein to form a new polymer of some industrial significance. Previous work by Chatterji (8) and others (13, 20) has shown the feasibility of such a reaction. The reaction product obtained was a polymer which showed some promise as a possible industrial adhesive in wood to wood bonding.

The purpose of this work was to investigate further the tensile strength characteristics of the adhesive polymer obtained from the reaction of dialdehyde starch and zein. Of particular interest was the determination of the effects of

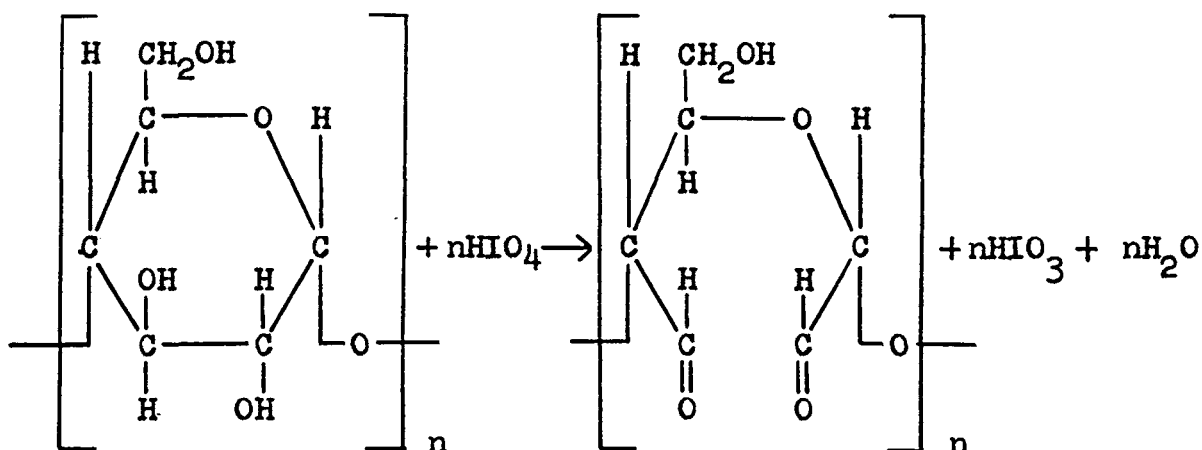
curing pressure, temperature, and time on the tensile strength of the glue in wood to wood bonding. Pressures ranging from 50 psi to 150 psi were employed, and temperatures from 40°C to 120°C were tried over times ranging between four and twelve hours.

In order to evaluate the results obtained in a meaningful manner, it also seemed advisable to interpret the results of this work in relation to various other adhesives already in use industrially. Such a comparison is, of course, essential in determining whether or not further development of the zein-dialdehyde starch reaction product as an adhesive is economically desirable.

LITERATURE REVIEW

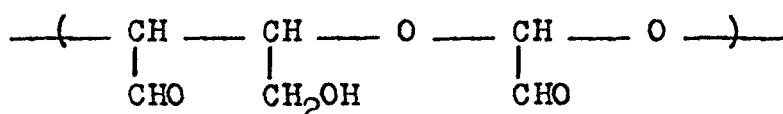
Dialdehyde starch, often referred to in the literature as oxystarch, is a finely divided, practically odorless solid which is almost identical in appearance and color to the original starch from which it is derived. While DAS is not a relatively new chemical discovery, recent developments in the manufacture and applications of dialdehyde starch have made it a subject of increasing industrial interest.

Dialdehyde starch was first prepared in the laboratory by Hudson and Jackson (17, 18). The oxidation reaction was carried out in solution using periodic acid as the oxidizing agent. The reaction is understood to proceed by the following mechanism.



The periodate ion selectively oxidizes the 1,2-glycol grouping of the second and third carbon atoms and breaks the bond between them. The starch chain is not ruptured, however, so the resulting compound can be accurately described as a polymeric dialdehyde. It should be noted that for simplicity the above

structure represents the amylose portion of the original starch (1, 4-branching), even though the amylopectin portion (3-, or 6-branching) is also present. To better emphasize the dialdehyde nature of the resulting polymer, and in order to discourage associating the polymer with ordinary starches, the following representation should probably be employed:



Dialdehyde starch remained a laboratory curiosity for many years due to the expensive oxidizing agent, periodic acid, required for its preparation. This problem was finally solved by Dvonch and Mehlretter (11) who in 1952 reported a practical electrolytic process whereby the expensive periodic acid could be regenerated for use over and over again. Two United States patents were granted to them in connection with this process (12, 23). The electrolytic process has been the subject of several experimental investigations since its conception, and today is a quite workable process as described in the literature (29, 24).

The electrolytic process is controllable to the extent that material of any level of oxidation can be produced. The level of oxidation of DAS is defined as the percentage of units in the original starch chain which have undergone oxidation. The higher the level of oxidation, the less the dialdehyde starch resembles ordinary starch in its properties. For

example, the higher level oxidation product will not gel when boiled in water, whereas the compound with a 50 per cent oxidation level will form a gel when heated with water. The dialdehyde starch used in this investigation had a high level of oxidation and was obtained from the Miles Chemical Company with the following specifications (27):

Aldehyde content-	greater than 93 per cent
Moisture content-	less than 10 per cent
Heavy metals	less than 10 ppm
Sulfated ash	less than 1 per cent
Bulk density	45 to 55 ml per oz.

The key to the great interest in dialdehyde starch lies of course in the reactive aldehyde groups. They have been shown (21) to react with or cross-link proteins, cellulose, methyl cellulose, starch, dextrans and other polysaccharides, polypeptides and polyhydroxy materials. DAS also has film forming properties and general usefulness as an intermediate for other chemicals. The properties of DAS have been thoroughly investigated by Sloan, et al. (31).

The use of dialdehyde starch as a tanning agent has been under investigation for some time (6, 14, 15). Results have shown that dialdehyde starch is comparable to other aldehydes in its ability to tan leather, and its use as a pretanning agent for the tanning of sole leather seems to be a very promising application.

Dialdehyde starch has also been widely investigated for

use in the paper industries. Meller (25) has shown that both the wet and dry strength of paper could be increased by using DAS as a beater additive. Jones et al. (19) have also studied the use of dialdehyde starch as an agent to improve the wet strength of papers.

The United States Department of Agriculture has studied for some time the use of dialdehyde starch in adhesive applications. Weakly et al. (37) have investigated the insolubilization or cross-linking of casein by DAS. They discovered that the slightly acidic protein-based adhesive could be used to give excellent water resistant bonds in veneers (35). A moderately alkaline soybean-blood glue containing a small percentage of dialdehyde starch has also been investigated (36). It was shown that while there was no apparent improvement in the dry strength of laboratory-prepared panels of plywood, the dialdehyde starch did increase the water resistance significantly and made the glue acceptable for interior plywood application.

For a further discussion of present and potential applications for dialdehyde starch, the reader is referred to the literature (21, 26).

Zein, a member of the alcohol soluble proteins known as protamines, is a fine powder, slightly yellow in color, which contains from 7 to 8 per cent of volatile matter and no more than 2 per cent of non-protein solids. It was first isolated by Gorham (16) in 1821 and was given the name "zein" by him.

Today zein is available only as a by-product of the corn processing industries. It is extracted commercially from corn gluten, a by-product of the starch industry which contains 35 per cent or more proteins classifiable as zein, with aqueous isopropyl alcohol (33). The extract is then treated with alkali and any oil present is separated from the alcohol solution with hexane. The zein is then precipitated, washed, and flash dried.

Zein, like all proteins, is a high polymer built up of amino acid units bound by peptide linkages. Glutamine and leucine are the major amino acid constituents of zein, being present 21.4 and 19.3 per cent by weight respectively (10). Cohn and Edsall (9) have established the molecular weight of zein to be about 37,000. Watson, Arrhenius, and Williams (34) report that the greater part of the zein has a molecular weight of approximately 35,000, while that of another constituent is approximately half this value. The zein used for this work, however, was obtained from Corn Products Sales Company with a reported molecular weight of only 25,000.

Zein is unique among industrial proteins in both its physical and chemical properties. These can be explained for the most part in terms of the amino acid composition of the zein molecule. One of the most outstanding chemical characteristics of zein is that it is relatively inert. Because of the lack of diamino acids in the molecule, zein has no apparent basic properties and therefore reacts slowly with

formaldehyde. Zein has very few acidic properties also because of the high proportion of the dicarboxylic acids present as amides. The large number of hydrocarbon side chains causes zein to be insoluble in water and soluble in many organic solvents which cannot be used for other industrial proteins such as casein, gelatine, and soybean protein (10).

One troublesome characteristic of zein is that it tends to become denatured when in solution (33). The denaturation, which is a change in the chemical nature of the zein rendering it insoluble in the usual solvents, is autocatalytic. The denatured insoluble material catalyzes the reaction to such an extent that in some cases, where considerable amounts are present, an otherwise stable solution may gel in a few hours. In general, the more nearly anhydrous the solvent becomes while still remaining a satisfactory solvent for zein, the more stable will be the solution.

Zein, like dialdehyde starch, has a wide range of industrial applications (10, 33). One major application for zein has been in the paper coating field. These coatings have a high gloss, excellent scuff resistance, flexibility, and water resistance which are all very desirable properties. Ready solubility in alcohol, rapid solvent release and excellent filmforming characteristics make zein particularly useful as a finish for wood. The hardness and toughness of these films are recognized as being outstanding. A new and interesting use for zein is in the pharmaceutical industry where its

edibility and binding characteristics have led to the wide usage of zein in tablets as binders and coatings. Zein has also been found quite useful in the manufacture of printing inks because of its rapid drying characteristics, hot scuff resistance, and pigment binding capacity.

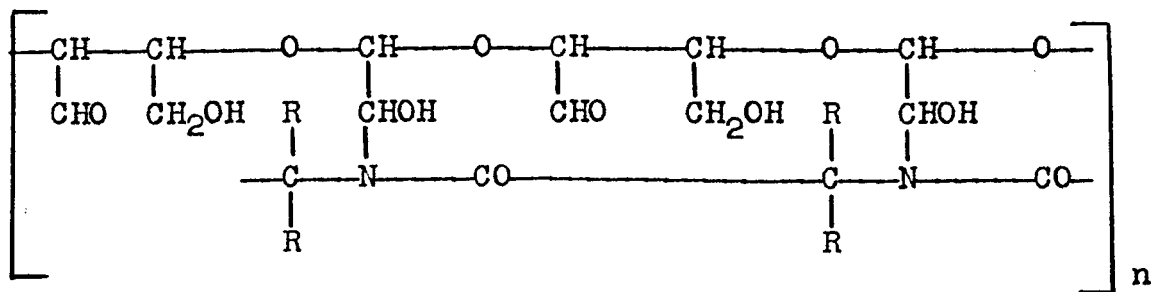
Zein can be used as an adhesive, but because of its cost, only where its specific properties can justify its use. One such example is in high grade veneers where it is very useful in that the adhesive does not strike through the wood (33). Zein adhesives have been made waterproof by combining them in solution with formaldehyde and an organic acid and curing under pressure at an elevated temperature (32). Corn gluten, the source of zein, has been used in the adhesive industry as an extender in phenolic resin plywood glues (4, 5). It has been found that corn gluten can be used in proportions up to 40 per cent of the total solids content of the glue without any apparent loss in water resistance or gluing properties of the original glue.

The fact that dialdehyde starch, a polymeric dialdehyde, had proven its ability to react with proteins led Chatterji (8) to investigate the possibility of reacting DAS with a high molecular weight protein in the hopes of producing a high polymeric compound of some industrial application. He chose to do his work with the complex wheat protein. Using various solvents Chatterji (8) performed over 130 reaction combinations between the DAS and the wheat gluten. His procedure

included alcohol drying of the reaction products to remove all water from them. They were then redissolved in glacial acetic acid to form an adhesive. The adhesive was then tested for tensile strength by applying it to hard maple test blocks which were clamped together and allowed to cure overnight at room temperature. An adhesive giving tensile strengths of over 900 psi was finally developed.

The high cost of alcohol drying was a serious problem which had to be overcome if the adhesive was ever to be developed commercially. Abegg (1) began working with the adhesive on a pilot plant scale and experimented with the use of a double drum dryer. On the pilot plant scale of production, the alcohol dried product gave tensile strengths of only 350 psi while the product off the double drum dryer could produce tensile strengths only 75 per cent of that value.

In his work, Chatterji (8) had found that the dialdehyde content of the reaction product was much lower than that of the original dialdehyde starch. He hypothesized that this was due to the cross-linking of the aldehyde groups with the wheat gluten to form a condensation polymer of the following form:



This structure indicates that a large number of additional aldehyde groups remain unaffected during the reaction process. Polymers which contain free aldehyde groups usually fall into the category of thermosetting resins.

Recognizing this fact, McCoy (22) and Erskine (13) tried curing the DAS-wheat gluten adhesive at elevated temperatures. Erskine (13) employed curing temperatures from 40 degrees centigrade to 160 degrees centigrade, and curing times from two to twelve hours. He was able to obtain tensile strengths of over 1125 psi with an adhesive prepared on a pilot plant scale.

Kalia (20) was the first to begin working on the reaction between DAS and corn gluten. He began his investigation by performing several solubility studies which led to the use of sodium bisulfite and isopropyl alcohol solutions as the solvents for dialdehyde starch and corn gluten respectively. He proceeded to make several reaction studies similar to those of Chatterji (8) in an attempt to produce an adhesive of similar quality to that prepared using wheat gluten. Using corn gluten, however, Kalia discovered that no adhesive with the desired tensile strengths could be obtained. Thinking that perhaps the protein content of the corn gluten was poor, he proceeded to investigate reactions of zein and dialdehyde starch. Using zein he was able to report an adhesive product having a tensile strength of over 1000 psi in wood to wood bonding. In his work, Kalia did some preliminary testing of

the reaction variables such as time, temperature, and reactant concentrations. He also studied two temperatures of curing which indicated that perhaps high temperature curing could make further improvements in the quality of the adhesive.

It would be impossible to present a thorough review of the aspects of adhesives and adhesion at this time. It might be well, however, to present a few basic concepts as they relate to the adhesive currently under study.

Adhesives can be classified according to the nature of their origin into the following three main areas (7): adhesives of animal origin, adhesives of vegetable origin, and synthetic adhesives. Adhesives of the first two types are generally unsuitable for industrial use unless modified by the addition of various substances to improve their adhesive qualities. The zein-dialdehyde starch adhesive under study would be an example of a chemically modified adhesive of vegetable origin.

It is impossible to designate a fixed set of desirable properties for adhesives as these may vary from application to application. Resistance to effects of moisture and changes in humidity, resistance to attack from molds and fungi, stability, and strength of bonding are a few characteristics generally considered important, however, in evaluating an adhesive.

The strength of an adhesive is based primarily on two distinct forces (1). The first of these forces is adhesion,

which is the force working between the molecules of the adhesive and the pasted surface. Hence, rough surfaces provide a greater surface area and allow for greater adhesion to occur. Secondly, there is the cohesive force. This is the force which works entirely within the adhesive itself and helps to keep the glue from pulling apart from within.

There are several standard tests which can be made on adhesives to determine their usefulness in particular industrial situations (28). The tensile strength test used in this research is just one of these tests which is quite useful in testing wood adhesives. Another common test for wood adhesives is the shear test which is an even more severe test than the tensile strength test in evaluating the strength of a particular glue. Tests for resistance to moisture and molds are also common tests made on adhesives being considered for plywood and veneer applications.

For a further discussion of adhesives, the reader is referred to the literature (2, 7, 28, 30).

EXPERIMENTAL PROCEDURE

Preparation of the Dialdehyde Starch Solutions

On the basis of previous investigations (8, 13, 20), a 5 per cent by weight solution of sodium bisulfite in water was chosen as the solvent for preparing the dialdehyde starch solutions. Using a 1000 ml volumetric flask, sufficient solvent was added to 13.333 grams of dialdehyde starch to prepare exactly one liter of solution. The suspension was transferred to a one liter flask which was placed in a water bath controlled at a temperature of 70°C. The neck of the flask was fitted with a rubber stopper through which a plexiglass stirring rod and bearing assembly was passed. This allowed the solution to be stirred and at the same time prevented the evaporation of solvent during heating. The mixture was stirred for a period of thirty minutes to allow for complete solution of the DAS. The color of the solution changed from a milky white to an almost translucent state at complete solution of the dialdehyde starch. Brown discolorations were checked for during the solution process to see if any degradation of the dialdehyde starch was occurring due to over or prolonged heating. Such discolorations were never observed. The viscosity of the solution did increase considerably during the heating; but upon removal from the water bath and subsequent cooling, the viscosity of the solution returned to near that of the original solvent. Finally, the cooled solution was put into

stoppered flasks for storage.

Preparation of the Zein Solution

As was the case for dialdehyde starch, the solvent for preparing the zein solutions was chosen on the basis of previous work (20). A 70 per cent solution by volume of isopropyl alcohol in water was employed. As before, a sufficient amount of solvent was added to 250 grams of zein in a 1000 ml volumetric flask to prepare exactly one liter of solution. After allowing the solids to disperse in the alcohol, the mixture was transferred to a small Waring blender. The blender was equipped with a copper tubing heating coil through which tap water of the desired temperature could be passed. A thermometer was also inserted through the top of the blender so that the temperature of the solution could be monitored. The blender was operated at a low speed to thoroughly mix the solution while it was heated to 55°C. After this temperature was obtained, the blender was allowed to run for an additional fifteen minutes to insure complete solution of the zein. The dark green solution which resulted was very tacky and quite viscous. It was transferred from the blender into tightly stoppered flasks for storage.

Preparation of the Reaction Products

Figure 1. illustrates the apparatus used to carry out the reactions between dialdehyde starch and zein. The reaction vessel was a 500 ml three-necked, round-bottom flask.

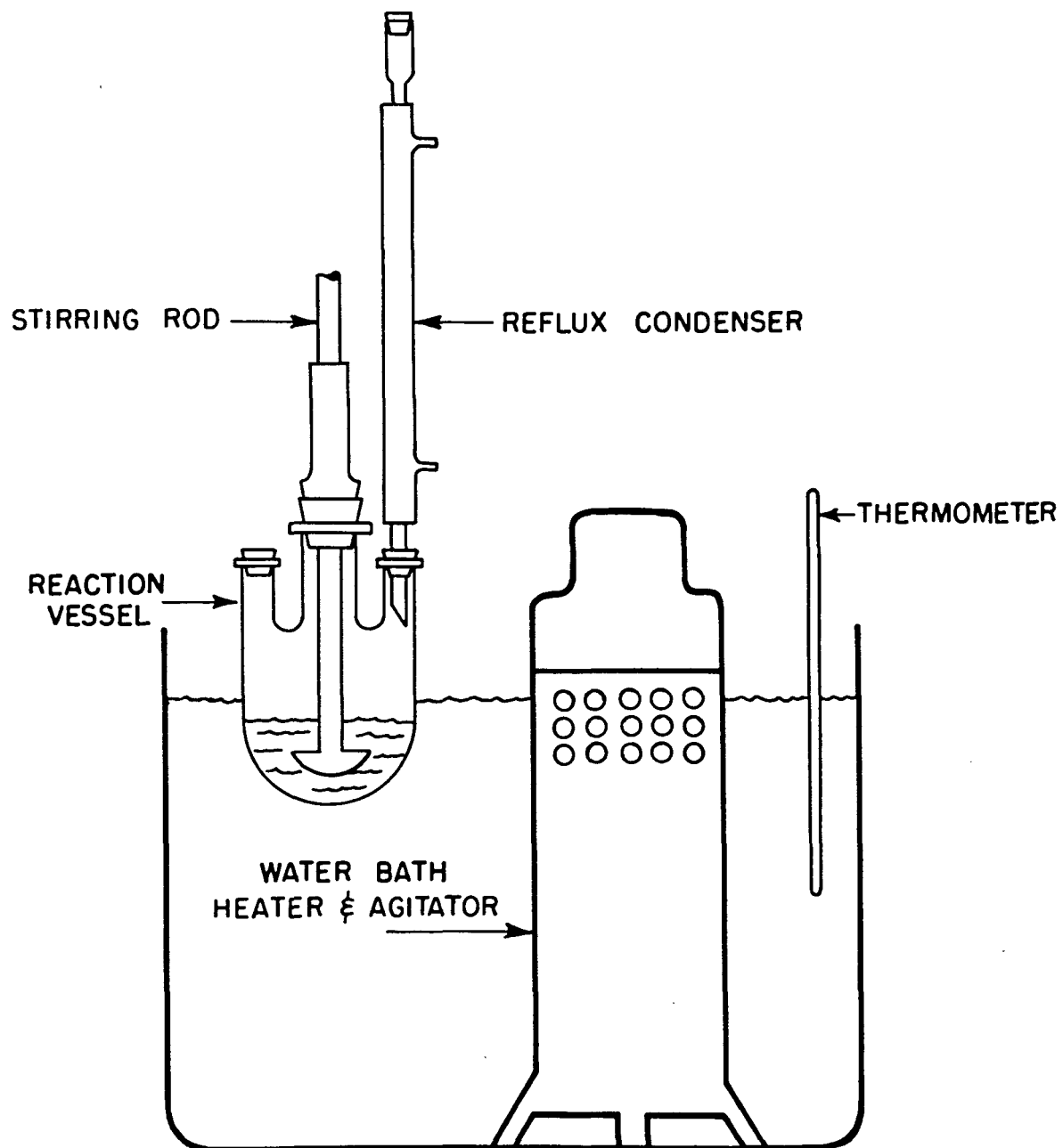


Figure 1. Apparatus used to react the zein and dialdehyde starch

It was placed in an agitated and temperature controlled water bath. A stirring rod assembly was placed into the middle neck of the flask so that the reactants could be heated and stirred without the loss of solvent by evaporation. To prevent pressure from building up within the reactor, a reflux condensor was fitted into one of the two remaining necks of the vessel. The third opening was fitted with a rubber stopper and was used for the adding of reactants.

With the bath at the desired temperature and the flask in place, the desired amount of zein solution was placed into the reaction vessel. Agitation was begun immediately to bring the zein up to temperature quickly and uniformly. The desired amount of dialdehyde starch solution was then added to the reaction vessel very slowly. Rapid addition of the DAS resulted in the precipitation of agglomerates of zein by the water in the dialdehyde starch solution. Upon completing the addition of the DAS, the timing of the reaction was begun.

After allowing the reaction to proceed for the desired length of time, the reaction vessel was removed from the water bath. The reaction product was quickly transferred to a one liter beaker. Distilled water at room temperature was then added to the solution until the reaction product was completely precipitated. Precipitation occurred in the form of a sticky, dough-like mass which was washed several times with distilled water to remove any remaining traces of the solvents. The doughy precipitate was then spread out into a

thin sheet and allowed to dry for a period of at least 48 hours. To prevent the product from adhering to anything while drying, it was found most convenient to simply hang the thin sheet of adhesive material over a string.

The final step was to grind the dried precipitate to a size where it could be easily handled and redissolved back into solution for application to test blocks. Two devices, a small ball mill and a small hammer mill, were tried for this purpose. Both accomplished approximately the same size reduction. The hammer mill, however, offered a great savings in time over the ball mill with no apparent adverse effects on the quality of the adhesive product. Therefore, the hammer mill was employed for the majority of the samples. Material of approximately -30 mesh was obtained in this way. Ground samples were stored in sample bottles to await testing.

Testing the Reaction Products for Tensile Strength

The American Society of Testing and Materials has established a standard procedure for testing the tensile strength of adhesives in wood to wood bonding (3). For reasons of practicality and convenience, however, it was considered necessary to alter certain steps in the standard procedure to better suit our own testing facilities.

The first step in preparing the samples for testing was to redissolve the samples in an appropriate solvent. On the basis of previous studies, both glacial acetic acid and a 70

per cent solution of isopropyl alcohol in water were considered (8, 13, 20). Following some preliminary investigations, the alcohol solution was found to be the best solvent for this purpose. It was used, therefore, throughout the remainder of the experimental work.

The desired amount of the sample to be tested was weighed out in a 50 ml sample bottle. Ten milliliters of the isopropanol solution were then added to the solids to begin the solution process. The solids were not readily soluble, however, and they tended to agglomerate into an adhesive mass, which with occasional stirring was slowly redissolved by the alcohol over a period of six hours. Except for those times when the solution was being stirred, the sample bottle was kept closed to prevent the loss of solvent. The resulting dark-green, homogeneous solution was quite sticky to the touch. The viscosity varied considerably with the amount of solids dissolved, but solutions as concentrated as 7 grams of solids per 10 ml of solvent still exhibited good flow characteristics.

The adhesive, once fully dissolved, was ready to be applied to the test blocks. The blocks of hard maple were machined on a lathe to the specifications as shown in figure 2. The test surface of each block was parallel to the grain of the wood and had a cross-sectional area of 0.5 square inches. After matching the blocks into pairs having similar grain structures, the adhesive was applied to the test face

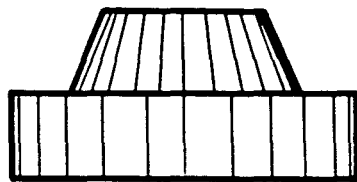
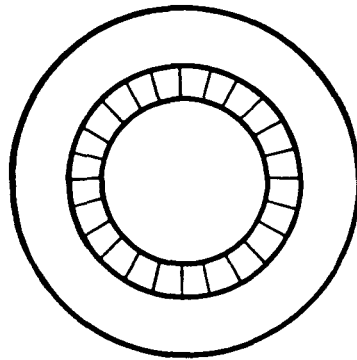


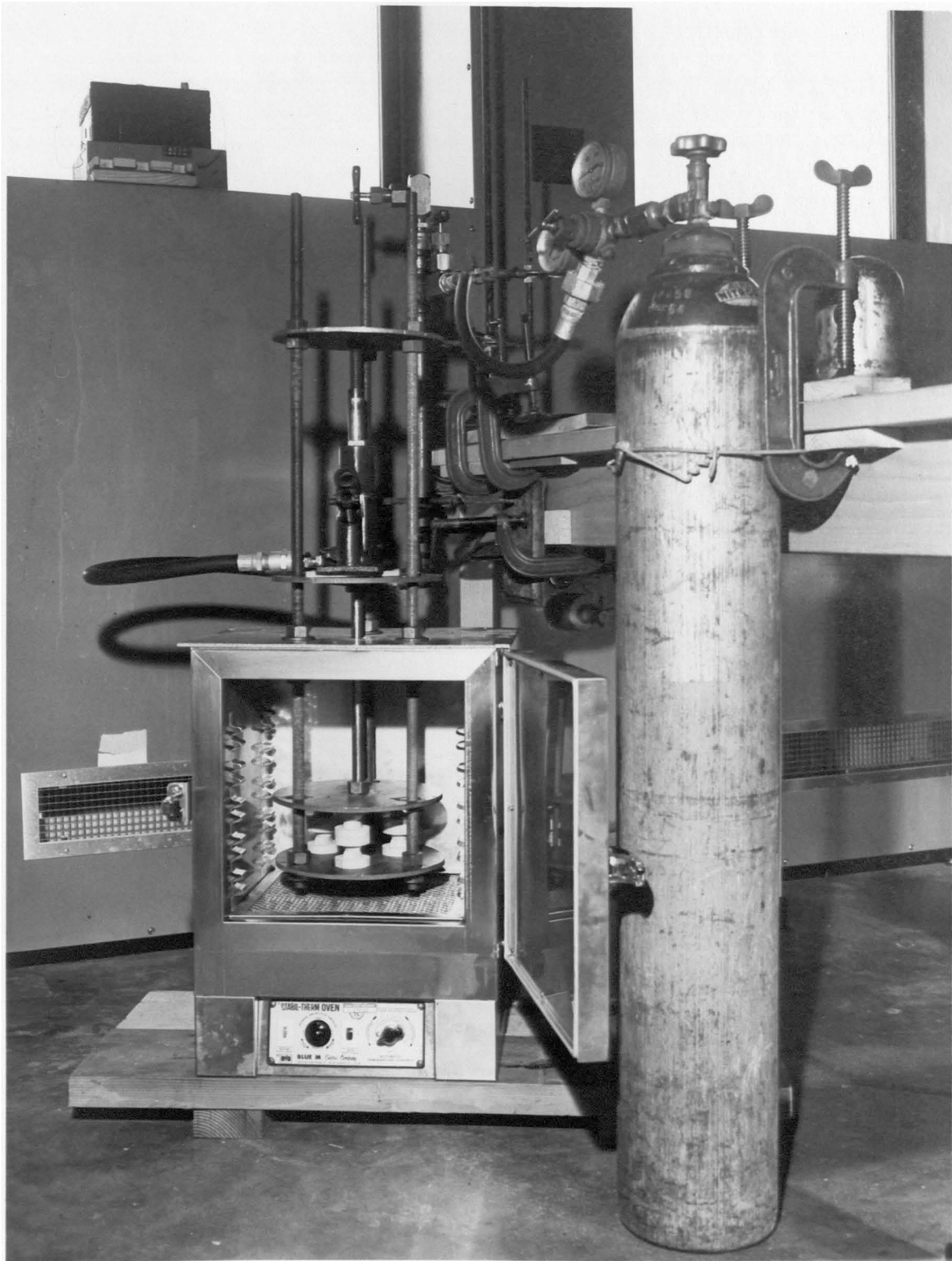
Figure 2. Hard maple test block

of both blocks. The blocks were then lined up with their grains parallel and pressed together lightly to initiate adhesion. Care had to be taken to insure perfect alignment of the block faces for maximum tensile strength readings on the test machine. It should be noted that no attempt was made to measure the amount of adhesive that was applied to the test surfaces. Instead, an excess amount of adhesive was applied and the quantity of glue retained between the faces was left as an undetermined function of viscosity and curing pressure. This procedure neglected, therefore, the testing of bonds where the interface was less than saturated with adhesive. However, such bonds seem of little interest where maximum results are desired.

After the blocks were joined together, they were placed in a specially designed press and oven to cure. The apparatus is illustrated in figure 3. A cylinder of compressed nitrogen was used to exert a regulated pressure on an oil reservoir which in turn generated a hydraulic pressure on the piston of the jack. The force of the jack extending itself between the upper two platens was transferred inside the oven and compressed the samples between the lower two platens. Using simple relationships of area, it was an easy matter to relate the pressure of the nitrogen to the pressure exerted on the blocks in the oven. In this way, both the temperature and pressure of curing could be controlled quite simply.

The only real drawback to the use of the apparatus was in

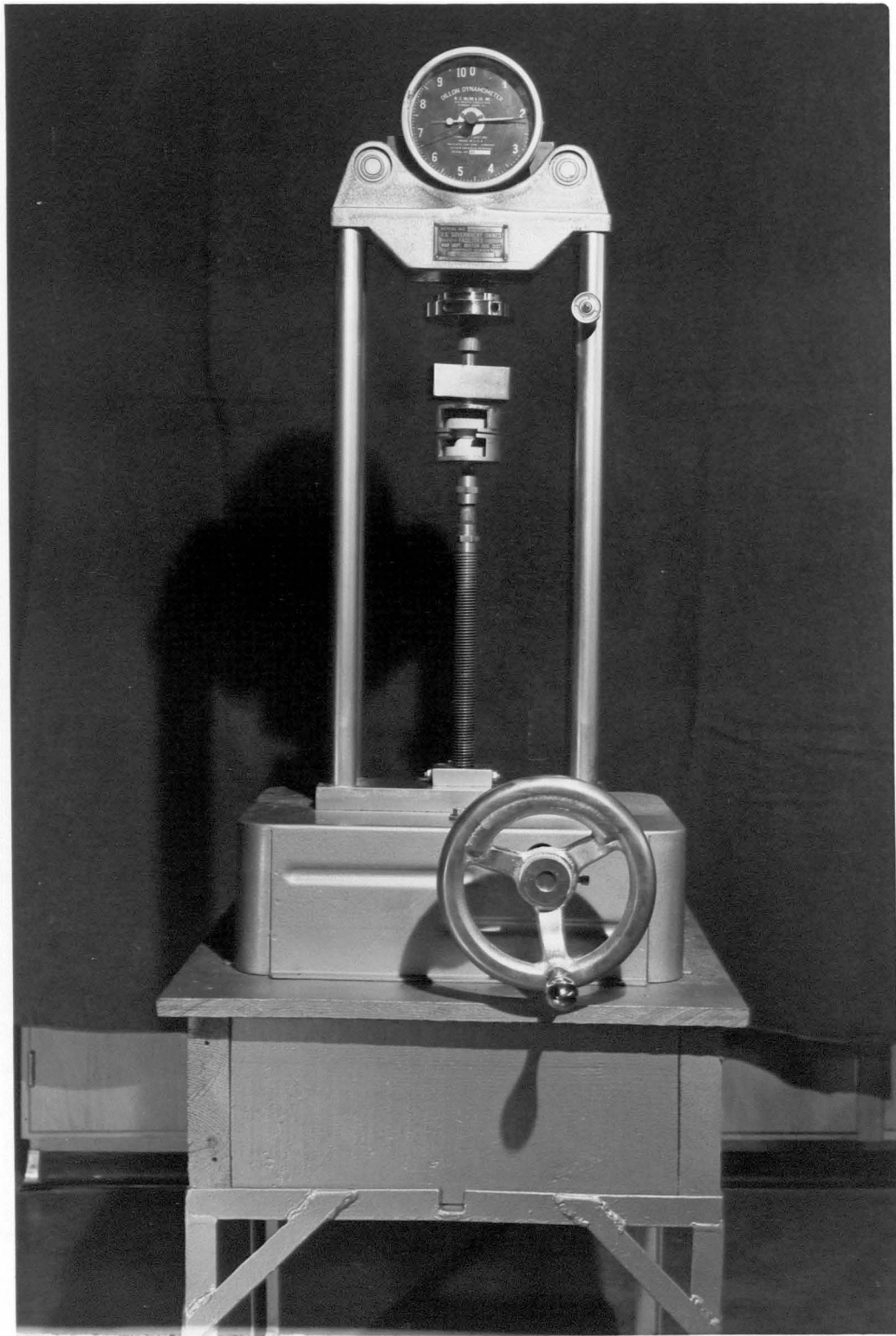
Figure 3. Apparatus used for curing test blocks under constant temperature and pressure



the pressure distribution over the samples in the oven. Even though the samples were placed in the oven in three stacks of two samples each, thus employing the principle that three points determine a plane, there was undoubtedly some pressure variations from stack to stack due to minute variations in wood thickness from sample to sample. However, the effect of this variation would probably be quite small if it could be compared to the variation between samples due to wood effects.

The final step in the test procedure was to measure the tensile strength of the cured samples. The samples were removed from the oven and allowed to cool for a period of several hours. They were then tested in a Dillon Dynamometer with a load capacity of 1000 pounds. Figure 4. illustrates how the blocks were placed in the machine between two jaws, and then pulled apart. The load was applied to the blocks at a rate of 600 pounds per minute. Since the cross-sectional area of the blocks is 0.5 square inches, the breaking load was doubled to get the tensile strength of the blocks in pounds per square inch.

Figure 4. Dillon Dynamometer used for measuring the tensile strength of adhesives in wood to wood bonding



RESULTS AND DISCUSSION

Preliminary Investigations

Preliminary investigations were undertaken in an effort to duplicate the results obtained previously by Kalia (20) who was the first to study the polymerization reaction between zein and dialdehyde starch. After a considerable period of time during which techniques were developed and refined, a large discrepancy was still found to exist between the values of tensile strength recorded previously and those observed under the present investigation. Using the same quality raw materials and procedures as was employed by Kalia (20), tensile strengths were obtained which were only 50 to 60 per cent of those previously recorded.

The reason for such a large discrepancy can not be fully explained. There is considerable reason, however, to believe that the primary source of the discrepancy lies in the tensile testing machines employed for the separate investigations. Kalia (20) used an older type shot-flow tensile tester which is a system of beams and levers by which the weight of shot flowing into a pan is used to find the tensile force required to break the test pieces. The accuracy of such a system is affected quite significantly by the accuracy used in measuring the various lever arms and also upon the amount of friction between the moving parts. The newer Dillon Dynamometer used in the current investigation simply recorded the deflection of a

steel beam in units of pounds force as tensile forces were applied to the test pieces. The newer mechanism is much simpler and would appear to be much more reliable.

Erskine (13) in his investigation of wheat gluten-dialdehyde starch adhesive polymers also reported a discrepancy between the two tensile testing machines. As yet, the magnitude of this discrepancy has not been fully determined. However, since the preliminary investigations yielded an adhesive comparable in strength to a similarly prepared wheat gluten adhesive tested on the Dynamometer, it was decided to proceed with the main testing program. The present results will have to be interpreted on their own merits until such time as the discrepancy between the two machines can be accurately determined.

Effects of Concentration and Pressure on Tensile Strength

Two variables which one would expect to be interrelated in their effects on tensile strength are the solids concentration of the glue and the curing pressure. This can be easily seen by reviewing the two forces which are involved in any adhesive bond. First, we have the force of adhesion which is a function of the attraction between the adhesive and the surface to which it is applied. Secondly, we have the force of cohesion which is a function of the internal strength of the adhesive itself. It follows then that the ultimate tensile strength of any adhesive bond is limited by the weaker of these two distinct

forces. If adhesion is the controlling force, then the bond fails at the interface between the surface and the adhesive. If, on the other hand, cohesion is the controlling force, then the bond tends to fail somewhere within the glue line.

Looking at concentration, we can see that by increasing the amount of solids in the glue, both the cohesive and adhesive forces would tend to increase also. After a certain point, however, the increased viscosity of the adhesive reduces the ability of the adhesive to penetrate the surface of the wood and a decrease in the adhesive forces would result. Thus we can see that if the adhesive forces are limiting over all values of concentration, then the effect of concentration on tensile strength should be quadratic in form.

Looking now at pressure, we can see its relation to solids concentration and tensile strength. As pressure is increased, penetration into the wood is increased while the thickness of the glue line is decreased. Thus if adhesion were again controlling, it is apparent an increase in pressure would increase the tensile strength of the glue up to a certain point. However, increasing the pressure beyond that point would result in a starved glue joint and severely weakened cohesive forces. Thus a quadratic effect of pressure would also be observed. If, on the other hand, the cohesive forces were limiting, then very high pressures and a very thin glue line would be very desirable.

With this in mind, it was decided to set up an experiment to test the effects of concentration and curing pressure on the

tensile strength of a zein-dialdehyde starch adhesive. A 5 by 5 factorial arrangement in a completely randomized design was selected for an experimental design. The adhesive tested was prepared by reacting 160 ml. of the standard zein solution (approximately 40 grams of zein) with 75 ml. of DAS solution (approximately 2 grams of DAS) at 70°C for a period of one hour. The concentrations tested ranged from 3 to 7 grams of solids per 10 ml. of solvent and the curing pressures ranged from 50 to 150 psi. Curing of the blocks was carried out at 80°C for 8 hours. The results of this experiment are given in Table 1. An analysis of variance was prepared for the data and it is given in Table 2.

From the analysis of variance table, the only significant variable on tensile strength appears to be the solids concentration of the glue. This effect also appears to be quadratic in nature, indicating that perhaps the adhesive forces of the glue are the controlling factors in determining its tensile strength. A visual inspection of the test pieces after testing also seems to support this hypothesis. However, a visual inspection cannot be considered as final evidence, because the presence of even a mono-molecular layer of adhesive over the surfaces of the test pieces would contradict the above hypothesis.

It is rather surprising that there are no apparent significant effects of pressure and pressure-concentration interaction. There are two possible explanations for this. The first is

Table 1. Tensile strength^a of a zein dialdehyde starch adhesive^b as a function of glue concentration and curing pressure

Curing Pressure ^c (psi)	Solids Concentration (grams/10 ml)				
	3	4	5	6	7
50	470	552	526	608	496
75	533	500	590	677	562
100	407	618	697	511	586
125	532	625	657	635	550
150	388	564	663	643	543

^aAverage values in psi

^bPrepared by reacting 40 grams of zein with 2 grams of DAS for one hour at 70°C.

^cTest blocks were cured for 8 hours at 80°C.

Table 2. Analysis of variance of tensile strength data taken as a function of glue concentration and curing pressure

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F Stastic
Treatments	860,037	24		
Concentration	472,632	4	118,158	4.49**
linear effect	121,508	1	121,508	4.62*
quadratic effect	349,059	1	349,059	13.26**
Pressure	79,829	4	19,957	0.76
Interaction	307,576	16	19,224	0.73
Error	3,106,007	118	26,322	
Total	3,966,044	142		

*Significant at .05 level

**Significant at .01 level

simply that the range of pressures studied was either above or below the range of pressures where pressure is a significant variable. A second explanation, and perhaps a more reasonable one, is that the overall effect of pressure is small and that the experimental design used in this experiment was not sensitive enough to detect it. Only six replications were used to determine each mean value instead of the fifteen to twenty replications recommended by the American Society of Testing and Materials (3). Had the additional replications been made, perhaps the sensitivity of the experiment could have detected smaller effects of pressure.

A study of the data does seem to indicate that perhaps a small quadratic effect of pressure does exist over the range of pressures studied. It was decided, therefore, to use the method of orthogonal polynomials to fit the data with a surface containing quadratic effects of concentration and pressure and an interaction term composed of the linear effects of both variables. The following relationship was obtained:

$$Y = 342C - 34.4C^2 + 0.771P - 0.00985P^2 + 0.284PC$$

Where: Y = tensile strength in psi

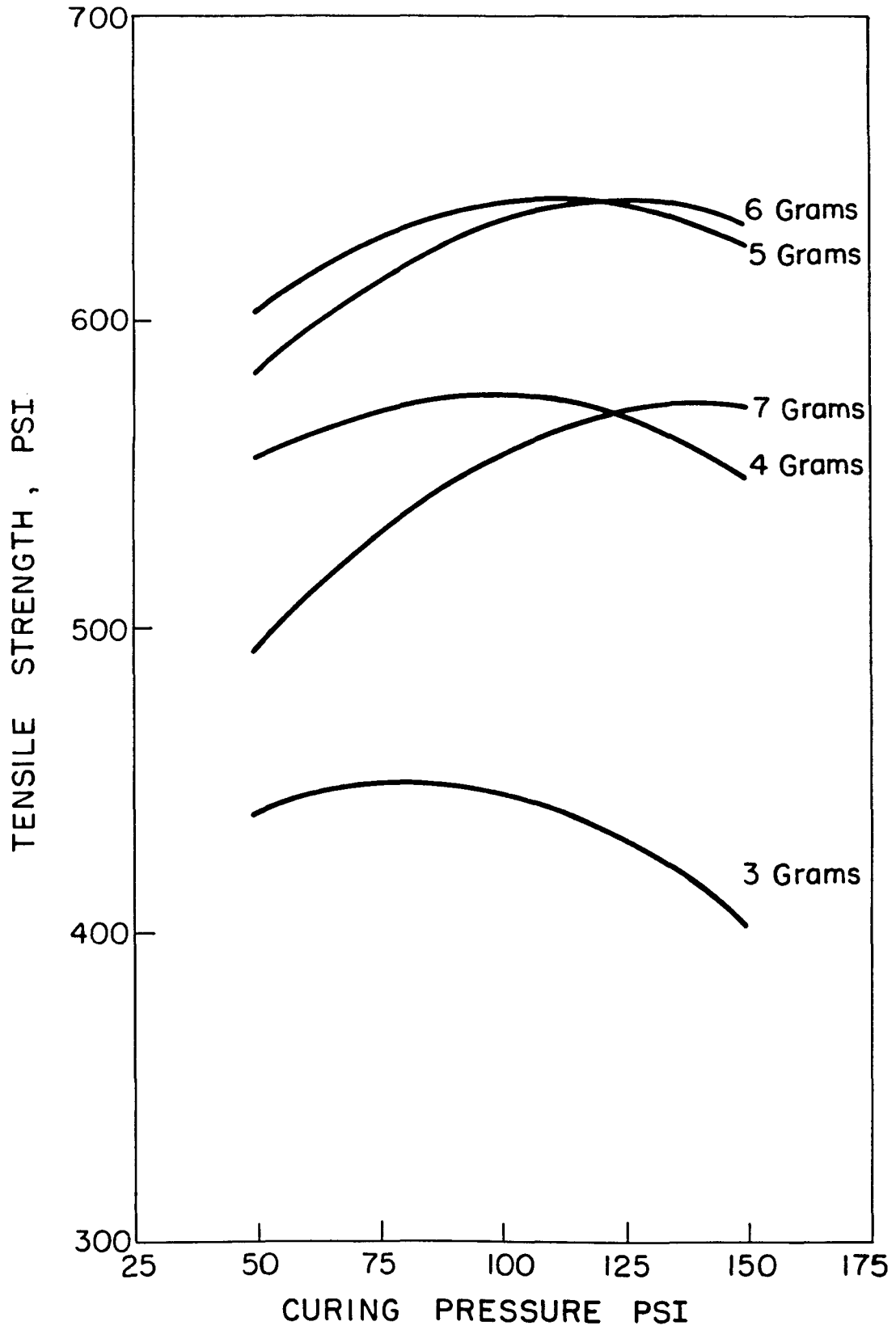
C = concentration in grams of solids per 10 ml solvent

P = curing pressure in psi

The surface obtained using this model is illustrated in Figure 5.

The coefficients on the various terms in the model indicate

Figure 5. Tensile strength of zein-dialdehyde starch adhesive versus curing pressure with concentration in grams per 10 ml of solvent as a parameter



why the pressure and interaction terms did not appear significant by the analysis of variance. However, the above model does appear to have a physical significance in terms of our earlier hypothesis. From the graph of the model it can be observed that as the viscosity increases due to the increase in the concentration of the glue, a higher pressure is required to optimize the tensile strength of the adhesive. Thus it would appear that the adhesive forces are definitely controlling the values of tensile strengths which are observed.

In order to determine a glue concentration and a curing pressure to be used for the remainder of the work, the above model was assumed correct. Using simple rules of calculus, the optimum values of concentration and pressure were determined to be 5.5 grams of solids per 10 ml of solvent and 120 psi respectively.

Effect of Reaction Time on Tensile Strength

A brief study was conducted to determine the effect of reaction time on tensile strength. In essence, this was done to measure the effect of the degree of polymerization in the adhesive prior to its application. The same study could have been conducted by varying the temperature of the reaction since this would affect the rate of polymerization. However, due to possible degradation effects over a wide range of temperatures, it was decided to keep the reaction temperature constant and vary only the reaction time.

Samples were prepared as for the preceding tests except that the reaction time for the samples was varied between 0.5 and 2.5 hours. A solids concentration of 5.5 grams per 10 ml of solvent was used in applying the glue, and curing was accomplished at 120 psi pressure for 6 hours at a temperature of 80°C. The results and an analysis of variance for the data are given in Tables 3 and 4 respectively.

Two things are rather surprising about the results of this experiment. Both the decrease in tensile strength with increasing reaction time and the significant cubic effect which appears in the analysis of variance are unexpected. Neither result is unreasonable, however. From the previous experiment it was observed that the adhesive forces of the glue seemed to be controlling the strength of the glue. If we accept the fact that the molecular size of the adhesive increases with reaction time, then for any given pressure it is obvious that after a certain molecular size has been attained that penetration into the small openings in the surface of the wood would decrease. There is no reason, therefore, to assume that increased cross-linking of the zein molecules should result in better adhesion. In fact it appears that the cross-linking of the zein may actually reduce its ability to adhere to the surface of the wood. It would be logical to assume that the cohesive forces would be increased by the polymerization reaction, but since cohesion is not the controlling factor this effect is lost.

The significant cubic effect can be explained by the

Table 3. Effect of reaction time on the tensile strength of zein-dialdehyde starch adhesives^a

Reaction time (hours)	Tensile strength (psi)
0.5	642
1.0	487
1.5	494
2.0	548
2.5	350

^aPrepared by reacting 40 grams of zein with 2 grams of DAS at 70°C.

Table 4. Analysis of variance of tensile strength data taken as a function of reaction time

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F Stastic
Among means	270,089	4	67,524	3.91*
linear effect	163,290	1	163,290	9.45**
quadratic effect	638	1	638	
cubic effect	103,330	1	103,330	5.98*
Within means	414,820	24	17,284	
Total	684,918	28		

*Significant at .05 level

**Significant at .01 level.

supposition that for each reaction time there is a unique relationship between tensile strength and the time and temperature of curing. It would not seem unlikely then that a constant time-temperature curing plane would intersect these surfaces in a third degree curve.

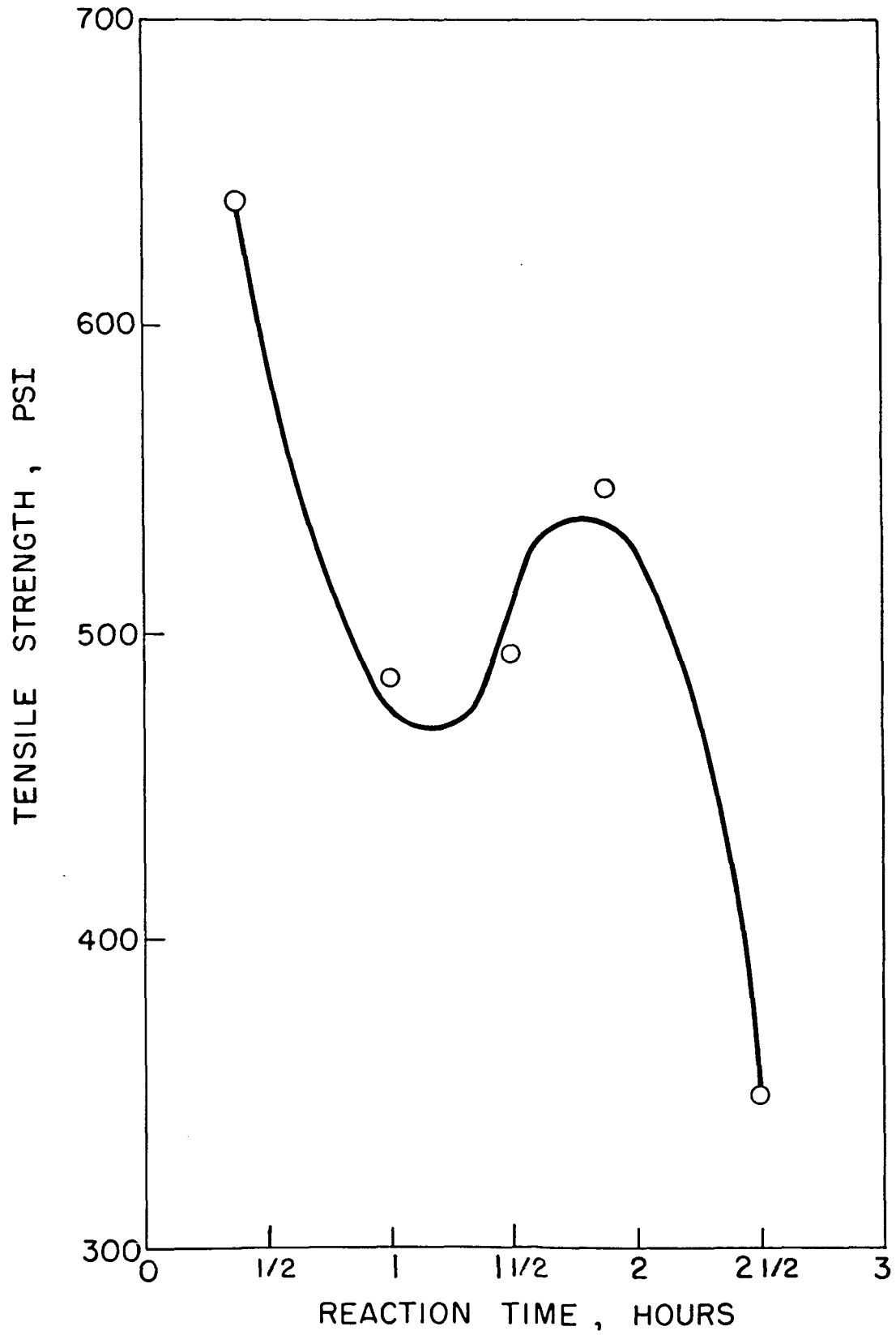
Again using the method of orthogonal polynomials, a cubic equation was used to fit the data to a smooth curve. The graph of this curve is given in Figure 6.

Effects of Curing Time and Temperature on Tensile Strength

In an attempt to improve the quality of the adhesive, it was decided to measure the effects of curing time and temperature on the tensile strength of the adhesive. Erskine (13) in his study of wheat gluten-dialdehyde starch adhesives was able to obtain a significant improvement in tensile strength at high curing temperatures. At 140°C curing temperature, results as high as 1125 psi were obtained.

It was again decided to use a 5 by 5 factorial arrangement in a completely randomized design as an experimental design. On the basis of Erskine's (13) work, curing times between 4 and 12 hours and curing temperatures between 40°C and 120°C were chosen for study. The reaction product chosen for study was the 0.5 hour reaction product as prepared in the preceding experiment. This sample was chosen for study on the basis of its superior tensile strength over the other samples. It should be noted, however, that because of the

Figure 6. Tensile strength of zein-dialdehyde starch adhesive versus reaction time



cubic nature of the curve, it could not be guaranteed that one of the other reaction products might not be superior under some other conditions of curing.

Again using 5.5 grams of sample per ml of solvent and a curing pressure of 120 psi, the necessary data was taken. The results are given in Table 5 and the analysis of variance in Table 6.

The results of this experiment are quite discouraging. Although the analysis of variance does reveal a highly significant quadratic effect of curing temperature on tensile strength, no improvement in the tensile strength of the adhesive was observed. The results of the experiment indicate that the 80°C curing temperature used in the previous experiments was the optimum curing temperature for this particular reaction product.

The fact that curing time is significant by the analysis of variance only in its interaction with temperature seems to indicate that at each temperature a different curing time is required to obtain the same tensile strength. By studying the tabulated results it appears that a higher curing temperature requires a shorter curing time to achieve the best results. It thus becomes a matter of economics as to which combination of time and temperature you choose to accomplish the curing of the adhesive.

The adhesive does not appear stable at elevated temperatures. This is indicated by the significant quadratic effect

Table 5. Tensile strength^a of a zein-dialdehyde starch adhesive^b as a function of curing time and temperature

Curing ^c Time (hours)	Curing Temperature (°C)				
	40	60	80	100	120
4	412	422	415	527	367
6	337	472	578	393	388
8	510	595	417	447	388
10	457	493	432	507	347
12	438	377	477	490	328

^aAverage values in psi

^bPrepared by reacting 40 grams of zein with 2 grams of DAS for one-half hour at 70°C

^cCured at a pressure of 120 psi.

Table 6. Analysis of variance of tensile strength data taken as a function of curing time and temperature

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F Stastic
Treatments	707,233	24		
Temperature	250,799	4	62,700	4.84**
linear effect	55,385	1	55,385	4.27*
quadratic effect	173,299	1	173,299	13.37**
Time	54,247	4	13,562	1.05
Interaction	402,187	16	25,137	1.94*
Error	1,580,838	122	12,958	
Total	2,288,071	146		

*Significant at .05 level

**Significant at .01 level.

of temperature as shown in the analysis of variance and by the low tensile strengths observed over all curing times at 120°C.

CONCLUSIONS AND RECOMMENDATIONS

There are several conclusions which can be made about the nature of the zein-dialdehyde starch adhesives. Perhaps the most important of these conclusions is that the addition of dialdehyde starch to zein does not significantly improve the tensile strength properties of the adhesive. There is even some evidence to indicate that the increased polymerization may actually reduce somewhat the tensile strength of the adhesive polymer. This conclusion can be supported by the evidence which indicates that the strength of the adhesive is limited by the forces of adhesion which exist between the adhesive and the surface of the wood. It is thus reasonable to assume that while the dialdehyde starch may increase the internal strength of the adhesive by cross-linking the zein molecules, the adhesive may actually be made less effective by the cross-linking due to a reduction in the adhesive forces between the glue and the wood.

This suggests that perhaps the real value in adding dialdehyde starch to zein lies in some other area than in its contribution to tensile strength. It has been pointed out previously that DAS has been used in the paper industry to improve the wet strength of papers (19,25). Dialdehyde starch has also been shown to increase the water resistance of other protein-based adhesives without having any significant effect on their tensile strengths (35, 36). The fact that a water

proof bond has been developed using zein with formaldehyde (33), indicates that the real value of the dialdehyde starch may be in its waterproofing ability. Therefore, it would seem advisable to begin investigating this aspect of the zein-dialdehyde starch adhesives.

This suggestion carries with it the implication that the adhesive may yet be of industrial importance. Zein is already considered an expensive industrial adhesive and is used only where its properties justify its use, as in the application of high grade veneers (33). As was just mentioned, a waterproof bond has been made for this purpose by using a mixture of zein and formaldehyde with an organic acid. It would seem advisable, therefore, to make a very thorough economic analysis of the entire adhesives market to determine the advisability of making further investigations.

The fact that the zein-dialdehyde starch adhesive did not respond to high temperature curing in the same way as the wheat gluten-DAS adhesive did is disappointing but not necessarily unreasonable. Zein is an unusual protein and is noted for both its unique physical and chemical properties. It should also be noted that the wheat gluten used was the crude wheat protein and that the zein is highly purified corn proteins. Kalia (20) was unable to produce any adhesive of sufficient strength using crude corn protein. This may serve to suggest that future study should be focused on developing the wheat gluten adhesive. It would appear to be the stronger and the

least costly of the two adhesives.

In conclusion it should be pointed out that the highest average tensile strength obtained during this study was approximately 700 psi. This was for a reaction product made from 40 grams of zein and 2 grams of DAS, reacted for one hour at 70°C, applied at a concentration of 5 grams per 10 ml of solvent, and cured for 8 hours at 80°C and 100 psi. Random individual observations exceeded 900 psi.

LITERATURE CITED

1. Abegg, C. F. The effect of double drum drying on the tensile strength of a dialdehyde starch-wheat gluten reaction product. Unpublished M.S. thesis. Library, Iowa State University of Science and Technology, Ames, Iowa. 1963.
2. Alner, D. J. Aspects of adhesion. University of London Press, Limited, London, England. 1965.
3. American Society of Testing and Materials. Standard method of test for tensile properties of adhesives (D897). American Society of Testing and Materials Vol. 6: 480. 1961.
4. Babcock, G. E. and Smith, A. K. Extending phenolic resin plywood glues with proteinaceous materials. Industrial and Engineering Chemistry 39: 85. 1947.
5. Babcock, G. E. and Smith, A. K. Extending resorcinol resin glue with corn gluten. Modern Plastics 24, No. 8: 153. 1947.
6. Beebe, C. W., Happich, M. L., Naghski, J., and Windus, W. A dialdehyde starch pretanning for rapid tanning of sole leather. American Leather Chemists Association Journal 54: 628. 1959.
7. Braude, F. Adhesives. Chemical Publishing Company, Brooklyn, New York. 1943.
8. Chatterji, A. K. Reactions of dialdehyde starches and wheat proteins. Unpublished Ph.D. thesis. Library, Iowa State University of Science and Technology, Ames, Iowa. 1963.
9. Cohn, E. J. and Edsall, J. T. Proteins, amino acids and peptides. American Chemical Society Monograph 90. 1943.
10. Corn Products Sales Company. Argo brand zeins G200 and G210. Author, New York, New York. 1960.
11. Dvonch, W. and Mehlretter, C. L. The electrolytic preparation of periodate oxystarch. American Chemical Society Journal 74: 5522. 1952.
12. Dvonch, W. and Mehlretter, C. L. Electrolytic preparation of periodate oxypolysaccharides. U.S. Patent No. 2,648,629. August, 1953.

13. Erskine, W. E. Effect of time and temperature on the reaction and curing of dialdehyde starch-wheat gluten adhesive. Unpublished M.S. thesis. Library, Iowa State University of Science and Technology, Ames, Iowa. 1965.
14. Fein, M. L. and Filachione, E. M. Tanning studies with aldehydes. American Leather Chemists Association Journal 52: 17. 1957.
15. Filachione, E. M., Harris, E. H., Fein, M. L., Korn, A. H., Naghski, J., and Wells, P. A. Tanning studies with dialdehyde starch. American Leather Chemists Association Journal 53: 77. 1958.
16. Gorham, J. Analysis of Indian corn. Quarterly Journal of Science, Literature and Art 11: 206. 1821.
17. Hudson, C. S. and Jackson, E. L. Application of the cleavage type of oxidation by periodic acid to starch and cellulose. American Chemical Society Journal 59: 2049. 1937.
18. Hudson, C. S. and Jackson, E. L. The structure of the products of the periodic acid oxidation of starch and cellulose. American Chemical Society Journal 60: 989. 1938.
19. Jones, E. J., Wabers, B., Swanson, J. W., Mehlretter, C. L., and Senti, F. R. Periodate oxystarches in paper applications. TAPPI (Technical Association of the Pulp and Paper Industry) 42: 862. 1959.
20. Kalia, K. K. Production of an adhesive polymer from zein and dialdehyde starch. Unpublished M.S. thesis. Library, Iowa State University of Science and Technology, Ames, Iowa. 1965.
21. Leffler, N. E. and Stanko, G. L. Dialdehyde starch: potential uses. Chemurgic Digest 19: 8. 1960.
22. McCoy, R. J. and Arnold, L. K. The reaction of wheat gluten and dialdehyde starch. Unpublished National Science Foundation report. Chemical Engineering Department, Iowa State University of Science and Technology, Ames, Iowa. 1965.
23. Mehlretter, C. L. Electrochemical production of periodate oxypolysaccharides. U.S. Patent No. 2,713,553. July 1955.

24. Mehlretter, C. L., Rankin, J. C., and Watson, P.R. Electrolytic preparation of periodate oxystarch. *Industrial and Engineering Chemistry* 49: 350. 1957.
25. Meller, A. The effect on paper wet strength of oxidized starches as beater additives. *TAPPI (Technical Association of the Pulp and Paper Industry)* 41: 648. 1958.
26. Miles Chemical Company. Sumstar dialdehyde starch. Technical Bulletin No. 6-129. Miles Chemical Company, Elkhart, Indiana. 1959.
27. Miles Chemical Company. Sumstar-190: data sheet 11-263. Miles Chemical Company, Elkhart, Indiana. 1959.
28. Perry, T. D. Modern wood adhesives. Pitman Publishing Company, Chicago, Illinois. 1944.
29. Pfeifer, V. F., Sohns, V. E., Conway, H. F., Lancaster, E. B., Dabic, S., and Griffer, E. L. Two stage process for dialdehyde starch using electrolytic regeneration of periodic acid. *Industrial and Engineering Chemistry* 52: 201. 1960.
30. Pinto, E. H. Wood adhesives. W. and F. N. Spon, Limited, London, England. 1948.
31. Sloan, J. W., Hofreiter, B. T., Mellies, R. L., and Wolff, I. A. Properties of periodate oxidized starch. *Industrial and Engineering Chemistry* 48: 1165. 1956.
32. Sturken, O. Adhesive. United States Patent No. 2,115,240. April, 1938.
33. Swallen, L. C. Zein: a new industrial protein. *Industrial and Engineering Chemistry* 33: 394. 1941.
34. Watson, C. D., Arrhenius, S., and Williams, J. W. Physical chemistry of zein. *Nature* 137: 322. 1936.
35. Weakly, F. B., Ashby, M. L., and Mehlretter, C. L. Casein-dialdehyde starch adhesive for wood. *Forest Products Journal* 13: 51. 1963.
36. Weakly, F. B. and Mehlretter, C. L. Low cost protein glue for southern pine plywood. *Forest Products Journal* 15: 8. 1965.

37. Weakly, F. B., Mehlretter, C. L., and Rest, C. E. Irreversible insolubilization of casein by dialdehyde starch. TAPPI (Technical Association of the Pulp and Paper Industry) 44: 456. 1961.

ACKNOWLEDGMENTS

I wish to express my sincere thanks to Professor L. K. Arnold for his guidance and direction throughout the duration of this investigation.

I also wish to express my thanks to Mr. William Erskine, Jr. who gave freely of his time in discussing his investigations of the wheat gluten-dialdehyde starch adhesives. His suggestions and advice were invaluable aids in conducting this investigation.

Many thanks go to Oscar who patiently prepared the thousands of test pieces used in making this study.

Financial support for the research was provided by the Iowa Development Commission and administered by the Engineering Research Institute at Iowa State University. Work was carried out in the Chemical Engineering Department using the facilities of both the Department and the Research Institute.