United States Department of Agriculture
Agricultural Marketing Service | National Organic Program
Document Cover Sheet
https://www.ams.usda.gov/rules-regulations/organic/national-list/petitioned

Document Type:

☐ **National List Petition or Petition Update**

A petition is a request to amend the USDA National Organic Program's National List of Allowed and Prohibited Substances (National List).

Any person may submit a petition to have a substance evaluated by the National Organic Standards Board (7 CFR 205.607(a)).

Guidelines for submitting a petition are available in the NOP Handbook as NOP 3011, National List Petition Guidelines.

Petitions are posted for the public on the NOP website for Petitioned Substances.

☒ **Technical Report**

A technical report is developed in response to a petition to amend the National List. Reports are also developed to assist in the review of substances that are already on the National List.

Technical reports are completed by third-party contractors and are available to the public on the NOP website for Petitioned Substances.

Contractor names and dates completed are available in the report.

Zein

Handling/Processing

Identification of Petitioned Substance

Chemical Names:
Zein

Other Names:
Corn prolamine
Confectioners glaze
Corn protein
Maize protein

Trade Names:
FloZein™

CAS Number:
9010-66-6

Other Codes:
ChemIDplus External ID: 0009010666
INS Number: n/a
E Number: n/a

Summary of Petitioned Use

The petitioned use of zein is as an allowed non-organically produced agricultural product, to be permitted as an ingredient in or on processed products labelled as organic through its addition to the National List. The petition identifies uses for zein as an ingredient and as a processing aid, including as a glaze, coating, taste masker, wheat gluten substitute, and for use in micro/nano-encapsulation. The specific petitioned use is as a food coating (Flo Chemical Corporation 2020).

Characterization of Petitioned Substance

<u>**Composition of the Substance:**</u>
Zein is the generic name of a class of proteins found in the corn kernel, where it represents about 50 percent of the total protein in the kernel (Shukla and Cheryan 2001). Zein proteins have low nutritional value because they lack two essential amino acids—tryptophan and lysine—and are low in threonine, valine, and the sulfur amino acids (Wilson 1987). Zein is classified as a prolamin, a group of simple storage proteins found in grains, including corn (zein), wheat (gliadin), and barley (hordein). The proteins found in the prolamin and glutelin fractions of wheat, rye, and barley possess celiac disease toxicity (i.e., they can trigger gluten intolerance) whereas zein, the prolamin protein in corn, does not.

<u>**Source or Origin of the Substance:**</u>
Most commercial zein is extracted from corn gluten, also referred to as corn gluten meal (CGM). Corn gluten is produced in the corn steep liquor process ("wet milling") used to separate corn starch from the corn kernel (Anderson and Lamsal 2011). The products of the wet milling process are corn starch, CGM, and corn steep liquor.

Zein can also be extracted from other corn processing byproducts, such as dry milled corn (DMC), distiller's dried grains with solubles (DDGS), and ground corn at the beginning of the dry-grind process, but these sources contain less protein than CGM. Some of these processes do not expose the zein to any reducing agent, such as sulfur dioxide, so the extracted zein is chemically unaltered (Cheryan 2002). In all cases, the extraction process employs an aqueous alcohol solution to selectively dissolve the zein protein. Ethyl alcohol or isopropyl alcohol are the most commonly employed aqueous solutions because they are easily recovered from zein (Anderson and Lamsal 2011). See *Evaluation Question #1* for more information.

Properties of the Substance:

Zein is a white to slightly yellow powder (Budavari 1996). Its most remarkable physical properties are that it is water-insoluble, but soluble in aqueous alcohol solutions (Anderson and Lamsal 2011). Zein is fully biodegradable. As mentioned above, the plant protein zein has a very poor essential amino acid profile. In addition, the amino acids in this water-insoluble plant protein are only about 60 percent available in human feeding studies (Calvez et al. 2020).

Specific Uses of the Substance:

These unique solubility characteristics of zein make it useful in many products as an edible food coating, as well as a component of paper coatings, plastics, textiles, and adhesives (Budavari 1996). When an aqueous solution of zein is applied to the surface of a food product, the solvent evaporates, leaving behind a water-insoluble (and edible) moisture barrier. This barrier hinders moisture loss from the food surface and hinders moisture pickup by a dry product, such as a food supplement capsule or tablet.

The petitioner is requesting that zein be allowed for use as a food coating and processing aid (Flo Chemical Corporation 2020). The petitioned substance is formulated as a 10 percent solution of zein dissolved in aqueous 85 percent alcohol and then used for coating by dipping, spraying, or panning (a process that uses rotating drums to cover items with a coating.) The petitioner mentions other uses for zein including:

- glaze for confections
- substitute for wheat gluten in baked goods
- processing aid for poultry
- micro/nano-encapsulation, taste masker, and processing aid for nutraceuticals

Newer applications taking advantage of zein's biological properties include cell culturing, degradable sutures, biodegradable plastics, and drug adjuvants (Anderson and Lamsal 2011).

Approved Legal Uses of the Substance:

Zein is a food substance Generally Recognized as Safe (GRAS) by FDA [21 CFR 184.1984] as a direct human food ingredient, for use as a surface-finishing agent, and for technical effects (i.e., as an anticaking agent or free-flow agent, a drying agent, and a humectant). Zein also is allowed as an indirect food additive used as a component of adhesives [21 CFR 175.105]. A major use of zein is for coating foods and pharmaceutical products. The most common production process for zein uses corn gluten, also known as corn gluten meal, as the starting material. Corn gluten itself is a GRAS food ingredient [21 CFR 184.1321].

Action of the Substance:

Zein is soluble in aqueous alcohol. When a zein solution is applied to a food or tablet surface, the alcohol vaporizes leaving behind a hydrophobic (water repellant) coating of zein that hinders moisture loss for a food and hinders moisture pickup for a pharmaceutical tablet.

Combinations of the Substance:

Zein is used to create a coating. Zein is typically dissolved in an aqueous solution of ethyl alcohol to enable utilization. The alcohol is volatile and quickly evaporates after application.. Formulations of zein other than those petitioned may include synthetic components, such propylene glycol.

Status

Historic Use:

Zein is an extracted, "value added" subfraction of corn gluten and represents about half of the protein in corn gluten. Corn gluten itself is widely used in organic production as a crop fertilizer and crop pesticide for pre-emergence weed control (USDA 2016a). Purified zein is not used in organic crop production.

Organic Foods Production Act, USDA Final Rule:

Zein is not listed anywhere in the Organic Foods Production Act of 1990 (OFPA) or the USDA organic regulations, 7 CFR Part 205. However, the agricultural substance corn gluten from which it is extracted is currently acceptable for use in organic crop production as a nonsynthetic substance per NOP Guidance 5034-1, *Materials for Organic Crop Production.* Both ethyl and isopropyl alcohol, which are most commonly used to extract the zein or enable its use as a food coating, are on the National List of synthetic substances allowed for crop and livestock production: ethyl alcohol (ethanol) at §205.601(a)(1)(i) and §205.603(a)(1)(i) and isopropyl alcohol (isopropanol) at §205.601(a)(1)(iii) and §205.603(a)(1)(ii).

International

Canada, Canadian General Standards Board – CAN/CGSB-32.311-2020, Organic Production Systems Permitted Substances List
http://publications.gc.ca/collections/collection_2020/ongc-cgsb/P29-32-311-2020-eng.pdf

Zein is not included in the Canadian General Standards Board—CAN/CGSB-32.311-2020, Organic Production Systems Permitted Substances List.

CODEX Alimentarius Commission – Guidelines for the Production, Processing, Labelling and Marketing of Organically Produced Foods (GL 32-1999)
http://www.fao.org/docrep/005/Y2772E/Y2772E00.HTM
Zein does not appear in the CODEX Alimentarius Commission—Guidelines for the Production, Processing, Labelling and Marketing of Organically Produced Foods (GL 32-1999).

European Economic Community (EEC) Council Regulation – EC No. 834/2007 and 889/2008
http://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX:32008R0889
Zein does not appear in the European Economic Community (EEC) Council Regulation—EC No. 834/2007 and 889/2008.

Japan Agricultural Standard (JAS) for Organic Production
http://www.maff.go.jp/e/jas/specific/criteria_o.html
Zein is not listed in Table 1 "Additives" of the JAS for Organic Processed Foods Notification No. 1606.

IFOAM – Organics International
http://www.ifoam.bio/en/ifoam-norms
Zein is not included in the IFOAM Norms.

Evaluation Questions for Substances to be used in Organic Handling

Evaluation Question #1: Describe the most prevalent processes used to manufacture or formulate the petitioned substance. Further, describe any chemical change that may occur during manufacture or formulation of the petitioned substance when this substance is extracted from naturally occurring plant, animal, or mineral sources (7 U.S.C. § 6502 (21)).

According to the Merck Index (Budavari 1996), "zein is extracted commercially from corn gluten meal with diluted isopropyl alcohol." The process is described in U.S. Patent No. 3,535,305 (Carter and Reck 1970). According to this patent, an aqueous solution of one of the solvents—isopropyl alcohol, ethyl alcohol, acetone, other ketones, or ethylene glycol—can be used. The alcohol proportion can range between about 60 percent to about 95 percent. The pH of the extracting liquid may be adjusted to 6.5 to 7 by adding a small amount of an aqueous alkali metal hydroxide solution such as sodium hydroxide.

The GRAS listing at 21 CFR 184.1984 specifies extraction with isopropyl alcohol. FDA provides this description of the commercial production of zein for food use: "[z]ein (CAS Reg. No. 9010-66-6) is one of the components of corn gluten." It "is produced commercially by extraction from corn gluten with alkaline aqueous isopropyl alcohol containing sodium hydroxide. The extract is then cooled, which causes the zein to precipitate." Note that the terms corn gluten and corn gluten meal are used interchangeably in the technical literature. Any small amount of the sodium hydroxide remaining from pH adjustment would be allowed under §205.605(b).

Isopropyl alcohol and ethyl alcohol are the solvents used most widely to manufacture food grade zein. As mentioned earlier, isopropyl alcohol is a synthetic substance on the National List allowed for use in organic crop production, as is ethyl alcohol. Isopropyl alcohol is also an allowed synthetic substance for use in organic livestock production, as is ethyl alcohol. FDA regulates that isopropyl alcohol is a "secondary direct food additive permitted in foods for human consumption" in 21 CFR 173.240. According to FDA, "[a] secondary direct food additive has a technical effect in food during processing but not in the finished food (e.g., processing aid)." In the case of zein coatings, the secondary food additive is ethyl alcohol, which evaporates and so is no longer present in the food.

Corn gluten itself is a GRAS substance [21 CFR 184.1321]. The FDA provides this description of the commercial production of corn gluten:

> *"Corn gluten (CAS Reg. No. 66071-96-3), also known as corn gluten meal, is the principal protein component of corn endosperm. It consists mainly of zein and glutelin. Corn gluten is a byproduct of the wet milling of corn for starch. The gluten fraction is washed to remove residual water-soluble proteins. Corn gluten is also produced as a byproduct during the conversion of the starch in whole or various fractions of dry milled corn to corn syrups."*

An Organic Materials Review Institute (OMRI) publication describes the corn wet milling process as follows (Organic Materials Review Institute 2011):

> *"Corn is soaked, or 'steeped' in 120°F to 130°F water containing 0.1%-0.2% sulfur dioxide for 24-48 hours. The sulfurous acid formed induces chemical and physical changes in the kernel, in effect separating the starch and insoluble protein by cleaving protein disulfide cross-links in the endosperm protein matrix. The sulfurous acid also helps to control undesirable microorganisms and allows dissolved sugars to be converted to lactic acid, which helps to maintain a pH near 4.0. During the steeping process, about 6% of the dry weight is dissolved, which is then evaporated to condense the steepwater into corn steep liquor. The remaining insoluble corn kernel is then further processed to produce many products used in foods, livestock feeds, and fertilizers."*

In the corn wet milling process, sulfur dioxide reacts with disulfide bonds in insoluble proteins, severing them and reducing the molecular weight of the resulting proteins. When a molecule of sulfur dioxide reacts with a disulfide bond, it "adds" itself to the new bond, artificially increasing the sulfur content of the protein. Chemical analyses of the corn protein zein isolated from the CGM byproduct of the corn wet milling process show two measurable anomalies compared to "zein" isolated from corn gluten derived from untreated corn. The first anomaly is a lower molecular weight (Parris and Dickey 2001) and the second anomaly is a sulfur content that is greater than the sum of the contributions of the sulfur-containing amino acids in zein (Boundy et al. 1967). Both anomalies indicate that sulfur dioxide has chemically changed the protein in corn gluten meal and consequently in the extracted zein.

A method for wet milling corn that does not employ sulfur dioxide uses ozone (O_3) instead (Ruan et al. 2004). Using ozone to replace sulfur dioxide avoids sulfur dioxide discharge to the environment. Ozone is a strong oxidant and disinfectant that controls the growth of putrefactive microorganisms in steeping systems. However, like sulfur dioxide, ozone chemically changes the endosperm protein matrix to achieve starch release. The protein content of ozone-treated corn is lower than that of untreated corn, indicating that protein is being destroyed in the ozonation process (Wang 2005).

Another alternative method that does not employ sulfur dioxide steeping is enzymatic corn wet milling (E-milling) (Ramírez et al. 2009). This process uses protease (protein hydrolyzing) enzymes to eliminate the need for sulfites and decrease the steeping time. During periods of high corn feedstock costs, this process is cost-competitive with the conventional sulfur dioxide steeping process, but it is not cost-competitive in normal times.

Other potential raw materials are DDG (distillers dried grains) or DDGS (distillers dried grains with solubles), which are by-products of the dry-grind ethyl alcohol industry(Kwiatkowski et al. 2006). The dry-grind ethyl alcohol process includes exposure to high temperatures during jet cooking and subsequent drying, potentially reducing the zein yield. The dry-grind ethyl alcohol process also exposes the corn to enzymes and two chemical reagents for pH control (lime and ammonia), but no sulfites are involved.

Dry-milled corn (DMC) is water-tempered corn grits where the corn endosperm has been separated from germ and pericarp through the milling process (Rausch et al. 2009). It would appear to be a good raw material for zein extraction because it has not been exposed to high heat, which may affect the zein protein. However, DMC contains very little protein: only 6.8–8.0 percent of the total protein in the milled corn (Anderson and Lamsal 2011). Recall that zein accounts for 50 percent of the protein in corn.

A relatively recent alternative process to produce zein is based on ethyl alcohol extraction from ground corn at the beginning of the dry-grind process. This avoids chemical changes due to use of sulfur dioxide. (Anderson and Lamsal 2011; Cheryan 2002). However, zein produced by this process is not commercially available (Prairie Gold 2020). Presumably, zein produced by this process is not available due to higher production cost and the small market for this process.

<u>Evaluation Question #2:</u> Discuss whether the petitioned substance is formulated or manufactured by a chemical process, or created by naturally occurring biological processes (7 U.S.C. § 6502 (21)). Discuss whether the petitioned substance is derived from an agricultural source.

Zein is derived from an agricultural source, either corn or corn gluten meal. As mentioned earlier, the corn kernel protein zein has unusual and useful solubility characteristics: it is insoluble in water but soluble in aqueous alcohol. Consequently, every process for the extraction of zein from corn kernels or corn processing byproducts requires dissolving the zein in aqueous alcohol and separating the zein-containing solution from the other components of the corn that are not soluble in alcohol. Both ethyl alcohol and isopropyl alcohol are common solvents for zein extraction. Other substances currently on the National List that require isopropyl alcohol extraction are xanthan gum at §205.605(b) and gellan gum at §205.605(a). The petitioner indicates that their extraction process uses ethyl alcohol exclusively to extract zein from corn gluten.

The extraction phase of the zein manufacturing process itself creates no chemical change in the zein as described in the definition of "synthetic" under 7 U.S.C. § 6502 (21). However, if the zein protein in the corn gluten has been chemically treated with sulfur dioxide or ozone, the zein will have experienced chemical change. If the raw material has undergone only enzymatic treatment or other methods of processing enumerated at 7 CFR 205.2, the zein will not have been chemically modified. The standards for determining "synthetic" and "non-synthetic" have been established by NOP in *Guidance 5033 Classification of Materials* (NOP 5033) (USDA 2016c).

Corn gluten, the most common zein starting material, is produced in traditional wet-milling of corn—"corn steeping"—and the zein within this starting material reflects the chemical action of sulfur dioxide on corn protein that is integral to this process (Neumann, Wall and Walker 1984). In 2013, NOP received a comment responding to the 2013 Guidance 5034-1 proposal [Docket AMS–NOP–12–0060; NOP–12–14], pointing out the chemical changes noted above.

In 2016, NOP rendered the following decision on the synthetic/nonsynthetic classification of corn gluten (USDA 2016b):

> *"Corn Gluten. One commenter requested that corn gluten produced by wet corn milling be classified as synthetic, rather than nonsynthetic, due to chemical changes that occur during manufacturing. Other comments claimed that corn gluten is nonsynthetic. We have retained classification as nonsynthetic due to the historical consideration of corn gluten as nonsynthetic; however, further consideration of this issue may be warranted by the NOSB. Parties interested in further consideration of corn gluten are encouraged to submit a petition to the NOSB according to the National List petition guidelines."*

Zein extracted from ground corn kernels at the beginning of the dry-grind process or corn byproducts that have not been exposed to sulfur dioxide, ozone, or another reducing agent presumptively have not undergone chemical change.

<u>Evaluation Question #3:</u> If the substance is a synthetic substance, provide a list of nonsynthetic or natural source(s) of the petitioned substance (7 CFR 205.600(b)(1)).

As stated above, zein extracted from ground corn kernels at the beginning of the dry-grind process or from corn byproducts not exposed to sulfur dioxide, ozone, or other reducing agents are presumptively nonsynthetic. At least two such zein materials extracted from these sources were industrialized (Anderson and Lamsal 2011). For example, zein produced by ethyl alcohol extraction of ground corn taken at the beginning of the dry-grind process (corn grits) avoided chemical changes (Cheryan 2002). However, zein produced by these two processes is not commercially available.

<u>Evaluation Question #4:</u> Specify whether the petitioned substance is categorized as generally recognized as safe (GRAS) when used according to FDA's good manufacturing practices (7 CFR 205.600(b)(5)). If not categorized as GRAS, describe the regulatory status.

Zein is a food substance generally recognized as safe (GRAS) by FDA [21 CFR 184.1984] The full text of 21 CFR 184.1984 reads as follows:

> PART 184 -- DIRECT FOOD SUBSTANCES AFFIRMED AS GENERALLY RECOGNIZED AS SAFE
> Sec. 184.1984 Zein.
>
> (a) Zein (CAS Reg. No. 9010-66-6) is one of the components of corn gluten. It is produced commercially by extraction from corn gluten with alkaline aqueous isopropyl alcohol containing sodium hydroxide. The extract is then cooled, which causes the zein to precipitate.
>
> (b) The ingredient must be of a purity suitable for its intended use.
>
> (c) In accordance with 184.1(b)(1), the ingredient is used in food with no limitation other than current good manufacturing practice. The affirmation of this ingredient as generally recognized as safe (GRAS) as a direct human food ingredient is based upon the following current good manufacturing practice conditions of use:
>
> (1) The ingredient is used as a surface-finishing agent as defined in 170.3(o)(30) of this chapter.
>
> (2) The ingredient is used in food at levels not to exceed current good manufacturing practice.
>
> (d) Prior sanctions for this ingredient different from the uses established in this section do not exist or have been waived.
>
> [50 FR 8999, Mar. 6, 1985, as amended at 73 FR 8608, Feb. 14, 2008]

Zein also is allowed as an indirect food additive used as a component of adhesives [21 CFR 175.105].

<u>Evaluation Question #5:</u> Describe whether the primary technical function or purpose of the petitioned substance is a preservative. If so, provide a detailed description of its mechanism as a preservative (7 CFR 205.600(b)(4)).

The primary technical function or purpose of zein is not as a chemical preservative, but as a food coating that can enhance food quality. Because zein is water-insoluble, it helps prevent moisture loss from the food, thus preserving food quality. Similarly, because zein is water-insoluble, a coating of zein on a nutritional supplement or other "pharmaceutical dosage form" hinders moisture pickup that reduces potency and shelf-life.

<u>Evaluation Question #6:</u> Describe whether the petitioned substance will be used primarily to recreate or improve flavors, colors, textures, or nutritive values lost in processing (except when required by law) and how the substance recreates or improves any of these food/feed characteristics (7 CFR 205.600(b)(4)).

Zein used as a coating has no direct effect on flavors, colors, textures, or nutritive values. Its effects are akin to those of packaging that separates a food from detrimental elements in the environment. For zein, the detrimental element it protects against is moisture (water).

<u>Evaluation Question #7</u>*:* Describe any effect or potential effect on the nutritional quality of the food or feed when the petitioned substance is used (7 CFR 205.600(b)(3)).

As mentioned above, zein used as a coating has no direct effect on flavors, colors, textures, or nutritive value. It retards moisture loss or moisture absorption, depending on the application. Its effects are akin to those of a metal can or a glass jar that separates the contained food from detrimental elements in the environment that adversely affect nutritional quality. A thin coating of zein contains a small amount of protein of relatively poor nutritional quality (Calvez et al. 2020).

<u>Evaluation Question #8:</u> List any reported residues of heavy metals or other contaminants in excess of FDA tolerances that are present or have been reported in the petitioned substance (7 CFR 205.600(b)(5)).

The Food Chemicals Codex standard for zein requires heavy metal levels measured as lead of not more than 20 mg per kg (i.e., ≤20 ppm) and of not more than 5 mg per kg for lead itself (i.e., ≤5 ppm) (Committee on Food Chemicals Codex 1996). Reports of heavy metal contamination in zein above these standards were not found in the writing of this report.

<u>Evaluation Question #9:</u> Discuss and summarize findings on whether the manufacture and use of the petitioned substance may be harmful to the environment or biodiversity (7 U.S.C. § 6517 (c) (1) (A) (i) and 7 U.S.C. § 6517 (c) (2) (A) (i)).

Zein is extracted from CGM. In its evaluation of CGM as an herbicide ((Office of Pesticide Programs 2003)), EPA stated:

> ***"All required toxicology data for this biochemical pesticide are waived. No additional toxicological data are needed. The decision to waive these data are based on: 1) the product is naturally occurring, 2) possesses a non-toxic mode of action, 3) corn gluten meal is considered GRAS (Generally Recognized As Safe) by FDA under 21 CFR §184.1321, and can be used without limitations, other than current Good Manufacturing Practices, and 4) under 40 CFR §180.1164, corn gluten is exempted from the requirements of a tolerance on food when used as a herbicide; and under 40 CFR §180.1001 (d), corn gluten meal is exempted from the requirement of a tolerance when used as an attractant on crops. Further, the registrant's request for data waivers was appended with abstracts from scientific journals discussing the use of corn gluten meal as a food and/or feed for dairy and beef cattle, cats, minks, foxes, sheep, horses, swine, poultry, trout, salmon, catfish, guinea pigs, hamsters, monkeys, mice, rats, rabbits, and dogs."***

Zein itself has been considered GRAS (Generally Recognized as Safe) since about 1960 and this status was confirmed in 1981 (Select Committee of GRAS Substances (SCOGS) 1981).

Zein is a fully biodegradable, edible protein extracted from corn milling byproducts (primarily corn gluten, a GRAS substance) with an alcohol and applied to food as an alcoholic solution. The alcohols involved are isopropyl alcohol (a major ingredient in hand sanitizers) and ethyl alcohol (grain alcohol). Zein manufacturing processes are designed to recover and reuse the alcohol for both economic and environmental reasons. An analogous substance is the purified protein gelatin, extracted from animal processing waste products.

<u>Evaluation Question #10:</u> Describe and summarize any reported effects upon human health from use of the petitioned substance (7 U.S.C. § 6517(c)(1)(A)(i), 7 U.S.C. § 6517(c)(2)(A)(i)) and 7 U.S.C. § 6518(m)(4)).

The petitioner describes the customary use of zein as a 10 percent solution in 85 percent aqueous ethyl alcohol applied by spraying, dipping, or panning to a variety of foods, including confections, nuts, dried fruits and meats, fresh fruits and vegetables, nutraceuticals, baked goods, poultry, and frozen potatoes, at a rate of 0.5–6.0 percent of the zein solution to the food. The alcohol solvent vaporizes within a few seconds or minutes. At the highest application rate, the amount of zein in the final product would not exceed 0.6 percent (6 percent of a 10 percent zein solution), or no more than 3 grams per pound of food.

Zein should not be a major contributor of protein in the human diet. Zein protein has limited digestibility. Only about 60 percent of its amino acids are available in human feeding studies (Calvez et al. 2020). More importantly, its poor essential amino acid pattern also detracts from its nutritional value. Zein itself has been considered GRAS (Generally Recognized as Safe) since about 1960 and this status was confirmed in 1981 (Select Committee of GRAS Substances (SCOGS) 1981).

Evaluation Question #11: Describe any alternative practices that would make the use of the petitioned substance unnecessary (7 U.S.C. § 6518(m)(6)).

The petitioned substance zein is used primarily for coating certain foods and pharmaceutical dosage forms with a nonsynthetic edible film that prevents moisture exchange—the food contact packaging itself becomes a plant-based food. Edible coatings on fresh produce provide an alternative to modified atmosphere packaging and reduce quality changes and quantity losses through modification and control of the internal atmosphere of the individual fruit (Smith et al., 1987). Synthetic plastic packaging can be used to prevent moisture exchange, which then becomes plastic waste that must be disposed of. The advantage of a moisture-barrier made with zein is that, as a corn protein and food, it is edible and completely biodegradable.

Evaluation Question #12: Describe all natural (non-synthetic) substances or products which may be used in place of a petitioned substance (7 U.S.C. § 6517(c)(1)(A)(ii)). Provide a list of allowed substances that may be used in place of the petitioned substance (7 U.S.C. § 6518(m)(6)).

An edible coating or film is a thin, continuous layer of material formed or placed, on or between, foods or food components that provides a barrier to mass transfer, serves as a carrier of food ingredients and additives, or provides mechanical protection (Gennadios et al., 1993). In general, the terms films and coatings are used interchangeably, although there is a technical difference in that films are preformed and freestanding, whereas coatings are formed directly on the food product (Ustunol 2009). The petitioned substance is used for coatings.

Edible (i.e., natural) substances used for coating certain foods and pharmaceutical dosage forms with an edible film include insect-produced shellac, waxes, gums, alginates, and proteins such as zein. Any alternative to zein for these food-coating applications must satisfy several critical criteria to ensure equitable performance when compared with the petitioned substance. The alternative substance must be insoluble in water but must also be soluble in volatile organic solvents and be biodegradable. Finally, the alternative substance must also carry the same public perception of zein as a non-animal derived, vegan food coating.

One edible alternative to zein is shellac. Interestingly, zein became popular as the substitute for shellac when shellac became unavailable due to supply shortages during World War II. "Orange shellac unbleached" is listed on the National List at §205.606(o) as a nonorganically produced agricultural product allowed as an ingredient in processed products labeled as organic. Shellac is insoluble in water but only very slowly soluble in alcohol. It forms films and is approved by FDA for inclusion in food coatings and is used for coating confections and medicinal tablets (Budavari 1996). Orange shellac (unbleached) was reviewed in a 2002 Technical Advisory Panel report created for the NOSB (USDA 2002):

> *"Specific Uses: In food shellac is used as a coating agent, color diluent, surface finishing agent, glazing/polishing agent, and used in confectionery, food supplement tablets, as well as chewing gum. Additional uses are as a component of adhesives for food contact, in packaging, inks, pharmaceutical coatings, cosmetics, lacquers and varnishes for wood, floor polish, manufacture of buttons, stiffening of hats, finishing of leather (Budavari, 1996; Ash 1995; Martin 1982). Action: Shellac is used as an ingredient in edible fruit coatings to limit water loss and prevent desiccation and weight loss, and prevent entry of pathogens. Shellac coatings are fairly impermeable to oxygen*

and water, and form a barrier on the fruit surface that reduces gas exchange. Reduction in oxygen levels will reduce the rate of respiration of fruits and vegetables and prolong shelf life by delaying the oxidative breakdown of the product. This also causes reduced production of ethylene; which normally triggers further maturation and ripening. Shellac waxes are also added to provide high-gloss finishes to fruit for cosmetic purposes (FDA 2001; Hagenmeier 2000; Kaplan, 1986)."

Shellac has certain shortcomings. For example, an experimental polyethylene–candelilla-wax coating formulation was superior to both a high-gloss shellac and a wood resin citrus coating for storage of Valencia oranges (Hagenmaier 2000). Another shortcoming is its identity and the public image of this identity. Unlike zein, shellac is not generally perceived to be a food. It is "the resinous excretion of the insect *Laccifer lacca*…[which] suck[s] the juice of different resiniferous trees in India and excrete[s] 'stick lac' almost continuously" (Budavari 1996)—this also prevents its use in vegetarian diets.

The proteins most commonly used as edible films and coatings are collagen, gelatin, caseins, whey proteins, corn zein, wheat gluten, soy protein, egg white protein, myofibrillar protein, some oilseed or grain proteins, and keratin (Chiralt et al. 2018). Most of these plant and animal proteins are water-soluble. As Chen et al. noted, "Films and coatings based on these proteins have excellent gas barrier properties and satisfactory mechanical properties. However, the hydrophilicity of proteins makes the protein-based films present poor water barrier characteristics. The application of plasticizers and the corresponding post-treatments can make the properties of the protein-based films and coatings improved. The addition of active compounds into protein-based films can effectively inhibit or delay the growth of microorganisms and the oxidation of lipids" (Chen et al. 2019). In contrast, zein is hydrophobic and thus does not require additives.

Two consumer-sensitive labeling issues that influence the selection of a particular protein for a food coating are vegetarian compliance and "major food allergens." The Food Allergen Labeling and Consumer Protection Act of 2004 (FALCPA) (Public Law 108-282) requires the labeling of foods that contain a "major food allergen." Under FALCPA, a "major food allergen" includes foods such as milk, egg, wheat, peanuts, and soybeans; food groups such as fish, Crustacean shellfish, and tree nuts; and ingredients containing protein derived from one of the mentioned foods or food groups. Of the vegetable proteins in the above listing (i.e., zein, wheat gluten, and soy proteins), only zein is not considered a "major allergen." This is an advantage for coating a food that will be consumed by the general public.

Waxes can be used to form water-insoluble food coatings. The FDA allows three waxes as surface-finishing agents for food coating: yellow and white beeswax (21 CFR 184.1973), candelilla wax (21 CFR 184.1976), and carnauba wax (21 CFR 184.1978). Certified organic beeswax and organic carnauba wax are commercially available, while non-organic carnauba wax is on the National List at §205.606(a). According to the 2014 Technical Report for carnauba wax (USDA 2014), "Carnauba wax is used in organic food handling and processing as a component of fruit coatings (Plotto and Narcisco 2006), candy coating (Weigand 2013) and as a component of an edible coating for nuts (Mehyar, et al. 2012)."

Plotto and Narcisco provide the following relevant guidance on the use of waxes, which extends to other natural substances used in organic food handling:

"A thorough understanding of materials and ingredients used in organic processing is necessary to interpret the National List. For example, even though substances such as carnauba wax and wood rosin are allowed, they actually cannot be applied to a fruit as such unless they are formulated into microemulsions. Microemulsions used for waxes applied to fruits are made with a fatty acid such as oleic, linoleic, palmitic, myristic, and lauric acid, and a balancing counterion such as the hydroxides of ammonium, sodium or potassium, morpholine, or, in the past, triethanolamine (Baldwin 1994)."

There are challenges to formulating microemulsions that satisfy both organic and commercial viability requirements for waxes. A carnauba wax microemulsion containing the monoglyceride glycerol monolaurate showed markedly stronger inhibition of sweet potato root rot than a traditional carnauba wax coating. Glycerol monolaurate, however, is a material that is not allowed in or on organic products (Yang, Li and Lu 2018). A carnauba wax-based fruit coating for organically grown fruits and vegetables has been verified by OMRI as compliant with USDA National Organic Standards, but no compositional information is publicly available other than that it is based on carnauba wax.

Many gums have been used as components of edible coatings, including xanthan gum (Mei et al. 2002) and pullulan (Diab et al. 2001). Xanthan gum is listed on the National List at §205.605(b) and the NOSB has recommended that pullulan be listed at §205.605. In general, however, coatings made with gums are not moisture resistant.

Alginates are on the National List at §205.605(b) and are produced from various genera of brown algae. Protective coatings for tomatoes can be made with sweet orange essential oil and sodium alginate (Das et al. 2020). Tomatoes coated with an alginate-based edible coating significantly enhanced firmness up to 33 percent, decreased total mesophilic bacteria including Salmonella and Listeria, and reduced weight loss up to three-fold less than uncoated ones. Sensory analysis also revealed that the use of the edible coating increased the total acceptance scores of tomatoes. However, creating a suitable vehicle for depositing a coating containing alginate generally requires a multiplicity of ingredients, including calcium sources, antibiotics, plasticizers, surfactants, and more (Senturk Parreidt, Müller and Schmid 2018).

Evaluation Information #13: Provide a list of organic agricultural products that could be alternatives for the petitioned substance (7 CFR 205.600(b)(1)).

Organic beeswax and organic carnauba wax are two commercially available alternatives.

Focus Areas Requested by the NOSB

Manufacturing Process

1. *Provide a detailed explanation of the manufacturing process of this material which covers the extraction, production, and composition of the product as applied (specifically which solvents and the amounts required for application).*

The manufacturing process used to produce the petitioned substance does employ an extraction method which uses ethyl alcohol. The composition of the product as applied includes zein in an alcohol solution. For further details on this process, including the amount of solvent required for application, see *Evaluation Question #1*.

Report Authorship

The following individuals were involved in research, data collection, writing, editing, and/or final approval of this report:

- Richard C. Theuer, Ph.D., Independent Contractor
- Peter Bungum, M.S., Senior Technical Coordinator, The Organic Materials Review Institute (OMRI)
- Doug Currier, M.Sc, Technical Director, The Organic Materials Review Institute (OMRI)
- Lindsay Kishter, Director, Nexight Group
- Rachel Lanspa, Communications Consultant, Nexight Group

All individuals are in compliance with Federal Acquisition Regulations (FAR) Subpart 3.11—Preventing Personal Conflicts of Interest for Contractor Employees Performing Acquisition Functions.

References

Anderson, T. J., and B. P. Lamsal. "Zein Extraction from Corn, Corn Products, and Coproducts and Modifications for Various Applications: A Review." *Cereal Chemistry* 88.2 (2011). 159-73. doi:10.1094/CCHEM-06-10-0091

Baldwin, E. A. "Edible Coatings for Fresh Fruits and Vegetables. Past, Present, and Future." *Edible Coatings and Films to Improve Food Quality*. Eds. Krochta, J.M., E.A.; Baldwin and M.O. Nisperos-Carriedo. New York: Technomic Publishing Co., 1994. 25-64.

Boundy, J. A., J. E. Turner, J. S. Wall, and R. J. Dimler. "Influence of Commercial Processing on Composition and Properties of Corn Zein." *Journal of Agricultural and Food Chemistry* 44.281-287 (1967).

Budavari, S. *The Merck Index*. Twelfth Edition ed. Whitehouse Station, NJ: Merck & Co., Inc., 1996. Print.

Calvez, J., S. Benoit, J. Piedcoq, N. Khodorova, D. Azzout-Marniche, D. Tome, R. Benamouzig, G. Airinei, and C. Gaudichon. "Very Low Ileal Nitrogen and Amino Acid Digestibility of Zein Compared to Whey Protein Isolate in Healthy Volunteers." *Am J Clin Nutr* (2020). doi 10.1093/ajcn/nqaa274. <https://www.ncbi.nlm.nih.gov/pubmed/33021640>

Carter, R., and D. R. Reck. Low Temperature Solvent Extraction Process for Producing High Purity Zein. U.S. Patent 3,535,305. 1970.

Chen, H., J. Wang, Y. Cheng, C. Wang, H. Liu, H. Bian, Y. Pan, J. Sun, and W. Han. "Application of Protein-Based Films and Coatings for Food Packaging: A Review." *Polymers (Basel)* 11.12 (2019). doi 10.3390/polym11122039.

Cheryan, M. U.S. Patent No. 6,433,146: Corn Oil and Protein Extraction Method. U.S. 2002.

Chiralt, A., C. González-Martínez, M. Vargas, and L. Atarés. "18 - Edible Films and Coatings from Proteins." *Proteins in Food Processing (Second Edition)*. Ed. Yada, Rickey Y.: Woodhead Publishing, 2018. 477-500.

Committee on Food Chemicals Codex, Food and Nutrition Board, Institute of Medicine, National Academy of Sciences,. *Food Chemicals Codex, Fourth Edition*. Washington, D.C.: National Academy Press, 1996. Print.

Das, S., K. Vishakha, S. Banerjee, S. Mondal, and A. Ganguli. "Sodium Alginate-Based Edible Coating Containing Nanoemulsion of Citrus Sinensis Essential Oil Eradicates Planktonic and Sessile Cells of Food-Borne Pathogens and Increased Quality Attributes of Tomatoes." *Int J Biol Macromol* 162 (2020). 1770-79. doi 10.1016/j.ijbiomac.2020.08.086.

Flo Chemical Corporation. *Petition for the Addition of Zein to the National List.* Ashburnham, MA: Flo Chemical Corporation, 2020. https://www.ams.usda.gov/sites/default/files/media/Zein_Petition_2192020.pdf.

Hagenmaier, R. D. "Evaluation of a Polyethylene–Candelilla Coating for 'Valencia' Oranges." *Postharvest Biology and Technology* 19 (2000). 147-54. doi 10.1.1.838.6196&rep=rep1&type=pdf. <http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.838.6196&rep=rep1&type=pdf>

Kwiatkowski, J. R., A. J. McAloon, F. Taylor, and D. B. 2006. Johnston. "Modeling the Process and Costs of Fuel Ethanol Production by the Corn Dry-Grind Process." *Industrial Crops and Products* 23 (2006). 288-96. doi:10.1016/j.indcrop.2005.08.004

Neumann, P.E., J.S. Wall, and C.E. Walker. "Chemical and Physical Properties of Proteins in Wet-Milled Corn Gluten." *Cereal Chemistry* 61.4 (1984). 353-56. http://online.cerealsgrains.org/publications/cc/backissues/1984/Documents/chem61_353.pdf

Office of Pesticide Programs. "Biopesticides Registration Action Document: Glutens, Corn (Corn Gluten Meal) (Pc Code 100137) ". Ed. US Environmental Protection Agency: EPA, 2003. 24 <https://www3.epa.gov/pesticides/chem_search/reg_actions/registration/decision_PC-100137_4-Mar-03.pdf>

Organic Materials Review Institute. *Omri Position on Corn Steep Liquor*. Eugene, OR: Organic Materials Review Institute, 2011. www.omri.org/news/96333/omri-position-corn-steep-liquor.

Parris, N., and L. C. Dickey. "Extraction and Solubility Characteristics of Zein Proteins from Dry-Milled Corn." *J Agric Food Chem* 49.8 (2001). 3757-60. doi jf0011790 [pii]. <http://www.ncbi.nlm.nih.gov/entrez/query.fcgi?cmd=Retrieve&db=PubMed&dopt=Citation&list_uids=11513661>

Prairie Gold, Inc. 2020. Personal communication of Richard C Theuer with Prairie Gold, Inc. September 21, 2020. Phone call.

Ramírez, E. C., D. B. Johnston, A. J. McAloon, and V. Singh. "Enzymatic Corn Wet Milling: Engineering Process and Cost Model." *Biotechnol Biofuels* 2.1 (2009). 2. doi 10.1186/1754-6834-2-2.

Rausch, K. D., L. E. Pruiett, P. Wang, L. Xu, R. L. Belyea, and M. E. Tumbleson. "Laboratory Measurement of Yield and Composition of Dry-Milled Corn Fractions Using a Shortened, Single-Stage Tempering Procedure." *Cereal Chemistry* 86 (2009). 434-38. doi doi.org/10.1094/CCHEM-86-4-0434.

Ruan, R., H. Lei, P. Chen, S.. Deng, X. Lin, Y. Li, W. Wilcke, and G. Fulcher. "Ozone-Aided Corn Steeping Process." *Cereal Chemistry* 81.2 (2004). 182-87.

Select Committee of GRAS Substances (SCOGS). *Evaluation of the Health Aspects of Wheat Gluten, Corn Gluten, and Zein as Food Ingredients*. Bethesda MD: Federation of American Societies for Experimental Biology, 1981. Available from https://www.faseb.org/Portals/2/PDFs/LSRO_Legacy_Reports/1981_SCOGS%20II-12%20Wheat%20&%20Corn%20Gluten%20&%20Zein.pdf

Senturk Parreidt, T., K. Müller, and M. Schmid. "Alginate-Based Edible Films and Coatings for Food Packaging Applications." *Foods* 7.10 (2018). doi 10.3390/foods7100170.

Shukla, R., and M. Cheryan. "Zein: The Industrial Protein from Corn." *Industrial Crops and Products* 13.3 (2001). 171-92. doi https://doi.org/10.1016/S0926-6690(00)00064-9. <http://www.sciencedirect.com/science/article/pii/S0926669000000649>

U.S. Department of Agriculture (USDA). 2014. "Carnauba Wax Technical Evaluation Report." [January 2014] Available from https://www.ams.usda.gov/sites/https://www.ams.usda.gov/sites/default/files/media/waxes%20report%20201_4.pdf

--. 2002. "Orange Shellac (Unbleached) Technical Report." Available from https://www.ams.usda.gov/sites/default/files/media/Or%20Shellac%20Technical%20Advisory%20Panel%20Report%20%282002%29.pdf

--. 2016a. Guidance - Materials for Organic Crop Production. Available from https://www.ams.usda.gov/sites/default/files/media/NOP-5034-1.pdf

--. 2016b. Response to Comments - Materials for Organic Crop Production. Available from https://www.ams.usda.gov/sites/default/files/media/NOP%205034-3%20-%20Response%20to%20Comments.pdf

--. 2016c. Guidance-Classification of Materials. Available from https://www.ams.usda.gov/sites/default/files/media/NOP-5033.pdf

Ustunol, Z. "Edible Films and Coatings for Meat and Poultry." *Edible Films and Coatings for Food Applications*. Eds. Embuscado, M. E. and K. C. Huber. Dordrecht: Springer-Verlag, 2009. 245-68.

Wang, Yu. "Evaluation of Lutein and Protein in Ozone Treated Corn." Louisiana State University, 2005. Print.

Wilson, C. M. "Proteins of the Kernel." *Corn: Chemistry and Technology*. Eds. Watson, S. A. and P. E. Ramstad. St. Paul, MN: American Association of Cereal Chemists, 1987. 273-310.

Yang, H., X. Li, and G. Lu. "Effect of Carnauba Wax-Based Coating Containing Glycerol Monolaurate on Decay and Quality of Sweet Potato Roots During Storage." *J Food Prot* 81.10 (2018). 1643-50. doi 10.4315/0362-028x.Jfp-18-017.