Reprinted with permission from
PROGRESS IN PAPER RECYCLING, Vol. 11, No. 3, May 2002

Recyclable Zein-Coated Kraft Paper and Linerboard

Nicholas Parris, Marguerite Sykes, Leland C. Dickey, Jack L. Wiles, Thomas J. Urbanik, and Peter H. Cooke

ABSTRACT

Recyclability of kraft paper and linerboard coated with commercial zein and paraffin wax or a zein–lipid mixture was evaluated using conventional recycling processes. Zein, an alcohol-soluble protein from corn, exhibits both grease and water vapor barrier properties. Strength properties, grease resistance, and water vapor barrier properties were measured on handsheets prepared from fiberized coated and recycled kraft paper and linerboard. The coating reduced water vapor transmission rates (WVTR) and grease permeation 16% and 100%, respectively, on handsheets prepared from reslushed kraft paper and 8% and 97% on kraft linerboard. Strength properties of reslushed zein-isolate-coated kraft paper were 12% to 19% lower than those of the reslushed uncoated control. However, strength properties of recycled paper, regardless of treatment or presence of enzyme, approximated those of reslushed uncoated paper. Handsheets from reslushed zein-isolate-coated linerboard were essentially as strong as reslushed control sheets. In contrast, strength values of handsheets from zein–wax-coated kraft paper reslushed in water were approximately 20% to 30% lower than those for reslushed uncoated paper. Pretreatment of coated paper with an enzyme solution of pancreatin 8x and sodium dodecylsulfate (SDS), followed by flotation removal of the coating, significantly improved strength properties of handsheets made from reslushed fibers.

KEYWORDS

Coating, Enzyme, Grease, Hydrolysis, Paper, Pulping, Recycle, Water vapor, Zein.

Parris, Dickey, and Cooke are with Eastern Regional Research Center, U.S. Department of Agriculture, 600 East Mermaid Lane, Wyndmoor, PA 19038.
Sykes and Urbanik are with USDA Forest Service, Forest Products Laboratory, Madison WI 53705.
Wiles is with Clemson University, Clemson, SC 29634.

INTRODUCTION

A major issue facing the food packaging industry is environmental "friendliness" of packaging materials. Waste disposal of coated packaging is a serious problem in the United States and many regions of the world. About one-third of municipal solid waste comes from containers and packaging, with 13% from plastic (1). Agriculturally derived alternatives to polyolefin packaging material currently used by the food industry offer an opportunity to strengthen the agricultural economy and reduce reliance on petroleum products. Materials that are recyclable have cost advantages that can offset the lower cost of petroleum products. Waxed paper products are not presently recycled, because wax particles cannot be cleanly separated from paper fiber during mechanical pulping. As a result, waxed corrugated boxes used for transport of perishable goods, such as fruits, vegetables, and frozen fish, are not recycled. Because recognizing wax barrier coatings is difficult in some cases, these containers unintentionally enter the recycling stream, resulting in unacceptable batches of recycled fiber and costly contamination of recycling equipment.

Wax is the most commonly used barrier coating. Various approaches have been taken to make wax-coated packaging more recyclable. Back and others (2) modified waxes with small amounts of fatty acids and a nonionic surfactant or other compounds to improve wax removal. Results indicated that old corrugated containers (OCC) could be recycled if container manufacturers replaced conventional waxes with modified waxes. Other researchers have focused on processing equipment, such as adding screens and flotation stages for increased wax removal, or altering process parameters, such as increasing pH and temperature paired with dispersion (3). Procedures have been reported for recycling waxed corrugated containers (4,5). Removal of stickies from recycled office paper by flotation, using ionically charged flotation aids, has been investigated (6). Parris and others proposed that corn zein–wax (7) or zein–lipid mixtures isolated from ground corn (8) could serve as wax or polyolefin alternatives. In those studies, grease resistance and water vapor barrier properties of coated brown kraft paper were examined as a function of coating level, method of application, and time of exposure. The effect of treatment conditions for various enzymes used to separate coating from paper fibers was also investigated. Although these experiments suggested the wax- and lipid-treated paper could be removed from small pieces of coated paper exposed to enzyme and surfactant within flasks, confirmation of these results on a larger laboratory scale using conventional recycling techniques was essential for evaluating these new coating materials.

The objective of the study reported here was to conduct a preliminary scaled-up laboratory evaluation of the recyclability of kraft paper and linerboard coated with commercial zein and paraffin wax or with a zein–lipid mixture using conventional recycling processes. Strength properties, grease resistance, and water vapor barrier properties were measured on handsheets prepared from fiberized coated and recycled kraft paper and linerboard.

MATERIALS AND METHODS

Materials/Equipment

Commercial corn zein F-4000 was obtained from Freeman Inc. (Tuckahoe, New York). Corn zein isolates were prepared by batch extraction with 70% ethanol from dry milled corn as described by Parris and others (8). Composition (dry basis) of the isolate used for this study was approximately 80% protein, 12% lipid, and 0% starch. Pancreatin (from porcine pancreas, activity equivalent to 8x, U.S.P. specification) and red oil dye were obtained from Sigma Chemical Co. (St. Louis, Missouri), oleic acid from Fisher Scientific (Fair Lawn, New Jersey), and paraffin wax from Cullen Industries, Inc. (Huntington Valley, Pennsylvania). The sprayer used was a 7.6-L Flowmaster PGX Model #1002V. Two kraft substrates, unbleached kraft paper (100 g/m^2) obtained from Uline (Waukegan, Illinois) and linerboard (180 g/m^2) from Green Bay Packaging (Green Bay, Wisconsin), made from 100% recycled kraft fibers were used. A 5-L capacity Hobart mixer (Hobart Co., Troy, Ohio) equipped with a jacketed mixing bowl for temperature control, a standard British disintegrator (Testing Hines, Inc., Islandia, New York), and a 50-kg capacity hydrapulper (Voith Sulzer, Appleton, Wisconsin) were used for fiberization in these trials. An 8-L capacity Denver flotation cell (Denver Co., Colorado Springs, Colorado) was also used for some of the experiments.

Chemical Analysis

Protein content (N × 6.5) for zein isolate was determined by the micro-Kjeldahl method, AACC, 1995 (9) and AOAC, 1995 (10). Starch content was determined according to a previously published procedure (11). Total lipid content was determined in our laboratory by packing a glass-wool-plugged pipet with approximately 100 to 300 mg sample, previously dried at 110°C. The micro column was eluted with 5 mL of hexane followed by 5 mL of chloroform. The eluates were evaporated with nitrogen gas to determine the weight of the extracts.

Sample Preparation

Commercial zein or zein isolate, 30 g, was dissolved with heating to approximately 70°C in 1 L of 90% (v/v) ethanol. The warm solution was filtered through cheesecloth into the spray tank and sprayed directly on approximately 3 m^2 of kraft paper or linerboard. Similarly, wax (30 g) was dissolved in 1 L of hexane with heat. The warm solution was transferred to a sprayer and applied directly to the zein-coated kraft paper. The coated papers were dried under ambient conditions. Small samples ofthe dry coated papers were weighed after each application to determine the amount of zein, zein isolate, or wax deposited. The amount of coating applied was sufficient to provide adequate grease and water vapor barrier properties as reported earlier (7,8).

Repulping

All the papers, coated and uncoated, were pre-soaked in warm water for several hours (overnight for the heavier linerboard) prior to fiberization. Batches of the coated paper were partially fiberized prior to adding the enzyme solution. Pancreatin 8x (1:50 w:w based on zein), 0.1% sodium dodecylsulfate (SDS), and pH 8.5 Tris buffer were added to adjust the pulp slurry to 8% solids and mixed for 30 min in the Hobart mixer at 38°C. The fiberized pulp subsequently was diluted and either washed thoroughly over a Buchner funnel or floated in the Denver cell. Flotation was done at 1% consistency, 38°C for 5 min, to remove waxy particles released from the fibers during enzyme hydrolysis of the coating. Either SDS, BRD-2340, or BRD-2367 surfactants (Buckman Laboratories, Inc., Memphis, Tennessee) served as the flotation aid in these experiments.

Reslushed trials on both coated and uncoated kraft paper used the British disintegrator at 2.5% solids for fiberization followed by dewatering on a Buchner funnel to preserve fines. A British disintegrator was used for the linerboard samples. These fiberized pulps were made into handsheets for the “reslushed only” experiments.

Testing

Handsheets were prepared according to TAPPI 205 sp-95 from each recycling process and tested at the Forest Products Laboratory (Madison, Wisconsin) for physical properties following TAPPI 403 om-91 for burst, T-414 om-88 for tear, and T-404 cm-92 for tensile strength. Water vapor permeability of coated paper was determined using the method described in ASTM E96–80 (102. A test temperature of 25±2°C and a relative humidity of 50±5% were controlled using an environmental chamber made by Hotpack Corp. (Model 317322) (Philadelphia, Pennsylvania). Grease resistance was determined using TAPPI T-507, "Grease Resistance of Flexible Packaging Materials," as described by Trezza (13). Test samples were placed into an oven at 60°C for 4 h. Afterward, the percentage of area stained by red oil dye on the stain-absorbing blotting paper was determined and recorded.

Scanning Electron Microscopy (SEM) Imaging

The coated surface of paper samples was imaged as describe earlier (8). Side views of reslushed paper were made by slicing the paper samples into 2- to 3-mm wide strips using a stainless steel razor blade and mounting each strip in a spring-loaded vertical mount #75915 (Electron Microcopy Sciences, Ft. Washington, Pennsylvania). Cut faces were coated with a thin layer of gold by direct current (DC) sputtering and examined in a Model JSM840 scanning electron microscope (JEOL USA, Peabody, Massachusetts) operating in the secondary electron imaging mode. Digital images were collected at 50× and 150× using an IMIX workstation (Princeton Gamma-tech, Princeton, New Jersey). Image analysis to determine the percentage area occupied by open spaces in projected images of the cut faces of paper samples was done using Image Pro Plus software (Media Cybernetics, Silver Spring, Maryland). Five replicates of images were segmented using the contour function by visually matching the areas of highlighted pixels with open areas in gray level images, then integrating the number of pixels in open areas and comparing with pixels corresponding to solid-filled areas of the paper samples.

DISCUSSION OF RESULTS

Data presented in Table 1 illustrate the influence of wax and zein on handsheet tensile, tear, and burst strength properties. The strength properties of zein–wax-coated kraft paper reslushed in water were 20% to 30% lower than the reslushed uncoated paper, indicating that the presence of wax and zein interfered with fiber bonding. Pretreatment of coated paper with a buffered solution containing pancreatin 8x and SDS and subsequent removal of the coated material by flotation improved the strength of these handsheets, which then better approximated that of the uncoated reslushed paper, indicating removal of most of the zein–wax coating. Strength properties of handsheets made by washing the recycled pulp after repulping with a buffered solution of pancreatin and BRD-2340 surfactant (typically used for enzymatic deinking) were lower than those measured when flotation followed the enzyme treatment. This is probably due to substitution of SDS with a surfactant that is less effective for wax removal. In addition, residual wax particles may be too large to be removed by washing but rather are in the particle size and density range suitable for flotation. With the use of BRD-2340, waxy material deposited on the pulping equipment and doler tank used for handsheet preparation. Deposition of waxy material on equipment would be unacceptable in large-scale mill recycling.

In contrast, Table 2 summarizes several successful approaches to recycling paper coated with a corn zein isolate as an extension of previous laboratory work (8). The strength of reslushed isolate-coated kraft paper was approximately 12% to 19% lower than the reslushed uncoated paper. However, the strength properties of the recycled isolate-coated paper, regardless of treatment or presence of the enzyme, more closely approximated those of reslushed uncoated paper than those of recycled zein–wax-coated paper. This result can be attributed to the presence of fatty acids in the lipid portion of the isolate that effectively solubilizes zein and enables subsequent removal by flotation or washing. Another advantage of the isolate coating is that no deposit was apparent on the process equipment after recycling. A smaller quantity of surfactant BRD-2340 could be used in place of a larger quantity of the more expensive SDS to produce comparable levels of coating removal. We also determined that buffering the system during enzymatic treatment was not necessary, because the

Table 1—Mechanical properties of handsheets[a] from zein–wax[b]-coated kraft paper

Treatment		Tensile index (kN m/g)	Burst index (kPa m²/g)	Tear index (mN m²/g)	Average % of control
Uncoated	Reslushed[c]	31.5	1.74	8.41	100
Coated	Reslushed[c]	24.5	1.15	5.79	71
Recycled	Enzyme[d]–flotation	27.2	1.51	7.62	88
	Enzyme[e]–wash	23.0	1.12	6.38	71

[a]60 g/m².
[b]4.26 g/m² commercial zein F-4000 plus 7.75 g/m² paraffin wax.
[c]Water.
[d]Pancreatin 8x, SDS, Tris buffer.
[e]Pancreatin 8x, BRD-2340, Tris buffer.

Table 2—Mechanical properties of handsheets[a] from zein-isolate[b]-coated kraft paper

Treatment		Tensile index (kN m/g)	Burst index (kPa m^2/g)	Tear index (mN m^2/g)	Average % of control
Uncoated	Reslushed[c]	31.5	1.74	8.41	100
Coated	Reslushed[c]	26.0	1.39	7.43	84
Recycled	Enzyme[d]–flotation	30.0	1.69	8.14	96
	Enzyme[d]–wash	27.7	1.44	7.63	87
	No enzyme[e]	30.7	1.73	8.67	100

[a]60 g/m^2.
[b]8.14 g/m^2 zein isolate 170-10.
[c]Water.
[d]Pancreatin 8H, BRD-2340, water.
[e]Pancreatin BRD-2340, water.

reslushed paper was approximately pH 8.5, within the pH range for optimum enzyme activity.

To explain the difference in strength properties of the handsheets, SEM digital images were prepared and recorded at 150×. No significant difference could be identified between the handsheets images from the surface of reslushed zein–wax-coated, zein-isolate-coated, and uncoated kraft paper (Figs. 1 to 3). Digital images of the edge view of the handsheets prepared from coated and uncoated paper indicated that there is more open area in the reslushed handsheets produced from the zein–wax-coated paper (21.9%) and zein-isolate-coated paper (23.8%) compared with the uncoated kraft paper (18.4±2.7%). This supports the assumption that residual coating interferes with bonding of paper fibers.

Because wax and other hydrophobic coatings are widely used on corrugated containers, a heavier grade kraft linerboard was coated with zein isolate and its recyclability examined. In this part of the study, SDS was replaced with BRD-2367, a surfactant recommended for more effective wax removal. Linerboard, more difficult to fiberize, was first pulped in a British disintegrator and subsequently treated at 8% solids with the enzyme preparation without continuous stirring. Handsheets from reslushed zein-isolate-coated linerboard exhibited strength values not substantially lower than those of reslushed uncoated linerboard (Table 3). A probable explanation for comparable values

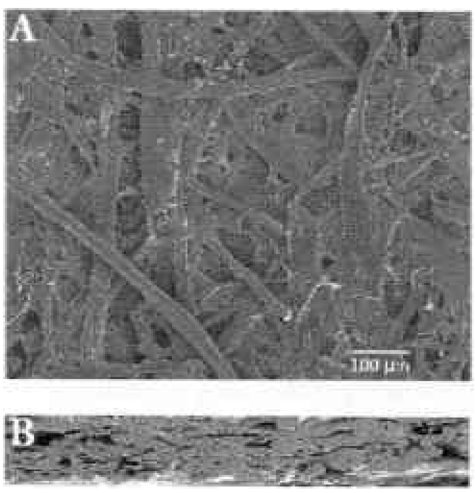

Figure 1. **SEM images of handsheets from reslushed kraft paper: (a) surface view, (b) edge view.**

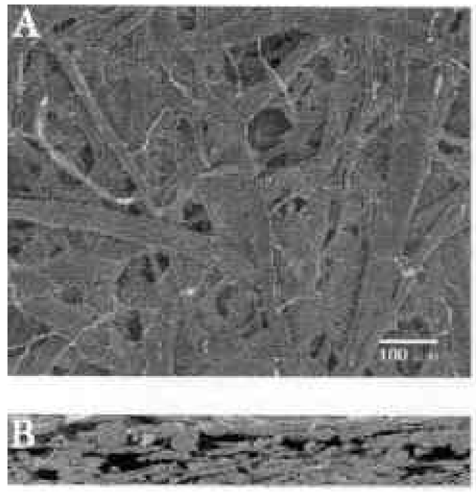

Figure 2. SEM images of handsheets from reslushed kraft paper coated with commercial zein and paraffin wax: (a) surface view, (b) edge view.

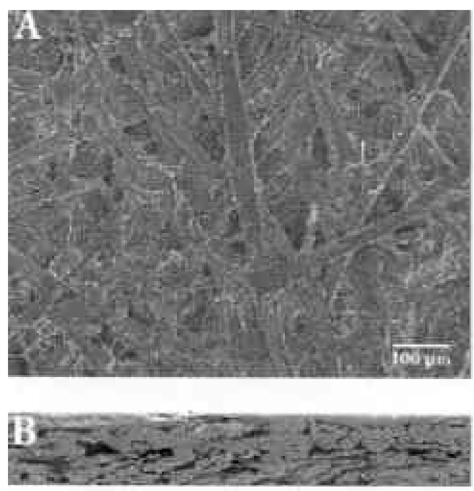

Figure 3. **SEM images of handsheets from reslushed kraft paper coated with zein isolate 170-10" (a) surface view, (b) edge view.**

Table 3—Mechanical properties of handsheets[a] from zein-isolate[b]-coated kreft linerboard

Treatment		Tensile index (kN m/g)	Burst index (kPa m²/g)	Tear index (mN m²/g)	Average % of control
Uncoated	Reslushed[c]	36.3	2.10	7.99	100
Coated	Reslushed[c]	35.6	2.00	7.90	97
Recycled	Enzyme[d]–flotation	30.4	1.40	7.50	81
	Enzyme[d]–wash	33.1	1.50	7.68	86
	No enzyme–wash[e]	32.3	1.50	7.76	86

[a]180 g/m².
[b]12.6 g/m² zein isolate 171-8.
[c]Water.
[d]Pancreatin 8x, BRD-2367.
[e]BRD-2367,water.

is that less isolate was applied to the linerboard than was used for coating the paper, even though adequate grease and water vapor barrier properties were maintained (Table 4). Because; the coating was applied based on weight per surface area, the linerboard (approximately twice the grammage of the paper used) contained less coating per unit mass of paper fibers. This is in contrast to reslushing the zein–wax-coated paper, which by itself definitely prevents good bonding of fibers (Table 1). Recycling [flotation or washing following pulping) the zein-isolate-coated liner appeared to offer no additional advantage. Regardless of recycling treatment, the loss in strength properties was between 5% and 30%. This loss possibly could be attributed to removal during recycling of strength-enhancing additives present in the linerboard as received from the mill.

It should be noted that barrier properties were tested on 180-g/m² handsheets, comparable to the grammage of the linerboard as received from the mill, and on 100-gm² handsheets for the kraft paper, also based on the grammage of the paper as received and presumably as used commercially. We previously reported that fatty acids in zein-isolate coatings on kraft paper contributed water vapor barrier properties and that zein reduced grease permeation (8). In Table 4, this was also demonstrated for zein-isolate-coated linerboard. At a coating level sufficient to protect kraft paper from water vapor and grease penetration, there was a 16% decrease in WVTR and a 100% decrease in grease permeation for reslushed coated paper compared with uncoated control paper. Untreated linerboard coated at approximately the same level had an 8% reduction in WVTR and a 97% reduction in grease permeation compared with the untreated control linerboard. Handsheets prepared from reslushed linerboard coated with 19.4-g/m² isolate exhibited a 16% decrease in WVTR compared with the untreated control linerboard. The principal reason for the lower WVTR and grease permeation values for the linerboard compared with the paper at comparable coating levels can probably be attributed to the additional thickness of the linerboard over kraft paper (0.244±0.003 mm to 0.126±0.004 mm, $n = 6$).

Based on the findings of this study, additional work needs to be done. We used strength, SEM, and barrier properties to determine recyclability. Other essential parameters—

Table 4—Water vapor transmission rates and grease permeation handsheets[a] from zein-isolate[b]-coated kraft paper and linerboard

Material	Coating (g/m²)	Treatment	WVTR (g/m² day)	grease permeation (% area stained)
Uncoated paper	—	Reslushed	1,409	67.0
Coated paper	12.6	Reslushed	1,185	0
Uncoated linerboard	—	None	1,251	28.5
Coated linerboard	14.5	None	1,148	0.7
Coated linerboard	19.4	Reslushed	1,055	0

[a]From 100-g/m² kraft paper and 180-g/m² linerboard. [b]Zein isolate171-8.

coefficient of friction and sizing—also need to be measured. This work was a laboratory study scaled up from Parris's earlier studies. While the results reported here confirm his previous findings, a pilot plant-scale investigation would need to be carried out to verify the effectiveness of the zein-isolate coating.

CONCLUSIONS

Zein-isolate-coated kraft paper shows good water vapor barrier and grease resistance properties, and this coated kraft paper appears to be recyclable using conventional recycling processes. Residual isolate coating would not compromise fiber bonding nor does it appear to deposit on processing equipment. If the isolate-coated kraft paper and linerboard are indeed recyclable, packaging coated with zein isolates probably could be commingled with uncoated OCC during reycling without reducing paper or linerboard strength or creating contamination problems. In contrast, our results indicate that commercially available zein- and wax-coated kraft paper cannot be recycled satisfactorily using laboratory-scale recycling equipment and typical processing conditions. Residual wax and zein particles interfere with fiber bonding, reflected by decreased paper strength properties. However, if flotation is added to the recycling process, removal of the zein–wax coating appears to be increased significantly. Based on evaluation of strength properties, this study suggests that isolates of zein could be a recyclable substitute for wax coatings. However, other physical properties, such as coefficient of friction and sizing, as well as pilot-plant scale studies need to be carried out to demonstrate the effectiveness of zein-isolate coating.

ACKNOWLEDGMENT

The authors thank Julie Hess, a summer student at FPL from the University of Wisconsin–Stevens Point, for handsheet testing of strength properties.

LITERATURE CITED

(1) EPA. Characterization of municipal waste in the United States: *1990 Update., Executive Summary*, U.S. Environmental Protection Agency, Office of Solid Waste. Washington, DC (1990).

(2) Back, E.L.; Laudi, B.; Elftonson, J. Effect of modifiers on wax properties and dispersability under hot alkaline conditions. Auto dispersible waxes for recyclable packaging papers. Part IV. *Nordic Pulp and Paper Research Journal* 10(2): 22–128 (1995).

(3) McEwen, J.G.E. Wax contamination in paper recycling: Understanding wax chemistry and recycling waxed papers, *Progress in Paper Recycling* 6 (1): 70–72 (1996).

(4) Byrd, M.V.; Heitman, J.A. Testing the recyclability of waxed-treated corrugated containers: A comparison of bench-and pilot-scale methods, In: *Proceedings, TAPPI* Pulping Conference, TAPPI Press, Atlanta, GA., Abstracts p. 45 (2000).

(5) Doshi, M.; Dyer, J.; Heise, O.; Cao, B. Removal of wax and stickies from OCC by flotation Part I: Green Bay Packaging trial, Progress in Paper Recycling 9(4): 71–76 (August2000).

(6) Hsu, N.N.; Dauplaise, D.L. Effectiveness of ionically charged chemicals as flotation aids in stickies removal during mixed office wastepaper recycling, In: *Proceedings of TAPPI Recycling Symposium*, TAPPI Press, Atlanta, GA., pp.249–255, (1996).

(7) Parris, N.; Vergano, P.J.; Dickey, L.C.; Cooke, P,H.; Craig, J.C. Enzymatic hydrolysis of zein-wax-coated paper. *J. Agric. Food Chem.* 46:4056–4059 (1998).

(3) Parris, N.; Dickey, L.C.; Wiles, J.L.; Moreau, R.A.; Cooke, P.H. Enzymatic hydrolysis, grease permeation and water barrier properties of zein isolate coated paper. *J. Agric. Food Chem.* 48:890–894 (2000).

(9). AACC, 19995 - American Association of Cereal Chemists. Approved Methods of the AACC, 9th ed.; American Association of Cereal Chemists: St. Paul, MN, 1995; Method 46-13.

(10). AOAC, 1995 - AOAC, Official Methods of Analysis, 16th ed.; Association of Official Analytical Chemists; Arlington, VA, 1995; Method 32.203.

(11) McCready, R.M.; Ducay, E.D.; Gauger, M.A. Automated analysis of sugar, starch and amylose in potatoes by measuring sugar–dinitrosalicylate and amylose-iodine color reactions. *J. AOAC* 57:336–342 (1974).

(12) ASTM. Standard test method for water vapor transmission of materials. In: *ASTM Book of Standards;* American Society for Testing and Materials: Philadelphia, PA., pp E96–80 (1980).

(13) Trezza, T.A.; Vergano, P.J. Grease resistance of corn zein coated paper. *J. Food Science* 59 (4): 912-915 (1994).■