Plastics from high pentosanocellulosic material

William Donald Harris
Iowa State College
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UMI
PLASTICS FROM HIGH PERFORMANCE RUBBER MATERIALS

by

William Donald Harris

A Thesis Submitted to the Graduate Faculty for the Degree of

DOCTOR OF PHILOSOPHY.

Major Subject: Chemical Engineering

Approved

Signature was redacted for privacy.

In charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

1934
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INTRODUCTION.

The development of a plastic molding compound from phenol-formaldehyde resin by Baekeland appears to have been the stimulus which popularized the field of research in synthetic resins and their plastics. As a result of this research, many new and valuable compounds have been produced. Among the most important are the urea-formaldehyde type, the vinyl types, and cellulose xanthate.

The chief advantage of a molding compound is its ease of fabrication into a finished, attractive product in one operation. This property has led to its use in the manufacture of a multitude of small articles. The plastic products of the above compounds have found a ready market in various specialty fields; for example, electrical insulators, handles, knobs and bottle caps. However, before plastic materials can be economically used for large articles and in building construction, their cost must be considerably reduced. This means that the resin or plastic binder cannot be made from costly, highly-refined chemical raw materials.

The possibility of the utilization of several agricultural waste products as cheap raw material in the formation of plastics is inviting. Corn is the leading agricultural product of the whole United States; and it is probably the most highly developed and exploited of the crop plants. The corn crop produced in the United States in 1931 was estimated at over 2,500,000,000 bushels (22). The basis for buying corn by elevators, in general, places the weight of a bushel of ear corn at 70 pounds, and allows
14 pounds for the weight of the cobs. Using these figures, the weight of corncobs produced in 1931 is calculated to be over 17,500,000 tons. Of this amount, the State of Iowa produced over 2,700,000 tons. It is almost unbelievable that this great amount of by-product is almost entirely wasted.

Corncobs are accumulated and classed as by-products in the corn products refining industries, at elevators and shelling stations. The possible construction of corn-alcohol plants for the production of fuel alcohol is likely to produce other points of accumulation. The high concentration coupled with the uniform annual production gives decided economic advantages for their use as a raw material. At the present time the most important uses of corncobs are for tobacco pipes and as a fuel.

Oat hulls and peanut shells are two other attractive raw materials. Since they are the by-product of food industries, they are also highly localized. In normal times, the plants of the Quaker Oats Co. produce about 400 tons of oat hulls per day, and the peanut industry has an available by-product of over 50,000 tons of peanut shells yearly. Cotton-seed-hull bran is another high pentosan waste material. It has been estimated that the cotton-seed oil plants produce over 1,000,000 tons of the bran yearly. These substances have decided advantages as raw materials in that they are clean, easy to handle, of small uniform size, free from impurities and stable in storage.

One significant common property possessed by these materials is the high percentage of pentosans. These pentosans (mainly
xylan) may be hydrolyzed with mineral acids to produce furfural, a compound capable of producing resinous condensation products with phenols.

Experimentation has shown that resinous pitches may be obtained by reaction between these high pentosan materials and phenolic bodies, such as phenol or cresols. The purpose of this research has been to determine: (1) the type of reaction between high pentosan material, such as corncobs and a phenolic body; (2) the products which may be produced by variation of experimental conditions and (3) the possibility of obtaining a valuable commercial plastic.
HISTORICAL.

A. Work Done by Previous Investigators.

In 1830, Dobereiner, a German, first obtained furfural while preparing formic acid by the action of sulfuric acid and manganese dioxide on sugar. During the distillation he noticed that the distillate came over milky and on standing a yellow "oil" separated out. He succeeded in obtaining only a small amount and did not make any extensive investigation of its nature. A short time later Emmet noticed that an "oil" was obtained when formic acid was prepared from rye or corn by treating with sulfuric acid.

Stenhouse, 1840, was the first to prepare a quantity of this "oil". He used Emmet's process, using oatmeal and sawdust as the material from which to make the "oil", and obtained enough for experimental use. The composition of the "oil" was determined and the formula \( \text{C}_5\text{H}_4\text{O}_2 \) given the compound.

Pownes, 1845, prepared the "oil" by distilling bran with sulfuric acid and suggested the name furfurol (furfur - bran, oleum - oil). Later when the aldehydic nature of the compound became known it was called furfur-aldehyde, later abbreviated to furfural. In 1928 the Quaker Oats Company, at Cedar Rapids, Iowa, started commercial production of furfural, which they produced from by-product oat hulls.

Chemical investigation of furfural showed that, like formaldehyde, it had a strong tendency toward polymerization.
and gave valuable resinous products when treated with phenols. Patents were granted Emil Novotny (20) in 1921 for a condensation product of furfural and phenol. At the present time, work is being carried on here at Iowa State College by R. W. Bruins on the use of polymers from furfural in the fabrication of molded products.

In 1922 and 1923, Robert Moscrip (19) and G. T. Williams (27) investigated the possible use of ground corncobs as a filler in moldable plastics. During their research, it was suggested that the furfural content of the corncobs be utilized to produce a plastic in the cobs. That is, the corncobs would be treated in the presence of phenol to produce a resin. The residue cobs would act as an inert filler. Investigation along the line of this suggestion gave promising results. When the ground corncobs and phenol were cooked together with a small amount of acid, a gummy, black plastic material was formed. By molding and baking in an oven, pieces of this material became very strong and hard; however, they retained some residual acid and would disintegrate in water.

Further work by Williams demonstrated that the reaction was better when no water was present and that sulfuric acid did not give as good results as hydrochloric acid. The use of higher temperatures and cooking in an autoclave were apparently desirable.

The research work was continued by James Williamson (28), who found that cathulls gave a better product than corncobs,
due probably to their greater uniformity, and that cresol could be substituted for phenol with equal success. He produced discs by cold-molding the dried plastic in a hydraulic press and baking in an oven. The discs would stand boiling water for one-half hour without decomposition.

H. A. Webber (26), in 1924, concluded that it was not certain whether the entire reaction was between furfural and phenol and that it was possible for the phenol to react with the pentoses, which are formed by the first step in the hydrolysis of the pentosans; also, that other reactions may occur due to the complicated structure of the corn cob. He tried many catalysts other than hydrochloric acid and sulfuric acid, but with no improvement. Cresylic acid was tried in place of phenol with no added success. Various solvents, were tried as media in which the reacting substances were soluble but no benefits were obtained.

Based on the results obtained by Webber, a patent was applied for and received on the process of making the molding composition. This process consisted of "reacting a solid pentosan-containing material and a phenol, the latter being in the proportion of approximately sixty percent by weight of the pentosan-containing material in the presence of hydrochloric acid, the latter being in the proportion of approximately ten percent of the weight of the pentosan-containing material, and then subjecting the mass to a temperature of approximately 100 deg. C. for approximately three hours".
In 1924, Josef Hovespian, H. L. Bowers (12), and J. E. McFarland (17) cooperated in the corncob plastic investigation. They used high-pressure cooking and catalysts which hydrolyzed to give hydrochloric acid. McFarland records the successful use of crude commercial cresol.

In the next year (1925), Albert J. Duden (6) worked toward making the plastic more waterproof and to improve on the other properties. Baking the molded product was found to increase its resistance to water.

W. E. Sillick (23) in 1931, in cooperation with the author, studied the effect of variation of molding temperatures on water-resistance. He came to the following conclusions: (1) that the optimum molding temperature was 210 deg. C.; (2) that considerable cooling of the mold was necessary before removal of the product; (3) that Halowax and paraffin were unsatisfactory as water-proofing agents; (4) that decomposition occurred at about 225 deg. C.
B. Resume of Investigational Work Carried On by the Author and Described in a Master's Degree Thesis.

The corn cob plastic which had been produced previous to the research work by the author was a brittle, black, resinous pitch containing some excess cresol and some residual acid. Molded objects of this material were repeatedly fusible and were affected by water. Accordingly, the first aims of the author's investigational work was directed toward overcoming these obvious faults.

It was first necessary to develop a suitable technique in carrying out the procedure of making and molding the plastic as developed by former workers. The molding operation was then improved by a study of the effect of molding temperature; by experiments on acid-proof mold surfaces, through work on the neutralization of residual acid in the plastic, and through experiments with the use of mold lubricants.

The individual reactions of cellulose, sugars, furfural, and lignins were studied in an attempt to understand their influence in the plastic reactions. The cellulose and sugars were found to react with phenol and the cresols to give a tarry pitch. Furfural was found to have only a slight tendency to combine with phenols in the presence of a very large quantity of water, and lignin did not appear to react with phenol under the conditions held in making the plastic.

Zinc chloride was found to make a very satisfactory catalyst. Its milder action helped to eliminate corrosion of the molds and
to eliminate sticking.

Water-resistance of the plastic did not appear to be increased by extraction of the soluble portions before molding. However, the addition of formaldehyde increased strength as well as water-resistance.
C. Related Literature.

Several workers have observed the fact that cellulosic materials have the property of reacting with phenols in the presence of acid catalysts to give resinous products. As early as 1909, Gustav Mauthner (18) received a German patent for a process making a resinous condensation product from cellulose and phenol. His process consisted of reacting together phenol, sawdust or cotton, and sulfuric acid; and he claims to have produced a resin which could be made insoluble and infusible.

A similar method was developed by Glaessen (9), 1919, who heated wood or wood waste with phenol in the presence of a small proportion of hydrochloric acid or other catalyst, and, in some cases, with a diluent such as water, alcohol, or benzene. Glaessen states that the product may be used as a substitute for various natural resins, pitch, asphalt and in making size.

Emil E. Novotny and Charles J. Romieux (21), 1932, disclosed a process for making a synthetic resin from phenol and a "natural vegetable product such as ground corncob, sawdust, or other substances". Their process provides for the reaction to proceed at temperatures above the boiling points of the constituents. They also state that urea, vinyl acetate, and other compounds may be used in place of phenol, that is, "substances which may be considered to have a carbon atom to which is linked a hydroxyl or a substituted hydroxyl group and either another carbon atom or a nitrogen atom through a double bond (=C-O-R)
such substances exhibit keto-enol tautomerism to varying degrees.

Novotny and Romloux claim that the resins made by their process may be made permanently fusible or convertible into hard, infusible, insoluble, acid and alkali-proof materials of great strength. The infusible resins are obtained by addition of 10-20 percent formalin to the phenol-sawdust resin and heating until reaction has taken place. The formalin would react with any excess phenol; however, there is a possibility of its reaction with some of the degradation products of the cellulose.

Hall, Slater and Acree (10), U. S. Bureau of Standards, in 1930, published the results of preliminary investigations on oat hulls and cotton-seed-hull bran as sources for xylose. They conducted a series of hydrolysis tests in which the xylan was hydrolyzed to xylose. The method consisted essentially of digesting the washed oat hulls or bran with dilute (0.3 normal) sulfuric acid for approximately two hours at ten pounds steam pressure.

Bryner (3), Iowa State College, (1934) made quantitative studies on the hydrolysis of oat hulls and pentosans. He gave the following conclusions: (1) The rate of hydrolysis of the oat hulls is increased by an increase of acidity at constant temperature. (2) There is an optimum acid concentration for a given temperature. (3) Above this optimum temperature the sugars are decomposed, some of the xylose being converted to furfural. By conducting the hydrolysis of oat hulls with 2 normal HCl at 98 deg. C. for three hours Bryner obtained 39.50 percent
of reducing sugars (mainly xylose).

It is interesting to note that experiments have been carried out in the Kaiser-Wilhelm Institute for Coal Research (1) for the purpose of producing synthetic plastic material with properties similar to those of Bakelite through the reaction of phenols on coal. Based on the fact that lignin dissolves in phenols in the presence of a small amount of a strong acid, various lignin-containing raw materials such as sawdust, peat, earthy and lignitic brown coal, humic acid and bituminous coal in a finely powdered form were each heated with a crude cresol mixture and after removal of the excess cresol subjected to a short extraction with benzol.

After removal of the solvent, the material could be molded into various shapes under pressure and at about 150 deg. C.
D. Analytical Data.

**Corncobs.** The structural basis of corncobs, as of all other plant materials, is cellulose. They are also known to contain pentosans, pentoses, lignins and other materials. The data on the composition of corncobs are not extensive. W. J. Suer (25), working in the Department of Chemistry, Iowa State College, in 1917 analyzed the cob by two methods for its cellulose content. The first was the chlorination process of Cross and Bevan (4), which gave the total cellulose. The second was the Konig process (16), which determined only the "cotton type" cellulose. Suer found the total cellulose to be 60.5 percent and that 32 percent was the "cotton type", leaving 28.5 percent furfural-yielding cellulose. He found the cobs yielded 23.3 percent furfural, which corresponded to considerably more than 28.5 percent pentose and assumes that the furfural-yielding material was not all pentose but that a part of it was present as pentosans, also that there was 8.47 percent pentosans in the cob. He made a crude fibre determination and obtained 36 percent and assumed the remaining 4 percent to be lignin. These assumptions are probably not correct, but his analytical data are of value.

**Oathulls.** Oathulls are known to contain somewhat higher proportions of lignin and pentosans than corncobs. L. C. Bryner, previously mentioned, made an analysis of oathulls for amount of reducing sugars obtained by acid hydrolysis and obtained the
following data:

Moisture loss (105° C.) ............ 5.60%
Ash................................... 7.32
Crude fibre.......................... 36.04
Lignin................................. 20.69
Reducing sugars (xylose)......... 39.10

He also recorded the amount of total soluble matter after hydrolysis to be 45.20 percent and the residue (unhydrolyzed) 52.60 percent. All figures are based on the weight of dry oat-hulls.
EXPERIMENTAL

The experimental work recorded here has been divided into two sections. The first includes the investigational work to gain knowledge of the reactions which the individual constituents of high pentosanocellulosic materials undergo when the latter are condensed with phenolic bodies, and the second is a record of experimental development of a plastic molding compound from corncobs or oat hulls and cresol.
Reactions of the Pure Constituents of Oat hulls and Corncobs.

This work has consisted of studying the possible variations of the reactions between phenol and the isolated and purified constituents of corncobs and oat hulls. The variations were made by the use of different catalysts, and by varying temperature and concentration of reacting substances.

The compounds studied were cellulose, pentosans and xylose and lignin. Furfural had been quite extensively investigated previous to the experimental work described in this paper and, therefore, was not taken up again.

Cellulose

Cellulose and phenol with sulfuric acid as catalyst.

Williams (9), in some of the earliest work at Iowa State College, tried sulfuric acid as a catalyst in the corncob-phenol reaction and found that it did not give as good results as hydrochloric acid. However, Mauthner (18) recorded the successful use of it in the manufacture of a resin from sawdust and phenol. Mauthner's process consisted of heating to 100 deg. C. a mixture of 1 kg. phenol, 100 gms. sulfuric acid and 350 gms. wood sawdust. By heating the resulting reaction product to 150 deg. C. or higher he obtained a resinous mass.

An experiment was made using Mauthner's procedure, with an exception that ground corncobs were substituted for sawdust.
The corncobs were found to give a resinous pitch similar to the sawdust. It was found necessary to heat and boil the reaction product to 180-200 deg. C. in order to obtain a solid resin at atmospheric temperatures. During the heating, considerable quantities of phenol and water were evaporated.

Cresol, when substituted for phenol, was found to react somewhat more vigorously, but it was found necessary to heat the mixture to a higher temperature to remove the excess cresol. A vacuum distillation was carried out to remove the cresol as completely as possible. When the distillation temperature was carried up to 300 deg. C. the softening point of the resin product was approximately 110 deg. C. This appeared to be the maximum distillation temperature since a slight charring took place.

In the procedure followed to determine how pure cellulose reacts with phenol, sulfuric acid was first used as the catalyst. A low-ash filter paper and surgical cotton were selected as representative types of pure cellulose. An experimental run was made using cellulose, phenol and sulfuric acid in the same proportions as when corncobs were used, that is, 100 gms. phenol, 35 gms. filter paper, and 10 gms. sulfuric acid. The mixture was then heated until the reaction was complete and the temperature had reached 200 deg. C. The solution and condensation of cellulose took place quite rapidly between 140 and 160 deg. C. to give a viscous black liquid. The further heating evaporated uncombined phenol and the water of decomposition. The large portion of water which came off at these high temperatures,
indicated that, although the cellulose had completely dissolved, condensation and decomposition reactions were still taking place. The resulting resinous product was, as near as could be determined, the same as that obtained from corncobs, except that it was slightly more free from impurities such as grit.

Another run was made in which the reaction was carried out at a slow rate at a temperature of 90-100 deg. C. The same proportions of constituents were used as in the preceding run. The object was to determine whether a plastic could be made without the complete decomposition of the cellulose and whether the brittleness and blackness of the resin was due to charring and the formation of carbon. The result was that darkening occurred simultaneously with the solution of the cellulose and appeared to be due to an attendant side reaction.

Three experimental runs were made to determine the maximum possible ratio of cellulose to phenol. The proportional amounts of constituents are given in Table I:

Table I.

Ratio of Cellulose to Phenol

With H₂SO₄ as Catalyst.

<table>
<thead>
<tr>
<th>Run</th>
<th>Cellulose</th>
<th>Phenol</th>
<th>H₂SO₄</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60 gms</td>
<td>30 gms</td>
<td>6 gms</td>
<td>Some unreacted cellulose</td>
</tr>
<tr>
<td>2</td>
<td>30 gms</td>
<td>30 gms</td>
<td>6 gms</td>
<td>Some unreacted cellulose</td>
</tr>
<tr>
<td>3</td>
<td>20 gms</td>
<td>30 gms</td>
<td>6 gms</td>
<td>Cellulose all reacted</td>
</tr>
</tbody>
</table>
These mixtures were placed on an electric hot-plate and digested until all reaction had ceased. In both run 1 and run 2 some of the cellulose remained unreacted, but in run 3 it had all reacted. The maximum amount soluble was estimated to be about 5 parts cellulose to 6 parts phenol. Even though in run 1 there remained some unreacted cellulose, there was also an appreciable amount of free phenol. It is probable that one molecule of phenol condenses with one \( C_6H_{10}O_5 \) unit of cellulose, but the viscous tar produced makes it difficult to secure intimate mixing and completion of the reaction.

**Cellulose and phenol with zinc chloride as a catalyst.**

During the part of the experimental work described in the Master's Thesis by the author, it was observed that zinc chloride had decided advantages for use as a catalyst in the reaction between cresol and corncoabs. Zinc chloride has been long known to act as a solvent for cellulose; hence an investigation was made of the possible reactions of the purified cellulose and phenol in the presence of it.

An experiment showed that 10 gms. of zinc chloride in a 50% water solution would gelatinize and dissolve approximately 3 gms. of filter paper cellulose. It was necessary, however, to digest with heating for 15-20 min. before complete solution was obtained. During the digestion some water was lost and the solution was obtained as a thick syrup. The cellulose could be reprecipitated by diluting with water.
A portion of phenol (5 gms.) was added to the syrupy solution and the digestion continued. A slow reaction occurred and the mixture gradually darkened until a black sticky mass was obtained. When the zinc chloride was washed out a black tar remained.

A portion of the mixture was removed from the digestion before much darkening had taken place. When this was diluted with water the cellulose was precipitated as a gummy mass containing free phenol. This mass could be easily molded and when dried over-night, in a warm place, it became very strong and tough. It had a pinkish color and was quite translucent. The phenol seemed to act partly as a solvent and partly as a plasticizing agent.

Using the zinc chloride as a catalyst, three experimental runs were made varying the proportion of cellulose. These runs were made in the same manner as those previously when sulfuric acid was used as a catalyst. The proportions are given in Table II:

Table II
ZnCl₂ as Catalyst.

<table>
<thead>
<tr>
<th>Run</th>
<th>Cellulose</th>
<th>Phenol</th>
<th>ZnCl₂</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>30</td>
<td>6</td>
<td>Some unreacted</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>30</td>
<td>6</td>
<td>Some unreacted</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>30</td>
<td>6</td>
<td>Cellulose all</td>
</tr>
</tbody>
</table>

...
As with sulfuric acid, the maximum amount of cellulose to react was approximately 5 parts to 6 parts of phenol. The reactions in this experiment were less violent and required a longer time than when sulfuric acid was used; however, the final products were very much the same. The zinc chloride acted in a very similar but considerably milder manner than sulfuric acid. Here also the reacting mixture darkened at the very start of the reaction, even though the temperature was raised very slowly.

Cellulose and phenol with sodium hydroxide as a catalyst. In this experiment an attempt was made to use an alkaline catalyst. 2 gms. of solid sodium hydroxide were dissolved in 10 gms. of warm phenol and 5 gms. cotton then added and the mixture allowed to digest on a steam hot-plate for an hour. At the end of this time part of the cellulose had dissolved and could be precipitated by dilution with water. Although the mixture colored slightly, there was no indication of any condensation taking place between the cellulose and phenol. The cellulose was but very slightly decomposed.

Effect of cellulose-cresol products on the polymerization of a furfural-cresol mixture. An experiment was made to find out whether the tarry material formed by the reaction of cellulose and cresol would have a deleterious action in the condensation of furfural and cresol. Two batches of the following proportions were weighed out:
The procedure was as follows: Batch I was mixed intimately and placed on a steam hot-plate to digest. For Batch II the cresol and zinc chloride were mixed and heated to boiling, the cotton then added and stirred until dissolved. Lastly the furfural was added and the mixture placed also on the hot-plate.

After 3-4 hours Batch I had polymerized to a rubber-like consistency, while Batch II was still liquid. When both batches were allowed to remain on the hot-plate over-night, I had set to a very tough strong solid, II was brittle, not so strong as I, and was full of bubbles.

It is evident that the product from cresol and cellulose did act as a negative catalyst in slowing the polymerization of furfural.

**Pentosans and pentoses.**

The pentosans used for these experiments were obtained from Bryner, previously mentioned, who had prepared a considerable quantity by extraction from oat hulls using the following process: Finely ground oat hulls were stirred into a 7% NaOH solution, stirred for one hour, allowed to stand over-night, stirred for another hour and filtered by suction. The residue was washed and the washings added to the filtrate. The filtrate was stirred
while 2 volumes of 95% ethyl alcohol were added. After complete mixing the NaOH was partly neutralized with HCl. The precipitated xylan was allowed to stand over-night and then filtered out. It was washed three times with alcohol and twice with dry ether, and finally dried in air.

The product was mainly xylan and had the following analysis:

- Moisture: 12.40%
- Ash: 19.50%
- Xylan (from xylose): 60.10%
- Lignins (by difference): 8.00%

The xylan was calculated from the maximum yield of xylose obtained by hydrolysis.

The reaction of the pentosans with phenol and cresol was tested by digesting a mixture of the two in the presence of a catalyst. Three runs were made and are shown in Table III. The first consisted of reacting a mixture of xylan, phenol and $H_2SO_4$; the second, a mixture of xylan, phenol and $ZnCl_2$; and the third a mixture of xylan, meta-para cresols and HCl.

Table III.

Reaction of Xylan With Phenols.

<table>
<thead>
<tr>
<th>Run</th>
<th>Xylan</th>
<th>Phenol</th>
<th>m-p</th>
<th>$H_2SO_4$</th>
<th>$ZnCl_2$</th>
<th>HCl</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gms.</td>
<td>gms.</td>
<td>gms.</td>
<td>gms.</td>
<td>gms.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>15</td>
<td></td>
<td>1.5</td>
<td></td>
<td></td>
<td>Black</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>15</td>
<td></td>
<td>1.5</td>
<td></td>
<td></td>
<td>no</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>15</td>
<td></td>
<td>2.0</td>
<td></td>
<td></td>
<td>reaction</td>
</tr>
</tbody>
</table>
The object of the first and second runs was to duplicate the conditions of previous runs with cellulose. The third run was made to find whether furfural could be produced in sufficient quantities to produce a furfural-cresol resin without having an appreciable amount of water present. HCl as a catalyst, did not have such a strong tendency to decompose carbohydrates as H_2SO_4, yet it was considerably more active than ZnCl_2. The cresol was a mixture of meta- and para-cresols and was used, in this case, because they are slightly more active than phenol or ortho-cresol.

The procedure consisted of mixing first the catalyst and phenol, then stirring in the xylan. It was necessary to dissolve the zinc chloride in an equal portion of water before it would dissolve in the phenol. The three mixtures were then placed on the hot-plate at 100-110 deg. C. for four hours.

The results were as follows: In run 1, the mixture gradually darkened and became pasty. At the end of 4 hours it had become a black solid. The solid was fusible with some decomposition and was completely decomposed by water, probably due to presence of xylose. Run 2 was very much like run 3. There was no reaction between the xylan and the phenol or cresol and after 4 hours the latter two had completely evaporated leaving the xylan as residue. By this it showed less tendency to condense with phenols than cellulose. Xylan was found to be readily soluble in warm phenol and cresol without sign of reaction, and in run 3 the addition of HCl seemed to precipitate
Xylose was treated with phenol in the same manner as was xylan. The mixtures were as follows:

<table>
<thead>
<tr>
<th></th>
<th>I. Xylose</th>
<th>II. Xylose</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 gms.</td>
<td>10 gms.</td>
</tr>
<tr>
<td>Phenol</td>
<td>20 &quot;</td>
<td>Phenol</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_4$</td>
<td>2 &quot;</td>
<td>$\text{ZnCl}_2$</td>
</tr>
</tbody>
</table>

Both mixtures were heated until reaction had started and then digested on a steam hot-plate until the reaction stopped. The two mixtures acted similarly, except that II required longer to react. In each case, the xylose appeared to carmelize and go into solution with decomposition and loss of water. It appeared to be somewhat more easily broken down than the xylan. The final products of these reactions were black tars which became brittle, black solids by evaporation of unreacted phenol and other volatile matter.

**Lignins.**

A sample of lignin was used which had been prepared from corn-cobs by Paul G. Bird of the Chemical Engineering Department, Iowa State College. He extracted the lignin from the ground corn-cobs with NaOH solution, precipitated the pentosans with alcohol, and then precipitated the lignin by neutralization with acid. The lignin was a brown powder of unknown purity.

A small portion of the lignin was heated with phenol without any catalytic material and it was found neither to be soluble
nor to react.

When 10 gms. lignin was mixed with 20 gms. phenol in the presence of 2 gms sulfuric acid and the mixture digested at 100-120 deg. C. the lignin went into solution with the formation of a black, tarry liquid. Although the viscosity increased, this material remained fluid when left in an open beaker on the hot-plate at 110-120 deg. C. for 12-14 hours. It finally became a brittle solid after considerable heating.
Development of the Process for Producing a Moldable Plastic.

Apparatus

Steam pressure-cooker. During the first part of the experimental procedure, the moldable plastic was made by using an excess of cellulosic material which acted as filler in the final product. Because of the large volume of solid material, it was necessary to devise a means for uniformly heating the reaction mixture, and wherein a number of small batches could be conveniently run. To do this a steam pressure-cooker was constructed from a 5 in. galvanized iron pipe. A diagram of the cooker is shown in Fig. 1. A 4 ft. pipe section (A) was threaded and capped at both ends, and securely fastened in a vertical position. In the top cap was placed a thermometer well (B) and steam connection (C); also, a pressure gauge (D) was placed in the steam line.

A number of cans were obtained as containers for the experimental batches, and were of a size which allowed five of them to be inserted into the pipe. Each can held approximately 100 gms. of cellulosic material. A small pressure-equalizing vent was made in the side of each can near the top.

Electrically-heated reaction vessel. In the improved procedure for making the plastic, a sufficient amount of cresol
was used to make fluid the reaction mixture. Later the excess cresol was distilled off under a 28.5-29 in. vacuum and at temperatures reaching 300 deg. C. The steam pressure necessary to attain this high temperature was unavailable, so a Stokes electrically-heated impregnating apparatus was adapted for making large batches of resin. A diagram is shown in Fig. 2. The apparatus consisted of a pressure vessel (A) of 7 gal. capacity, a condenser and receiver (B) and a vacuum pump. The pressure vessel was equipped with a drain (C) at the bottom, two sight glasses (D), a thermometer well (E) and pressure gauge (F) at the top; also a thermostat (G) controlled the heating element. It was rated at 100 lbs. maximum pressure. The top was hinged and could be bolted tightly. Sight glasses were very important since it was difficult to control foaming during the first part of the vacuum distillation.

Steam-heated mold. The plastic molding compound was produced as a thermo-plastic powder and it was necessary to cool the mold before removing the product. The first molds were heated with a gas burner or electric element and had no provision for rapid cooling. Approximately two hours were required to mold one test piece. Two other disadvantages were the difficulty of close temperature control and the inconvenience of transferring the hot mold to the press. These disadvantages were overcome by the construction of a cored mold which could be heated with steam and cooled with water. Fig. 3
**Fig. 1**

*Steam Pressure Cooker*

A- 5" pipe section
B- thermometer
C- steam connection
D- pressure gauge
E- removable cap
F- condensate outlet
G- container
H- support

*By W.D.H.*
Fig 2.
Electrically-Heated Reaction Vessel.

A - Reaction Vessel
B - Condenser & Receiver
C - Drain
D - Sight glasses
E - Thermometer Well
F - Pressure Gauge
G - Relief Outlet
H - To Vacuum Pump
I - Condensate Drain
J - Thermostat
K - Heating Unit
Fig. 3
Steam-Heated Mold
and
Hydraulic Press

A - Mold
B - Steam inlet
C - Water inlet
D - Outlet

By W. C. H.
shows a diagram of the mold and hydraulic press. Because of the large contraction of the molding powder during molding, it was necessary to make the mold of the "positive" or closed type. The body of the mold (A) consisted of a 4-in.-square, steel block with a 1\(\frac{3}{8}\)-in. hole in the center. The core was made by drilling inter-connecting holes around the center hole and plugging all except two openings, an inlet (B) and outlet (D). A plug was made to fit the bottom of the mold. It and the molded product were forced out by raising the mold and forcing the plunger through.

The hydraulic press was a Carver laboratory type capable of applying 20,000 lbs. total pressure on the ram.

Procedure for producing a molding material.

During the experimental investigation a standard procedure was developed for making the plastic molding compound. The following steps in the process will be taken up in detail:

Grinding the corncobs, bringing about the reaction, preparation of the molding powder and the molding operation.

Grinding the corncobs. The grinding of the corncobs presented quite a difficult operation. When it was only necessary for the particles to pass a quarter-inch screen, a small swing-hammer mill operated very satisfactorily. However, because of the extreme toughness of the cobs and tendency of the particles to ball up, much time and power
were necessary to reduce them to a fine state of subdivision.

A quantity of fine material was obtained for experimental use by wet grinding in a rod mill. The rod mill consisted of a heavy steel cylinder revolving on trunnions. It was about one-third filled with steel rods approximately 3 in. in diameter and the length of the inside of the mill (approximately 6 ft.). The corncobs and a stream of water were introduced at one end of the mill and they passed through by gravity to the other end of the mill. As the mill revolved the rods tumbled down and ground the material between them and the shell of the mill. The crushed material discharged from the mill into a revolving screen which separated the water from the cobs.

It was found necessary to dry the ground cobs immediately to prevent fermentation. This was done by spreading the materials on trays and drying in a shelf dryer. When dry the lumps were broken up in a hand-operated disc mill and the various-sized particles separated by screening.

Later a considerable quantity of ground corncobs in various sizes was obtained from Arnold and Whittemore (2) who were studying the practicability of grinding them for use as a cleaning material. A record was kept of the material ground and the power costs.

Whole cobs were fed dry to the rod mill at a rate of 222 lb. per hour (1 ton in 9 hours). The power consumed was 17.4 Kwh, per hour, or 156.6 Kwh. per ton of cobs. At 2.5¢ per Kwh. the power cost was $3.92 per ton. The product of
this first grinding was screened and separated as follows:

Coarse 53.9% retained on 8 mesh screen
Medium 26.5% passed 8 mesh retained on 40 mesh
Fine 7.7% passed 40 mesh.
Total 88.1%

The loss was 11.9% and was estimated to be mainly fines.

The coarse material or that retained on the 8 mesh screen was re-run through the mill and screened again. This gave a total yield of 54 percent for the medium material and approximately 20 percent for the fine material. There was a considerable loss of the fine material. The cost of grinding 1 ton of corn cobs, including the re-running of the coarse material once, was $5.26 for power only.

Method of carrying out the reaction. The reaction between the cellulosic materials and cresol was carried out by two methods. The procedure for the first method is outlined in the following steps: (1) 5-10 parts by weight of ZnCl₂ are dissolved in an equal weight of water and the solution mixed well with 100 parts of cresol or phenol. (2) The mixture is placed in a closed container and that placed in a pressure autoclave. Live steam is admitted to the autoclave at 90lbs. per sq. in. pressure for 2 hours. (3) The cob-cresol mixture becomes quite sticky and plastic. It is spread out on pans and dried at 100-120 deg. C. for 8-10 hours. (4) The dried
material is ground to pass a 40 mesh screen and is then ready for molding.

The other method produced a somewhat superior product to that previously described. The procedure is as follows: (1) 5 parts by weight of ZnCl₂ or H₂SO₄ are dissolved in an equal weight of water and then combined with 100 parts of cresol or phenol. The solution is then heated to boiling in an autoclave. (2) 30 parts of ground corn cobs (preferably 8 mesh or smaller) or 30 parts of oat hulls are introduced gradually with stirring. (3) The autoclave is closed and the temperature kept at 140 deg. C. for 3 hours. Care must be taken with large batches, as the reaction is exothermic and may cause excessive pressure. (4) Any pressure is then released and the material is subjected to a vacuum distillation until the temperature rises to 250-300 deg. C., depending on the desired melting point of the resin. (5) The resin is run out into flat pans and cooled until solid.

This latter method was used as a standard to prepare resin for molding experiments. Tests of molded products of the plastic made by the first method showed a lower water resistance than those made from resin produced by the last process.

The amount of water soluble material in the powdered resin was determined by extraction in a Soxhlet apparatus. The data are given as follows:
Wt. filter thimble plus resin ........... 14.622 gms.
Wt. filter thimble .................... 4.203
Wt. resin .................. 10.419 gms.

Wt. filter plus resin after extraction .... 14.096 gms.
Wt. filter thimble .................... 4.203
Wt. extracted resin .................. 9.893 gms.

Loss in wt. of resin .................. .526 gms.
Percent soluble matter ................ 5.05 %

Preparation of the molding powder. When the plastic material was made by the first method described, it contained sufficient unreacted corncob to act as filler. After drying and grinding it could be molded directly. However, some batches retained a slight amount of acid which caused sticking. This was neutralized by treating the dry plastic powder with NH₃.

To prepare a molding compound from the resin produced by the second reaction method, the resin was ground to pass a 60 mesh sieve and then incorporated with a filler by grinding the two together. When wood flour was used as filler, the optimum ratio was approximately 55 parts by weight of wood flour to 45 parts by weight of resin. With too much wood flour the resin did not come to the surface sufficiently during molding to give a shiny appearance, and when too much resin was used the material became too fluid and extruded from the mold.

The molding compound prepared from resin and filler had the property of flowing well in the mold, and no plasticizer was needed; however, when the material was prepared by the first method it did not always flow well in making thin objects. To
overcome this, stearic acid and zinc stearate were used as plasticizers, and a test was made of the effect of these on the molded product. At the same time the effect of fineness of the mix was studied to ascertain whether it, too, had some influence on the plasticity. A plastic material was made by mixing together 100 gms. cathulls, 40 gms. cresol and 2 gms. ZnCl₂ and cooking for 4 hours at 150 deg. C. in the steam pressure-cooker. The cooked material was dried 2 hours at 100-110 deg. C. and ground to pass a 40 mesh screen. The powder was then divided into several portions; 2 percent stearic acid being added to one portion and 2 percent zinc stearate added to another. The plasticizers were well mixed with the molding powder by grinding for 1 hour in a ball mill. To determine the effect of fineness, another portion was ground in the ball mill until it passed a 200 mesh sieve. The treated materials were molded at 190 deg. C. under 3000 lbs. per sq. in. pressure. The pressure was applied for 1 hour and at the end of that time the mold had cooled so that the product could be removed. The product was a disc 1.25 in. in diameter and approximately 1/8 in. thick.

Strength tests were made on a Page impact-testing machine. In this machine, the test disc was placed on a solid block and a half-inch ball point placed on the center of the disc. A shock was transmitted through the point from a falling 2Kg. weight. The machine would lift the weight 1 cm. higher each time before dropping it. The strength recorded was the distance in cm. that the weight was dropped when the disc broke.
Table IV
Effect of Plasticizers and Fineness.

<table>
<thead>
<tr>
<th>Run</th>
<th>Plasticizer</th>
<th>Percent by Weight</th>
<th>Fineness</th>
<th>Molding Temp.</th>
<th>Pressure</th>
<th>Strength</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zinc Stearate</td>
<td>40</td>
<td>190</td>
<td>3000</td>
<td>27</td>
<td></td>
<td>Average disc.</td>
</tr>
<tr>
<td>2</td>
<td>Stearic Acid</td>
<td>200</td>
<td>190</td>
<td>3000</td>
<td>11</td>
<td></td>
<td>Excellent surface</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>40</td>
<td>190</td>
<td>3000</td>
<td>27</td>
<td></td>
<td>Good flow, Dull surface</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>2</td>
<td>40</td>
<td>190</td>
<td>3000</td>
<td>22</td>
<td>Best flow, Greasy appearance</td>
</tr>
</tbody>
</table>
The data obtained from the tests are shown in Table IV.

The results showed that both zinc stearate and stearic acid aided the flow of the plastic in the mold without greatly lessening the strength. However, they caused a greasy surface to form on the product. Fine grinding helped the flowing quality some and gave a very polished surface, but caused a loss of strength.

**Variation of molding temperature.** This experiment was run before the completion of the steam-heated mold, and the mold used in this case was heated on an electric hot-plate to the desired temperature. The plastic powder was introduced into the hot mold, which was then transferred quickly to the hydraulic press and molded under a pressure of 3000 lbs. per sq. in. Pressure was maintained for approximately 1 hour. At the end of that time the mold had cooled to about 40 deg. C. and the disc was removed. The discs were 2\(\frac{3}{8}\) inches in diameter and approximately 1/8 in. thick. One run was made varying the molding temperature from 100 deg. C. to 130 deg. C. with a plastic powder containing 40 percent resin, and another run was made varying temperature from 110 deg. C. to 130 deg. C. with a plastic powder containing 50 percent resin. Wood flour was used as the filler.

Strength tests of the molded discs were made in the Page impact-testing machine. The treatment and results of these tests are shown in Table V.
Table V.
Variation of Molding Temperature.

<table>
<thead>
<tr>
<th>Run</th>
<th>Resin (gms)</th>
<th>Wood Flour (gms)</th>
<th>Molding Temperature (°C)</th>
<th>Pressure (lbs. per Sq. in.)</th>
<th>Strength (cm)</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>60</td>
<td>100</td>
<td>3000</td>
<td>18</td>
<td>Resin did not flow sufficiently</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>60</td>
<td>110</td>
<td>3000</td>
<td>17</td>
<td>Disc good</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>60</td>
<td>120</td>
<td>3000</td>
<td>13</td>
<td>Disc good</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>60</td>
<td>130</td>
<td>3000</td>
<td>22</td>
<td>Disc good</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>50</td>
<td>110</td>
<td>3000</td>
<td>11</td>
<td>Disc good</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>50</td>
<td>120</td>
<td>3000</td>
<td>9</td>
<td>Disc good</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>50</td>
<td>130</td>
<td>3000</td>
<td>13</td>
<td>Resin too fluid; extruded from mold.</td>
</tr>
</tbody>
</table>
The results of the strength tests were not uniform enough to use as a basis for judgment of best molding temperature. However, the plastic containing 40 percent resin was shown to be stronger than that containing 50 percent resin.

Only a qualitative moisture absorption test was made on the discs. The results showed the discs with 50 percent resin to be more water-resistant than those with 40 percent resin and, with the same composition, those molded at lower temperatures, were the least resistant.

In Run 1 the resin did not flow sufficiently to give the disc a smooth, shiny surface, and in molding the disc in Run 7 the material became so fluid that it extruded from the cracks of the mold.

**Comparison of various fillers.** In this experiment a study was made to determine the effect of various fillers on the molding operation and on the physical properties of the molded plastic. Wood flour was considered a standard since it had been used for filler in most of the other molding experiments.

A supply of resin, for use as binder, was prepared according to the procedure already given; that is, ground corn cobs were reacted with cresol and a sulfuric acid catalyst and the excess cresol removed by vacuum distillation. The melting point of the resin was approximately 110 deg. C.

The resin was ground in a ball mill and screened with an 80 mesh sieve. It was then compounded with the filler by grinding
the resin and filler together for 2 hours in a ball mill.

The materials used for filler were wood flour, corncob flour, soya-bean meal, Sil-o-cel, asbestos, and precipitated calcium carbonate. Soya-bean meal was tested to observe the effect of the oil content on molding and water-proofing. The asbestos was used in two sizes; that which had passed a 40 mesh screen, and some which was approximately 8 mesh size. The grinding during the mixing with resin probably reduced these sizes somewhat.

Mixing and molding conditions were kept as uniform as possible. The molding temperature was kept 135-140 deg. C. for a period of 10 min., and the mold then cooled with cold water to 20-30 deg. C.

The molded product was a disc 1 1/2 inches in diameter and thickness varying from 0.3 to 0.7 inches. The thickness of the disc could not be kept uniform because of the varying density and compressibility of the fillers.

Comparisons were made of the strength and water absorption. The Page testing machine was used for the strength tests and water absorption determined by immersing weighed samples in water for 2 hours, blotting off the surface moisture and re-weighing. It was not intended to obtain the total amount of moisture that the discs could absorb, but rather a comparison of the water-resistance of the discs.

The specific gravities of the discs were calculated from their weights and volumes. Experimental data are recorded in
### Table VI

**Use of Various Fillers.**

<table>
<thead>
<tr>
<th>Run</th>
<th>Composition of Plastic:</th>
<th>Wt.</th>
<th>Wt.</th>
<th>Wt.</th>
<th>Wt.</th>
<th>Water</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>corn cob flour</td>
<td>50</td>
<td>50</td>
<td>17.440</td>
<td>decomposed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>soya bean meal</td>
<td>50</td>
<td>50</td>
<td>16.467</td>
<td>17.460</td>
<td>0.993</td>
<td>6.0</td>
</tr>
<tr>
<td>3</td>
<td>Sil-o-cel</td>
<td>50</td>
<td>50</td>
<td>20.802</td>
<td>20.812</td>
<td>0.010</td>
<td>0.05</td>
</tr>
<tr>
<td>4</td>
<td>calcium carbonate</td>
<td>55</td>
<td>45</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>asbestos fine</td>
<td>60</td>
<td>40</td>
<td>34.749</td>
<td>34.751</td>
<td>0.002</td>
<td>0.0058</td>
</tr>
<tr>
<td>6</td>
<td>asbestos coarse</td>
<td>60</td>
<td>40</td>
<td>23.466</td>
<td>23.468</td>
<td>0.002</td>
<td>0.0085</td>
</tr>
<tr>
<td>7</td>
<td>asbestos coarse</td>
<td>65</td>
<td>35</td>
<td>17.497</td>
<td>17.505</td>
<td>0.008</td>
<td>0.046</td>
</tr>
<tr>
<td>8</td>
<td>wood flour</td>
<td>40</td>
<td>60</td>
<td>15.246</td>
<td>15.353</td>
<td>0.107</td>
<td>0.70</td>
</tr>
<tr>
<td>9</td>
<td>wood flour</td>
<td>45</td>
<td>55</td>
<td>17.065</td>
<td>17.434</td>
<td>0.369</td>
<td>2.16</td>
</tr>
<tr>
<td>10</td>
<td>wood flour</td>
<td>50</td>
<td>50</td>
<td>15.474</td>
<td>15.730</td>
<td>0.256</td>
<td>1.66</td>
</tr>
<tr>
<td>11</td>
<td>flour</td>
<td>55</td>
<td>45</td>
<td>13.347</td>
<td>13.790</td>
<td>0.443</td>
<td>3.32</td>
</tr>
<tr>
<td>12</td>
<td>flour</td>
<td>60</td>
<td>40</td>
<td>14.038</td>
<td>14.390</td>
<td>0.352</td>
<td>2.50</td>
</tr>
</tbody>
</table>
Table VI
Use of Various Fillers.

<table>
<thead>
<tr>
<th>wt.</th>
<th>wt.</th>
<th>percent</th>
<th>thick.</th>
<th>specific gravity</th>
<th>strength</th>
<th>cm.</th>
<th>remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>17.440</td>
<td>decomposed</td>
<td>:</td>
<td>:</td>
<td>:</td>
<td>9</td>
<td>Decomposed completely in water</td>
</tr>
<tr>
<td>50</td>
<td>16.467</td>
<td>17.460</td>
<td>0.993</td>
<td>6.00</td>
<td>.47</td>
<td>1.21</td>
<td>2</td>
</tr>
<tr>
<td>50</td>
<td>20.802</td>
<td>20.812</td>
<td>0.010</td>
<td>0.05</td>
<td>.5</td>
<td>1.44</td>
<td>3</td>
</tr>
<tr>
<td>45</td>
<td>:</td>
<td>:</td>
<td>:</td>
<td>:</td>
<td>:</td>
<td>:</td>
<td>Too brittle to remove from mold</td>
</tr>
<tr>
<td>40</td>
<td>34.749</td>
<td>34.751</td>
<td>0.002</td>
<td>.0058</td>
<td>.66</td>
<td>1.82</td>
<td>3</td>
</tr>
<tr>
<td>40</td>
<td>23.466</td>
<td>23.468</td>
<td>0.002</td>
<td>.0085</td>
<td>.44</td>
<td>1.84</td>
<td>24</td>
</tr>
<tr>
<td>35</td>
<td>17.497</td>
<td>17.505</td>
<td>0.008</td>
<td>.046</td>
<td>.31</td>
<td>1.94</td>
<td>Resin ran out disc stuck</td>
</tr>
<tr>
<td>60</td>
<td>15.246</td>
<td>15.353</td>
<td>0.107</td>
<td>0.70</td>
<td>.41</td>
<td>1.28</td>
<td>16</td>
</tr>
<tr>
<td>55</td>
<td>17.065</td>
<td>17.434</td>
<td>0.369</td>
<td>2.16</td>
<td>.44</td>
<td>1.33</td>
<td>15</td>
</tr>
<tr>
<td>50</td>
<td>15.474</td>
<td>15.730</td>
<td>0.256</td>
<td>1.66</td>
<td>.41</td>
<td>1.30</td>
<td>11</td>
</tr>
<tr>
<td>45</td>
<td>13.347</td>
<td>13.790</td>
<td>0.443</td>
<td>3.32</td>
<td>.34</td>
<td>1.35</td>
<td>28</td>
</tr>
<tr>
<td>40</td>
<td>14.038</td>
<td>14.390</td>
<td>0.352</td>
<td>2.50</td>
<td>.38</td>
<td>1.27</td>
<td>31</td>
</tr>
</tbody>
</table>
Table VI.

The strength tests showed that the only fillers which gave a good strength were wood flour and coarse asbestos. The Sil-o-cel, calcium carbonate, and soya-bean meal gave practically no additional strength to the resin. It was observed that the disc containing 60 percent wood flour was the strongest. This was due to fact that the surface gave and cushioned the shock without transmitting it.

The water absorption by the asbestos-filled discs was very much less than by the others. These discs retained their shiny surface at the end of the 2 hours immersion whereas the water had dulled the surface on all of the other discs. The oil content of the soya-bean meal did not make the disc water-resistant.

It was found necessary to use a higher weight proportion of the asbestos filler than with the other fillers. This was due to its greater density as indicated by the specific gravities of the molded pieces.

The effect of paraformaldehyde and hexamine as hardening agents. In preparing the resin from corn cobs (or oat hulls) and cresol it was very difficult to remove all of the unreacted cresol, and its presence lowered the melting point of the finished product. There were also present in the resin decomposition products of the cellulosic material which did not react with the cresol. They were also deleterious. In pre-
vious work, formaldehyde was tried and found to react with some of these materials. In this experiment, paraformaldehyde and hexamine were incorporated into the molding compound in order that they would react during the molding operation.

The procedure was as follows: the resin and hardening agent were dissolved in acetone and to the solution was added wood-flour filler. The object of the acetone solution was to insure uniform distribution of the resin and hardening agent and to impregnate the wood particles if possible. The acetone was evaporated by drying the mixture on a steam hot-plate at 100-110 deg. C. for 4 hours, and the dry material ground twice in a hand-operated disc mill to insure uniformity. Discs were molded in the steam-heated mold at 135 deg. C. and 5000 lbs. per sq. in. pressure for 10 min.

The discs were tested for strength in the Page impact machine and for moisture absorption. Moisture absorption was determined by immersing a weighed sample in water for 2 hours and then reweighing. The experimental data are shown in Table VII.

Only one disc was broken for each run and the experimental error was rather large. However, the results of the strength tests show that the addition of paraformaldehyde did not appreciably increase the strength while the hexamine increased it considerably.

The moisture absorption determination did not show any
Table VII

Use of Paraformaldehyde and Hexamine (hexamethylenetetramine).

<table>
<thead>
<tr>
<th>Run</th>
<th>Resin</th>
<th>Wood Flour</th>
<th>WT. Parafomaldehyde</th>
<th>WT. Discs</th>
<th>WT. Discs</th>
<th>WT. Hexamine</th>
<th>Dry</th>
<th>Wet</th>
<th>Moisture</th>
<th>% Absorption</th>
<th>Strength</th>
<th>cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>55</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>55</td>
<td>10</td>
<td></td>
<td></td>
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<tr>
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<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

Values in grams (gms).
advantage for the addition of either paraformaldehyde or
hexamine. Run 3, using only 20 percent paraformaldehyde,
showed the lowest moisture gain (0.37 percent), but this may
have been due to a slight excess of mold lubricant.

The discs containing paraformaldehyde stuck rather badly
and were with difficulty removed from the mold. Lubrication
of the mold with mineral oil or a mixture of beeswax and
stearic acid helped but did not overcome the difficulty. The
hexamine discs did not stick at all.

**Materials cost data for manufacture of a molding compound.**
The calculations for material costs are based on the materials
used and the resin obtained from a large experimental batch.
The total raw materials used is as follows:

- 40 lbs. crude cresol (cresylic acid)
- 10 lbs. ground corncobs
- 0.4 lbs. $\text{H}_2\text{SO}_4$

The yield was:

- 17 lbs. resin
- 22.5 lbs. recovered cresol.

The cost of cresylic acid on the market averages at approximately $120.00 per ton, and sulfuric acid $16.00 per ton. An estimated cost for corncobs is $10.00 per ton. From these figures the cost of materials for producing 1 ton of resin is
as follows:

1.04 ton cresol @ $120.00 $125.00
.59 ton corn cobs @ $10.00 5.90
.024 ton H₂SO₄ @ $16.00 .40
Total cost $131.30

For a molding compound containing 55 percent wood flour and 45 percent resin the cost per ton of compound is as follows:

.45 ton resin @ $131.50 $59.00
.55 ton wood flour @ $30.00 16.50
Total cost $75.50
This amounts to $.0378 per pound.

For a molding compound containing 65 percent asbestos and 35 percent resin, the cost per ton is as follows:

.35 ton resin @ $131.30 $46.00
.65 ton asbestos @ $25.00 16.25
Total cost $62.25
The cost per pound is $.0311
The complex nature of corncobs and cathulls makes difficult the satisfactory explanation of the results obtained in their reactions with phenolic bodies. These cellulosic materials contain, in addition to the cellulose, a large percentage of encrusting materials known as ligno-celluloses. Included in the ligno-celluloses are the lignins and the pentosans. Any of these compounds may enter into reaction with the phenols, and the presence of the non-reactive compounds can greatly affect the physical characteristics of the resulting products of reaction.

The pure cellulose and the pentosans are the most important constituents, since they are present in the greatest concentration. Alpha-cellulose is partially dissolved by hot phenol and in time decomposed. If the temperature is raised to 150-160 deg. C. and a small amount of sulfuric acid added as a catalyst, a violent reaction takes place, resulting in the decomposition and solution of the cellulose. Removal of the excess phenol by vacuum distillation, or extraction, leaves a black, resinous pitch. The action of the sulfuric acid appears to decompose the cellulose in such a way that a mixture of compounds are formed. Some of these condense with the phenol, and the others are inert. According to Cross and
Bevan (4), the chemical decomposition of cellulose may be grouped under two headings.

1. Decompositions determined by the non-oxidizing acids—the changes resulting from addition or subtraction of H₂O.

2. Decomposition by oxidants, with attendant or secondary effects of hydrolysis and condensation.

The effect of sulfuric acid is that of a non-oxidizing acid and produces compounds having active CO groups. These groups may be effective in the condensation with phenol; however, at the high reaction temperature there is considerable loss of water, which results in the formation of unsaturated compounds, colloidal carbon particles and possibly anhydride groupings. The formation of unsaturated compounds and colloidal carbon is probably detrimental and the anhydride beneficial to the formation of a good resin.

The pentosans are assumed to be condensation products of the oxycelluloses. Upon partial hydrolysis they form five-carbon sugars called pentoses, and further hydrolysis produces furfural, a five-carbon, ring aldehyde. Furfural, being an aldehyde, has the property of condensing with phenol to form a valuable resinous compound. It is difficult to determine whether furfural is formed in the reaction between pentosans and phenol where no excess of water is present. Under the conditions of this reaction any furfural formed would condense with the phenol with extreme rapidity.
and, therefore, be difficult to detect. However, a hydrolytic reaction, resulting in the addition of water, is necessary for the production of furfural and this is not the type of reaction which produces the best resin from oathulls or corncobs and phenol.

When oathulls are hydrolyzed with dilute acids they yield a mixture of sugars along with other soluble products. Xylose is the chief sugar formed, but there is also formed an appreciable amount of glucose. The xylose is formed by hydrolysis of xylan, and the glucose by the hydrolysis of starches and possibly by some degradation of the cellulose. The xylose and glucose will also condense with phenols at high temperatures to give resinous pitches.

Lignin is difficult to isolate from plant materials in an unchanged form and its structure is uncertain; however, the lignin molecule is known to consist of a benzenoid structure and to contain several hydroxyl groups. Several workers have also recorded the presence of one or more carbonyl groups. The existence of these carbonyl groups may explain the condensation reaction between phenol and lignin, for it is known that the two compounds will condense in the presence of a mineral acid to give a tarry black material. Jonas (13) found that lignin obtained by acid treatment of wood would condense with boiling phenol to form a product which could be distilled, without decomposition, between 230 and 240 deg. C. at 10 mm. pressure. According
to Kalb and Schoeller (14) the lignin residue obtained by
hydrolysis of wood, when condensed with phenol, gives a
product having the character of a phenol. They also obtained
a similar product by heating wood with phenol and a small
amount of hydrochloric acid. It is probable that the
hardening action of formaldehyde on the corncob-cresol
condensation product is due to a reaction with phenolic
groups attached to the lignin rather than to a reaction
with residual cresol.

In summing up the results of the reactions of the
cellulose, lignins and pentosans with phenols, it is seen
that each will produce a resinous product containing un-
known impurities, and that the aggregate, which results from
the reaction of corncobs or like material with phenols,
consists of an indefinite mixture of compounds difficult
to separate because of a resinous nature.
Discussion of Results.

Two methods were described for producing a plastic molding compound; one in which cresol was reacted with an excess of corncobs or insight, and the other wherein the cellulosic material was reacted with an excess of cresol and a resin formed by distilling off the excess cresol at an elevated temperature, this resin then being mixed with a filler.

In the first method, it was not necessary to add a filler, as the excess corncobs served the purpose. Another advantage of this method, which was not emphasized before, is that the cresol and catalyst dissolve and plasticize a part of the cellulose without decomposing it to a black tarry material. The cooked material is brown and gummy, rather than black and tarry. When this is dried and molded it produces stronger discs than material prepared from resin and filler.

The chief disadvantage of this method is poor water resistance. It has been established that this is at least partially due to the formation and presence of sugars. These sugars are probably formed by hydrolysis of starches and pentosans due to accumulation of water during the reaction. In the second method the sugars are decomposed and reacted with the cresol. When an attempt was made to extract the sugars with water, the material became no longer plastic and could not be molded. The water had evidently extracted
the ZnCl₂ and most of the cresol which were mainly acting as solvents, the ZnCl₂ acting also as catalyst. In the early experiments, when it was found that molding at high temperatures increased water resistance, the sugars were probably decomposed in the mold.

The second process, in which an excess cresol is used, overcomes the difficulty due to presence of soluble compounds. The reaction is carried out at a high enough temperature to cause decomposition and condensation with cresol of all of the constituents of the corn cobs, and the high temperature (260-300° C.) of the following vacuum distillation removed, in addition to the excess cresol, most of the water of combination of any remaining carbohydrates. The resin which is left has only a very small portion (5%) of water-soluble compounds, and pieces can be immersed in water for long periods of time without being affected.

When the molding compound is made by mixing the resin with a wood-flour filler and products molded from it, they are not very water resistant. A study for the cause of this has led to the belief that the resin does not impregnate or "wet" the wood fibres and the moisture penetrates through them, causing them to swell and destroy the product. A test of various materials for use of filler has shown that asbestos serves very well. Molded products containing it as filler have a much lower water absorption and are stronger than wood flour.

One property of the resin which is most desirable to im-
prove is the strength. The resin itself is rather weak and brittle; far from approaching the strength and toughness of Bakelite resin. This is probably due to the presence of carbonized material and compounds which fail to condense with cresol. As a remedy, 10-20% of either paraformaldehyde or hexamine was mixed in with the resin before molding. The hexamine considerably improved the strength, but only slightly improved the water resistance.

At first it was believed that the formaldehyde reacted with residual cresol, but the extent of the reaction indicated that there was an additional effect. Under theoretical consideration it was brought out that phenol condensed with lignin to give a compound having phenolic characteristics. It is probable that the formaldehyde reacts with this and other similar compounds.

Much trouble was experienced through sticking of the material in the mold. This may have been due either to entrapped air or to the acidic character of the plastic. The plastic made by the process using an excess of corncobs was greatly benefited by treating the dry powder with NH₃. The resin made by the other process using cresol was neutral to litmus and thought to be free from acid; yet the fact that hexamine gave freedom from sticking while paraformaldehyde did not, indicates that the heat of molding may increase some slight acidic action and that it probably would be better to have the plastic slightly on the alkaline side.
CONCLUSIONS.

The conclusions drawn from the knowledge obtained by this investigation are as follows:

1. Cellulose, pentosans, pentoses and lignins can all be condensed with phenol to produce a resinous material.

2. It is most difficult to produce a hard resin from cresol and lignin, but the lignin resin can be hardened by reaction with an aldehyde.

3. A plastic material can be made from high pentosan substances by the combined solvent actions of zinc chloride and cresol, however, it has the disadvantage of not being very water-resistant.

4. The method of preparing the plastic wherein an excess of cresol is used during the reaction and that excess later removed by distillation is more practical and gives a better product than the method in which an excess of oat hulls or corncobs is used.

5. Oat hulls are more desirable than corncobs, since they give an equal product and do not have to be ground.

6. The only advantage of ZnCl₂ over H₂SO₄ in the condensation reaction is due to the lower acidity of the resinous product.

7. The plastic products containing asbestos as filler were much more water-resistant than those containing
wood flour. The other fillers tested were decidedly inferior to these two.

8. The use of zinc stearate or stearic acid as plasticizing agents only slightly improved molding but left the surface somewhat greasy.

9. The optimum molding temperature for the plastic compound, without a hardening agent, is approximately 140 deg. C.

10. The use of paraformaldehyde as a hardening agent was not desirable as it caused sticking in the mold without an appreciable increase in strength.

11. Here the addition of hexamine was decidedly beneficial as it reduced sticking and increased the strength.
SUMMARY

The investigational work was divided into two parts. In the first part, information was obtained as to the nature of the reactions of the individual constituents of high pentosanocellulosic materials with phenol or the cresols in the presence of a catalyst.

Cellulose was found to act in two ways; it would either dissolve in phenol and zinc chloride, the zinc chloride acting as a solvent instead of catalyst, or it would undergo decomposition and condense with phenol to form a black, resinous material. Sulfuric acid served also as catalyst in the condensation, while sodium hydroxide did not. The presence of the condensation products of cellulose and cresol was found to exert a retarding action on the condensation and polymerization of a cresol-furfural mixture.

The pentosans were found to be soluble in phenol and cresol without reaction or, at an elevated temperature and in the presence of sulfuric acid, they would condense similarly to cellulose to give a resinous material.

Xylose would also condense with phenol like the pentosans, but at a somewhat lower temperature.

Lignins were not directly soluble in phenol but would dissolve with condensation to give a tarry liquid which remained fluid after considerable heating.

In the second part of the experimental work, a steam pressure cooker and an electrically-heated reaction vessel
were adapted for carrying out the reaction between corncobs
or oathulls and cresol.

A standard process was developed for carrying out the
reaction, and for preparing a molding compound from the
plastic material. This process consisted of the following:
(1) Five parts by weight of \( \text{H}_2\text{SO}_4 \) were dissolved in an
equal weight of water and then combined with 100 parts of
cresol. (2) The solution was heated to boiling in an auto­
clave and 30 parts of ground corncobs introduced gradually.
(3) The autoclave was closed and the temperature kept at
140 deg. C. for 3 hours. (4) The pressure was then released
and a vacuum distillation carried out to remove excess
cresol and other volatile materials. (5) When the distillation
temperature had reached 250-300 deg. C., the residual liquid
was run into flat pans and cooled until solid. (6) The solid
resin was ground to pass a sixty mesh sieve and then in­
corporated with 55 percent wood flour filler to produce the
molding compound.

The properties of the molding compound were improved
by a study of the effect of the molding temperature; by
experiments with the use of plasticizers; by an investigation
of various fillers, and through experiments on the effect
of paraformaldehyde and hexamine as hardening agents.
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A method of obtaining resins by heating wood waste with molten phenol and hydrochloric acid.


The pentose and furfural yields from cotton-seed-hull bran, peanut hulls, and oat hulls. A modified process for the production of xylose from
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Studies on the use of high pressure cooking, the removal of unreacted constituents by vacuum, and the successful use of crude cresol in the production of the corncob-cresol plastic.


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