United States Green Chemistry Challenge Awards Program

Project Title: Generally Recognized As Safe ("GRAS") Coatings

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I. **Abstract:** Using materials that are generally regarded as safe – GRAS - for human consumption, we have developed coatings which can be applied to food or used in food packaging. Our GRAS coatings protect food from outside elements, are safe for human consumption and use natural ingredients without any plastics or other chemicals derived from fossil fuels. GRAS coatings have barrier properties to air, water and solvents which will allow them to replace coatings originating from fossil fuels, especially plastics made using acrylates and methacrylates. GRAS coatings have the potential to make food packaging "greener" and more sustainable through the elimination of toxic plastics and will enable an increase in recycling of food packaging.

II. **Patent Application:** Because we believe that this technology is novel and unique, in 2010, Ecology Coatings filed a WCT patent application for its GRAS coatings - PCT/US10/44011.[1] The U.S. Patent Office in May 2011 agreed the claims made by Ecology were indeed novel, non-obvious and have industrial utility, corroborating the unique nature of the technology. This action allows Ecology to file for accelerated patent approval which is expected in 2012.

Ecology Coatings has been awarded five other patents and has a sizable trade secret portfolio.

III. **Milestones:** The patent application is pending. An article discussing the technical aspect of our GRAS coatings was published in the May 2010 issue of *Paint & Coatings Industry* magazine. The article can be found here: Bio-Based Materials For UV-Cured Coatings. We are engaged in testing the technology with several potential customers.

IV. **Award Category U.S. Nexus:** We believe our GRAS coatings also fall within "Design of Greener Chemicals" category. We are a startup headquartered in Warren, Michigan with eight employees and modest revenues thus far. Most of our research has occurred in our Akron, Ohio laboratory. We clearly fall within the "Small Business" Award Category.

We expect GRAS coatings to have a positive effect on health in the United States by reducing toxic chemicals used in food packaging used by U.S. residents. In addition, when these components are substituted for those with potential toxicity, less toxic waste will be introduced into the environment.

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[1] Ecology's patent application can be found by searching the U.S. PTO website at: http://portal.uspto.gov/external/portal/pair.

The science in the use of GRAS materials is completely original. When examination was done for the PCT patent, no prior art was discovered. The chemical mechanisms, however, are well known. Sulfhydral bridges from sulfur containing amino acids such as cysteine are made available as proteins are opened by denaturization with a lower pH.
Cys-S -H +H-S-Cys in the presence of $2H^+ \rightarrow$ Cys-S-S-Cys. Crosslinking is accomplished by the use of UV light. Previous research has shown that other forms of radiation, such as gamma, can cause this type of crosslinking in these types of proteins. Reference: The Effect of Irradiation on the Molecular Properties of Egg White Protein, Food Sci. Biotechnol., Vol 9, No 4, pp. 239-242 (2000).

The scientific claims from the GRAS patent application are shown below:

1. A method for preparing a coated article, comprising:
   (a) coating a substrate with a composition comprising:
      (i) a polypeptide, wherein the polypeptide is selected from: albumin, transferring, ovomucin, lysozyme, cystein, or combinations thereof, and
      (ii) a denaturing agent; and
   (b) curing and cross-linking the composition by exposing the composition to shortwave actinic radiation to form a coated article;

wherein the temperature of the composition during the curing process is less than about 70°C; and wherein the composition does not coagulate during the curing process.

2. The method of claim 1, wherein the composition further comprises a polar solvent.
3. The method of claim 1, wherein the polar solvent is water.
4. The method of claim 1, wherein the composition is safe for human consumption, safe for contact with food, or a combination thereof.
5. The method of claim 1, wherein the curing comprises exposing the composition to actinic radiation having a wavelength from about 200 nm to about 400 nm.
6. The method of claim 1, wherein the curing comprises exposing the composition to actini radiation having a wavelength of about 280 nm.
7. The method of claim 1, wherein the composition further comprises an acid.
8. The method of claim 1, wherein the composition further comprises: 2,3-dihydroxysuccinic acid; ethanoic acid; 3-hydroxypentanedioic acid; salts thereof; partial salts thereof; or combination thereof.
9. The method of claim 1, wherein the polar solvent has pH of about 7 or below.
10. The method of claim 1, wherein the composition further comprises a natural gum, a flavoring agent, a dye, a de-foaming agent, or a combination thereof.
11. The method of claim 1, wherein the composition further comprises maltodextrin, an oil, or a combination thereof.
12. The method of claim 1, wherein the substrate is paper, plastic, metal, food, or a combination thereof.

13. The method of claim 1, wherein the polypeptide is provided in the form of a powder.

14. A coated article comprising:

(a) a substrate; and

(b) a polypeptide composition, wherein the polypeptide composition comprises a a polypeptide composition, wherein the polypeptide composition comprises a polypeptide selected from: albumin, transferrin, ovomucin, lysozyme, cysteine, or combinations thereof coating the substrate; and

wherein the polypeptide composition is cross-linked after coating the substrate; and wherein the polypeptide compositions not coagulated.

15. The coated article of claim 14, wherein the polypeptide composition further comprises a polar solvent.

16. The coated article of claim 14, wherein the polypeptide composition further comprises water.

17. The coated article of claim 14, wherein the polypeptide composition further comprises a denaturing agent.

18. The coated article of claim 14, wherein the polypeptide composition is safe for human consumption, safe for contact with food, or a combination thereof.

19. The coated article of claim 14, wherein cross-linking the polypeptide composition comprises exposing the polypeptide composition to shortwave actinic radiation.

20. The coated article of claim 14, wherein cross-linking the polypeptide composition comprises exposing the polypeptide composition to actinic radiation having a wavelength from about 200 nm to about 400 nm.

21. The coated article of claim 14, wherein cross-linking the polypeptide composition comprises exposing the polypeptide composition to actinic radiation having a wavelength from about 280 nm.

22. The coated article of claim 14, wherein the polypeptide composition further comprises an acid.

23. The coated article of claim 14, wherein the polypeptide composition further comprises: 2,3-dihydroxysuccinic acid; ethanoic acid; 3-hydroxypentanedioic acid; salts thereof; partial salts thereof; or combinations thereof.

24. The coated article of claim 14, wherein the polar solvent has a pH of about 7 or below.

25. The coated article of claim 14, wherein the polypeptide composition further comprises natural gum, a flavoring agent, a dye, a de-foaming agent, or a combination thereof.

26. The coated article of claim 14, wherein the polypeptide composition further comprises maltodextrin, an oil, or a combination thereof.

27. The coated article of claim 14, wherein the substrate is impregnated with the composition.

28. The coated article of claim 14, wherein the substrate is paper, plastic, metal, food, or a combination thereof.

29. The coated article of claim 14, wherein the polypeptide is in a form of a powder.

30. A method for preparing a coated article, comprising:

(a) coating a substrate with a composition comprising:

(i) a monomer, an oligomer, or a combination thereof, and

(ii) a polypeptide, wherein the polypeptide is selected from: albumin, transferrin, ovomucin, lysozyme, cysteine, or combinations thereof; and

(b) curing and cross-linking the composition by exposing the composition to shortwave actinic radiation to form a coated substrate;

wherein the temperature of the composition during the curing process is less than about 70° C; and wherein the composition does not coagulate during the curing process.

31. The method of claim 30, wherein the composition is safe for human consumption, safe for contact with food, or a combination thereof.

32. The method of claim 30, wherein the monomer is trimethylolpropane triacrylate (TMPTA), ethoxylated TMPTA (TMPTEOA), tripropylene glycol diacrylate (TRPGDA), or a combination thereof.

33. The method of claim 30, wherein the oligomer is epoxy diacrylate.

34. The method of claim 30, wherein the composition further comprises: a photoinitiator, a diluent, a surfactant, a pigment dispersion, a natural gum, a dye, a de-foaming agent, or a combination thereof.

35. The method of claim 30, wherein the composition further comprises maltodextrin, an oil, or a combination thereof.

36. The method of claim 30, wherein the curing comprises exposing the composition to actinic radiation having a wavelength from about 200 nm to about 400 nm.

37. The method of claim 30, wherein the curing comprises exposing the composition to actinic radiation having a wavelength of about 280 nm.

38. The method of claim 30, wherein coating comprises impregnating the substrate with the composition.

39. The method of claim 30, wherein the substrate is paper, plastic, metal, food, or a combination thereof.

40. The method of claim 30, wherein the polypeptide is in the form of a powder.

41. A coated article comprising:

(a) a substrate; and

(b) a composition coating the substrate comprising:

(i) a cross linked monomer, oligomer, or a combination thereof, and

(ii) a polypeptide selected from albumin, transferrin, ovomucin, lysozyme, cysteine, or combinations thereof;

wherein the composition is cross-linked after coating the substrate, and wherein the composition is not coagulated.

42. The coated article of claim 41, wherein the composition is safe for human consumption, safe for contact with food, or a combination thereof.

43. The coated article of claim 41, wherein the monomer is trimethylolpropane triacrylate (TMPTA), ethoxylated TMPTA (TMPTEOA), tripropylene glycol diacrylate (TRPGDA), or a combination thereof.

44. The coated article of claim 41, wherein the composition further comprises: a a diluent, a surfactant, a pigment dispersion, a natural gum, a flavoring agent, a dye, a de-foaming agent,

or a combination thereof.
45. The coated article of claim 41, wherein the composition further comprises maltodextrin, an oil, or a combination thereof.
46. The coated article of claim 41, wherein cross-linking the composition comprises exposing the composition to shortwave actinic radiation.
47. The coated article of claim 41, wherein cross-linking the composition comprises exposing the composition to actinic radiation having a wavelength from about 200 nm to about 400 nm.
48. The coated article of claim 41, wherein cross-linking the composition comprises exposing the composition to actinic radiation having a wavelength of about 280nm.
49. The coated article of claim 41, wherein the substrate is impregnated with composition.
50. The coated article of claim 41, wherein the substrate is paper, plastic, metal, food, or a combination thereof.
51. The coated article of claim 41, wherein the polypeptide is provided in the form of a powder.

GRAS COATING POTENTIAL USES:

I. COATING AS A PHOTOINITIATING FILM FORMER:

SUMMARY: Our GRAS coating uses mixtures of proteins available in food that can be used as a self-photoinitiating film former. To make natural proteins available for cross-linking, they can be relaxed or denatured using a mild acid available in food such as lemon juice. When cured at a rate of up to 400 feet per minute using 300 – 600 Watt UV lamps, polymerizing occurs resulting in a coating with barrier properties to air, solvents, water or grease.

Our GRAS coating can be used to coat a substrate using (i) a polypeptide, where the polypeptide - albumin, transferrin, ovomucin, lysozyme, cysteine, or combinations thereof - (ii) a denaturing agent; and (iii) curing and cross-linking the composition by exposing the composition to shortwave actinic radiation (UV) from 200 nm to about 400 nm to form a coated article. The coating uses water as a polar solvent with a pH of 7 or below. The coating can also use a natural gum, a flavoring agent, a dye, a de-foaming agent, or a combination thereof. The composition can also use maltodextrin, an oil, or a combination thereof.

USES: There are many potential uses of our GRAS coating. For example, because it is essentially "food" and edible, it can be used as a coating on dried fruit. The barrier properties of the GRAS coating will inhibit oxygen exposure of the fruit which will extend its shelf life. GRAS coating would also be useful on food wrapping – such as deli meat, cookies, muffins and desserts. Since the barrier properties of the coating will resist grease, the food will be presented in a cleaner, more appealing package. Most importantly, since none of the ingredients would be viewed by the FDA as an adulterant, these coatings may form grease barriers inside packaging, substituting for polyethylene or other petroleum based products.

II. GRAS COATING AS A PHOTOINIATOR:

SUMMARY: Our GRAS coating can be also used photoinitiator with conventional UV-curable materials which can have direct contact with food such as the monomers trimethylolpropane triacrylate (TMPTA) and trimethylolpropane ethoxylate triacrylate (TMPEOTA). These monomers have been approved by the FDA for direct food contact under Food Contact Notification 772 on March 7, 2008.

USES: UV curable inks and coatings are used on many types of food packaging including cereal boxes. Photoinitiators from these coatings have been found as adulterants in food. The substitution of a GRAS photoinitiator will alleviate this problem.

III. GRAS COASTING USED TO EXTEND PIGMENT COVERAGE:

SUMMARY: Our GRAS components, when used in a powdered form, can be used to extend the coverage of pigments while promoting – rather than interfering with - the UV-curing process. Silica fillers are used for this purpose. These fillers, when inhaled, can cause silicosis. They can also present an explosion hazard when fine dusts in air pick up a static charge. These fillers also interfere with cure, requiring more energy. We substitute a safer and more energy efficient filler for these silicas.

USES: The uses are many and varied from pigmented coatings on metal to textured coatings on plastics. One use being explored is textured coatings for food preparation surfaces.

IV. GRAS COATING USED AS A MATTING AGENT:

SUMMARY: Our coating can be used as a matting agent, curing into the finished film and enhancing the UV-curing process. When combined with other bio-based additives, the coating can produce a rough surface that still resists water or grease migration.

USES: Silcas are also used as matting agents. Matting agents scatter light, reducing the gloss of a coating. Our GRAS components can substitute for the silicas with the advantages cited above for a pigment extender. Matting agents are used to give many UV coatings a flatter, richer appearance. Our GRAS materials may be used in many ways to improve health and reducing hazards. Health is improved by reducing adulterants in food through the use of safer components for coatings that may have direct or indirect contact with food. The use of silicas and petroleum products may be reduced. Energy usage may be reduced as well. These materials present a truly innovative approach to the field of UV curable coatings. The development of these materials for the use in a variety of consumer products can open the door to growth, jobs, and a healthier environment.