The Industrial Uses of Corn Protein

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The bulk of our corn crop is used directly as feed for farm animals. About 120 million bushels is processed each year by the wet-milling industries, however, to provide starch and oil for human food and for many industrial applications. Corn gluten, a byproduct of the starch refineries, contains about 50 percent protein.

Like other high-protein products, corn gluten is used without further change, mainly in feed concentrates and in small amounts as extenders for commercial resins and glues. It is sometimes destarched by acid or enzyme hydrolysis to yield a product that is almost entirely protein and is used in paints. Sometimes it is broken down by complete hydrolysis to yield monosodium glutamate, a seasoning for food.

The gluten is also processed to yield zein, a pure protein that has many commercial uses. Zein belongs to a class of proteins called prolamines, which have several unique properties. In fact, the special properties of zein make it widely acceptable for a number of industrial uses for which other proteins are inferior or unsuited.

Zein has been produced commercially since 1938. It is one of the few alcohol-soluble proteins; alcohol is used to extract it in pure form from the corn gluten. Originally, the gluten occurs mixed with starch in the endosperm of the corn kernel, the starchy part outside the germ. Most of the gluten is concentrated in a layer next to the hull of the kernel.

In commercial processing, isopropyl alcohol (about 15 percent water) is used to extract the zein from the gluten meal. The extract is subjected to a complicated process to obtain the isolated protein. It must be clarified by filtration to remove undissolved particles and then mixed with an oil solvent (hexane) to remove oil and coloring matter. The result is two phases, or layers. One contains the oil. The other contains the concentrated zein. After these are separated by centrifugation, the zein phase is squirted into large volumes of cooled water to precipitate the zein as a fibrous solid. The zein, when filtered from the water, must be dried by a carefully controlled process, because wet zein when heated forms a gummy dough that cannot be worked successfully. The final product is a light-yellow, durable powder.

Zein was a relatively expensive protein during the first years of its production because the method of making it was complicated. Its price, however, remained steady during the war years while the price of other commercial proteins increased until there was no difference in cost.

Up to 1950, only one company produced zein, and its capacity was below the actual demand. It is to be expected that the number of producers and their capacities will increase as demand dictates. Based on the amount of corn wet milled by the starch refineries, the potential supply of zein is 100,000 to 150,000 tons annually.

Corn contains proteins other than zein, and methods have been developed for their isolation. The Northern Regional Research Laboratory developed a process whereby corn gluten is first wetted with only a small amount of alcohol instead of the large amount
The proteins are then extracted with a relatively inexpensive alkaline solution. The pretreatment with alcohol is necessary to make the zein soluble. The process not only extracts the other proteins of corn along with the zein, but also greatly increases the efficiency of zein recovery. Because of greatly increased yields, the process would undoubtedly result in a less expensive protein for potential industrial uses.

The properties of zein and most other proteins are solubility in dilute alkali, tackiness (which enables them to adhere to other materials), ability to form films and fibers, susceptibility to coagulation by heat and other forces, and susceptibility to hydrolysis by chemicals and enzymes of organisms.

But zein, which belongs to the prolamine class of proteins, has some characteristics that distinguish it from most other proteins. It is deficient in some of the most reactive side groups, such as amino and carboxyl groups. Those groups have a great attraction for water, and zein therefore has relatively good resistance to water. Zein, on the other hand, contains an abundance of less reactive groups, such as amide and hydroxyphenyl groups. For that reason it is soluble in dilute alkali and, as the distinguishing feature of the prolamine class, it is soluble in low-boiling organic solvents, such as alcohols, ketones, and acids. That solubility factor makes zein useful in varnishes because, when a solution is spread on a surface, the solvent quickly evaporates to leave a coating, or film, of zein. Zein is also soluble in higher-boiling organic solvents, such as glycol ethers, and forms solutions that are used in the formulation of hot melts, cork binders, and printing inks. The constitution of its molecule is such that zein also has good oil resistance and imparts valuable greaseproofness to materials when applied as a coating.

Another noteworthy property of zein, which is unusual for proteins, is its thermoplasticity—the property of softening when heated. Thermoplastic materials are readily formed into inexpensive articles in molds by an application of heat and pressure. Moist zein readily flows under molding conditions to form articles that hold their shape under normal conditions. In combination with rosin and similar materials, it forms hot melts, which can be used as another method for applying coatings. Such formulations are also useful because of their heat-sealing properties.

Zein is resistant to hydrolysis and to putrefaction by micro-organisms. Many proteins, when dissolved in dilute alkali, start to deteriorate and to give off ammonia; zein, however, is relatively stable in alkaline solutions. Also, zein can be stored for a long time in a wet or dissolved state without acquiring the disagreeable odor of putrefaction so evident with other proteins. The resistance to spoilage is convenient in manufacturing plants where wastes are bound to accumulate.

The zein molecule seems to have a relatively long, effective chain length, which enhances the film- and fiber-forming properties of this protein. Though relatively inert, zein is reactive to chemicals, such as formaldehyde, which tie molecules together and thus harden and improve the water-resistance of coatings and shaped articles. It has remarkable adhesive properties, which are necessary in many of its applications.

The most troublesome property of zein has probably been the gelation of its solutions. Varnish in bottles, for example, would solidify, or coating solutions would turn to a gel in the paper coater. This gelling property is inherent in proteins and is closely related to the film- and fiber-forming properties. Solutions of zein can be stabilized against gelation by a special formaldehyde treatment. Also, the zein now sold commercially is a modified protein that forms relatively stable solutions.

Zein itself has become an important industrial protein because the
combinations of certain of its properties favor its use for specific purposes. For example, its solubility in alcohol makes it a good ingredient of varnishes; furthermore, the coating it forms adheres to the surface, is durable, resists water and chemical agents, is flexible to a certain degree, and has satisfactory color.

Patents cover the use of zein for many products—from a hair-wave set to chewing gum. It can be molded into hard, resistant plastics or converted into sheets of rubbery material. It forms a tough film or coating on other materials. It makes an excellent textile fiber. It can be used as an adhesive to bind other substances together or in compounding printing inks. It has been used in making beer and improving flour.

The most important industrial users take advantage of the properties already discussed and use the commercially supplied product without much further modification. For novelty uses, such as replacements for rubber, celluloid, or linoleum, the properties are often modified by chemical reactions and physical treatments. Zein is seldom used alone—it is generally mixed with such materials as resins and plasticizers, which contribute their own desirable properties to the mixture. Many formulations are available to fit the various needs.

During the Second World War, when imports of shellac were greatly curtailed, zein was used extensively as a replacement in varnishes and phonograph records.

As a varnish, zein was used in an alcohol solution along with other ingredients, generally including rosin. The recommended ratio of zein to rosin ranged from 1:1 to 1:3 parts by weight. The higher proportions cost more, but they make more durable finishes. Various formulations are useful as wood primers, which have excellent sanding qualities, or as gloss finishes. They can be used on a variety of surfaces—wood, paper, asphalt compositions, leather, cloth, glass. Outstanding properties are a high gloss, fast rate of drying, suitable hardness, flexibility, brushability, resistance to water and grease, and good dielectric characteristics. Pigments can be added to the spirit varnishes to make decorative as well as protective coatings.

Zein replaced shellac in phonograph records because it supplied the needed thermoplastic material for the molding process; it was found that zein could be used with very little change in the process. It is said that the zein records wear better and have superior tone qualities.

In the paper industries, zein has value for sizing, impregnating, coating, laminating, and gluing paper. One of the uses is as a glossy protective coating, which is applied as zein varnish and known as overprint or label varnish. It gives a glossy finish and resists scuffing, water, alcohol, and grease.

Zein is also used as size for paper and cardboard. The treatment is usually called tub sizing because the paper is immersed in a water dispersion of the zein formulation before rolling and drying. Good water resistance is given the paper. The addition of materials like oleic acid imparts excellent water resistance to the paper. Zein-sized papers also have the useful property of resistance to penetration by the oils, greases, and waxes. They can be used as wrapping papers and cardboard containers for greasy foods.

Another way to make paper proof against grease is to coat it with an alcoholic solution of zein.

Proteins are generally used as binders in clay coating papers. Zein is a good binder because of its excellent adhesive character and its good water resistance. The coating slurry (which contains clay, zein, and dispersing agents for the zein, such as alkali or rosin soaps) is applied with ordinary equipment. Advantages are that mixtures high in solids can be used and less heat is needed to effect drying.

Zein is used to bind cork particles together to form composition cork. Granulated cork is first mixed with zein
in a glycol solvent and with a curing agent, such as paraformaldehyde. The mixture is then molded by slight pressure into blocks, rods, or sheets, which are cured at high temperatures. The finished products have many different uses—as gasket materials, bottle-cap liners, polishing wheels, shoe fillers, textile spinning cots, and novelty and specialty items. A particular advantage of zein as a binder is its resistance to molds in hot, damp weather.

Other adhesive applications include the binding of paper, glass, wood veneer, and materials like nitrocellulose, to which ordinary glues will not adhere. Zein can be used successfully in making impregnated and laminated paper gasket material. It is used in printing inks where it must adhere to the paper and be quick-setting to allow for rapid printing.

An excellent textile fiber is being made from zein. (See p. 469.)

Other uses are numerous. As a sealer for asphaltic compositions, zein protects the surface coating from penetration by the asphalt. It is one of the foaming agents used in fire extinguishers. Some foundries use it as binding material in sand molds. It is used as a binder to stiffen hard felts and as one of the ingredients of oil-cloth and linoleum. It serves as backing for photographic films and makes a useful sizing for fibers in the weaving industry.

Thus, corn protein has many applications besides its major use as feed. After zein became commercially available, its industrial utilization expanded rapidly as improved processes and new industries developed. Successful use depends on a sound understanding of its unique properties and how to use those properties to advantage. The great potential availability encourages continued and increased utilization in a wide range of commercial applications for which zein is suited.

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Cyril D. Evans joined the Department of Agriculture in 1941, when the protein section of the Northern Laboratory was established. His major work has been on the industrial utilization of plant proteins—as fibers, films, plastics, coatings, adhesives, and plasticizers.

### Strength of four glues applied to various woods

**Shear strength (pounds per square inch) when applied to—**

<table>
<thead>
<tr>
<th>Glue mix</th>
<th>Birch Dry</th>
<th>Birch Wet</th>
<th>Tupelo Dry</th>
<th>Tupelo Wet</th>
<th>Red gum Dry</th>
<th>Red gum Wet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peanut-meal glue 1</td>
<td>364</td>
<td>157</td>
<td>327</td>
<td>91</td>
<td>382</td>
<td>150</td>
</tr>
<tr>
<td>Commercial soybean meal prepared for use as plywood glue</td>
<td>367</td>
<td>147</td>
<td>374</td>
<td>138</td>
<td>373</td>
<td>110</td>
</tr>
<tr>
<td>Casein-glue mix ready for use upon addition of water</td>
<td>393</td>
<td>151</td>
<td>401</td>
<td>o</td>
<td>328</td>
<td>33</td>
</tr>
<tr>
<td>Casein-glue mix containing blood and soybean meal</td>
<td>396</td>
<td>142</td>
<td>268</td>
<td>112</td>
<td>352</td>
<td>105</td>
</tr>
<tr>
<td>Casein-glue mix containing blood and soybean meal</td>
<td>396</td>
<td>142</td>
<td>268</td>
<td>112</td>
<td>352</td>
<td>105</td>
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1 All commercial mixes.