

REVIEW

Zein: A History of Processing and Use

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ABSTRACT

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Corn is the largest and most important agricultural commodity in America. Zein, one of the components in corn, has long been investigated for uses other than food and feed. Zein is a unique and complex material, and it is one of the few cereal proteins extracted in a relatively pure form. Today, because of environmental concerns, interest in zein utilization is again growing. Some of the more important research on zein is more than 50 years old. Most of this work has been either forgotten, lost, or difficult

to locate. Much of this work was done at the USDA laboratory in Peoria, IL. Since most early zein literature is still easily accessible at that laboratory, this review on zein has been prepared making use of this old literature. This review reexamines the old literature and reconciles it with new zein research to illustrate some of the unique properties of and opportunities for zein.

Zein has been examined as a possible raw material for polymer application since the early part of the 20th Century. Gorham (1821) first described zein after isolating the protein from maize. He named the material "zeine". The description that Gorham gave to zein would easily be recognized today. It resembled bees' wax and to be soft, ductile, tenacious, and elastic. It had some of the properties of wheat gluten and was analogous to resin. The same material was later described as "maize fibrin" by Ritthausen (1872). Other early work on zein was conducted by Bizzo (1822) and Stepf (1859). Chittenden and Osborne (1891a,b) and Osborne (1897; 1908; 1924) placed zein in its present classification as a prolamin. Osborne (1891b, 1902) also was granted two patents on the extraction of zein. During this same period, there were numerous patents granted relating to the extraction and uses of zein (Rathmann 1954). However, commercial production of zein did not start until the mid-1930s (Anon 1944). For the next 20 years, a number of uses were found for zein in all fields (Rathmann 1954), including the manufacture of buttons, fiber, adhesives, coatings, and binders, etc. Commercial production of zein peaked in the late 1950s, approaching 15 million pounds a year in the United States (Anon 1978). By 1978 the production of zein had dropped to one million pounds a year and has remained fairly constant since then.

Renewed interest in zein as a polymeric material has been stimulated, in part, by the perceived negative impact of plastic on solid waste disposal. Zein offers several potential advantages as a raw material for film, coatings, and plastics applications. It is biodegradable and it is annually renewable. The annual surpluses of corn provide a substantial raw material resource. However, there are also some problems with the use of zein as a plastic material. Zein is a biological material and, like most biological materials, it is affected by water. This, coupled with the fact that water is a plasticizer for zein, means that zein's properties are subject to change with humidity. The cost of zein is also a major limitation in its use as a polymeric raw material. Indeed, cost was one of the reasons for zein's loss of markets in the late 1950s and early 1960s.

Interest in zein utilization is growing again. Zein is a unique and complex material, and it is one of the few cereal proteins extracted in a relatively pure form. This review will reexamine the old literature

and reconcile this with the new zein research to illustrate some of the unique properties of and opportunities for zein.

ZEIN EXTRACTION

Osborne (1891b) was the first to be granted a U.S. patent for extraction of zein. His method, which he deemed a commercial process, was essentially the same as that used for laboratory extraction of zein; the only real difference was the starting material. Laboratory methods started with corn meal or whole kernel corn, whereas Osborne's method started with gluten meal, a coproduct of the then new corn wet-milling process. This gave the method an economy of scale. Whereas the laboratory method only gave yields of 5–6%, the new method had potential yields of 30–40%. Osborne's method called for extraction in a batch operation using 95% aqueous ethanol. This method was never commercialized as the method was batch-oriented and 95% aqueous ethanol is not the best solvent for commercial extraction of zein.

Other early patents were also granted for zein extraction. Wulkan (1902) received a patent for recovery of zein and starch from degermed corn meal. This method called for the use of strong aqueous alcohol containing alkali to dissolve zein. Soluble zein was decanted from the remaining starch. This method also would not give pure zein and starch as claimed by the author. It is now known that some protein would not dissolve with an alcohol-alkali extraction, thus contaminating the starch fraction with unextracted protein. Alkali would also extract other proteins besides zein. Zein extraction from ground corn by hot amyl alcohol was patented in 1902 (Donard and Labbé) and was patented in the United States in 1903. Pure zein was extracted from corn meal or gluten meal if the meal was first extracted with benzene or ether (Donard and Labbé 1903). By removing oily and fatty substances from the meal, a purer zein with a better appearance was obtained. Osborne and Cornelison were granted a United States patent in 1902 for extracting corn gluten meal using dilute aqueous alkali. This method had the advantages of using a less costly solvent, eliminating distillation and evaporation steps, and increasing yields of zein. Of course, as Osborne pointed out, some of the increased yield was probably due to extraction of proteins besides zein.

Except for some laboratory methods (Mason and Palmer 1934; Nolan and Vickery 1936), little research was done on extraction of zein for the next 30 years, probably because there was no real use for zein until the mid-1930s. Then there was an explosion in the amount of research on zein. Many of the uses for zein that were found will be discussed in this review. These new uses of zein prompted the need for commercial quantities of zein.

From 1938 until 1943, Swallen and coworkers were granted numerous patents covering extraction processes for zein. The first patent

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(Swallen 1938a) was not much different from the extraction process of Osborne 40 years earlier. The main differences in Swallen's process were better control of temperature during extraction, and adjusting the pH to ≈ 6 or 7. Swallen called for the extraction to take place at $<70^{\circ}\text{C}$, and preferably between 55 and 65°C . Refinements of the original patent were added over the next five years. Toluol (Swallen 1938b) and later hexane (Swallen 1942a) were added to the extraction procedure to remove lipids and pigments from the zein. In this step, an equal volume of hexane is added to the alcoholic zein solution, causing two layers to form. The top layer contains lipids, pigments, and alcohol. The second layer is a more concentrated zein solution. The addition of the toluol or hexane extraction had the added benefit of concentrating the alcohol zein solution without evaporation. Zein was precipitated from solution by spraying the solution into moving water (Horesi et al 1941). This was an advantage over the laboratory method of precipitating the zein in the form of a dough. Because the precipitated zein was in the form of small particles, the drying process was much more efficient and economical.

For zein production really to be a commercial process, extraction must be continuous. This was achieved by using a countercurrent extractor. Countercurrent extractors were specially developed to be used with corn gluten meal (Swallen and Reintjes 1941, 1942). Aqueous isopropanol (88%) was just as effective for extracting zein as 93% aqueous ethanol (Swallen 1942b). The use of isopropanol had two major advantages over ethanol for extraction. First, it made possible the use of hexane as a color and oil solvent, replacing benzol or toluol. Second, no government license is needed for using isopropanol. A patent very similar to the Swallen patents was granted in 1936 to Buron and MacDonough. Their patent included countercurrent aqueous alcohol extraction and a water precipitation step.

Commercial production of zein was finally achieved using the processes described in these patents. A small pilot plant was started in 1938 (Anon 1939) by Corn Products Refining Company. At the time, the interest in zein was for use in plastics and coatings. However, after the start of World War II, shellac became in short supply, and zein was in demand as a replacement in lacquers and coatings. To keep up with zein demand, Corn Products Refining Company built a much larger plant located in Pekin, IL, in 1943 (Anon 1944) that had several times the capacity of the original plant. By 1944, more than half of the new plant's output was going to the paint, varnish, and lacquer industries, principally as a replacement for shellac (Anon 1944). Figure 1A shows the process flow as it was in 1944.

The zein extraction process was changed slightly in the late 1940s to produce a product called Zein A (Northern Regional Research Laboratory, internal memo dated August 9, 1948). The new procedure added an alkali treatment. After the initial zein extraction, sodium hydroxide was added to the alcoholic zein solution to adjust to pH 9–11 (Swallen and Hamilton 1943). The solution was then aged and filtered before the extract was adjusted back to pH 6 using hydrochloric acid. The neutralized extract was then mixed with hexane and the process continued as before. The alkali-treated zein was more stable against gelation (Anon 1968). The addition of alkali to the zein solution during extraction resulted in the destruction of 80% of its cysteines which improves its stability in solution (Boundy et al 1967). Zein A was used primarily for fiber production, with about 100,000 pounds per month going to Virginia-Carolina Chemical Corporation (Northern Regional Research Laboratory, internal memo dated August 9, 1948). In later years the alkali treated zein was sold under the trade name G200 (CPSC 1960).

In the mid-1950s, in an effort to reduce costs and to meet customers' requirements for zein, the zein extraction process was modified yet again (Forbath 1957). The two main changes involved extraction of zein from corn gluten meal. First, the number of extraction vessels was reduced from seven to four, and the alcohol and the corn gluten meal moved concurrently down the extraction line. Second, the temperature at which extraction takes place was increased from $\approx 60^{\circ}\text{C}$ to just below the boiling point of aqueous isopropanol ($\approx 88^{\circ}\text{C}$). These steps reportedly reduced the extraction time from 3.5 hr to 0.5 hr, increased extraction efficiency by 20%, and cut solvent losses by 30%.

Morris and his coworkers (1956 and 1959) developed a zein extraction process that eliminated the need for hexane treatment. The process consisted of extracting corn gluten meal with 28–33% (w/w) aqueous isopropanol and 6% lime. The extraction was most effective if it took place between 70°C and just below the boiling point of aqueous isopropanol. After 10 additional purification steps, the recovered zein contained only 2% nonprotein impurities. Other methods proposed for extracting zein included extracting with different organic solvents (Martin 1940), using multiple solvents (Coleman 1947), extracting with alkali solvents (Pearce 1948), and extracting in a series using aqueous alcohol followed by an alkali solvent (Evans and Ofelt 1947).

The zein extraction method most commonly used now is a modification of Swallen's process, which was patented by Carter and Reck (1970) (Fig. 1B). A single extraction of corn gluten meal is made with 88% (w/w) isopropanol containing 0.25% sodium hydroxide. The extraction takes place at a ratio of 4:1 alcohol to gluten at 55 – 65°C . Total time for extraction is 1 hr. Zein is precipitated from the solvent by chilling the extract to -10 to -20°C . An increase in zein purity results from repetition of the extraction process, followed by cooling and decanting cycles. The improved process benefits by not using a second solvent for oil and pigment removal, and not requiring a distillation step for alcohol recovery.

In recent years, there has been a renewed interest in using zein as a raw material for environmentally friendly products. One limitation of using zein has been its prohibitive cost, which ranges from $\$10.00$ to $\$27.00/\text{lb}$ (Chemical Market Reporter 8/11/00). Zein is too expensive to compete against synthetic polymers that cost well

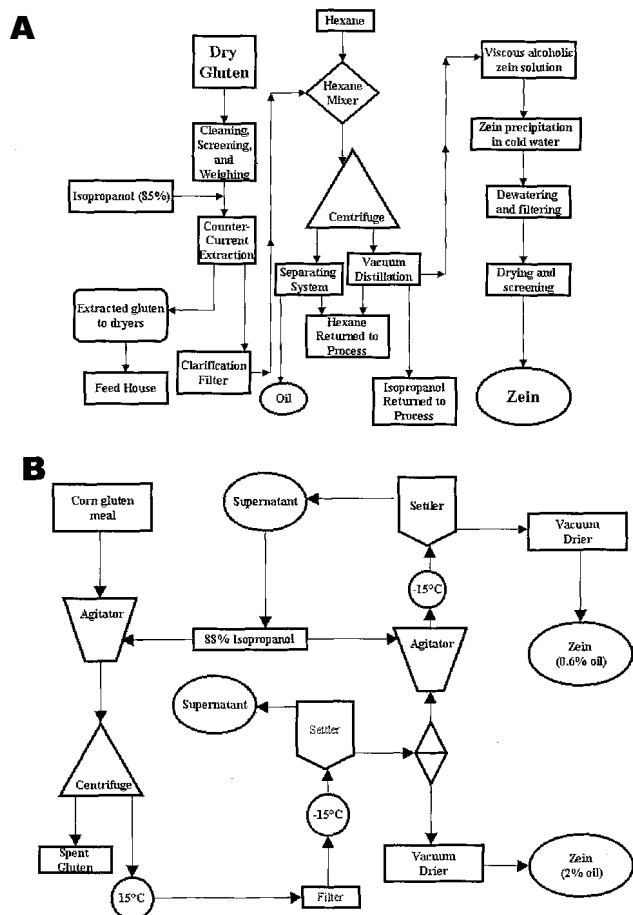


Fig. 1. Commercial flow process of zein isolation from corn gluten meal. **A**, Original flow process (Anon 1944); **B**, Process based on patent (Carter and Reck 1970).

under \$1.00/lb. Some of the high cost of zein, no doubt, comes from its current low demand. Current production is ≈ 1.2 million pounds a year (Shukla 1992). More new uses for zein would help lower this cost. A greater demand for zein would lead to increased production, resulting in lower zein costs. However, just increasing the demand for zein and using the present extraction methods will probably not decrease zein cost enough to justify its use in applications in which it competes with synthetic polymers. Indeed, at the height of zein production (>15 million pounds/year), the cost of zein was becoming too great to compete with newly developed synthetics such as Orlon (acrylic). In 1959, zein was selling for \$0.28 to \$0.35/lb. Adjusting for inflation, today this would be \approx \$1.10 to 1.40/lb, making it still too expensive to compete with synthetics in most markets.

To address the cost of zein manufacturing, there has been renewed activity in zein extraction research. Research has been undertaken that investigates the extraction of zein from whole ground corn rather than corn gluten meal (Lawhon 1986; Chen and Hoff 1987; Hojilla-Evangelista 1992; Dickey et al 1998; Shukla et al 2000). Lawhon (1986) used batch extraction of ground corn to isolate corn proteins. His method entailed suspending ground corn in 45–60% aqueous ethanol that contained either no NaOH or 0.1N NaOH. Extractions were also performed with only 0.1N aqueous NaOH. Lawhon's extraction temperatures ranged from ambient to 60°C, the preferred temperature being 49°C. Extraction times ranged from 30 min to 2 hr. These extraction methods recovered 45–85% of the endosperm protein, depending on the solvent used and the extraction time.

Chen and Hoff's (1987) method for zein recovery called for grits to be extracted with either 50% aqueous ethanol or 50% aqueous alcohol containing 0.08N NaOH, and passing the solvent through a corn grit-packed column. The method could also use the two extraction solvents in series, depending on the type of zein desired. They claimed that 60–80% of the total endosperm protein could be extracted.

Hojilla-Evangelista and coworkers (1992) removed corn proteins from flaked corn with 45% aqueous ethanol containing 0.1M NaOH.

Dicky and coworkers (1998) investigated extracting corn flour or grits with 70% aqueous ethanol. Russell and Tsao (1982), while studying the removal of zein from endosperm, found that the extraction of zein depended on the diffusion of ethanol into the endosperm. Because of the rate-limiting effect of diffusion, smaller endosperm particles are needed to quickly extract zein. They found that extracting zein with 55% aqueous ethanol from pin-milled corn could be done in 30 min, whereas larger endosperm particles could take as long as 4 hr to extract 80% of the zein. Dicky and coworkers (1998) found that during extraction, vigorous mixing along with raising the solvent temperature to 50°C disintegrates the endosperm and thereby diminishes diffusion limitations on extraction rates.

High yields of zein (60% of the zein in corn) could be extracted from ground corn with a particle size of 200–800 μm in 30–40 min when extracted at 50°C with 70% aqueous ethanol (Shukla 2000). Shukla and coworkers found that an 85% recovery of zein could be achieved by using four extractions of fresh solvent. High concentrations of zein (15 g/L) could be achieved by multiple extractions of fresh corn with the same solvent.

A number of advantages could make ground corn extraction attractive to alcohol producers. Ethanol producers already have distillation equipment needed for recovery of the alcohol. Starch used for fermentation does not have to be free of protein, unlike other applications for starch. The extraction solvent will already be on hand and would not have to be purchased. Corn grits can be used to dehydrate ethanol (Ladisich and Dyck 1979; Ladisich et al 1984). Corn grits are already being used in some large-scale fermentation plants to dehydrate fuel grade ethanol (Anderson et al 1996). Chen and coworkers (Chen and Hoff 1987; Chien et al 1988) have demonstrated that extraction of corn grits with ethanol can simultaneously dehydrate ethanol and extract oil from corn grits.

A major drawback of using whole corn extraction is the final purity of the zein. Whereas yields of extracted protein are good, with some methods extracting up to 85% of the total endosperm protein, the purity of the recovered protein is $\approx 65\%$, which is only mediocre

TABLE I
Primary Solvents for Zein^a

Solvent	Temp. °C ^b	Solvent	Temp. °C ^b
Acetamide	82	Furfuryl alcohol	≤ 40
Acetic acid	14	Glycerol	139
2-amino-2-ethyl-1,3-propanediol	38	Glycerol furfuryl	≤ 40
2-amino-2-methyl-1-propanol	24	Glycerol- α - γ -dimethyl ether	≤ 40
Aniline	Gels	Glycerol- α -monochlorohydrine	≤ 40
Benzyl alcohol	-18	Glycerol- α -methyl ether	≤ 40
Benzyl Cellosolve	≤ 40	Glycerol- α -phenyl ether	> 54
Butylamine	≤ 40	β -Hydroxyethylaniline	-30
Butyl tartrate	≤ 40	Hydroxyethylethylenediamine	≤ 40
1,3-Butylene glycol	39	2-Hydroxymethyl-1,3-dioxolane	≤ 40
<i>o</i> -Cyclohexylphenol	> 55	Lactic acid	≤ 40
1,3-Diaminopropanol	40	Methanol	63
Di[- β -hydroxyethyl]aniline	> 59	Methyl lactate	≤ 40
Diethanolamine	30	Monoethanolamine	6
Diethylene glycol	≤ 40	Monoisopropanolamine	-4
Diethylene glycol monoethyl ether	≤ 40	Morpholine	-6
Diethylene glycol monomethyl ether	≤ 40	Morpholine ethanol	> 2
Diethylenetriamine	≤ 40	Phenol	40
Diglycolchlorohydrine	≤ 40	Phenylethanolamine	-15
Diisopropanolamine	32	Propionic acid	60
Dipropylene glycol	≤ 40	Propylene chlorohydrin	-30
Ethyl ether tripropylene glycol	-20	Propylenediamine	≤ 40
Ethyl lactate	-24	Propylene glycol	≤ 40
Ethylphenylethanolamine	-25	Pyridine	≤ 40
Ethylene chlorohydrine	≤ 40	Resorcinol monoacetate	0
Ethylene glycol	18	Triethanolamine	> 21
Ethylene glycol monoethyl ether	≤ 40	Triethylenetetramine	≤ 40
Ethylene glycol monomethyl ether	≤ 40	Tetrahydrofurfuryl alcohol	≤ 40
Ethylenediamine	11	Triethylene glycol	≤ 40
Formic acid	7	Triisopropanolamine	> 46

^a Table from Evans and Manley (1941).

^b Temperature at which the 10% (w/v) zein solution became cloudy.

(Lawhon 1986; Hojilla-Evangelista et al 1992). Hojilla-Evangelista and coworkers (1992) greatly improved the purity of their extracted protein by dialyzing the extracted protein against water. Percentages of crude protein went from 66% before dialysis to 79% after dialysis. Using NaOH as part of the solvent also affects the purity of the final zein due to the alkali extracting γ -zein, lipoproteins, and non-protein nitrogen (Landry and Moureaux 1980; Coleman and Larkins 1999). Protein purity could thereby be improved by extracting with only aqueous ethanol without NaOH, thereby eliminating alkali-soluble materials. This would, of course, lower the yield of protein recovered and leave more protein with the starch fraction. Extracting first with absolute ethanol, as proposed by Chen et al (1987) and Hojilla-Evangelista (1992), would also produce purer zein extracts by removing the oils and pigments before zein extraction. Zein recovered from whole grain extractions may also be different chemically from that extracted from corn gluten meal.

Research is still underway to refine the traditional zein extraction from corn gluten meal. Takahashi and Yanai (1994) demonstrated that aqueous acetone could be exchanged for aqueous ethanol or isopropanol for extracting zein. The extracted zein was odorless and nearly white. The final precipitation of zein in absolute acetone also simplified drying, since the zein contains virtually no water. Using aqueous acetone was tried by Evans et al (1945) 50 years previously, but without the same success. They found that aqueous acetone could only extract about half the zein from corn gluten meal compared with aqueous ethanol, and that the zein obtained had different solubilities. The two research groups did use slightly different acetone concentrations; Evans et al used 70% (w/w) aqueous acetone, whereas Takahashi and Yanai (1994) used 65% (w/w) aqueous acetone. In a similar process, Takahashi and Yanai (1996) demonstrated that fats and oils could be extracted from corn gluten meal using short chain hydrocarbons before zein extraction, improving the extraction process. Extraction of fats and oils is then followed by extraction of the zein and pigments in acetone containing only a small percent of water. By extracting oils and fats before zein extraction, the process improves the purification of zein and aids in keeping filters clean. Also, by removing fats and oils from the corn gluten meal before zein extraction, pigments can be obtained that are unadulterated with fats and oils. Pigments in the supernatant can be concentrated and sold as a food ingredient.

Cook et al (1996) developed a zein extraction process that removes zein from enzymatically modified gluten meal. Corn gluten meal is subjected to enzymatic treatment to hydrolyze residual starch. The removal of starch improves the subsequent removal of off-flavors and colors. The method then treats the enzymatically treated corn gluten meal with a mild alkaline buffer to facilitate subsequent removal of fatty acids and oils. Pigments in the corn gluten meal are removed by extracting with absolute ethanol. Because fats and oils had been removed previously, the by-products of this depigmentation step could be further purified and sold as a food grade colorant. Zein is finally removed from the treated corn gluten meal using a standard aqueous alcohol extraction. The resulting zein is a white, odorless and de-flavored material.

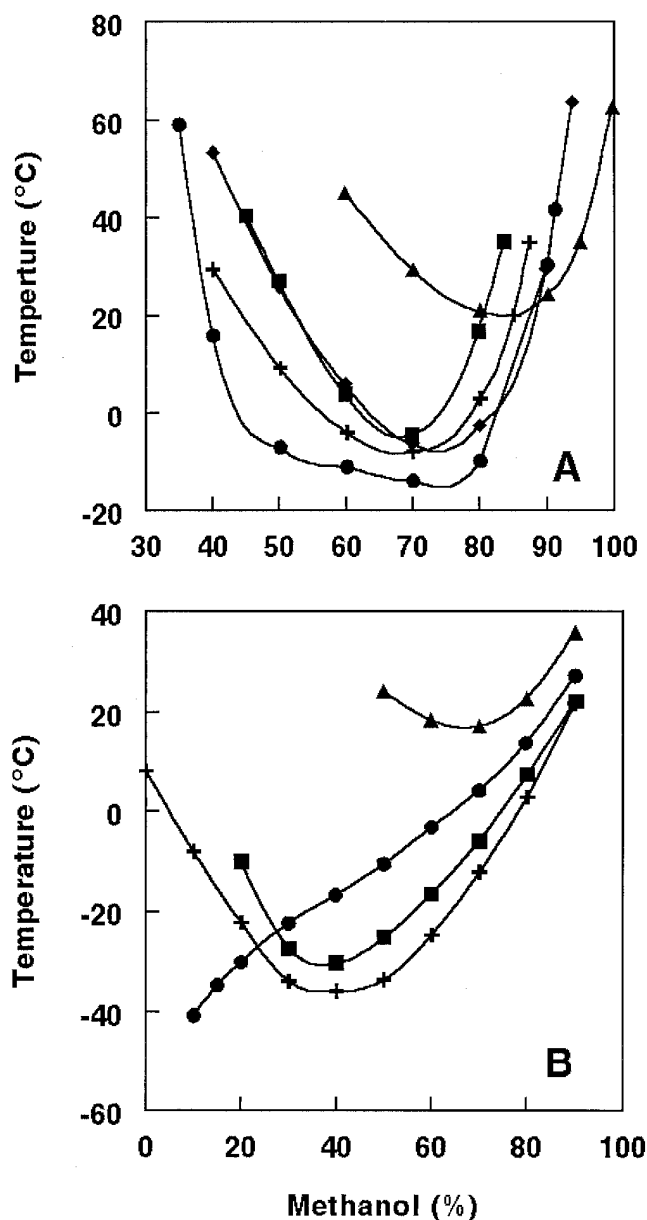


Fig. 2. Cloud point temperature curves for binary solvents and commercial zein (SO₂ treated). A, Mixture of water and solvents (+, isopropanol; ●, *n*-propanol; ▲, methanol; ■, acetone; ◆, ethanol). B, Mixture of methanol and solvents (+, ethylene glycol; ●, propylene glycol; ▲, acetone; ■, acetylaldehyde (Manley and Evans 1943).

CHARACTERISTICS OF ZEIN

Zein is the alcohol-soluble protein of corn and is classified as a prolamin (Osborne 1924). Prolamin zein and commercial zein are not the same material. Zein is the principle storage protein of corn and constitutes 44–79% of the endosperm protein, depending on the corn variety and separation method used (Larkins 1981; Hoseney 1994; Hamaker et al 1995; Landry et al 2000). In the kernel, zein is located in protein bodies $\approx 1 \mu\text{m}$ in size (Duvick 1961). Biologically, zein is a mixture of proteins varying in molecular size and solubility. These proteins can be separated by differential solubilities and their related structures into four distinct types: α , β , γ , and δ (Coleman and Larkins 1999). α -Zein is by far the most abundant, accounting for $\approx 70\%$ of the total (Thompson and Larkins 1989). The next most abundant zein is γ -zein, contributing $\approx 20\%$ to the total. α -Zein can be extracted using only aqueous alcohol, whereas the other zeins need a reducing agent in the solvent to be extracted. Zein solubilized from whole kernel corn without using a reducing agent will consist of mixtures of aggregates and monomers (Tsai 1980). Zein that is extracted without using reducing agents is known as native zein. α -Zein that is extracted with a reducing agent shows up as two bands with apparent migration rates (M_r) of 19 and 22 kDa on SDS-PAGE (Coleman and Larkins 1999).

Commercial zein is made up of α -zeins (Wilson 1988). The fact that only α -zein is found in commercial zein in large amounts is both beneficial and understandable. The other types of zeins (β , γ , and δ) are thought to contribute to gelling, which is a shortcoming of commercial zein. The old literature divides zein into two classes: α -zein and β -zein (McKinnery 1958, Pomes 1971). α -Zein was soluble in 95% aqueous alcohol or 85% aqueous isopropanol, whereas

β -zein was soluble in 60% aqueous ethanol (Mckinnery 1958). Only α -zein is suitable for commercial use as β -zein is prone to gelation. (Pomes 1971). α -Zein in today's classification scheme contains the two polypeptides: 19 kDa and 22 kDa. The β -zein fraction contains α -zeins and β , γ , and δ -zeins.

α -Zein is the major zein found in commercial zein primarily because of the solvent used and the material from which zein is extracted. Commercial zein is not extracted from whole corn but from corn gluten meal. Corn gluten meal is a coproduct of corn wet-milling. Corn wet-milling uses SO₂ to help soften the kernels and facilitate removal of starch. SO₂ weakens the matrix structure by breaking disulfide cross-links (Hoseney 1986). The SO₂ also reduces the disulfide bonds found in β , γ , and δ -zein. Once reduced, γ -zein is water-soluble (Paulis and Wall 1977) and would be eliminated with the steep water. The extraction solvent used for recovering commercial zein (86% aqueous isopropanol) also decreases the amounts of β , γ , and δ -zeins being solubilized. Esen (1986) showed that β and γ -zein were not soluble in solvents containing 90% isopropanol alcohol.

ZEIN SOLVENTS

Zein is known for its solubility in binary solvents containing a lower aliphatic alcohol and water, such as aqueous ethanol and aqueous isopropanol, and for its insolubility in water alone (Wilson 1987). Indeed, it is zein's solubility in aqueous ethanol and the high yield of proline upon hydrolysis that distinguishes it as a prolamin (Osborne 1908, 1924). Aqueous alcohols are the most common solvents for zein today, probably because of the prolamin classification. Also, zein isolation procedures all use aqueous alcohols because alcohols are easily recovered from the zein (Swallen 1941). However, for commercial purposes, other solvents and solvent combinations may also be important.

Osborne (1897) reported that zein completely dissolves in glycerol at 150°C. He also noted that a zein glycerol solution could be heated to 200°C without undergoing any apparent change. Osborne also reported that zein could be dissolved in glacial acetic acid and phenol. Both solvents leave a clear film of unchanged zein after evaporation. A study to find other primary solvents for zein was conducted by Evans and Manley (1941). In their study, solvents had to make at least a 10% solution to be classified as a primary solvent. Table I lists the primary solvents for zein and their critical cloud points (peptization). [Note: term used by the authors in the original manuscript. First used by Dill to describe the effect of temperature on the turbidity of gliadin and zein solutions.] The cloud point is the temperature at which the solution turns cloudy upon cooling. It is of interest that all of the primary solvents are glycols, glycol-ethers, amino-alcohols, nitro-alcohols acids, amides, and amines. For a single substance to be a good solvent for zein, the molecule needs to have the proper balance between polar and nonpolar groups (Swallen and Danehy 1946). Glycols have considerably greater solvent power than do their corresponding monohydric alcohols (CPSC 1960). Propylene glycol is a good solvent for zein but absolute propanol is not. Adding additional hydroxyl groups seems to lower the solvent power. Propylene glycol can dissolve zein at room temperature, whereas glycerol needs to be heated to 150°C, and polypropylene glycols with a molecular weight >3,000 do not dissolve zein at all (Evans and Manley 1941).

As noted previously, the initial observations of binary solvents for zein were made by Osborne (1891), and Chittenden and Osborne (1892). They noted that zein was freely soluble in aqueous methanol, ethanol, and propanol. In 1927, Dill performed a more extensive study of the solubility of zein in binary solvents. He showed that temperature and the ratio of the solvent mixture had a dramatic affect on the cloud point of zein. Once a suitable alcohol water mixture was found, Dill could not find a limit to zein's solubility in that solvent. Indeed, when zein is soluble in a solvent or mix solvent, the only limitation on the amount that can be dissolved is

the viscosity that can be handled by the mixing equipment (Pomes 1971). Due to the fact that Dill could not find a saturated solution for wheat gliadin (Dill and Alsberg 1925) and zein (Dill 1927), he was uncertain if these were true solutions. He believed these mixtures were more related to colloidal systems. Therefore, Dill used critical peptization to describe the temperature at which the zein solution turned turbid. In colloidal chemistry, peptization is used to describe the point where a sol gels. The literature today uses cloud point to describe the temperature at which a sol turns turbid.

Swallen (1941) stated that zein's solubility was similar to that of other polymers, and that improved solubility could be obtained by adding secondary liquids, which themselves are not solvents. Examples would be the addition of water to alcohols. Besides water, aromatic hydrocarbons improve the solvent power of anhydrous alcohols. Swallen also found that ketone and water mixtures made good binary solvents.

A comprehensive investigation of binary solvents for zein was completed by Manley and Evans (1943). They studied the solubility of zein in a binary solvent system where lower aliphatic alcohols, ketones, or glycols were the primary component and water, aromatic hydrocarbons, chlorinated hydrocarbons, nitroparaffins, aldehydes, or cyclic ethers were the secondary components (Table II). Again, just as in Dill and Swallen, this study showed that the solvating power of these binary solvents depended on the ratio of the two components and the temperature (Fig. 2). Manely and Evans concluded that aqueous *n*-propanol was the most effective solvent due to its low cloud temperature and broad range of mixture ratios. Besides the aqueous alcohols, Manley and Evens found that aqueous solutions of acetone, acetyl-acetone, dioxane, and dioxolane are effective solvents for zein. Zein solutions of acetone and water mixtures are distinguished by very low viscosities. Zein solutions (20%) in 70% aqueous acetone had a viscosity of 20 cp, whereas a 20% zein solution in 70% aqueous ethanol had a viscosity of 83 cp (Manley

TABLE II
Secondary Solvents for Zein^a

Water in combination with one of the following

Acetone
Acetyl acetone
n-Butanol
t-Butanol
s-Butanol
Dioxalane
Dioxane
Ethanol
Isobutanol
Isopropanol
Methanol
n-Propanol

A lower aliphatic alcohol and one of the following

Acetaldehyde
Acetone
Benzene
Butyl lactate
Chloroform
Dichloromethane
Diethylene glycol monoethyl ether
Ethyl lactate
Ethylene dichloride
Ethylene glycol
Ethylene glycol monoethyl ether
Furfural
Methyl ethyl ketone
Methylene chloride
Nitroethane
Nitromethane
Propylene glycol
1,1,2,2-Tetrachloroethane
1,2,3-Trichloroethane
Toluene

^a Data from CPSC (1949) and Manley and Evans (1943).

and Evans 1943). Manley and Evans further found that nonaqueous binary solvents for zein constitute a much larger group than the aqueous mixtures and are considerably different in character. The nonaqueous mixtures were less prone to gel under the influence of time and heat, did not foam as did water-containing mixtures, and were resistant to precipitating agents such as tannins and picric acid. In contrast to the aqueous alcohol mixtures, the mixtures of methanol and aromatic or heterocyclic aldehydes make better zein solvents than do the higher alcohols. The same trend holds for hydrocarbons, chlorinated hydrocarbons, and glycols.

Zein solutions and dispersions gel with time and heat (Evans and Manley 1946). This tendency to gel increases as the concentration of the zein solution increases (Manley and Evans 1943). Swallen (1941) reported that alcoholic zein solutions containing a lower concentration of water gelled at a slower rate. In a series of patents, Collman (1939a,b) stressed that zein coating solutions should contain $\leq 5\%$ water to retard gelling. Swallen (1941) found that addition of acid resins, such as rosin or shellac, reduced the rate of zein gelation. Evans and Manley (1943) found that alcoholic solutions of zein could be stabilized against gelling by adding an aldehyde to the solution. Unfortunately, more than 20% aldehyde was needed to retard gelation, but the addition of aldehyde delayed gelation for as long as several months.

The first use of a ternary solvents to extract zein was by Galeotti and Giampalmo (1908). They observed the solubility of zein in five

ternary mixtures, all of which included ethanol and water. A more extensive study of ternary solvent mixtures for zein was conducted by Evans and Manley (1944) (Table III). They examined aqueous alcohol and aldehyde mixtures as in their previous work (1943), but also examined nonaqueous ternary mixtures. The addition of acet-aldehyde to aqueous alcohol greatly reduces the cloud point temperature of the solvent mixture (Fig. 3); however, large amounts of acetaldehyde are needed for this reduction. Ternary solvent mixtures containing acetone, water, and aldehyde were similar to the aqueous alcohol and aldehyde mixtures, but were superior in their resistance to gelling. As little as 5% aldehyde was needed in the aqueous acetone system to retard gelling. A ternary mixture of ethanol, acetone, and rosin made a good solvent for zein with a cloud point temperature of less than -60°C for some ratios.

Zein solutions can be stabilized against gelation by adding a processing step (Swallen 1940; Evans and Manley 1943, 1946). Zein in aqueous alcohol and aldehyde mixtures could be stabilized against gelling by heating the mixture to $>120^\circ\text{C}$ for 15 min. Unheated samples would gel in a few days, while heated samples could be stabilized for 20 to 70 days. The exact reduction in gelation depended on the ratio of the solvent mixture and the amount of zein dissolved. This method was an advantage over other stabilizing procedures because only 5% aldehyde was needed instead of 20%.

Conditions used to isolate the zein will also affect the resolu-bility of the zein (Fig. 4). Zein from ground corn that was isolated using the traditional Osborne method (no reducing agents or alkali) had to be heated to 40°C to dissolve zein in an 82% (w/w) aqueous methanol solution (Dill 1927). In contrast, zein isolated from corn gluten meal that had been treated with SO_2 during wet-milling was soluble at 20°C in 82% aqueous methanol (Manley and Evans 1943). Zein isolated from corn gluten meal and then treated with alkali was soluble at 7°C in 82% aqueous methanol (CPSC 1960).

TABLE III
Ternary Solvents for Zein^a

Water, a lower aliphatic alcohol, and one of the following	
Acetaldehyde	Dioxane
Acetone	Ethylene glycol monoethyl ether
Acetylacetone	Formaldehyde
Benzene	Methyl acetate
Butyraldehyde	Nitroethane
Diacetone alcohol	Nitromethane
Water and any two of the following	
1,3-Butanediol	Dipropylene glycol
1,4-Butanediol	Ethylene glycol
2,3-Butanediol	Hexylene glycol
Diethylene glycol	Propylene glycol

^a Data from CPSC (1949) and Evans and Manley (1944).

PLASTICIZERS

As with solvents for zein, plasticizers for zein need a polar group and a proper balance between polar and nonpolar groups. A perfect plasticizer, satisfactory for all applications, has yet to be found. Zein plasticizers were classified into seven diverse groups (Table IV) by Hansen (1938). Some of the more effective plasticizers are non-volatile solvents such as triethylene glycol. Substituted aryl sulfon-

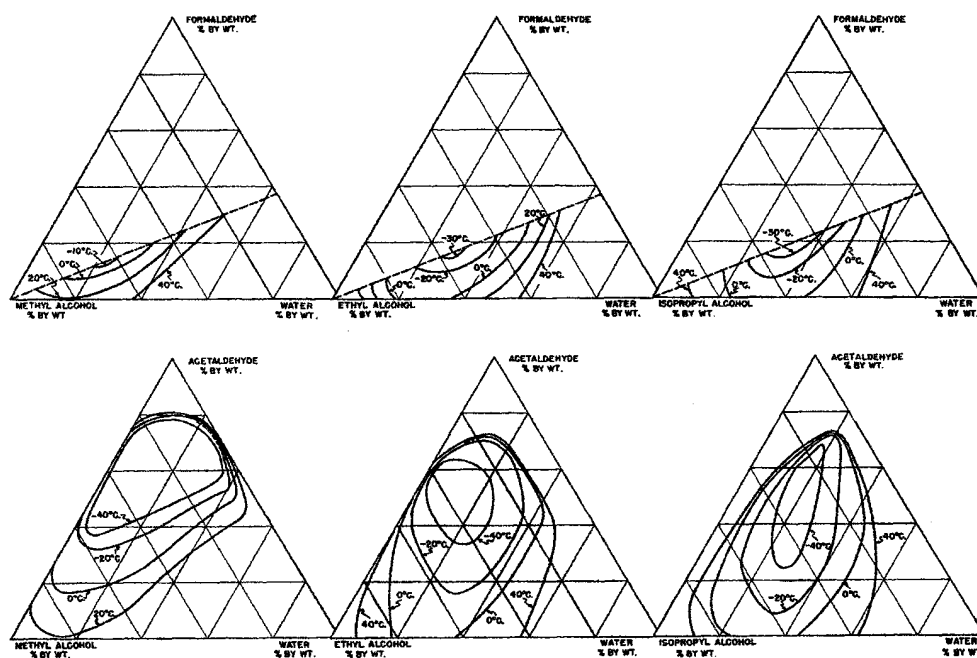


Fig. 3. Ternary graphs of cloud point temperatures for ternary solvents and commercial zein (SO_2 treated) (Evans and Manley 1944).

amides, lactic acid, dibutyl tartrate, oleic acid, and acetanilide are some of the more useful plasticizers for zein (CPSC 1960). Zein also has what the old literature calls secondary plasticizers. These plasticizers have limited effect on zein alone, but when used in combination with other compounds they become effective plasticizers. Although water is generally not added to zein for its plastication effect, water may be zein's most effective plasticizer. Numerous studies (Lawton 1992; Kokini et al 1995; Madeka and Kokini 1996) have reported the great effect water has on zein's glass transition temperature. Like other cereal proteins, zein will gain or lose moisture from the air, depending on the relative humidity, so water must be considered when evaluating plasticizers effects on zein.

USES

Applications for zein were not fully developed until a commercially viable product was realized. However, research into the possible uses of zein were well underway early in the 20th Century. Zein's soft, ductile nature after being precipitated from solvent no doubt lead to it being tried as a plastic, either alone or in mixtures. One of the first to promote zein as a plastic was Goldsmith (1909a,b). He proposed that zein could be mixed with compounds that he described as converting agents and then heated. His converting agents were, in all likelihood, plasticizers. Once heated, the zein softened and other materials such as other resins or fillers could be added. The soft mixture could then be shaped into finished articles. Later,

Goldsmith (1910, 1912) showed that adding formaldehyde to a mixture of zein and converting agents produced a tougher and more stable composite. Desvaux and Allaire (1909) showed that zein could replace part of the nitrocellulose or camphor used in the production of celluloid. The new plastic was less flammable and expensive while retaining the properties of celluloid. Later, other patents were granted using zein in the production of plastic or celluloid-like materials (Satow 1917a; Swett 1921). Zein was also mentioned for uses in fabric stiffeners (Swett 1920), artificial leather (Satow 1917b), lacquer (Satow 1917c), filament, and film (Ostenberg 1919) during this same period. These early patents did not establish much use for zein, but they did set the stage for the research to come in the next two decades by showing what could be produced from zein. These patents also demonstrated that chemical and physical methods affected zein's properties .

The 1930s and 40s saw an explosion in the amount of research done on zein. This was probably spurred on by the chemurgy movement of the time. The fact that a commercial zein plant began operation in 1938 also probably helped fuel research on zein.

COATINGS FROM ZEIN

The first major commercial use of zein was for coatings. When shellac was in short supply during World War II, zein was in great demand as a replacement for shellac in lacquers, varnishes, and coatings (Anon 1944). Of zein total production in 1943, more than half was used as a replacement for shellac (Anon 1944). Indeed, because of zein's importance as a coating during World War II, its supply and use were regulated by the War Production Board (Anon 1943). Nearly 2 million pounds of zein were sold for floor covering in 1943 (Reiners et al 1973). It was common for zein to be used as a floor coating for steamship engine rooms because of its good durability and grease resistance (Morgan 1943). Most floor covering formulations contained other resins in addition to zein because of its water sensitivity. The Chemical Formulary (Bennett 1945) called for zein to be mixed with two-thirds rosin to make an effective shellac substitute. Usually, the recommended ratio of zein to rosin was 1:1 to 1:3 parts by weight (Croston and Evans 1950). Zein's water resistance could be greatly increased with the addition of formaldehyde and heat treatment when used alone (Meigs 1943). When compared with shellac floor coatings, zein-resin coatings had

TABLE IV
Plasticizers for Zein^a

Primary Plasticizers	Secondary Plasticizers ^b
Glycols	Glycerol
Triethylene glycol	Sorbitol
Propylene glycol	Diphenylamine
Ethylene glycol	Dibutyl phthalate
Polyethylene glycol	Dibutyl sebacate
Polypropylene glycol	Triphenyl phosphate
Sulfonamides	
Benzene sulfonamide	
N-Ethyl benzene sulfonamide	
p-Toluene sulfonamide	
N-Ethyl p-toluene sulfonamide	
Fatty acids	
Oleic acid	
Palmitic acid	
Myristic acid	
Stearic acid	
Amides	
Acetamide	
Acetanilide	
Urea	
Amines	
Triethanolamine	
Diethanolamine	
Glyceryl esters	
Glyceryl monooleate	
Glyceryl monopalmitate	
Glyceryl monostearate	
Glycol esters	
Glycol monooleate	
Glycol monopalmitate	
Glycol monostearate	
Esters	
Dibutyl tartrate	
Monobutyl phthalate	
Monomethyl azelate	
Monomethyl sebacate	
Miscellaneous	
Ethylene glycol monophenyl ether	
Tricresyl phosphate	
Tall oil	

^a Hansen (1938), CPSC (1949).

^b Secondary plasticizers are poor plasticizers for zein when used alone, but are effective in mixed plasticizer systems.

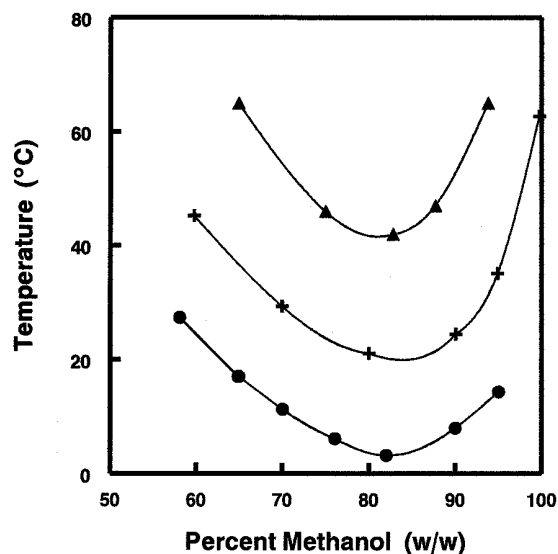


Fig. 4. Cloud point temperature curves for zein extracted from different sources and by different methods: laboratory prepared zein (no reducing agents or alkali) (▲), (Dill 1927); commercial zein extracted from corn gluten meal (SO₂ treated) (✚) (Manley and Evans 1943); commercial zein extracted from corn gluten meal and treated with alkali (●) (CPSC 1960).

improved wear resistance and retained higher gloss (Maher and Struthers 1955). The greater the percentage of zein used in the coating, the greater the abrasion resistance. In fact, the durability of the coatings described by Maher and Struthers failed to pass the test for removability, as set in Federal specifications.

Coatings were also produced that contained both zein and shellac (Weber 1944). These coatings were an improvement over coatings using either zein or shellac alone. Shellac improved zein by making it more water-resistant, and zein improved shellac by making it tougher and more scuff resistant (Maher and Struthers 1955). During World War II, sizable amounts of zein were used as a replacement for shellac in wood varnishes. Zein was most often used with other resins in varnishes with zein to resin ratios of 45:55. However, zein's tendency to gel in solution made it less than ideal. Lowering the pH of the varnish with hydrochloric acid solved the problem (Anon 1968). Alkali-treated zein, and later deaminated zein, produced a solution-stable zein. Despite zein's success as a shellac replacement during World War II, consumers had an overwhelming preference for shellac after the war (Anon 1951) despite the fact that zein cost substantially less than shellac (\$0.52/lb for shellac and \$0.30/lb for zein). The unfavorable experiences of gelation using zein made the trade wary of using even the more stable zein (Anon 1968).

Grease and solvent resistance is one of zein's most important characteristics. Because of this, zein found use as protective coatings in packaging resin. Coatings were put onto carton stock for doughnuts, crackers, pies, and cookies. The coatings were a mixture of zein and rosin along with fatty acid plasticizers (Anon 1968). Zein was also used as a protective coating on paperboard salt containers to prevent the penetration of wax that was added for moisture resistance (Anon 1951). Zein coatings of fiberboard containers were of interest because of their good grease resistance, printability, and dispersing effect on waxes. For a time, zein coatings were able to compete with laminated glassine, but their poor aging properties (embrittlement after 30–90 days of storage) prevented wide use (Anon 1968). Other disadvantages of using zein for these types of coatings included inferior water resistance, tendency toward putrefaction and insect infestation (Anon 1951). Paper coated with zein was used during World War II to wrap airplane and machine parts

for shipment (Morgan 1943). These coated papers were grease resistant and prevented the escape of oil and grease into packaging. To protect labels on bottles and cans, a combination of zein and other resins was used in overprint varnishes (Clark and Gralow 1949). Because alcohol was used as the solvent for the overprint varnish, drying took as little as 15 sec (Clark and Gralow 1949). In 1949, zein varnishes represented the largest single outlet for zein, with about 2 million pounds per year used for coatings (Anon 1951).

Zein was once used in sizable quantities in the paper industry. The main uses of zein were for pigment coatings (Stewart 1942; Casey 1961a) and protective coatings (Davis et al 1953; Casey 1961b). In pigment coatings, zein is used as an adhesive to bond the pigment to the base paper. Pigment coatings are usually used in the manufacture of papers for magazine publications. Stewart found that zein could effectively replace casein in pigment coatings containing clay (Stewart 1942). The best dispersing agents for zein in aqueous systems are sodium resinate, sulfonated castor oil, and sulfonated tall oil (Casey 1961a). If alkali is used to dissolve zein, the zein is more water resistant if ammonia is used (Keim 1949). Speed and cost were the advantages of using zein. Zein dispersed faster in water than did casein. Zein not only cost less than casein, but also required less zein to effectively bind the clay. However, zein-coated paper performance was unsatisfactory in the waxy pick test compared with casein-coated paper, and dispersing agents used in the zein coating were believed to harm printing plates (Anon 1968).

James (1942) also found that pigment coatings made with zein were not sufficiently water resistant for lithographic paper so zein was not used often in pigment coatings. Zein was used in glossy protective coatings for catalogues, children's books, and "pocket" books (Anon 1951). This application was more of a varnish than a traditional paper coating. The coatings had a slightly amber color but were satisfactory for use in decorative coatings and in food packaging where grease resistance was desired (Davis et al 1953). Glycols had to be used because of aging problems with fatty acid plasticizers. Although the resulting coatings were satisfactory for grease resistance, water resistance was extremely poor, and coated paper would stick together (blocking) during storage. (Anon 1968). The estimated market for this type of zein coating did not exceed

TABLE V
Casting Conditions for Zein Film

Reference	Solvent	Solution (w/v)	Plasticizer	Other	CastingMedium	Drying Conditions
Hansen 1937	90% aqueous ethanol	20% zein	Dibutyl tartrate	Monoethanolamne formaldehyde	Metal andglass	60°C
Hansen 1938	70% aqueous ethanol	12% zein	Monoglycerides	Glycine ethyl esterand glyoxal	Mercury	60°C
Anon 1943	90% aqueous ethanol	20% zein	Fatty acid dimers	Formaldehyde	Polished chromium	10–20 min at 120°C
Gennadios et al 1993a	95% aqueous ethanol	16.6% zein	Glycerol	NA	Glass	15 hr at 35°C
Wei and Baianu 1999	90% aqueous ethanol	30.7% zein 25% (w/w)	Glycerol, PEG, and lactic acid	NA	Teflon	Overnight at room temperature
Yamada et al 1995	70% aqueous acetone	10% zein	NA	1,2-epoxy-2-chloropropane	Plastic plate	30°C
Park et al 1994b	95% aqueous ethanol	16.6% zein	Glycerol and PEG	NA	Glass	55°C
Takahashi et al 1996	70% aqueous acetone	10% zein	NA	NA	Plastic sheet	6 hr at 25°C, 70% rh
Aydt et al 1991	aqueous ethanol	NA	Glycerol	NA	Aluminum	24 hr at 23°C
Paris and Coffin 1977	80% aqueous ethanol & 70% aqueous acetone	10% zein	Polypropylene glycol	Gluteraldehyde	Polystyrene orteflon	Vacuum oven at 40–60°C
Weller et al 1998	95% aqueous ethanol	17% zein(w/w)	Glycerol and PEG	NA	Glass	18 hr at room temp 24 hr at 25°C C, 50% rh
Buffo et al 1997	95% aqueous ethanol	24% zein	Glycerol and PEG	NA	Glass	48 hr at 25°C, 50% rh
Herald et al 1996	95% aqueous ethanol	10% zein	Lactic acid, triethylene glycol, and sorbitol	NA	Polyethylene	Overnight room condition
Tillekeratne and Easteal 2000	95% aqueous ethanol	20% zein	PEG400 and PEG1000	NA	Poly(methyl methacrylate)	Room condition 24 hr

250,000 lb annually (Anon 1951). Zein use for grease proofing vanished by 1954 (Anon 1968).

More recently, zein-coated paper has been considered as a replacement for polyolefin coated materials currently used in the food industry (Trezza and Vergano 1994; Trezza et al 1998). They found that even though zein-coated paper was not as effective a barrier to hot beef fat as free films, it was equal to polyolefin laminates used for quick-service packaging. Zein-coated paper showed adequate grease resistance in quick service sandwich packaging for 1–2 hr. Similar results were found for the grease resistance of zein-coated paper (Parris et al 1998). The water vapor transmission rates of zein-coated paper could be significantly lowered by incorporating paraffin wax into the coating.

In the mid-20th Century, most pharmaceutical tablets were coated with sugar (Winters and Deardorff 1958). Sugar coating the tablets was laborious and time-consuming. Because of zein's film-forming ability and microbial resistance, it was a natural choice for tablet coating. Coating tablets with zein was rapid, taking less than 30 min (Winters and Deardorff 1958). Zein-coated tablets adequately resisted heat, abrasion, and humidity. The coatings also concealed the taste and odors of the original tablets without interfering with solubility. Tablets completely coated with zein showed hardness increases of >100% (Stern 1976). The added strength zein gives to tablets is equivalent to those of other conventional pharmaceutical coatings (Stern 1976). Zein films provide an excellent gas barrier against oxygen at low water contents (Beck et al 1996). When compared with ethyl cellulose (DS ≈ 2.5), dry zein has an oxygen permeability coefficient of ≈20% less. Because of zein's sensitivity to water, zein coatings release active ingredients at high relative humidities and are not capable of slow release (Beck et al 1996).

Zein has been used as a food coating for the last 40 to 50 years. One of the first reports of using zein in food involved its use as a protective coating in fortified rice (Mickus 1955). Milled white rice was wetted with thiamin, niacin, and iron in an acidic solution and dried. Then an alcoholic solution of zein and stearic acid was applied. Zein was a particularly good choice in this application because rice is usually rinsed in cold water and the rice cannot lose >15% of its added vitamins and minerals. Cosler (1957; 1958) was the first to report on zein's ability to protect nuts against rancidity. Pecan pieces coated with as little as 1% zein (w/w) could be stored for nine months without becoming soggy, stale, or rancid. Similar results

were obtained with walnuts, almonds, peanuts, and with nuts incorporated into chocolate bars. The zein coatings contained acetylated monoglycerides and antioxidants. They were equal or superior to gloss and moisture vapor resistance of shellac used in confectioners glaze for hard gums, sugar-coated confections, and hard candies. (Cosler 1959) and had the added advantage of being edible and nutritious.

Cosler (1957), in his patent, stressed the necessity of using acetylated monoglycerides as plasticizers in food coatings. However, other plasticizers have been used in these coatings with considerable success (CPSC 1960; Alikonis 1962). Alikonis et al (1962) reported that coating raw nuts with zein before roasting reduced the tendency of the skins to flake off. Because of the importance of the pericarp and water plays in the popping of popcorn (Hoseney et al 1983), zein was tried as a coating to improve popping volume (Wu and Schwartzberg 1992). Zein did slightly decrease the rate of moisture loss during heating, and increased the expansion bulk volume 15%, but only when the popper was not preheated. The zein coating was not strong enough to mend broken and damaged pericarp, so it did not improve the expansion bulk volume and unpopped ratio for kernels with damaged pericarp. Tomatoes have been coated with zein to increase shelf life (Park et al 1994a). Zein coatings on tomatoes at the pink stage of maturity could delay color change, maintain firmness, and reduce weight loss during storage. Shelf life of the coated tomatoes was extended by six days. Zein coatings have been tried as a protective coating for eggs, enhancing the mechanical strength of eggshells (Wong et al 1996). Eggs coated with zein also exhibited low moisture loss and maintained an "A" grade through 21 days of storage at room temperature (Wong et al 1996).

Free-standing films are required for the evaluation of zein's barrier and mechanical properties, and are required for mulch and bags. Researchers have been studying and producing free-standing zein films since the mid-1930s. Even though solvent type, plasticizer content, type substrate used for casting, and drying conditions vary among studies, the general film-forming procedure is always the same. Zein is dissolved in an appropriate solvent, plasticizers and other agents (such as cross-linkers or anti-blushing) are added to the solution, the solution is cast onto a nonstick substrate, the solvent is allowed to evaporate, and the free-standing film is peeled off the nonstick substrate. Table V reviews the various zein films described in the literature, showing solvents used, plasticizers and other agents added to the films, and their drying conditions. For

TABLE VI
Tensile Properties of Zein Films

Reference	Plasticizer ^a	Conditioning	Crosshead Speed (mm/min)	Tensile Strength (MPa)	% Elongation
Anon 1943b	50–90% fatty acid dimers	Not reported	nr ^d	17–23	27–136
Aydt et al 1991	glycerol	72 hr at 26°C, 50% rh	30	0.4	too brittle to measure
Gennadios et al 1993a	42% glycerol	2 days at 25°C, 50% rh	500	13.2	nr
Park et al 1994b	17–39% total plasticizer ^b mixtures of GYL and PEG	48 hr at 25°C, 50% rh	500	8.4–35.5	3–94
Herald et al 1996	≈42% total plasticizer, 16.6% lactic acid, 16.6% triethylene glycol, 8.3% sorbitol	2 hr at 23°C, 55% rh	25	3.9	213.3
Buffo et al 1997	≈46% total plasticizer 24% GYL, 22% PEG	48 hr at 25°C, 50% rh	nr	2.6	84.4
Parris and Coffin 1997	0 and 30% total plasticizer ^c mixture of GYL and PEG	overnight at 52% rh	5	4.9–14.4	1.5–117.8
Weller et al 1998	≈52% total plasticizer 27% GLY and 25% PEG	2 days at 25°C, 50% rh	150	1.05	130.2
Santosa and Padua 1999	50–100% oleic acid or linoleic acid	48 hr at 25°C, 50% rh	25.4	1.6–9.4	2.8–165
Tillekeratne and Eastal 2000	≈30% PEG 400 or ≈30% PEG 1000	48 hr at 22°C, 50% rh	nr	≈16 for 400 ≈23 for 1,000	≈1.5 for 400 PEG ≈2 for 1,000 PEG

^a % Plasticizer based on zein (w/w).

^b % Plasticizer based on mL/g of zein.

^c How % plasticizer was calculated was not reported.

^d Not reported.

zein to be used in mulch or bags, alternatives to casting are needed for film production. Solution casting to produce films is only suitable for laboratory testing.

Recently, researchers have begun to prepare zein films or sheets by a molding process (Lai and Padua 1997; Lai et al 1997). Zein sheets are prepared by mixing zein with plasticizers and then kneading the mixture. Depending on the plasticizer content, heat may be necessary to soften the mixture. In the final step, the softened zein mixture is either compression molded or rolled out into sheets. To date, no research has been published where zein films have been produced through extrusion technology.

The tensile properties of zein reported in the literature are almost as varied as the authors reporting them. Literature values for tensile strength of zein cast films range from a low of 1.05 MPa (Weller et al 1998) to a high of 13.3 MPa (Genadios et al 1993a) for comparably plasticized films. Film elongation ranges from 2.6% (Parris and Coffin 1997) to 213% (Herald 1996) for comparably plasticized films. Table VI summarizes tensile properties described in the literature. Lee et al (1998) found that they could increase the tensile strength of a 50% plasticized zein film to 14 MPa by the addition of silica. The tensile strength could be further increased to 43 MPa by refluxing zein with tetraethoxy silane.

Zein is a polymer and is going to behave as a conventional polymer. Zein films will be affected by the type and amount of plasticizer they contain. This means that as the percentage of a plasticizer increases, tensile strength will decrease and percent elongation will increase (Bolker 1974). This was demonstrated for zein in 1943 (Anon 1943b) and later confirmed by Park and coworkers (1994c) and numerous others (Table VI). Padua and coworkers (Lai and Padua 1997; Lai et al 1997; Santosa and Padua 1999) showed that the tensile strength of zein sheet plasticized with fatty acids decreased as fatty acid content increased. The type of plasticizer also affects the tensile properties of zein films. Park and coworkers (1994) showed that polyethylene glycol was a more effective plasticizer for zein than glycerol; this was later corroborated by Parris and Coffin (1997). In the zein literature distributed by Corn Products Company (the original manufacture of zein), polyethylene glycols were called primary plasticizers while glycerol was called a secondary plasticizer (CPSC 1950). For glycerol to be an effective plasticizer for zein, it needs to be used in conjunction with other plasticizers. Parris and Coffin (1997) demonstrated that a 1:1 mixture of polypropylene glycol and glycerol was a more effective plasticizer than either alone.

Zein is hygroscopic and will lose water to or gain water from its surrounding environment, depending on the environment's relative humidity. Zein can absorb > 20% of its dry weight when stored at a water activity <0.8 (Gennadios and Weller 1994). Water is a very effective plasticizer for zein (Lawton 1992; Beck et al 1996; Kokini 1996). This means that zein films stored at different relative humidities will have different tensile properties. Genndaios and coworkers

(1993a) demonstrated that the tensile strength of zein films decreased linearly as relative humidity increased. One of the inadequacies of all the reported literature about tensile properties of zein is that the plasticizing effect of water is not addressed. Water needs to be accounted for when assessing the tensile properties of zein films. Another aspect of producing zein films with plasticizers is that some zein plasticizers themselves are hygroscopic, such as triethylene glycol, glycerol, polyethylene glycol, and levulinic acid. Water absorbed by the plasticizer will be available to plasticize the zein.

Two other issues also make comparing different zein films difficult. First, zein films are cast from solutions of differing concentrations (Table V). This variable will result in films of different thicknesses. Unless thickness is accounted for, it will affect the physical properties of the film. In theory, accounting for the size of the sample makes the results independent of size, but in practice, a consistent standard sample size is necessary for reproducible results. Second, the crosshead speeds (strain rates) used in tensile testing zein films varied from 5 to 500 mm/min (Table VI). Crosshead speeds must be used that allow the polymers to be tested in the same time scale. The speed at which the films are tested are known to influence tensile behavior dramatically (Flanagan 1993). Extensible material tested at slow speeds has generally lower tensile strengths and moduli and greater elongation than the same material tested at faster speeds. Specimens always need to be conditioned before testing. This involves keeping the specimens under the specified test conditions for a specific amount of time before testing so they can reach equilibrium with the test environment. The standard method for testing thin plastic sheeting (ASTM D 882-97) calls for conditioning time not less than 40 hr.

Barrier properties are also important to the end uses of zein, whether for stand-alone films such as bags and packaging or for coatings of pharmaceuticals and food. Zein films have low permeabilities to oxygen and carbon dioxide. Low oxygen permeabilities are particularly important for coating and packaging applications. Published oxygen permeabilities are 1.8–34.8 amol/m²·s·Pa (Aydt et al 1991; Gennadios et al 1993b; Park and Chinnan 1995) [1 amol = 10⁻¹⁸ mol]. Oxygen permeability values are lower than those reported for polyethylene and poly(vinyl chloride). Aydt et al (1991) reported an average carbon dioxide permeability through zein films of 216 amol/m²·s·Pa. Park and Chinnan (1995) reported carbon dioxide permeability through zein films of ≈267 amol/m²·s·Pa. A possible reason for the large difference in carbon dioxide permeability between the two reports may be the level of plasticizer. Park and Chinnan (1995) showed that as the plasticizer level increased in films, oxygen permeability increased.

A shortcoming in the reported gas barrier properties of zein is that the barrier properties were measured on dry films at 0% rh. Plasticizer levels affect oxygen barrier properties of zein and wheat

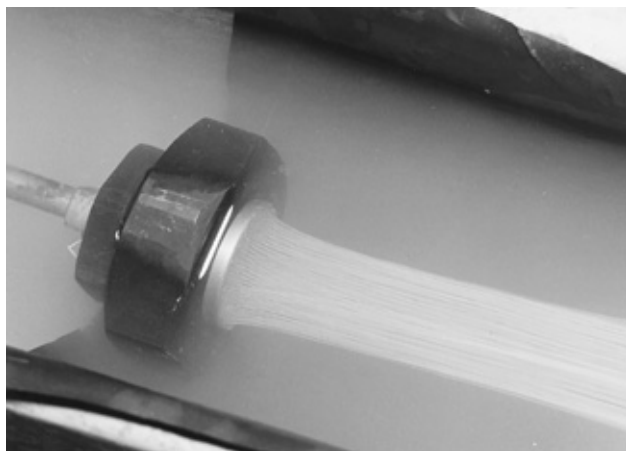


Fig. 5. Spinneret used for zein fiber formation.

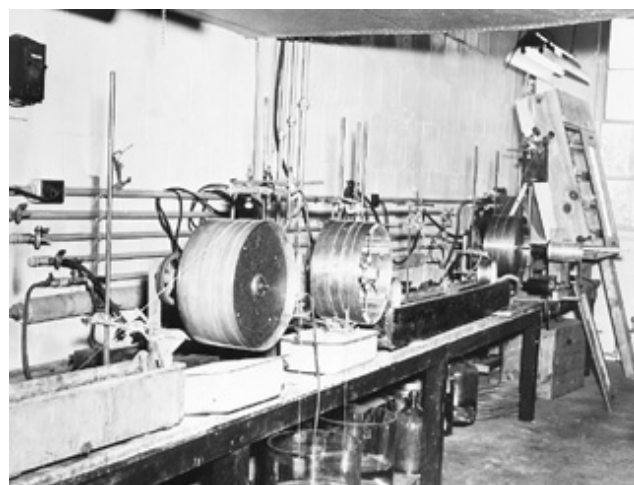


Fig. 6. Laboratory equipment for making zein fiber (Evans et al 1950).

gluten (Park et al 1994b) and permeation of synthetic films (deV Naylor 1989). Because water is a very effective plasticizer for zein, it would be expected to have an effect on zein's barrier properties. For other natural films, gas permeabilities increase when moisture level or plasticizers level increases (Arvanitoyannis et al 1996). Water vapor permeability of zein films is high compared with those of plastics (Park and Chinnan 1995). Published rates are 1.8–9.07 g/mm⁻¹/m²/hr⁻¹/k⁻¹Pa (Gennadios et al 1993b; Herald et al 1996; Buffo et al 1997; Weller et al 1998). The permeability of zein to water increases as relative humidity increases (Tillekerate and Eastale 2000). This is probably due to the plasticizing effect of water and absorbed water swelling the film. Because water permeability of zein is so poor, a concerted effort has been made to protect zein films from water and water vapor. Veatch (1938) found that adding ≈4% paraffin wax to zein films can substantially increase water resistance. Laminating zein films with wax reduced the water vapor permeability to 0.115–9.07 g/mm⁻¹/m²/hr⁻¹/k⁻¹Pa (Weller et al 1998). Similar coatings reduced the water vapor permeability of wheat gluten films (Gontard et al 1995), methyl cellulose films (Greener and Fennema 1989; Martin-Polo et al 1992), and pectinate films (Schultz et al 1949). Santosa and Padua (1999) demonstrated that increased amounts of oleic acid in zein films retards water absorption. Decreasing water absorption in zein films would be expected to have a favorable effect on water vapor permeability.

FIBERS

The first use of zein for the production of fibers (filament) was patented by Ostenberg in 1919. Ostenberg showed that filaments (what he called artificial silk) could be made from a solution of dissolved prolamins of corn using any of the known mechanical processes. Swallen (1939) patented a more commercial operation for the production of zein fibers which described the process in greater detail. The Swallen process called for a zein solution to be extruded either into air (dry spinning), where the coagulation would take place due to evaporation of solvent, or that the zein solution be extruded into water or some other coagulation medium (wet spinning). Swallen described two types of zein solutions used to produce fibers. The first solution called for zein to be dissolved in aqueous ethanol or similar organic solvent mixtures (mixtures of water and methanol, diethylene glycol, ethylene glycol monoethyl ether, or diacetone). This solution generally contained 2–5% by weight of free formaldehyde, although Swallen claimed that ≤50% by weight could be used. Swallen also recommended that the solution contain ≤20% of a zein plasticizer to give the zein fibers flexibility and resilience. This solution could be extruded either into air or a liquid coagulating bath. An alternative method calls for zein to be dispersed into aqueous solutions of formaldehyde without organic solvents. This mixture was then extruded into a coagulating medium. If zein fibers were produced from solutions containing no formaldehyde, then the coagulating medium needed to contain formaldehyde. Once the fibers were produced, the method called for them to be baked at 60–90°C for 8 to 10 hr to complete the zein formaldehyde reaction. The fibers had excellent water resistance after the final cure and satisfactory wet strength. These fibers were generally superior to the artificial fibers of the day.

Other patents for the production of zein fibers quickly followed. Meigs (1940) showed that stretching the fiber before drying improved the tensile strength and flexibility of the fiber. Graves (1942) described extruding zein with linear polyamide to increase the tensile strength of the fiber. Zein fibers were produced by extruding a solution containing zein, urea, and formaldehyde in aqueous methanol (Sitzler 1943). Because extruding zein filaments directly into a coagulating bath of formaldehyde caused the outer surface of the filament to become tacky, Stuken (1944) proposed adding inorganic matter to the bath to prevent the tackiness. Biehn and Cline (1947) found that the filaments could be partially hardened by immersing them in a mixture of formaldehyde, aluminum sulfate, and sodium chloride.

The textile industry at that time was very interested in protein fibers that would resemble wool. The pre-World War II domestic production of wool was not great enough to meet demand (Harold 1940). There were numerous publications in the trade magazines of the day describing the production of zein and other protein fibers and their properties (Anon 1939b; Harold 1940; Von Bergen and Krauss 1940; Worden 1941).

At about this same time, basic research addressing the production of fibers from zein was started by Croston, Evans, and Smith (USDA-Agricultural Research Service scientists), who were credited with most of the scientific contributions of zein fibers production (terHorst 1949). Croston et al (1945) described a wet-spinning method for production of zein fibers which called for an alkaline, aqueous, dispersion of zein to be extruded through spinnerettes. The dispersions contained 13–16% zein and 0.5–1% formaldehyde with a dispersion between pH 11.3 and 13.7. For satisfactory spinnerette operation, a highly viscous dispersion was needed. The dispersion needed to be at the incipient gel stage, which the authors described as the point where the protein mass slowly flows together when cut. To get to this stage, the dispersion needed to age for seven days, or an agent such as urea was added to accelerate the aging process. Once the desired viscosity of the dispersion was obtained, it was extruded through the spinnerettes (Fig. 5). The spinnerettes contained 100 to 300 holes with diameters of 0.003–

TABLE VII
Physical Properties of Vicara and Wool^a

Characteristics	Vicara	Wool
Price of staple, lb	\$1.00	\$1.77 ^b
Specific gravity	1.25	1.28–1.33
Dry tensile strength	1.1–1.2 g/denier	1.0–1.7 g/denier
Wet tensile strength	0.53–0.57 g/denier	0.9 g/denier
Strength	17,000–20,000 PSI	20,000–29,000 PSI
Dry elongation	25–40%	25–35%
Wet elongation	30–50%	50%
Elastic recovery at 4%	99%	99%
Stiffness	2.8 g/denier	3.9 g/denier
Moisture at 65% rh, 23°C	10%	9.6–12.2%
Water absorption at 90% rh	25%	21.9%
Weakening point	178°C	decomposes at ≈130°C
Softening point	243–246°C	na

^a Data compiled from Karh (1950), Anon (1952, 1953), Mauersberger (1954).

^b Price of wool March 7, 1952 (Anon 1952).

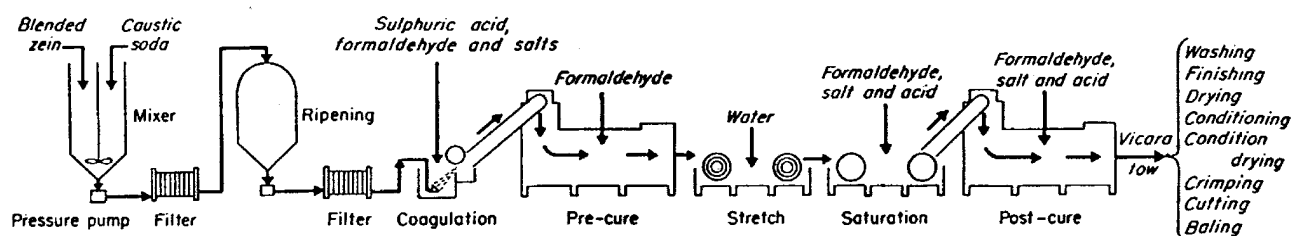


Fig. 7. Commercial flow process for zein fiber production (Anon 1952).

0.006 in. The coagulating bath composition usually consisted of 4.7% sulfuric acid, 3.1% acetic acid, and 4.4% zinc sulfate. After leaving the coagulating bath, the filaments are pulled through a mild formaldehyde (1.3%) precuring bath. The precuring treatment was necessary for the filaments to be effectively stretched. Filaments were stretched in a water tank at 45–60°C. The filaments were generally stretched 200–350% but depended on the formulation of the zein dispersion, the amount of precure, and the temperature of the stretching bath. From the stretching bath, the filament went into the dryer. The filament was dried at 65°C for 5 min. Figure 6 shows Evans and Croston's original fiber-making equipment.

Croston et al (1945) found that the extent of precure influenced fiber elongation and strength. Fibers that precured for longer times had greater strength but less elongation. Fibers that precured in more concentrated formaldehyde also had lower elongations and greater strength. Fibers that were not precured broke easily and could be stretched indefinitely without showing an acceptable increase in strength. The wet strength of the zein fibers was $\approx 3\times$ lower than the strength of the dry fiber. The wet strength could be improved with longer precure times. The strength of the zein fibers was much better than those of the other regenerated protein and synthetic fibers of the day, being comparable to wool fiber. Zein fibers prepared by this method would shrink back to their prestretched length when immersed in hot water. The shrinkage could be greatly reduced if the fiber was treated with a strong formaldehyde solution (postcure).

Acetylation of the zein fibers increased the water resistance and produced a softer fiber (Evans et al 1947). The acetylation was accomplished with acetic acid and a catalyst (sodium acetate or sulfuric acid) after the precure and stretching. Acetylation was not a remedy for shrinkage. In order for zein fiber not to shrink back to the prestretched length, the fiber must be postcured.

Later, Evans and Croston (1949) found that for rapid curing of the zein fiber, a two-stage curing procedure was needed. The first stage (precure) consisted of a mild cure to introduce $\approx 0.75\%$ formaldehyde into the fiber. The second stage (postcure) occurred after fiber stretching. The postcure introduced and additional 3% formaldehyde into the stretched zein fiber, which stabilized its length. They found that only under acid conditions (pH 0–4), did any curing take place. Postcuring at 60°C with ammonium salts reduced curing times to 15–30 min. Zein fibers cured under these conditions were stable to boiling in mild alkali, and when cured under highly acidic conditions were stable to both acid and alkaline boiling. Greater stabilization of the zein could be achieved if the curing was done

under anhydrous conditions (Croston 1950). The curing mixture consisted of an organic solvent (that does not swell excessively or dissolve the fiber), aldehyde, and a strong acid. The cure was rapid when the temperature was raised to 100°C. Curing at that temperature was complete in 15 min. Zein fibers were quite resistant to shrinkage ($\approx 2\text{--}3\%$) and had unusual strength after boiling in acid dye baths. Evans, Croston and coworkers were later granted patents on the procedures outlined above (Croston and Evans 1949; Croston et al 1950; Evans et al 1950).

Zein fibers were produced by the Virginia-Carolina Chemical Corporation (V-C) from 1948 until 1957 (Moncrieff 1963). Pilot-plant operations began in 1948 and were followed by commercial production of zein fiber at Taftville, CT, in late 1949 (Anon 1953). Zein fibers were commercialized under the trade names Vicara, Zycon, and Wavecrape (Anon 1951b; Anon 1952; Koch 1954). Vicara was a textile fiber, Zycon was a fiber for the hat industry, and Wavecrape was a fiber used by hairdressers. Vicara fiber was produced in the greatest quantity. The commercial process for Vicara production was similar to the process outlined by Evans and Croston (Anon 1952). This is not surprising because research on Vicara was done in cooperation with the Northern Regional Research Laboratory, where Evans and Croston worked (Anon 1953). The commercial process differed from Evans and Croston's method in that formaldehyde was used in the coagulation bath and the postcure. Using two curing baths containing formaldehyde ensured full saturation of the fiber with formaldehyde. A flow chart of the process is shown in Fig. 7. Vicara was produced by forcing the spinning solution through spinnerettes (each with $\approx 5,000$ holes) into the coagulation bath. The filaments were lifted from the bath as a composite tow. The tow could contain as many as 270,000 individual filaments. The tow then proceeded to curing and stretching. After the postcure, the tow moved to the washers and dryers. It was given as many as 60 consecutive washings and squeezings before being cut and baled. Drying took place in steam-heated ovens. After the initial drying, the fibers were humidified to a constant moisture content. The total process for making Vicara was lengthy and required rigid controls. Zein traveled 7–14 miles from the time it entered the plant until it left as staple or tow (terHorst 1949; Anon 1953). The staple fiber was shipped in bales of 300–1,000 lb, and continuous tow was shipped in cartons of 125 lb each.

Some properties of Vicara were similar to those of wool (Table VII). Under the microscope, Vicara appears as a cylindrical, translucent rod with a nearly circular cross-section as well as a smooth surface and uniform shape (Fig. 8) (Anon 1953; Wormell 1954). Vicara was resistant to acids and alkalis and had a good affinity for most dyes. Because of Vicara's resistance to most chemicals and its

TABLE VIII
Vicara Fibers^a

Denier	Number of Filaments	Total Denier Weight
2	270,000	540,000
3	270,000	810,000
5	108,000	540,000
7	84,000	588,000
15	39,600	594,000

^a Values are approximate.

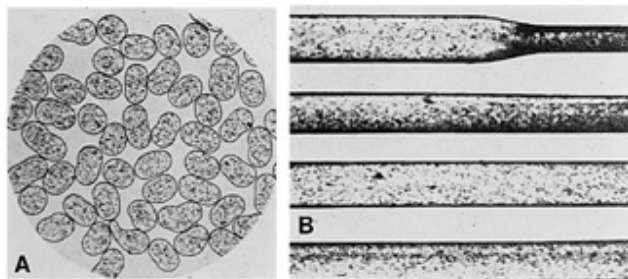


Fig. 8. Zein fiber ($\times 300$) cross-section (A) and longitudinal (B). (Wormell 1954). Reproduced with permission of publisher.

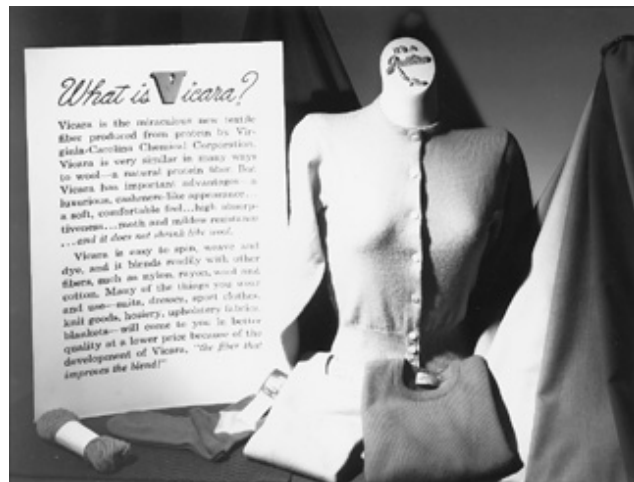


Fig. 9. Store window display from 1951 in Peoria, IL, showing sweaters made of 40% Vicara and 60% wool.

stability at high temperatures, no caution was necessary in laundering and ironing (Mauersberger 1954). Vicara was produced in four types of fibers which differed with their intended uses (Table VIII). The staple length could vary from 0.5 to 6 in., as designated by the customer. Vicara could be used alone in the production of fabrics. The 100% Vicara fabrics were soft and full (Anon 1953). However, Vicara mostly was blended with other fibers, both natural and synthetic (Fig. 9). Zein fibers were first used to replace 10–15% of rabbit fur in felt hats (Smith 1952). The fiber added draping qualities to rayon, warmth to nylon, and softness to wool (Croston 1952; Mauersberger 1954).

In 1949, V-C opened a plant in Taftville, CT, with a capacity of 2.4 million pounds a year. In 1952, V-C scaled-up the Taftville plant's capacity to produce 12 million pounds a year with future plans to boost output to 20 million pounds a year by 1954. By 1955, V-C planned to open another plant that would increase the output of Vicara to 50 million pounds a year (Anon 1952). This was contingent on obtaining sufficient amounts of zein with no problems. Some textile professionals even thought the near-future potential of Vicara was close to 100 million pounds a year (Anon 1952). In its best year, 1954, only four million pounds of Vicara were sold (Reiner et al 1973).

Two main problems led to Vicara's collapse. The first was that Vicara had the lowest tensile strength of any common fiber of the time (Anon 1968). Secondly, Vicara did not have the same dyeing characteristics as wool. It was restricted to darker shades as it could not be bleached to a clear, pure white. During the early 1950s, Vicara did very well despite its recognizable weaknesses because there were no alternatives. By 1955, Orlon (acrylic), with greater tensile strength (4–5.5 g/denier) and an ability to be used in common dyeing systems, essentially replaced Vicara in wool blends (Anon 1968). In February 1958, the V-C Taftville plant was closed.

Even though Vicara's production has stopped, there is still some interest in producing fibers from zein. Though the tensile strength of Vicara was good compared with other regenerated protein fibers, it was too low for usable fibers. Morgan (1962) showed that the tensile strength of zein fibers could be doubled if fibers were saturated with a salt solution before and after stretching. The first saturation (before stretching) called for the fiber to be immersed for 5 min at 50°C in an aqueous saturated salt solution containing 10% sulfuric acid, 5% formaldehyde, and just enough sodium chloride to keep the solution saturated. The fiber was then stretched in a saturated ammonium sulfate solution. It was resaturated at 60°C in a solution of 5% sulfuric acid, 0.75% formaldehyde, and excess sodium chloride. The fiber was then postcured by heating at 44.5°C and 95% rh for 115–125 min. This procedure produced a fiber with a dry tensile strength of 2.17 g/denier.

The chemicals used to produce zein fibers also are problematic. Formaldehyde, alkali, and acid are all environmentally unfriendly. Alternatives need to be found before zein fibers can be produced in today's market.

Uy (1994) showed that zein fibers could be produced from a hydrated zein mixture, eliminating the alkali-spinning solutions and acid used in the coagulation bath. The mixture was prepared by mixing zein with water at 0–18°C until a free-flowing particulate mixture was formed. The mixture was then heated to 45–80°C and simultaneously extruded through a spinnerette to form zein fibers. The fibers then were treated in a stabilizing bath containing only 3% formaldehyde and drawn. The tensile strength of these fibers was lower than that of Vicara, but the fibers had greater elongation.

Dry spinning can also produce zein fiber without formaldehyde, acid, or alkali (Yang et al 1996). In this procedure, zein was dissolved in a solution of aqueous isopropanol or ethanol, and a polycarboxylic acid (citric acid or butanetetracarboxylic acid) was added as a cross-linker for the zein. The added polycarboxylic acid was needed as a precross-linking treatment. Without the acid, the fiber could not be oriented effectively during stretching. The alcoholic zein solution was extruded through a spinnerette into air and wound on a drum.

The fiber was dried at 90°C for 60 min. The temperature was then raised to 150°C, and the zein was dried for an additional 30–60 min. After drying, the fiber was stretched in a water bath containing citric acid at 40°C. The fiber was dried at 90°C for 5 min and then cured at 170°C for 3 min. Fibers created with this method had tensile strength and elongation values (1.06 g/denier and 30%, respectively) similar to those reported for Vicara. The fibers also showed good resistance to boiling in an aqueous acetic acid solution. Tensile strength and elongation were 0.98 g/denier and 42%, respectively, after boiling, and shrinkage was <10%. Recent research (Zhang et al 1997) has shown that the tensile strength of zein fibers can be greatly improved by using acetic acid (pH 2.5) in the coagulation bath. Treatment of fibers after coagulation included separate curing in 95% acetic anhydride followed by curing in 20% glutaraldehyde solution and then stretching the fibers. This treatment increased the tensile strength of the fiber fivefold. Even fibers tested at 100% rh showed only a small decrease in strength.

INKS

Zein was used in three types of printing inks: heat set, vapor set, and flexographic (Coleman 1941; Bernardi 1942; Leekley 1952; Leekley and Stiles 1954; Weber and Permut 1960). All three types of inks have zein performing the same function, which is forming a film and binding the pigment to the paper. Heat set and vapor set inks generally had zein dissolved or dispersed in organic solvents. In heat set zein inks, zein and pigment were dissolved in low boiling glycols. The ink set once the solvent was boiled off. Heat set zein inks had good stability on the press and were well suited to the letterpress process.

Vapor set zein inks are analogous to heat set zein inks. Sometimes ink manufacturers would combine heat set and vapor set in a single ink. Vapor set inks are set by moisture or water vapor. Zein is dissolved in a glycol along with a modifying resin and the pigment is dispersed in the solvent. The choice of solvent is critical because the solvent must dissolve both the zein and modifying resin, but then precipitate the zein on the addition of water. Modifying resins are added to harden the ink. The ink is set by subjecting the printed material to steam or water vapor. (Bernardi 1942; Kroeger and O'Connor 1945). Once the ink sets, the water and glycol are absorbed by the substrate (Carlick 1971). Moisture set inks are fast drying, odorless, and useable on letterpress equipment (Carlick 1971). Flexographic inks are fast drying and have low viscosity. Zein flexographic inks differ from the heat set and vapor set inks by using alcohol or water-based solvents (Sulzberg and Kveglis 1988). Flexography, a type of letterpress process, was largely developed to print on flexible packaging. Indeed, the principle advantage of flexography is its ability to print on a wide variety of substrates, including plastic film, foils, coated and uncoated paper, paperboard, and corrugated board (Sulzberg and Kveglis 1988). Zein was usually dispersed in alkaline water solutions containing shellac or rosin (Olhof 1967). Alcohols were usually added to decrease the viscosity, improve flow, and adjust drying rates. Flexographic inks set when the solvent evaporates. Because water-based inks are slower to dry, they are used on substrates that can absorb water readily, such as tissue paper and paperboard. Zein was also used in alcohol-based flexographic inks but not to the same extent as the water-based inks. Zein inks were had good heat and oil resistance, fair to good rub and water resistance, but only fair ink stability, flexibility, and gloss (Olhof 1967). Zein lost this market, like others, to synthetic film formers. Carboxylated acrylic polymers, usually containing styrene, have largely replaced all natural resins because they provide better abrasion resistance and have better water resistance (Bassemir et al 1995). About 200,000 to 300,000 lb of zein were used to produce inks in 1950 (Anon 1951). It was estimated that potential use could be as high as 5 million lb/year if costs could come down. However, costs remained high, and in 1966, zein was sharing a 1 million lb/year ink market with casein (Olhof 1967).

MOLDED ARTICLES

One needs only to precipitate a zein solution in water to see why some of the first suggested uses for zein were for molded articles. Freshly precipitated zein, with water as a plasticizer, is soft, ductile, elastic, and easily molded into shapes. There were numerous patents early in the 20th Century that discussed zein's thermoplastic nature and its compatibility with other resins (Rathmann 1954). However, zein did not really begin its use as a plastic until the late 1930s. Zein plastic was first manufactured as a replacement casein-type plastic (Simonds et al 1949). The main advantage of using zein over casein was that zein was slower curing, which allowed incorporation of formaldehyde into the plastic before forming (Sturken 1939; Swallen and Danehy 1946; Simonds et al 1949). This eliminated the lengthy formaldehyde bath required for casein plastic. Zein plastics were also more water-resistant than casein plastics (Simonds et al 1949). Zein plastic was manufactured by mixing zein with $\approx 20\%$ water and 5% formaldehyde along with pigments, plasticizer, or other materials. The mixture was then softened, mixed on heated rolls, and formed into sheets by hydraulic presses. A partial cure was sometimes used by pressing at 100°C for a short time. Forming or machining, such as cutting, punching, or stamping was done on the partially cured plastic, which was then cured completely by baking. Further machining could then be done. Shorter molding cycles were possible by mixing zein and paraformaldehyde with a gasoline-insoluble fraction of pine resin. This mixture was molded at 160°C and 4,000 psi for 3–5 min (Bers 1945). The molded article was stable even after immersion in alcohol for 48 hr. Like casein plastic, zein plastic could not be used to make large articles because moisture absorption made the articles dimensionally unstable (Brydson 1966). Zein plastic never achieved the commercial success that casein plastic did (Anon 1951, Brydson 1966) because casein plastic production was already in decline before zein began commercial production (Simonds et al 1949).

A rosin-zein compound to be used as a substitute for traditional shellac-type phonographic records was in development before 1942 (Hunter 1942). A typical formulation for records is 100 parts zein to 400 parts terpene resin and 20 parts plasticizer (Corn Products 1959). Filler or color could also be added. Zein composite records wore better and had better tone qualities than shellac-based records (Croston and Evans 1951). Unfortunately, at about the same time that zein started being used as a substitute for shellac in phonographic records, unbreakable vinyl records started being produced and eventually took over the industry (Anon 1951).

Recently, scientists have renewed attempts at using zein in molded articles. Polosi (1997) showed that zein containing $\approx 40\%$ water and molded at $>130^\circ\text{C}$ for 5–10 min had insolubilities in alcohol and acetic acid similar to those of zein cross-linked with melamine-formaldehyde. Lim and Jane (1994) have injected molded articles containing thermoplastic starch and zein plasticized with glycerol and water. These samples initially had tensile strengths of 20–25 MPa, but lost significant strength when dried. Using potato starch or anionic starches improved the tensile strength of dried molded samples, but tensile strengths were still lower than those of undried samples. In an effort to increase tensile strength and water resistance of molded articles, zein was processed with dialdehyde starch (Jane et al 1994; Spence et al 1995), which significantly increased tensile strength and decreased water absorption. Molded articles containing 25% zein and 75% dialdehyde starch (90% oxidized) had an average tensile strength of 38 MPa, with water absorption of $\approx 5\%$ after submersion in water for 24 hr (Spence et al 1995).

MISCELLANEOUS USES

Zein was described as a possible adhesive or binder even in the first patents (Osborne 1891a; Takamine and Satow 1917; Satow 1919). Solutions of zein containing formaldehyde were tried as adhesives to bond wood (Sturken 1939). Zein adhesives were

strong and, unlike casein glues, did not use alkali and did not stain the wood. Zein adhesives were thought to be a good choice for adhering veneers. Because of its prohibitive cost, zein was not used as a wood adhesive except for adhering high-grade veneers (Simonds et al 1949).

Zein was used as an adhesive to form composition cork (Cooke and Ryan 1945; Croston and Evans 1951; Bridges 1958). Granulated cork was mixed with zein in a glycol solvent and a curing agent (paraformaldehyde, glyoxal, formaldehyde, trioxane or furfural). Cork to zein ratio was usually $\approx 4:1$. The mixture was usually heated to 90–100°C to facilitate solubilization of zein. The mixture was then molded into blocks, rods, or sheets, and cured at 135–150°C. Composition cork was used in gaskets, shoe fillers, and, because it inhibited mold growth, in bottle cap liners. Moisture is needed for the cork bottle liners to seal properly, and in other binders of the day, such as animal glue or casein, that water would allow mold growth. When zein was used as a cork binder, the cork could be stored at 23°C at 65% rh for two years without showing signs of mold growth. In the early 1950s, $\approx 1,000$ lb per month were used in cork gaskets and liners (Anon 1951).

Because zein is not soluble in water and there are no proteases in human saliva, numerous patents have been granted to use zein as a chewing gum base (Hatherell 1932; Weber 1939; Lougovoy 1949). More recently, zein was investigated as a coating for sweeteners in chewing gum (Zibell 1989; Courtright and Barrett 1990). Addition of zein to chewing gum also reduces bitterness and harshness during prolonged chewing (Patel et al 1993).

Zein has several uses in photographic film. It was used as part of the backing coating for film (Renwick 1928). Zein coated on the backing paper of rolled film provided as much protection against fog, mottle, and offset as gelatin, and provided as effective protection from moisture as did cellulose esters (Baxter 1941). The coating also protected the film's light-sensitive layer from contact with the backing strip.

Zein was also used as a binder and a protective coating for single-sheet photographic paper (Baxter 1953). About 200,000 lb a year of zein were once used as backing in photographic film (Reiners et al 1973). Zein was also used in the light-sensitive layer of film for producing color (Jennings 1946; Fierke and Chechak 1949). It is a water-insoluble peptizer for silver halide. The zein-peptized silver halide can be used in mixed grain emulsions where the grains enveloped in zein are separately developed from those enveloped in gelatin (Lowe 1951).

Zein-epoxy baked coatings were proposed for use as linings in cans (Pomes 1971). Zein and 5–30% epoxy resin were dissolved in solvent and cast into films. The dried films were then baked to cure. The films were flexible, hard, and tough (Howland 1961). The zein-epoxy mixture could be coated onto tin and baked. There was strong adhesion of the coating to the tin, and the coating was not affected by water (Howland 1961). Zein and bisphenol-A mixtures were thought to be a particularly good choice for can coatings. Cured zein-bisphenol-A coatings on tin plates had sufficient flexibility and adhesion so that cans could be formed without debonding the coating (Holand and Reiner 1962).

In the human mouth, there is a perceptual threshold. Particles of ≈ 1 μm diameter will not be perceived as individual particles. Rather, they have the texture of a creamy fatlike fluid (Iyengar and Gross 1991). The protein bodies of corn are ≈ 1 μm (Wilson 1987) and could be used to mimic fat. A process for the enrichment of protein bodies from corn gluten meal was patented by Cook et al in 1996. Opta Food Ingredients tried to extract the protein bodies intact but could not do so on an industrial scale. They were able to extract zein under controlled conditions and with a microgrinding step were able to produce a colloidal suspension of microparticles of 0.3–3 μm . Opta Food Ingredients marketed the fat substitute under the trade name Lita (now discontinued). Food products such as mayonnaise, ice cream, and spreads could be prepared with Lita, replacing 75–100% of the normal fat (Iengar and Gross 1991).

OUTLOOK

The current industrial use of zein is small but growing. There are currently two producers of zein: Freeman Industries, Inc., of Tuckahoe, NY, and Showa Sangyo Corp., Japan. Zein has had a long and prominent research history. An extraordinary amount of research has been done on this corn component. A bibliography of zein compiled by Rathman (1954) listed some 942 citations between 1891 to 1953. The research certainly did not stop there. A quick search of the U.S. patent literature from 1972 to date found 158 hits for zein. Most older uses of zein were lost to synthetic polymers because of superior properties and lower cost of the synthetic polymers. In this day of environmentally friendly products, however, zein again may find a niche that synthetic polymers cannot fill. But for zein to realize its full potential, research must find ways to overcome two main problems: prohibitive cost and poor resistance to water. In 1959 (CPSC 1959), zein was selling for \$0.28 to \$0.35/lb, making it too expensive for some applications. Adjusting for inflation, \$0.28 to \$0.35 in today's dollars would be \$1.10 to \$1.40, which is much less than what zein sells for now (\$10.00 to \$27.00/lb, Chemical Market Reporter 8/11/00). [Author's note: Based on Producer Price Index Inflation Calculator, www.jsc.nasa.gov/bu2/inflation/ppi/inflatePPI.html] No doubt, part of the problem for the extreme price of zein today is its lack of production. Interestingly, zein has been estimated to cost \$1.00 to \$1.50/lb if extracted as one of the products from an ethanol production plant (Dickey et al 1999). It should be kept in mind that prices in this range were too expensive for most applications when zein was losing its markets in the 1950s (Anon 1951).

The second problem with zein is its susceptibility to water. As discussed earlier in this review, zein is hygroscopic and will lose or gain water with changes in relative humidity. This phenomenon makes zein unacceptable for some applications for which it had shown great promise in the past, such as films and coatings. A large potential market for zein is in food coatings, and indeed this is its only market now (Shukla 1992). Today, zein coatings are only used for material such as nuts and pharmaceuticals that are packaged to stay dry. Water will not be much of a factor for these coatings. For zein to truly make inroads as a food coating or for other uses, requires a way to make zein less susceptible to water.

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