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PLASTICS FROM SOYBEAN MEAL AND FURFURAL

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It is well known that most protein substances may be hardened to form relatively hard, tough, and water resistant materials by suitable chemical treatment. Perhaps the oldest application of this type is the tanning of leather. Much more modern and of much more popular appeal is the production of some 10,000 tons casein annually to be made into such items as buttons, buckles, fountain pens, and various novelties in an attractive array of pastel colors. While milk casein, hardened by formaldehyde, makes excellent plastics the casein is higher in cost than some available proteins so that the possibility of using other proteins has been given considerable study.

Of these other proteins soybean oil meal is very attractive from the standpoint of availability and cost. The production of soybean meal in the United States is about 1,300,000 tons a year and the cost is less than two cents a pound. Meal from which the oil has been removed by pressure in an expeller contains about 5 per cent residual oil and therefore is less attractive from the plastic standpoint than the solvent extracted meal containing not over one per cent oil. The extracted meal has a protein content of about 50 per cent. While the protein may be extracted from the meal and used in plastics, because of the high protein content of the meal it seems possible that the whole meal might be used, allowing the non-protein material to remain as a filler.

In the manufacture of plastics from casein the fat-free casein is mixed into a plastic mass with water and extruded into the desired shapes such as sheets or rods. These are hardened by immersing in a formaldehyde solution. However, to date the only commercial plastics from soybean protein are those made from a mixture of phenol, formaldehyde, and soybean meal. Patents (2) have been obtained on a method of making plastics from soybean protein in a manner similar to that used with milk casein but these patents apparently have never been commercialized.

Brother and McKinney (1) at the U. S. Regional Soybean Laboratory, Urbana, Illinois, studied the hardening action of aldehydes on commercial soybean "alpha" protein over a wide range of hydrogen ion concentrations. They found that the optimum hydrogen ion concentration for the protein-formaldehyde reaction to be pH 4.3.

Forster (3), working in the Chemical Engineering Laboratory at Iowa State College, plasticized water extracted soybean meal with dilute sodium hydroxide and then molded the resulting material. The product was brittle and cracked.

Myers (4) in the same laboratory produced fair plastics by plasticizing soybean meal with caustic soda and hardening with formaldehyde, paraformaldehyde, and furfural. These plastics had a high water absorption.

Since the Iowa Engineering Experiment Station has been actively engaged in developing new uses for agricultural products and by-products the authors studied the use of furfural as a hardening agent on soybean meal. Furfural is at present produced commercially at an Iowa plant from oat hulls by steam distillation with dilute sulfuric acid but it may be produced from any of the high pentosan-containing agricultural by-products such as corn cobs, cornstalks, and various straws.

Since it was not considered desirable to attempt to use pure furfural directly on the meal a saturated or seven percent solution in water was used. Seven thousand one hundred and fifty cubic centimeters of the solution containing a total of 500 grams of furfural were placed in a 5-gallon stoneware jar and sodium hydroxide added to give a hydrogen ion concentration of pH 4.3, the optimum found by Brother and McKinney when formaldehyde was used to harden soybean protein. To this solution was added 500 grams of solvent extracted soybean meal which was kept in suspension for 48 hours at room temperature. At the end of this time the hydrogen ion concentration had dropped to pH 4.1 and the concentration of furfural to 3.2 per cent. The hardened meal was washed free from furfural with water on a Buchner funnel. Because of the large amount of fine material present this was a very slow procedure. The material was next dried at 100° C. for 36 hours. The hardened soybean meal was then ground to pass a 60-mesh screen and mixed in a pebble mill with an equal weight of wood flour filler.

The molding powder thus prepared was formed into test disks in the "button" mold used for this purpose. This mold consisted essentially of a block of steel 4 inches by 4 inches by 3.25 inches with a vertical hole 1.5 inches in diameter. The bottom of the hole was closed by a steel disk and the pressure was applied to the molding powder by a steel piston operating in the hole. The block was provided with channels for steam heating and water cooling. Since satisfactory molding temperatures could not be secured with the steam pressure available the mold was heated by four Meker gas burners. The temperature was determined by an ordinary mercury-in-glass thermometer inserted in a hole in the block but due to a lag effect there was an apparent rise in temperature after the burners were shut off. Pressure was applied in a Carver laboratory type hydraulic press operated by hand.

The product, which proved to be thermoplastic, was molded into disks 0.32 to 0.33 inches thick under pressures from 2,000 to 4,000 pounds per square inch, temperatures from 146° C. to 210° C., and curing time from 3 to 4 minutes. In each case the disk was cooled 3 minutes before removal. None of these samples cured entirely satisfactorily although the ones at 2,500 pounds and 210° C. for 4 minutes were fair.

To produce a plastic which would cure more satisfactorily, batches were made containing one, two, and four percent hexamethylenetetramine. At the temperature of molding the hexamethylene tetramine broke down liberating formaldehyde which reacted with the protein completing the hardening effect of furfural. The best results were secured with one and two percent hexamethylene tetramine. Because of the large amount of gas produced it was necessary to "breathe" the mold, that is release the pressure after the first closing to allow the escape of gases formed.

The best molding procedure for the plastic was as follows: A weighed amount of powder was placed in the button mold and slowly heated with Meker burners to 170° C. The burners were turned off; the mold breathed; and 2,500 pounds per square inch pressure was applied. The temperature rose to 200° to 210° C.; and after a 4 minute cure, cold water was run through the mold for about 3 minutes. The disk was then removed.

Four batches containing one percent hexamethylene tetramine were tested for strength and moisture absorption. The strength test was made in an impact tester. The disk to be tested was placed on a steel block at the base of the machine and a pin one inch in diameter with a rounded end placed on top of the disk. A 5-pound weight, which was held in place by guides, was allowed to fall and strike the pin. The height at which the weight fell was increased one inch at a time from an initial setting of 5 inches until the impact blow caused the disk to crack. The strength was reported as the inches of fall required to break the sample. The average strength of 20 samples from 4 batches was 19.7 inches. This strength compares very favorably with that secured by high grade commercial phenolic plastics tested under the same conditions. The moisture absorption was determined by immersing weighed disks in distilled water at room temperature for 48 hours and reweighing. The average absorption from the four batches was 12.4 percent. This high absorption limits these plastics to uses away from contact with water. While no accurate yield figures are available for this plastic approximate cost figures can be calculated. During the treatment of the meal with the furfural solution there is doubtless some loss of soluble material from the non-protein portion of the meal. Yields, however, should be in excess of 75 percent. If the cost of the meal is calculated at 2 cents a pound, the yield at 75 percent, furfural cost at 10 cents a pound, and hexamethylene tetramine at 40 cents a pound, the raw material cost for the plastic without filler would be 3.5 cents a pound. When molded using an equal amount of wood flour filler costing 1.5 cents a pound, the raw material cost would be 2.6 cents a pound. This makes the plastic very attractive from the cost standpoint.

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