

**POLYMERIC FILM FOR AGRICULTURAL PRODUCT STORAGE,
CONTAINERS MADE THEREFROM AND RELATED METHODS OF
AGRICULTURAL PRODUCT STORAGE**

Inventor: Rachel Dove

FIELD OF THE INVENTION

[00001] The present invention relates to polymeric laminate materials and more particularly to polymeric laminate materials exhibiting functional properties. The present invention further relates to barrier and cushioning films, in particular, barrier and cushioning films exhibiting functional properties proving advantageous for the management of adverse conditions, pertaining particularly, but not limited to, food storage. The present invention further relates to cushioning films in which the chambers contain active ingredients to be deployed on contact. The present invention further relates to the lamination of the cushioning film for increased functional properties.

BACKGROUND OF THE INVENTION

[00002] Polymeric laminates exhibiting functional properties have a wide variety of applications in multiple industries ranging from healthcare to modified atmosphere packaging to construction and others. For the purposes of the present invention, more specifically, food storage, recent technological advancements in flexible packaging and barrier films provide stored product and end user benefits such as moisture absorbency, odor absorbency, odor blocking, oxygen transmission and water vapor transmission management, all of which contribute to maintaining freshness and resisting contamination.

[00003] Post harvest practices have significant outcomes in human and animal health as well as agribusiness and the economic sustenance of farmers and overall food security. Poor handling, poor storage, insect infestations, mold, bacteria, fungus and or other contaminants pose significant health risks when contained within foodstuffs intended for human or animal consumption. Post harvest losses resulting in such infestations significantly hinder income generation, more specifically for small-scale farmers in Sub-Saharan Africa. "In Tanzania, maize losses of up to 35% may occur due to *Prostephanus truncatus* (Larger Grain Borer) within 5 to 6 months if improperly stored (Mallya, 1992) and up to 60% losses may occur after 9 months of storage (Keil, 1988), a situation which may result in serious famine" according to the FAO's Paper on Insect Damage, Post Harvest Compendium. In Kenyan highlands, total losses due to pests in maize were estimated at 57% with insects being more important than disease (Grisley, 1997). In Zimbabwe, grain damage of 92% in stored maize was reported due to insect pests, treatment with malathion reduced damage by only 10% (Matrio, et al. 1992). Infestations of stored cowpeas can be as high as 90% in markets and in village stores (Alabeek, 1996). A wide variety of food stuffs are affected by insects, mold and fungi infestation is not limited to maize grains and pulses. Insect pests, in addition to fungal diseases, are responsible for 50% damage in cassava (Maninek, 1994). Losses of up to 70% in dried cassava roots after 4 months of storage were reportedly due to *P. truncatus*. (Hodges, et al., 1985).

[00004] Insect pests inflict their damage on stored products mainly by direct feeding. Some species feed on the endosperm, causing loss of weight and quality, while other species feed on the germ, resulting in poor seed germination and less viability

(Malek & Parveen, 1989; Santus, et al. 1990). In addition to direct consumption of the product, insect pests contaminate their feeding media through excretion, molting, dead bodies and their own existence in the product, which is not commercially desirable. Damage done by insect pests encourages infection with bacteria and fungal disease through transmission of their spores (Cravedi & Quaroni, 1982; E. Kundayo, 1988; Dunkel, 1980). The presence of insects also raises the stored product temperature, due to their feeding activity, resulting in hot spots (Appert, 1987; Mills, 1989). These "hot spots" can lead to condensation and excessive moisture, resulting in the growth of mold or fungi. Insects' activity can have profound effects on the spread of fungal diseases through transmitting the spores and increasing the surface area susceptible to fungal infection, which eventually increases production of mycotoxins (Dunkel, 1988).

[00005] Despite the physical damage of insect pests, infestations resulting from poor post-harvest storage can have economically devastating effects on farmers, communities, and the economies of several countries and ultimately international food security, depending on exportation of maize, wheat and other food stuffs. For example, *P. truncatus* cost Tanzania roughly US \$91 million annually in lost maize intended for consumption or export (Bionet International & Global Invasion Species Program). Farmers in sub-Saharan Africa are frequently forced to sell stored produce prematurely because of the deterioration due to insect damage that occurs if storage periods are extended (Global, et al. 1996, Brice et al. 1996, Marsland & Golob 1996, Donaldson, et al., 1996). Inability to store and protect post-harvest leads to significant income reduction as farmers do not have the flexibility to wait for the higher price as the market fluctuates. The combined difficulties of on-farm food storage and the economic burden

of post-harvest loss are devastating for farmers in developing countries, particularly due to the lack of available resources for building insect and rodent proof storage units, the lack of information regarding insecticide/pesticide use, as well as lack of affordability for materials which can mitigate external environmental and climatic conditions.

[00006] On-farm storage difficulties and post-harvest losses occur mainly as a result of temperature, moisture, respiration of stored contents, infestation of insects, infestation of rodents and fumonisins, mycotoxins and aflatoxins resulting from mold and fungi growth, due to lack of oxygen transmission and water vapor transmission of storage containers presently employed. Whether intended for human consumption, or used as animal food stock, stored product contamination poses serious health risks. Aflatoxin consumed by dairy cattle, though altered in their body, still remains toxic and shows up in the milk (Christensen & Meronuck, 1986, Gwinner, et al., 1996). *A. fumigatis* is report to result in high levels of abortion in cattle feeding on contaminated food; also infects human lungs (Darwish, et al., 1991; Pandey & Prasad 1993; Abud, et al., 1995).

[00007] The use of plastic sacks, bag storage, prefabricated iron halls and flexible plastic silos are increasingly gaining ground among farmers for short term storage (Peterson & Simila, 1990; Compton, et al., 1993; Bartali, 1994). However, none of the current storage mechanisms effectively manage the comprehensive set of factors including moisture management, barrier to or effective transmission of oxygen, and contact release mechanisms for active ingredients, which more specifically, when properly released, promote desired effects such as but not limited to insect and or rodent repellency and or moisture management and or bacteriostatic or fungicidal properties..

[00008] Accordingly, there remains a need for improved polymeric materials for

maintaining acceptable and FAO recommended moisture levels for stored product and on-farm storage of dry foodstuffs to obtain optimal storage conditions for the prevention and reduction of post harvest losses.

[00009] In addition, there remains a need for effective dosing of insecticides or pesticides within a laminate structure, such as that used in a food container.

[00010] Polymeric laminates which have raised portions, membrane structures, air pockets, gaps, quilting, pillowing, three dimensional raised, conical, round, honeycomb membranes and different shapes, dimensions, and interconnected air pathways contained within the laminates have a wide variety of uses and was patented in July, 1968, US Patent Number 3,142,599, Method for Making Laminated Cushioning Material, becoming trademarked and commonly known as “Bubble Wrap,” from which the product line has expanded to include films exhibiting functional properties such as anti-static and anti-flammability.

[00011] Patents exist for the encapsulation of Holiday confetti and graffiti, associated holiday prints, as described in US Pat. No. 20100143614 “Holiday and Event Bubble Wrap” and holiday-inspired or event-themed scents for bubble wrap as seen in Patent No. 806255 filed on 02/21/1997, “Scented Bubble Wrap” as well as multiple patents detailing differences in pocket structure, load strength and wall thickness of the air pocket, bubble dimension and shape and interconnectedness of air pockets, air pathways, structural design and incorporation into other containment units and free standing containment units.

[00012] The foregoing patents are hereby incorporated herein by reference.

[00013] However, there exists no prior art which uses the air pocket as a contact

release mechanism for releasing substances to include but not limited to active ingredients in whatsoever state such as vapors, liquids, oils, pheromones, gels, hydrogels, gases or gaseous components, solids, waxes, powders or particulates of whatsoever size, admixtures and combinations of either chemical, inorganic, and or organic materials and or derivatives of natural or synthetic materials whatsoever for the purposes of managing adversities related to stored product conditions.

[000014] Such laminates which exhibit contact release mechanisms, with or without a barrier layer or alternative laminate substrate, may be used for the storage of agricultural products and the like, such as harvested grain, maize, cowpeas and silage, whereby such laminates function as mechanical barriers to pests, rodents and insects while mitigating the effects of temperature and humidity variations, stored product transpiration and moisture management as a result of contact pressure which enables the release of the food-safe active ingredient contained within the air cushioned membrane .

[000015] There are several concomitant problems attendant to on-farm storage of dry foodstuffs (e.g., grain and maize), such as water ingress and the subsequent moisture accumulation in the surface layer of the grain adjacent the innermost layer of the container and the effects of external temperature and humidity on internal stored product atmosphere, creating conditions for mold, fungus, and bacteria contamination and the resulting toxins such as aflatoxin, mycotoxins and fumosins.

[000016] Free-standing storage units for bagged agricultural commodities are prone to both insect and rodent infestation. Insect infestation may exacerbate the proliferation of mold and fungal growth due to the insect's respiration, excretions, and transmission and further distribution of the mold, fungal, and bacterial spores while migrating through

the stored product. Accordingly, it is beneficial to provide on-farm storage containers that prevent or reduce both infestation and manage moisture transmission to prevent fungal growth. To reduce fungal growth, the containers should maintain some degree of oxygen permeability in a manner which permits complementary moisture vapor diffusion or a form of hermetic storage with use of the novel substrate detailed herein as a component of a hermetic approach whereby the polymeric layer either retains moisture or functions to achieve acceptable levels of difference between external and internal temperatures and relative humidity to prevent moisture accumulation and its related effects such as hot spots and areas of decomposing foodstuff due to centralized moisture.

[000017] In the preparation of polymeric materials of this type for these purposes, there has been a deficiency in the prior art to attempt to manage the adverse effects of combined infestations of insects of differing speciation and or rodent populations as well as fungal, bacterial and mold proliferations for stored products observing the storage condition parameters recommended by the FAO for foodstuffs intended for human or animal consumption with relation to moisture content at time of storage.

[000018] In the preparation of polymeric material of the air cushioned, chambered, quilted, raised, textured or three dimensional type whatsoever, there has been a deficiency in the prior art to encapsulate an active ingredient for the purposes of promoting a desired effect as a result of penetrating the bubble or raised portion for the controlled-by-contact release of the active ingredient, ingredients, or combinations thereof, more specifically for the controlled release of active ingredients which, when employed, have a desired effect to promote optimal conditions for the protection of stored products, more specifically, dry foodstuffs.

SUMMARY OF THE INVENTION

[000019] It is therefore an object of the present invention to provide a new polymeric laminate incorporating, encapsulating or otherwise containing active ingredients released on contact so as to bring about the intended effect of the active ingredient at the time of, during, or as a result of its release via penetrative contact.

[000020] The present invention features the use of air cushioned film encapsulating or otherwise containing active ingredients or bioactive substances or components thereof specifically for the purpose of a release by penetration either used singularly, as an insert, and or in combination with polymeric films incorporated, coated, laminated, infused, coextruded or somehow containing active ingredients to provide one of the following or a combination of the following for the distinct purpose of promoting or contributing to the promotion of a desired effect; moisture management, oxygen transmission, water vapor transmission, fungal, bacterial and mold growth inhibitors or scavengers of whatsoever nature, and insecticides of whatsoever nature and class or family, whether natural or synthetic, to include but not limited to, insect sterilization, excito-toxins, dessicants, pheromones, attractants, scents, and rodent repellents of whatsoever nature as well as additives contributing or pertaining to material properties such as UV blockers or stabilizers, colors, or additives of whatsoever nature.

[000021] The present invention includes multilayer structures, laminates, co-extruded films or substrates and or air cushioning films and or three dimensional films having raised, quilted or pocketed structures or texturized substrates of whatsoever nature, encapsulating active ingredients which are released on contact by penetration of the raised portion, such laminates may be employed for use as films singularly, as liners,

inserts, special placement strips, or additional components to existing storage mechanisms, as multi-dimensional laminates combining one or more polymer layer, or manufactured as containers comprising the same for the storage of agricultural products and the like either for human or animal consumption such as harvested grain, maize, silage and feedstock as well as methods of storing foodstuffs for a period of time to permit on-farm storage and ultimately to promote the subsequent economic benefits related to timely market approach.

[000022] In another aspect of the present invention, there is provided a polymeric laminate comprising adapted to contact an insect of a given dimensional shape with a dose of an insecticide: an innermost layer comprising a bubble plastic thermoplastic polymeric material layer comprising bubbles containing at least one insecticide, the bubbles having a shape and an inter-bubble distance adapted to resist the movement of the insect thereabout. The bubbles may face inward or outward, and may also be incorporated as a double layer.

[000023] In this regard, it has been found that the shape, size and/or inter-bubble distance can be chosen so as to resist the movement of the insect about the bubbles, so as to relatively increase the resident time the insect spends within a gnawing distance from the bubble(s). Because many boring insects will continue to gnaw or bore into nearby material, it is desirable to tune these parameters based upon the physical dimensions of the target insect(s) to make the spatial environment more difficult for the insect(s) to navigate.

[000024] In a preferred embodiment, the insecticide is in powder form, and preferably comprises a material selected from the group consisting of diatomaceous earth and cuticle desiccants.

[000025] It is also preferred that the burst strength of the thermoplastic bubbles of the bubble plastic thermoplastic polymeric material allows the insect to burst the thermoplastic bubbles so as to expose the insect to the at least one insecticide. Although the bubble layer may be made of any suitable polymeric material designed to allow the insect to gnaw, bore or otherwise pierce, preferably the bubble plastic thermoplastic polymeric material comprises a polymer selected from the group consisting of LDPE, LLDPE, VLDPE and may include one or more of the other thermoplastic group of polymers.

[000026] It is a further object of the present invention to provide a new polymeric laminate which has the capacity to exhibit multifunctional properties while providing an effective barrier to pests and insects indiscriminate to the type of insect and food product stored, as a result of having taken into account varying speciation and or diverse infestations and or erratic insect behavior resulting in the discovery of a variety of novel and interconnected parameters directly contributing to the effectiveness of the film's mechanical barrier to include but not limited to; the depth and width of the depressed channels in between the raised air pockets of the film in relation to the thoracic dimensions, mandible positioning and or mode of feeding, mandible strength and mouthpart construction, leg span, thrusting capacity, mobility, flexibility and maneuverability, tenacity, and overall interaction of the insect with the textured substrate such as scratching, burrowing, as well as the impacts of penetration to include but not

limited to, the rate of penetration of the raised portion upon differing techniques and methods of penetration and the subsequent rate of active ingredient release and volume in relation to the insect body dimensions, the differences in penetrability of different shapes due to mandible positioning and insect dimensions and thus maneuverability, and other mechanical properties distinct to the construction and properties described herein which act as the initial barrier before the active ingredient release.

[000027] It is a further object of one variation of the present invention to provide a method of entrapment and or reactions whatsoever which alter and or impede the maneuverability of the insect, immediately prior to, upon, during or shortly thereafter the release of the active ingredient, especially on insects whose mode of infestation are tenacious and persistent whereby the innate behavior of such insects will cause their entrapment, exposure to a laminate-incorporate insecticide or pesticide, and ultimate suffocation within the singular celled air pockets.

[000028] It is yet another object of another variation of the present invention to allow, in some embodiments, the encapsulation of a variety of one or more active ingredients to be released on contact by penetration and this may or may not, depending on the climactic and existing storage conditions and insect speciation present in the environment in which the film is to be deployed, require the dosing of multiple active ingredients in one air pocket, or singular air pockets containing singular active ingredients yet located in close proximity or adjacent to air pockets which may contain an alternative singular active ingredient or a combination of different active ingredients so that one film may contain either multiple air pockets encapsulating singular active ingredients, or selected air pockets may contain multiple active ingredients, while other

air pockets may contain no active ingredients.

[000029] It is yet another object of still another embodiment of the invention to provide insect-specific shape, volume, height, and strategic positioning of the air pockets within an array so that interconnectedness of air pathways can, if desired, distribute active ingredients in a pre-determined manner or in exact locations for increased effectiveness upon release.

[000030] It is yet another object of the invention to provide for a mix-on-release capacity whereby the air pockets containing one active ingredient and air pockets containing alternative ingredients can be, if such outcome is desired, interconnected via air pathways to allow for simultaneous penetration whereby the separate active ingredients are mixed upon release.

[000031] Films of the present invention and those of slight variation described herein may also find beneficial use in building applications, such as in grain storage facilities, such as in grain or food storage warehouse floor applications, ceiling or easement coverings, or for use within residential construction to mitigate infestation while providing insulation,.

[000032] A related embodiment of the present invention may also include a polymeric film used as a wrap deployed around tree trunks as barriers to burrowing wood pests and other forest diseases with the alternative active ingredients or combinations of active ingredients exhibiting properties including to but not limited to repellency, sterilization, growth regulation, contact killer, cuticle dessicant, propagate or other type of active ingredient or any mixtures or combinations whatsoever whether natural or synthetic or mechanically or chemically manipulated, for specific applicability and

effectiveness with consideration to the vector strain, speciation, insect behavior, resistance, reproduction, mode of action, etc as well as the modifications required for material properties to withstand environmental conditions and application requirements.

[000033] Another related embodiment of the present invention may be polymeric film substrates dosed with active ingredients for contact release to include but not limited to fertilizers, agricultural inputs, pesticides, herbicides, and or other active ingredients whereby direct release of active ingredients enhances or somehow imparts desired results to include but not limited to soil quality, enriches plant nutrient uptake, or other beneficial properties on contact release, such films may be used underneath the soil as a catchment unit or as a protective covering.

[000034] The polymeric substrate and combinations thereof of the present invention may be produced by coextrusion, coextrusion blown film, double bubble blown film, texturized geomembrane film extrusion, profile extrusion, thermoforming, vacuum forming, void fill forming, film extrusion, film lamination, coating by stenter, saturation, spray, powder dusting, hot roll pressing, or other means of incorporation, impregnation, or infusion whereby the laminate substrates can, if desired for increased end product effectiveness, undergo further manufacturing process to include but not limited to heat fusing,, bonding of all types to include thermal point bonding, sheet bonding, electrostatic bonding through coating mechanisms known to those skilled in the art and or other coating mechanisms intended to adhere substrates, and or thermal seaming, thermal embossing, calendarization, or stenter fixation, and or bonding methods known and used in the art not mentioned herein.

[000035] Separate laminates may be used in accordance with environmental

conditions, and further bonding or lamination may be done in view of such environmental or cost considerations.

[000036] An alternate product which may utilize alternative fixation methods may include the use of adherents, glues, or other epoxies, resins, or mixtures thereof or other materials adequate to form a seal and intended to affix either portions and or sheets of whatsoever dimension of one laminate substrate to another may be included. Such locations of placement for adherents, glues, epoxies, and or resins or other materials intended to affix substrates not mentioned herein may be placed at the edges during manufacture for later use as a method of post-manufacture, consumer assembly of a bag-like structure or containment unit.

[000037] The method employed for dosing active ingredients within the air pockets may be dependent upon the composition, viscosity, heat index and other properties of the active ingredient whether it be in powder, liquid, gel, or any other substance whatsoever such as respective flow rates and other physical and chemical properties, and such dosing of active ingredients preferably should take place at the crucial phase in film manufacturing where the hot melt plastic sheet has conformed the desired depressions and dimensions after coming off the perforated roller with sufficient cooling at a temperature adequate so as not to entirely embed the active ingredient in the hot plastic but before moving onto the process whereby the second sheet second is to be laid so as to suspend the active ingredient between the raised portion and the flat laminate, thus enclosing, encapsulating, or otherwise containing the active ingredient in a manner sufficient so as to be released from the raised portion upon penetration.

[000038] Dispensing mechanisms appropriate for this technology may range from

simple to complex, based on the desired accuracy of the dosage of active ingredient and or precision of placement and affordability for the end product. Automated overhead mounted gravimetric dispensing units which precisely and accurately dose active ingredients, such as those commonly used in the pharmaceutical industry, as well as in-line spray coating, wet or dry powder coating and other dispensing units of high precision are examples of effective manufacturing apparatus for some variations of this invention, most preferably used when active ingredients are in liquid, gel, or format other than dry powder or particulate, although such high precision fill mechanisms may not be the most effective method of manufacture for providing affordable solutions for mitigating post harvest losses in developing economies.

[000039] The preferred method to reduce manufacturing costs and thus end product cost for dispensing active ingredients within the air pockets of the bubble film employs a metal drum roller set, most preferably a non-stick metal which may have an anti-static coating or pre-treatment, and most preferably with perforations and or meshes, whereby such drum roller set is designed for use as a dispensing unit affixed to braces welded to the machine frame in a manner which allows interchangeability with other roller sets, most preferably located after the perforated vacuum suction roller and even more preferably located directly after a cooling unit positioned so as to sufficiently cool the raised portions before passing to the dispensing drum roller set, most preferably containing two drums, one outer and one inner, most preferably with an outer metal drum having perforations of a larger diameter, shape and dimension sufficient for releasing the powder and or particle size to be released, most preferably circular in shape, whereby the inner drum, acting as the distributor of active ingredient to the outer drum is affixed yet

rotating independently of and most preferably affixed in a manner to cause the internal drum to rotate opposite the outer drum, with the inner drum most preferably having a smaller mesh size so as to filter and allow for even mixture and distribution of the powders or particulates upon rotation.

[000040] Depending upon the powder or particulate sizes, dosing may come from an automatic, gravimetric and or pressurized pump unit attached to the inner drum, dispensing the active ingredient into the inner drum in metered doses through a perforated central pipe whereby the pressurization forces the powder and or particulates through the perforations releasing the active ingredient to the inner drum. Through alignment of holes and or mesh apertures between both drums during opposite rotation, the outer drum ultimately releases the active ingredient into the air pocket.

[000041] Alternative methods of manufacture for dispensing multiple active ingredients may include multiple active ingredients dosed together through one central hopper and external feed unit, and or by a segregation mechanism whereby the external dispensing unit has a partitioned hopper which contains and distributes multiple active ingredients into separate and respective chambers, pumped through respective hoses to the segregated perforated pipe within the inner drum depositing the active ingredients into segregated chambers of the inner drum and through the alignment of the holes and or mesh between both drums during opposite rotation, the active ingredient is released. For larger industries producing wider width films, it is most preferable for the even distribution of active ingredient to have two separate external dispensing units located on either side of the drum for the purpose of reducing the distance of travel of active ingredient, economizing air supply and speed of manufacturing so as to reduce the time

of film under dosing process. Such dual location of external dispensing units may also provide for further differentiation and or multiplicity of active ingredients.

[000042] Alternative methods of manufacture to provide multiple active ingredients dosed in a segregated manner for cost conscious considerations may include a mechanism whereby the inner drum is segregated with a partition of the desired amount of allocations, resulting in separated chambers to be fed manually.

[000043] Alternative methods of manufacture to provide multiple active ingredients dosed in a segregated manner may include the manual loading of active ingredients desired per chamber within the segregated inner drum.

[000044] Partitioning and segregating chambers of the drums may be done either in horizontal or vertical manner, containing and dosing any singular, and or multiple, and or mixtures of active ingredients to provide the intended pattern of active ingredient dosing.

[000045] Portions of the polymer laminates and air cushioned laminates may include different or combined active ingredients to impart different or collective properties to different portions of the laminate as the dosing environment requires. This may include design features to include but not limited to air pocket dimensions, structures, pocket or quilting shapes of different geometry and may include interconnected air passages or aesthetics commonly used in various industries, such as colored film packaging, or other color and text associations such as printing and laminating for brand identification or pictographic representation or imagery or design of whatsoever nature whereby such printing of specific areas may be done with inks, paints, solvents, laminates, and/or adhesives containing active ingredients, so as to provide a combination of different active properties on one substrate.

[000046] In a further preferred embodiment, the polymeric laminate additionally comprising a mesh material layer disposed adjacent the mesh material having openings of sufficient size to permit the partial passage of the insect through the mesh material so as to hold an insect of the dimensional shape. It is preferred that the inter-layer distance between the innermost layer and the mesh material layer is less than the length of the insect so as to permit only the partial passage of the insect through the mesh material so as to hold an insect of the dimensional shape between the innermost layer and the mesh material layer.

[000047] The polymeric laminate may incorporate any of the features and layers otherwise described herein not inconsistent with this aspect of the invention. Optionally, the polymeric laminate may additionally comprise an outermost layer comprising a thermoplastic polymeric material containing at least one ultraviolet blocking material. It may also include a bio-composite absorbent layer comprising super-absorbent polymers, and a bio-composite compatibilizer layer comprising activated [bamboo] carbon and a compatibilizer. Likewise, additionally comprising a rodent repellent intermediate layer comprising a thermoplastic polymeric material, a rodent repellent material and ethyl vinyl acetate. It may also incorporate an oxygen barrier intermediate layer comprising ethylene vinyl alcohol and EMMA inorganic/organic additives. For instance, the polymeric laminate may additionally include: (a) an outermost layer comprising a woven thermoplastic polymeric material containing at least one rodent repellent material and an ultraviolet blocking material, and a layer comprising at least one pesticide and/or insecticide; and (b) an innermost layer comprising a food grade polymer and an adhesive; and, interposed between the outermost layer and innermost layers, the following layers: a

bio-composite layer comprising a thermoplastic yarn mesh containing at least one super-absorbent polymer and activated carbon. The bio-composite layer may be of an HDPE mesh containing at least one super-absorbent polymer, and a second layer comprising an HDPE mesh containing a biocomposite material and activated bamboo carbon. The polymeric laminate may be incorporated into a multi-layer laminate comprising: (a) an outermost layer comprising a thermoplastic polymeric material containing at least one rodent repellent material; (b) an innermost layer comprising a food grade polymer and an adhesive; and, interposed between the outermost layer and innermost layers, the following layers: (1) a woven thermoplastic polymeric material; (2) a bubble plastic thermoplastic polymeric material layer comprising bubbles containing at least one insecticide as described herein; and (3) a bio-composite layer comprising a thermoplastic yarn mesh containing at least one super-absorbent polymer and activated carbon.

Polymeric Laminate – Coextruded Version

[000048] In general terms, the invention includes a polymeric laminate comprising: (a) an outermost layer comprising a thermoplastic polymeric material containing at least one of the following and within a multilayer sheet or a substrate comprised of multiple layers, but most preferably the combination of rodent repellent material, at least one pesticide and/or insecticide and an ultraviolet blocking material; (b) an innermost layer comprising a food grade polymer and an adhesive; and, interposed without respect to order between the outermost layer and innermost layers, the following layers: (c) an oxygen barrier intermediate layer comprising a thermoplastic polymeric material containing at least one additive that functions as a desiccant, a free radical scavenger or an oxygen barrier; and (d) a bio-composite absorbent/compatibilizer layer comprising a

thermoplastic polymeric material containing at least one super-absorbent polymer and activated carbon, such as activated bamboo carbon charcoal or another antifungal additive (such as Triclosan). Examples are shown in Figures 1 – 1e.

[000049] It is preferred that the outermost layer comprises a first layer comprising a polyolefin, a rodent repellent (as per environmental demand in areas of use) and an ultraviolet blocking material; and a second layer comprising a thermoplastic polymeric material and at least one insecticide or pesticide material. It is further preferred that the bio-composite absorbent/compatibilizer layer comprises a first layer comprising at least one super-absorbent polymer; and a second layer comprising an anti-fungal or another organic material or combination thereof exhibiting both moisture absorbency and anti-fungal properties such as activated bamboo carbon.

[000050] The outermost layer and other layers within the multilayer substrate may comprise a polyolefin, polymer, thermoplastic or thermoset selected from the group consisting of polypropylene, HDPE, LDPE, LLDPE, VLDPE and copolymers and homopolymers thereof or blends with other materials or varying ratios thereof, including recycled materials, or compatibilizers for ease of manufacturing to add desired properties providing further mechanical barrier to pests, additives determined by humidity, temperature, pest behavior, and pest penetration and migration methods per environmental conditions and stored product conditions .

[000051] Active ingredients for pest control and insecticides may be selected, depending upon the pest behavior, from the group consisting of synthetic pyrethroids, such as permethrin and deltamethrin and/or organophosphorous compounds, pirimiphos methyl, chlorpiriphos methyl, fenitrothion, malathion and/or composition or mixtures

thereof and or from other pertinent and applicable insecticide families and/or ethnobotanical mixtures, including without limitation to and in environments whereby organic methods are preferred neem plant or oil, sweet flag worm seed and peppers, geranium oil and menthol and its derivatives, and/or other plant-based or naturally derived materials with reported repellency or efficacy of pest control exhibited and known to those skilled in the art..

[000052] In another related variation of the present invention, the polymeric laminate comprises: (a) an outermost layer comprising a polyolefin, a rodent repellent and an ultraviolet blocking material; (b) an innermost layer comprising a food grade polymer and an adhesive; and, interposed without respect to order between the outermost layer and innermost layers, the following layers: (c) an insecticide/pesticide intermediate layer comprising a thermoplastic polymeric material and either an insecticide or a pesticide material; (d) an oxygen barrier intermediate layer comprising ethylene vinyl alcohol and preferably EMMA with inorganic/organic additives; (e) a bio-composite absorbent layer comprising super-absorbent polymers; and (f) a bio-composite compatibilizer layer comprising a naturally occurring anti-fungal, and absorbent such as activated bamboo carbon kapok fibers or others.

[000053] The compatibilizer(s) used in accordance with the present invention may include any compatibilizer effective to render the additive compatible with the surrounding polymer, such as those selected from the group consisting of chitin and citric acid for compatibility with ethylene vinyl copolymers or naturally derived components such as granulated activated bamboo carbon

[000054] In still another variant of the present invention, the invention includes a

polymeric laminate comprising: (a) an outermost layer comprising a polyolefin, an insecticide/pesticide material, a cuticle desiccant and an ultraviolet blocking material; (b) an innermost layer comprising a food grade polymer and an adhesive; and, may or not be interposed, most preferably included in high moisture areas, without respect to order between the outermost layer and innermost layers, the following layers: (c) an rodent repellent intermediate layer comprising a thermoplastic polymeric material, a rodent repellent material and ethyl vinyl acetate; (d) an oxygen barrier intermediate layer comprising ethylene vinyl alcohol and/or EMMA and at least one inorganic/organic additives, (e) a bio-composite absorbent layer comprising at least one super-absorbent polymer(s); and (f) a bio-composite compatibilizer layer comprising activated bamboo carbon charcoal or another antifungal additive, and a compatibilizer.

Polymeric Laminate – Mesh Version

[000055] In still another variation of the present invention, the invention includes a polymeric laminate comprising, as shown for example in Figure 2: (a) an outermost layer comprising a woven thermoplastic polymeric material containing at least one rodent repellent material and an ultraviolet blocking material, and a layer comprising at least one pesticide; (b) an innermost layer comprising a food grade polymer and an adhesive; and, interposed without respect to order between the outermost layer and innermost layers, the following layers: and (c) a bio-composite layer comprising a thermoplastic yarn mesh containing at least one super-absorbent polymer and activated carbon, such as an activated bamboo carbon charcoal or another antifungal additive.

[000056] It is preferred that the bio-composite layer be of a mesh structure comprised of either a thermoplastic, polyester, or monofilament yarns of either HDPE,

PP, PE, PET or other mesh containing at least one super-absorbent polymer, and a second layer comprising a thermoplastic, more preferably an HDPE mesh containing a biocomposite material and antifungal additive, such as activated bamboo carbon.

[000057] Another variation of the present invention is a polymeric laminate comprising (a) an outermost layer comprising a thermoplastic polymeric material containing at least one rodent repellent material; (b) an innermost layer comprising a food grade polymer and an adhesive; and, interposed without respect to order between the outermost layer and innermost layers, the following layers: (c) a woven thermoplastic polymeric material; (d) a thermoplastic polymer layer containing at least one pesticide; (e) a bio-composite layer comprising a thermoplastic yarn mesh containing at least one super-absorbent polymer and activated carbon.

[000058] In one variation, the bio-composite layer comprises a thermoplastic mesh, such as HDPE or polypropylene mesh containing at least one super-absorbent polymer, and a second layer comprising an HDPE or polypropylene mesh containing a biocomposite material and activated bamboo carbon.

[000059] Still another variation of the invention is a polymeric laminate comprising (as exemplified in Figures 2b and 2c): (a) an outermost layer comprising a woven thermoplastic polymeric material containing at least one rodent repellent material and an ultraviolet blocking material, and a layer comprising at least one pesticide; (b) an innermost layer comprising a food grade polymer and an adhesive; and, interposed without respect to order between the outermost layer and innermost layers, the following layers: (c) a bio-composite layer comprising a thermoplastic yarn mesh containing at least one super-absorbent polymer and activated carbon such as activated bamboo carbon

charcoal or another antifungal additive.

[000060] A further variation is a polymeric laminate comprising (see Figure 3): (a) an outermost layer comprising a woven thermoplastic polymeric material containing at least one ultraviolet blocking material as well as, optionally, the rodent repellent and the at least one pesticide; (b) an innermost layer comprising a food grade polymer and an adhesive; and, interposed without respect to order between the outermost layer and innermost layers, the following layers: (c) a first bubble plastic thermoplastic polymeric material layer comprising bubbles containing at least one rodent repellent material; (d) a second bubble plastic thermoplastic polymeric material layer comprising bubbles containing at least one pesticide; (e) a non-woven or other equivalent layer, such as a filter membrane, that encapsulates cellulosic or other naturally absorbent materials and/or superabsorbent polymers, and (f) an optional bio-composite layer comprising a thermoplastic yarn mesh containing at least one super-absorbent polymer and activated carbon or other antifungal additive.

[000061] A variant of this embodiment additionally comprises a layer of a thermoplastic polymeric material containing calcium carbonate or equivalent material as a filler/blocking agent, and disposed between the second bubble plastic thermoplastic polymeric material layer and the a non-woven or other equivalent layer or within the layers of the coextrudate film.

[000062] Preferably, the first bubble plastic layer comprises a polymer selected from the group consisting of LDPE, VLDPE, polypropylene or other suitable polymeric material, adhered to the outermost layer by an adhesive such as EVOH, and wherein second bubble plastic layer bubbles are provided with an insecticide in powder form,

such as diatomaceous earth or other cuticle desiccants or mixtures of different insecticides from different families to include but not limited to pyrethroids, organophosphates, or admixtures and varying insecticide cocktails to achieve effective results and avoid resistance with repeat contact.

[000063] Yet another embodiment of the present invention includes a polymeric laminate comprising: (a) an outermost layer comprising a thermoplastic polymeric material containing at least one ultraviolet blocking material as well as, optionally, the rodent repellent and at least one pesticide; (b) an innermost layer comprising a food grade polymer and an adhesive; and, interposed without respect to order between the outermost layer and innermost layers, the following layers: (c) a first bubble plastic thermoplastic polymeric material layer comprising bubbles containing at least one rodent repellent material; (d) a second bubble plastic thermoplastic polymeric material layer comprising bubbles containing at least one pesticide; (e) a bio-composite absorbent layer comprising at least one super-absorbent polymer(s); and (f) a bio-composite compatibilizer layer comprising activated carbon such as bamboo carbon, and a compatibilizer.

[000064] With respect to all of the embodiments of the present invention, it will be recognized that the layered substrates, or mixtures thereof may include recycled material in place of or in addition to biobased material in an amount of up to 100% of the biobased material. As used herein, "recycled" materials encompass post-consumer recycled (PCR) materials, post-industrial recycled (PIR) materials, and a mixture thereof.

A Polymeric Storage Container for Harvested Agricultural Products

[000065] The present invention also includes a polymeric storage container for harvested agricultural products, the container comprising a polymeric laminate according

to any of embodiments of the invention. These may be produced by any methods and through the use of machinery known and used in the art for creating polymeric bags and other containers made from or incorporating polymeric sheet or woven sheet material and may or may not be fit within or supported by a framed structure.

System for Storage of Harvested Agricultural Products

[000066] A system for storage of harvested agricultural products, the system involving the use of such laminates, sections or portions of the laminate to be strategically placed within existing storage containers to provide spatial effectiveness or containers made therefrom and/or bags for on-farm storage at a farm.

[000067] Laminates of the present invention may be used in a system and method for free-standing hermetic storage of bulk, boxed or bagged commodities, such as that described for instance in U.S. Patent No. 8,141,328, which is hereby incorporated herein by reference.

[000068] The present invention may also be considered an improvement upon the materials and methods described in Korean Patent Application No. KR10109267, which is hereby incorporated herein by reference.

[000069] The foregoing and other objects, features, and advantages of this invention will become more readily apparent from the following detailed description of a preferred embodiment which proceeds with reference to the accompanying drawings, wherein the preferred embodiment of the invention is shown and described, simply by way of illustration of the best mode contemplated of carrying out the invention.

[000070] As will be realized, the invention is capable of other and different embodiments, and its several details are capable of modifications in various obvious

respects, all without departing from the invention. Accordingly, the drawings and description are to be regarded as illustrative in nature, and not as restrictive. It will also be appreciated that the detailed description represents the preferred embodiment of the invention, and that individual steps of the process of the invention may be practiced independently so as to achieve similar results; and likewise that variations of the described laminates and containers may be made by modifications in the design or manufacturing process to achieve similar results.

BRIEF DESCRIPTION OF THE DRAWINGS

[000071] Figure 1 is a schematic of a polymeric laminate in accordance with one embodiment of the present invention.

[000072] Figure 1a is a schematic of a polymeric laminate in accordance with an alternative embodiment of the present invention.

[000073] Figure 1b is a schematic of a polymeric laminate in accordance with yet another alternative embodiment of the present invention.

[000074] Figure 1c is a schematic of a polymeric laminate in accordance with yet another alternative embodiment of the present invention.

[000075] Figure 2 is a schematic of a woven material laminate in accordance with one embodiment of the present invention.

[000076] Figure 2a is a schematic of a woven material laminate in accordance with an alternative embodiment of the present invention.

[000077] Figure 2b is a schematic of a woven material laminate in accordance with yet another alternative embodiment of the present invention.

[000078] Figure 2c is a schematic of a woven material laminate in accordance with

yet another alternative embodiment of the present invention.

[000079] Figure 3 is a schematic representation of the production of a polymeric laminate in accordance with one embodiment of the present invention.

[000080] Figure 3a is a schematic representation of the production of a polymeric laminate in accordance with one embodiment of the present invention.

[000081] Figure 4 is a schematic of a grain storage bag containing grain, in accordance with one embodiment of the present invention.

[000082] Figure 5 is a detailed perspective view of a thermoplastic bubble-containing material containing active ingredients, in accordance with one embodiment of the present invention.

[000083] Figure 6 is a detailed perspective view of a double-layered thermoplastic bubble-containing material containing multiple active ingredients, in accordance with one embodiment of the present invention.

[000084] Figure 7 is a detailed longitudinal view of a metal drum unit that may be used to make the thermoplastic bubble-containing material containing multiple active ingredients, in accordance with one embodiment of the present invention.

[000085] Figure 8 is a partially sectioned view of a metal drum with powder dispensing unit that may be used to create and fill the thermoplastic bubble-containing material containing multiple active ingredients, in accordance with one embodiment of the present invention.

[000086] Figure 9 is a partially sectioned view of a metal drum with powder dispensing unit that may be used to create and fill the thermoplastic bubble-containing material containing multiple active ingredients, in accordance with one embodiment of

the present invention.

[000087] Figure 10 is a perspective view of a metal drum which may be used to dose a single active ingredient into the thermoplastic bubble-containing material, in accordance with an embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[000088] In accordance with the foregoing summary, the following provides a detailed description of the preferred embodiment, which is presently considered to be the best mode thereof. It is understood that multiple variations or combinations of properties desired differs according to environment and climatic conditions, types, presence and life cycle of insects, respiration rates and transpiration intensities of stored product.

[000089] Features and advantages of the invention will now be described with occasional reference to specific embodiments. However, the invention may be embodied in different forms and should not be construed as limited to the embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete and will fully convey the scope of the invention to those skilled in the art

[000090] As used throughout this application, the term "polymer" refers to a material which is the product of a polymerization or copolymerization reaction of natural, synthetic or combined natural and synthetic monomers and/or co-monomers and is inclusive of homopolymers, copolymers, terpolymers, etc. In general, the layers of the multilayer film described in the present application may comprise a single polymer, a mixture of a single polymer and non-polymeric material, a combination of two or more polymers blended together, or a mixture of a blend of two or more polymers and non-

polymeric material. It will be noted that many polymers may be synthesized by the mutual reaction of complementary monomers. It will also be noted that some polymers are obtained by the chemical modification of other polymers such that the structure of the macromolecules that constitute the resulting polymer may be thought of as having been formed by the homopolymerization of a hypothetical monomer.

[000091] Polymers and thermoplastic raw materials may be selected for their barrier properties, mechanical properties, rheological properties, or other factors influencing barrier functions such as the climatic conditions, intended conditions of stored product, insects, pests, and or risk of fungal contamination.

[000092] As used throughout this application, the term "thermoplastic" refers to a polymer or polymer mixture that softens when exposed to heat and then returns to its original condition when cooled to room temperature. In general, thermoplastic materials may include natural or synthetic polymers.

[000093] Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, reaction conditions, and so forth as used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless otherwise indicated, the numerical properties set forth in the specification and claims are approximations that may vary depending on the desired properties sought to be obtained in embodiments of the present invention.

Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical values, however, inherently contain certain errors necessarily resulting from error found in their respective

measurements

[000094] Figure 1 is a schematic of a polymeric laminate in accordance with one embodiment of the present invention which may be produced by co-extrusion and film-blowing, such as by using multilayer coextrusion blown film equipment commercially available from Kung Hsing of Taiwan. This may be made as a multi-layer coextrusion wherein the substrate and the different active ingredients used is not limited to the number or order of the layers.

[000095] The typical thickness range of the laminates used as singular layers, or as multilayers of the present invention made from coextrusion is from about 50 microns to 600 microns, although other thicknesses may be produced. The thicknesses of the individual layers may be determined to obtain overall laminate dimensions, but typically will be in the general range of 80 to 150 microns.

[000096] The outermost layer 1 may be produced of a thermoplastic material, such as a polyolefin selected from the group consisting of polypropylene, HDPE, LDPE, LLDPE, VLDPE and copolymers and homopolymers thereof. An example of the LLDPE is PLEXAR 800 commercially available from Lyondell Basel.

[000097] The rodent repellent(s) that may be used in accordance with the present invention may include without limitation any synthetic or natural rodent repellent partially or wholly miscible with the polyolefin and/or thermoplastic base layer, such as denatonium benzoate, trinitrobenzene-aryl amine complexes, and tributyl tin chloride. Natural rodent repellents may include, without limitation, salicylic ester, menthol, corn mint oil, eucalyptus, camphor, terpene, peppermint oil, citronella oil, rosemary oil, clove oil, geranium oil, cayenne pepper, methyl nonyl ketone, or combinations thereof.

[000098] The ultraviolet blocking material(s) may be any material effectively miscible with the base polymer, and in an effective amount known in the art such as, for instance, from about 2% to about 5% percent by weight. An example of such a material is Optiblock 10 commercially available from Specialty Minerals, Inc. Other materials providing UV reflection or absorbency may be used such as carbon black or titanium dioxide of 18-150nm particle size or other UV stabilizers.

[000099] The pesticide intermediate layer 2 may comprise a thermoplastic polymeric material or polyolefin, and at least one insecticide or pesticide material that may include any synthetic or natural insecticide or pesticide or combinations partially or wholly compatible or miscible with the polymeric material, provided in an effective amount to reduce or eliminate infestation. Examples include those selected from the group consisting of synthetic pyrethroids, such as permethrin, or deltamethrin. Most preferably, the insecticide is a combination of either synthetic or natural compounds or admixtures thereof to include but not limited to pirimiphos-methyl (sold commercially under the name Actellic Superdust), with permethrin at a concentration of 3% by weight and pirimiphos-methyl at 14% by weight, or other silicone dioxide plus synthetic pyrethroids or mixtures thereof, specifically to repel *Prostephanus truncatus* and *S. zeamis* in tropic and sub tropic zones, particularly for maize storage. It is understood that other admixtures of active ingredients may be used, to include but not limited to; malathion + permethrin, fenitrothion + deltamethrin, or either of such compounds mixed with alternatives of similar insecticide families

[0000100] The insecticide may also include a cuticle desiccant material, or materials that sterilize insects, inhibit their growth or retard their reproduction or to cause excito-

repellency, mortality, or to attract for migration and proprigation, or combinations thereof.

[0000101] The thermoplastic polymeric material may be selected from among any material that may be amenable to co-extrusion while being able to contain the active ingredients at an effective level. Examples may include ethyl vinyl acetate or a thermoplastic polymer mixed with natural starches so as to form a biocomposite. An example of such a starch-blended polyester is Ecoflex from BASF.

[0000102] The oxygen barrier intermediate layer 3 preferably may comprise any thermoplastic material, though it is preferred to use ethyl vinyl alcohol (EVOH), ethylene methyl acrylic co-polymer (EMMA) or ethylene-methacrylic acid (EMAA) owing to their increased adhesion with the other layers. An example of such an EMMA material is PXL 164 commercially available from Lyondell Basel as PLEXAR. This layer includes at least one oxygen barrier material, such as inorganic or organic additives or materials that function as desiccants, free radical scavengers or oxygen barriers, and provided in effective amount to inhibit oxygen ingress. This amount will vary with the foodstuff volume to laminate surface area ratio of the specific application, but generally will be in the range of from about 2% to 75% by weight. Such inorganic additives may include iron, ascorbic acid, calcium hydroxide, activated carbon, sodium chloride, potassium chloride, magnesium oxide, titanium oxide, aluminum oxides, chromium oxide, calcium oxide, silica, bentonite, zeolites, montmorillonite, mullites, wollastonites and agalmatolite clay or admixtures thereof in either particle, powder, or masterbatch form.

[0000103] Organic additives may include such substances as are known in the field,

such as compatibilizers including but not limited to metal alcoholates and alkoxysilanes. Typical content of these materials will be in the range of from about 1% to about 25% percent by weight, or otherwise, depending upon the rate of adherence and or miscibility of the material to be incorporated into the polymeric structural layer.

[0000104] The bio-composite absorbent layer 4 comprises one or more super-absorbent polymers, such as sodium polyacrylates commercially available from Shanghai Dinghan Chemical Co., Shanghai, PRC, or from Teijin Limited of Taiwan, and provided in an effective amount to absorb moisture respiring from the dry foodstuff to be contained or from the moisture diffusion caused by changes in relative humidity and temperature. This amount may be determined by both the preference for placement within the multilayer co-extrudate or within the layered structure and with reference to local climatic conditions and the amount of moisture to be generated through transpiration of the stored product, such as in the context of contained corn or maize stored outdoors in tropical regions having different transpiration intensities compared to wheat or grain stored in bunkers in colder climates.

[0000105] The bio-composite absorbent layer 4 may preferably be provided with micro perforations of a valve type, of angled, conical, or otherwise shaped structure to manage oxygen transmission and moisture vapor transmission, in accordance with methods known in the art. Such valve perforations, when preferably placed at approximately a 45 degree angle to the laminate surface, are effective to permit moisture migration from this layer to reach the outside of the laminate, yet prohibitive of in-flow.

[0000106] The bio-composite compatibilizer layer 5 comprises a thermoplastic polymer material as the base material, with addition of antifungals preferably activated

bamboo carbon, and a compatibilizer, in an amount effective to such as chitin, citric acid, such as Ciroflex A4, commercially available from Vertellus. Typical content of these materials will be in the range of from about 1% to about 25% percent by weight.

[0000107] Any of the foregoing layers 3, 4 or 5 may contain a blocking ingredient or an additive which prohibits the migration of active ingredients such as calcium carbonate, silica or talc, that restrict the mobility of the pesticide or rodent repellent ingredient to prevent them reaching the contained dry foodstuff. A stabilizer may also be contained within, such as Uvinul 4050H which is FDA approved.

[0000108] The innermost layer 6 comprises preferably a food grade polymer and an adhesive adapted to affix this layer to the immediately adjacent intermediate layer, such as layer 5. Examples of food grade polymers may include Sabic 6135 NE.

[0000109] It will be understood that each of the individual layers shown and described may be combined and/or amalgamated along with the active ingredients contained within or affixed to each such layer so as to produce a functional laminate not inconsistent with the integration of the constituent layers and the function of the active ingredients. Examples of such variation are described herein.

[0000110] Figure 1a is a schematic of a polymeric laminate in accordance with an alternative embodiment of the present invention. This embodiment is similar to that of Figure 1 except that the outermost layer contains the pesticide and the UV blocker ingredient, while the first intermediate layer contains the rodent repellency ingredient(s).

[0000111] Figure 1b is a schematic of a polymeric laminate in accordance with yet another alternative embodiment of the present invention. This embodiment is similar to that of Figure 1 except that layers 1 and 2 have been effectively combined by being

coextruded as a single layer.

[0000112] Figure 1c is a schematic of a polymeric laminate in accordance with yet another alternative embodiment of the present invention. This embodiment is similar to that of Figure 1 except that arrangement of layers 4 and 5 has been reversed.

[0000113] Figure 1d is a schematic of a polymeric laminate in accordance with yet another alternative embodiment of the present invention. This embodiment is similar to that of Figure 1 except that layers 4 and 5 have been effectively combined by being coextruded as a single layer.

[0000114] Figure 1e is a schematic of a polymeric laminate in accordance with yet another alternative embodiment of the present invention. This embodiment is similar to that of Figures 1 – 1d except that layer 6 is produced as a single layer and inserted as liner when the film is converted to a bag through the use of such techniques as horizontal or vertical form, fill and seal, or manually.

[0000115] Figure 2 is a schematic of a woven material laminate in accordance with one embodiment of the present invention. This Figure shows outermost layer 1 which is a tape-woven layer 7 of an HDPE (or polypropylene) flat yarn containing the pesticide and rodent repellent ingredients which is thermally laminated with a EMMA thermoplastic layer 8 also containing a pesticide. It is preferred that the pesticide in the warp or weft of layer 7 be different from that of layer 8. Additionally, the warp (or weft) of layer 7 may contain the pesticide while the weft (or warp) of layer 7 contains the rodent repellent. Additionally, the warp (or weft) of layer 7 may contain different active ingredients than the weft (or warp) of layer 7 so that two different active ingredients and the desired different properties may be contained on one substrate with actives of one

complementary to the adjacent active ingredient to produce a desired combined effect, or for one active ingredient to enhance or decrease the effect of the opposite. The HDPE (or polypropylene) flat yarn may come from post-industrial or post-consumer recycled material and this recycled material may or may not contain active ingredients.

[0000116] Figure 2 also shows the HDPE monofilament yarn mesh layer 9 which has the superabsorbent polymer chemically incorporated into the yarn. Layer 10 is a biocomposite mesh prepared from a monofilament yarn of HDPE with activated carbon contained in the polymer. Layer 11 is a sheet of food grade polymer with an adhesive to bind it to the mesh layer 10. The laminate of Figure 2 is prepared by first assembling sub-laminates of layers 7 and 8 and 9 – 11, respectively, followed by thermal point bonding the two sub-laminates together, as indicated by the series of X's in Figure 2.

[0000117] Figure 2a is a schematic of a woven material laminate in accordance with an alternative embodiment of the present invention. This embodiment is similar to that of Figure 2 except that layers 1 and 2 have been effectively combined by being coextruded as a single layer.

[0000118] Figure 2a is a schematic of a woven material laminate in accordance with an alternative embodiment of the present invention. This embodiment is similar to that of Figure 2 except that the woven layer 13 contains no active ingredients while additional layer 12 laminated on the outside of the woven layer 13 contains a rodent repellent and layer 14 contains an insecticide. This embodiment also shows layers 15 and 16 that are similar to layers 9 and 10 of Figure 2, and layer 17 that may be produced as a single layer and inserted as liner when the film is converted to a bag through the use of such techniques as horizontal or vertical form, fill and seal, or manually.

[0000119] Figure 2b is a schematic of a woven material laminate in accordance with yet another alternative embodiment of the present invention. This embodiment is similar to that of Figure 2 with layers 18 and 19 similar to layers 7 and 8, and with the exception that layers 9 and 10 have been combined as a single layer 20, and layer 21 being produced as a single layer and inserted as liner when the film is converted to a bag through the use of such techniques as horizontal or vertical form, fill and seal, or manually.

[0000120] Figure 2c is a schematic of a woven material laminate in accordance with yet another alternative embodiment of the present invention. This embodiment is similar to that of Figure 2b with layers 24 and 25 being coextruded as a single sub-laminate prior to thermal point bonding.

[0000121] Figure 3 is a schematic representation of the production of a polymeric laminate formed in accordance with yet another alternative embodiment of the present invention. Figure 3 shows outermost layer 30 which would be the same construction as layers 7 and 8 of Figure 2. Layer 31 is a bubble plastic layer of LDPE, VLDPE, polypropylene or other suitable polymeric material, adhered to layer 30 by an adhesive such as EMMA, or EVOH, and wherein the bubbles are encapsulating an insecticide in powder, particulate or granular form, such as diatomaceous earth (such as is sold under the trade name Protect-It from Headley Technologies) or other cuticle desiccants and insecticide cocktails and may or may not include one or more of the synthetic pyrethroids or synthetic organophosphate insecticides or insecticide families exhibiting preferred properties which may or may not include sterilizing effect,s, growth regulator effects, repellency effects, propagation effects or other desired effects for pest and insect control.

Layer 32 is an opposing layer of bubble plastic (such as may be produced by thermoforming in combination with layer 31) wherein the bubbles are provided with a rodent repellent such as those described herein. Layer 33 is a separate layer of a thermoplastic material containing a filler/blocking agent (such as calcium carbonate) provided so as to prevent any liberated rodent repellent and/or insecticide/pesticide from migrating toward the food grade layer.

[0000122] Layer 34 is a non-woven or other equivalent layer, such as a filter membrane or porous substrates, that encapsulate cellulosic or other naturally absorbent materials (such as bamboo fiber, kapok fiber, coconut husks, apricot pits, and the like) and/or synthetic absorbants such as superabsorbent polymers, to provide a moisture barrier while retaining and absorbing moisture diffusion from the contained foodstuff, such as that of transpiration of grain and the like and from changes in relative humidity, transpiration, respiration intensity and other conditions prone to moisture.

[0000123] Layer 35 is an adhesive layer, such as EVOH or other equivalent materials, such as those described herein. Layer 36 is a food grade polymer that is attached to layer 34 by adhesive layer 35. Layers 34/35/36 may then thermal point bonded to layers 30 – 33.

[0000124] Figure 3a is a schematic representation of the production of a polymeric laminate formed in accordance with yet another alternative embodiment of the present invention. This embodiment is similar to that of Figure 3 with layers 37, 38 and 39 being equivalent to layers 30, 31 and 32; and wherein layers 34 and 35 have been replaced with layers 40 and 41 which are the same as layers 4 and 5 of Figure 1, and wherein layer 43 is the same as layer 6 of Figure 1 with optional adhesive layer 42 where the food grade

layer is separately produced.

[0000125] Figure 4 is a schematic representation of the production of a polymeric laminate of the construction shown in Figure 3a, and wherein like reference numerals indicate the respective layers, and formed into a bag and containing grain 44, in accordance with one embodiment of the present invention. This schematic shows the detailed construction of the cooperative layers 38 and 39 which provide an insecticide in powder form, and a rodent repellent, respectively.

[0000126] It will be appreciated that the logical order of the steps are used for purposes of illustration only, and that the constituent layers, their measurements and active ingredient determinations may be varied where not otherwise inconsistent with the purpose and result obtained in the practice of the invention.

[0000127] The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The foregoing embodiments are therefore to be considered in all respects illustrative rather than limiting on the invention described herein. The scope of the invention is thus indicated by the appended claims rather than by the foregoing description, and all changes that come within the meaning and range of equivalency of the claims are intended to be embraced therein.

[0000128] Figure 5 is a schematic representation depicting multiple active ingredients dosed on one substrate wherein Figure 5a depicts one bubble encapsulating multiple active ingredients adjacent to another bubble containing only one active ingredient as shown in Figure 5b.

[0000129] Figure 6 is a schematic representation of active ingredients encapsulated or otherwise contained within raised portions on two sides, portraying the film having the

capacity to encapsulate multiple active ingredients on both sides.

[0000130] Figure 7 is the schematic representation to display one method, a horizontal partitioning of the metal drum roller for dosing multiple active ingredients on one substrate. Figures 7a, 7b and 7c represent the centrally located but partitioned containment units which receive the active ingredient from the external feed unit which is also partitioned as indicated in 7d. After the active ingredients have been transferred to their respective containment units, the active ingredient is released through the perforated pipes of the containment unit segregating the active ingredients into their respective units as portrayed in figures 7e, 7f and 7g, while the drum is rotating, the active ingredients then pass through to be dosed on the substrate.

[0000131] Figure 8 is a schematic representation of another method of segregating the distribution of active ingredients to combine multiple active ingredients on one substrate with the use of a pressurized, automatic dosing units which separates the active ingredients, as depicted by Fig 8a, 8b, 8c, 8d, 8e, which are then transferred through the channeled core and dosed in a segregated release as portrayed in figures 8f, 8g, 8h, 8i, and 8j.

[0000132] Figure 9 is a schematic representation of vertically partitioning the drum rollers as depicted in figures 9a, 9b and 9c, being fed from overhead mounted containment units receiving the active ingredient from an external unit which is also segregated as depicted in 9e. As depicted in 9f and 9g, the two drums rotate in opposite directions, resulting in the active ingredients being released when the perforations and or mesh apertures align.

[0000133] Figure 10 is the schematic representation of the drum roll set which is fed

with one active ingredient as depicted in 10a, by an external feed unit whereby the active ingredient travels through the hollow core depicted in figure 10b to the inner drum portrayed in figure 10c, rotating in one direction as portrayed in figure 10e, releasing the active ingredient through the perforations, whereby the active ingredient flows to the second drum as displayed in figure 10d, which is rotating in the opposite direction as depicted in figure 10f, upon which the active ingredient is dosed on the surface of the substrate.

Claims to Polymeric Laminates, a Polymeric Storage Container for Harvested
Agricultural Products and a System for Storage of Harvested Agricultural Products

What is claimed is:

1. A polymeric laminate comprising adapted to contact an insect of a given dimensional shape with a dose of an insecticide:

an innermost layer comprising a bubble plastic thermoplastic polymeric material layer comprising bubbles containing at least one insecticide, said bubbles having a shape and an inter-bubble distance adapted to resist the movement of said insect thereabout.
2. A polymeric laminate according to claim 1 wherein said insecticide is in powder form.
3. A polymeric laminate according to claim 1 wherein said insecticide comprises a material selected from the group consisting of diatomaceous earth and cuticle desiccants.
4. A polymeric laminate according to claim 1 wherein the burst strength of the thermoplastic bubbles of said bubble plastic thermoplastic polymeric material allows said insect to burst said thermoplastic bubbles so as to expose said insect to said at least one insecticide.
5. A polymeric laminate according to claim 1 wherein said bubble plastic thermoplastic polymeric material comprises a polymer selected from the group consisting of LDPE, VLDPE and polypropylene.
6. A polymeric laminate according to claim 1 additionally comprising a mesh material layer disposed adjacent said thermoplastic bubble layer, having openings of sufficient size to permit the partial passage of said insect through said mesh material so as to hold an insect of said dimensional shape.

7. A polymeric laminate according to claim 2 wherein the inter-layer distance between said bubble layer and said mesh material layer is less than the length of said insect so as to permit only the partial passage of said insect through said mesh material so as to hold an insect of said dimensional shape between said innermost layer and said mesh material layer.
8. A polymeric laminate according to claim 1, additionally comprising an outermost layer comprising a thermoplastic polymeric material containing at least one ultraviolet blocking material.
9. A polymeric laminate according to claim 1, additionally comprising a bio-composite absorbent layer comprising super-absorbent polymers, and a bio-composite compatibilizer layer comprising activated [bamboo] carbon and a compatibilizer.
10. A polymeric laminate according to claim 1, additionally comprising a rodent repellent intermediate layer comprising a thermoplastic polymeric material, a rodent repellent material and ethyl vinyl acetate.
11. A polymeric laminate according to claim 1, additionally comprising an oxygen barrier intermediate layer comprising ethylene vinyl alcohol and EMMA inorganic/organic additives.
12. A polymeric laminate according to claim 1, additionally comprising:
- a) an outermost layer comprising a woven thermoplastic polymeric material containing at least one rodent repellent material and an ultraviolet blocking material, and a layer comprising at least one pesticide and/or insecticide;
 - b) an innermost layer comprising a food grade polymer and an adhesive; and, interposed between said outermost layer and innermost layers, the following layers: a bio-

composite layer comprising a thermoplastic yarn mesh containing at least one super-absorbent polymer and activated carbon.

13. A polymeric laminate according to claim 1, wherein said bio-composite layer of an HDPE mesh containing at least one super-absorbent polymer, and a second layer comprising an HDPE mesh containing a biocomposite material and activated bamboo carbon.

14. A polymeric laminate polymeric laminate according to claim 1 comprising:

- a) an outermost layer comprising a thermoplastic polymeric material containing at least one rodent repellent material;
- b) an innermost layer comprising a food grade polymer and an adhesive; and, interposed between said outermost layer and innermost layers, the following layers:
- c) a woven thermoplastic polymeric material;
- d) a bubble plastic thermoplastic polymeric material layer comprising bubbles containing at least one insecticide; and
- e) a bio-composite layer comprising a thermoplastic yarn mesh containing at least one super-absorbent polymer and activated carbon.

Polymeric Laminate – Coextruded Version

15. A polymeric laminate comprising:

- a) an outermost layer comprising a thermoplastic polymeric material containing at least one rodent repellent material, at least one pesticide and/or insecticide and an ultraviolet blocking material;
- b) an innermost layer comprising a food grade polymer and an adhesive; and, interposed

between said outermost layer and innermost layers, the following layers:

- c) an oxygen barrier intermediate layer comprising a thermoplastic polymeric material containing at least one additive that functions as a desiccant, a free radical scavenger or an oxygen barrier; and
- d) a bio-composite absorbent/compatibilizer layer comprising a thermoplastic polymeric material containing at least one super-absorbent polymer and activated carbon.

16. A polymeric laminate according to claim 15 wherein said outermost layer comprises a first layer comprising a polyolefin, a rodent repellent and an ultraviolet blocking material; and a second layer comprising a thermoplastic polymeric material and at least one insecticide or pesticide material.

17. A polymeric laminate according to claim 15 wherein said bio-composite absorbent/compatibilizer layer comprises a first layer comprising at least one super-absorbent polymer; and a second layer comprising activated bamboo carbon.

18. A polymeric laminate according to claim 15 wherein said outermost layer comprises a polyolefin selected from the group consisting of polypropylene, HDPE, LDPE, LLDPE, VLDPE and copolymers and homopolymers thereof.

19. A polymeric laminate according to claim 15 wherein said outermost layer comprises a rodent repellent selected from the group consisting of synthetic pyrethroids, such as permethrin.

20. A polymeric laminate comprising:

- a) an outermost layer comprising a polyolefin, a rodent repellent and an ultraviolet blocking material;
- b) an innermost layer comprising a food grade polymer and an adhesive; and, interposed

between said outermost layer and innermost layers, the following layers:

- c) an insecticide/pesticide intermediate layer comprising a thermoplastic polymeric material and either an insecticide or a pesticide material;
- d) an oxygen barrier intermediate layer comprising ethylene vinyl alcohol and EMMA and inorganic/organic additives;
- e) a bio-composite absorbent layer comprising super-absorbent polymers; and
- f) a bio-composite compatibilizer layer comprising activated bamboo carbon and a compatibilizer.

21. A polymeric laminate according to claim 20 wherein said outermost layer comprises a polyolefin selected from the group consisting of polypropylene, HDPE, LDPE, LLDPE, VLDPE and copolymers and homopolymers thereof.

22. A polymeric laminate according to claim 20 wherein said outermost layer comprises a rodent repellent selected from the group consisting of synthetic pyrethroids, such as permethrin.

23. A polymeric laminate according to claim 20 wherein said bio-composite compatibilizer layer comprises activated carbon selected from the group consisting of bamboo activated carbons.

24. A polymeric laminate according to claim 20 wherein said bio-composite compatibilizer layer comprises a compatibilizer selected from the group consisting of chitin and citric acid.

Polymeric Laminate – Version 2

25. A polymeric laminate comprising:

- a) an outermost layer comprising a polyolefin, an insecticide/pesticide material, a cuticle desiccant and an ultraviolet blocking material;
- b) an innermost layer comprising a food grade polymer and an adhesive; and, interposed between said outermost layer and innermost layers, the following layers:
- c) a rodent repellent intermediate layer comprising a thermoplastic polymeric material, a rodent repellent material and ethyl vinyl acetate;
- d) an oxygen barrier intermediate layer comprising ethylene vinyl alcohol and EMMA inorganic/organic additives;
- e) a bio-composite absorbent layer comprising super-absorbent polymers; and
- f) a bio-composite compatibilizer layer comprising activated bamboo carbon and a compatibilizer.

Polymeric Laminate – Mesh Version

26. A polymeric laminate comprising:

- a) an outermost layer comprising a woven thermoplastic polymeric material containing at least one rodent repellent material and an ultraviolet blocking material, and a layer comprising at least one pesticide and/or insecticide;
- b) an innermost layer comprising a food grade polymer and an adhesive; and, interposed between said outermost layer and innermost layers, the following layers:
- c) a bio-composite layer comprising a thermoplastic yarn mesh containing at least one super-absorbent polymer and activated carbon.

27. A polymeric laminate according to claim 26 [Figure 2 detailed] wherein said bio-composite layer of an HDPE mesh containing at least one super-absorbent polymer, and a second layer comprising an HDPE mesh containing a biocomposite material and

activated bamboo carbon.

28. A polymeric laminate comprising:

- a) an outermost layer comprising a thermoplastic polymeric material containing at least one rodent repellent material;
- b) an innermost layer comprising a food grade polymer and an adhesive; and, interposed between said outermost layer and innermost layers, the following layers:
- c) a woven thermoplastic polymeric material;
- d) a thermoplastic polymer layer containing at least one pesticide and/or insecticide;
- e) a bio-composite layer comprising a thermoplastic yarn mesh containing at least one super-absorbent polymer and activated carbon.

29. A polymeric laminate according to claim 28 [Figure 2a detailed] wherein said bio-composite layer of an HDPE mesh containing at least one super-absorbent polymer, and a second layer comprising an HDPE mesh containing a biocomposite material and activated bamboo carbon.

30. A polymeric laminate comprising:

- a) an outermost layer comprising a woven thermoplastic polymeric material containing at least one rodent repellent material and an ultraviolet blocking material, and a layer comprising at least one pesticide and/or insecticide;
- b) an innermost layer comprising a food grade polymer and an adhesive; and, interposed between said outermost layer and innermost layers, the following layers:
- c) a bio-composite layer comprising a thermoplastic yarn mesh containing at least one super-absorbent polymer and activated carbon.

31. A polymeric laminate comprising:

- a) an outermost layer comprising a thermoplastic polymeric material containing at least one ultraviolet blocking material;
 - b) an innermost layer comprising a food grade polymer and an adhesive; and, interposed between said outermost layer and innermost layers, the following layers:
 - c) a first bubble plastic thermoplastic polymeric material layer comprising bubbles containing at least one rodent repellent material;
 - d) a second bubble plastic thermoplastic polymeric material layer comprising bubbles containing at least one pesticide and/or insecticide;
 - e) a non-woven or other equivalent layer, such as a filter membrane, that encapsulates cellulosic or other naturally absorbent materials and/or superabsorbent polymers
 - f) an optional bio-composite layer comprising a thermoplastic yarn mesh containing at least one super-absorbent polymer and activated carbon.
32. A polymeric laminate according to claim 31 additionally comprising a layer of a thermoplastic polymeric material containing calcium carbonate or equivalent material as a filler/blocking agent, and disposed between said second bubble plastic thermoplastic polymeric material layer and said a non-woven or other equivalent layer.
33. A polymeric laminate according to claim 31 wherein said first bubble plastic layer comprises a polymer selected from the group consisting of LDPE, VLDPE, polypropylene or other suitable polymeric material, adhered to said outermost layer by an adhesive such as EVOH, and wherein second bubble plastic layer bubbles are provided with an insecticide in powder form, such as diatomaceous earth or other cuticle desiccant.

34. A polymeric laminate according to claim 31 wherein said first bubble plastic layer comprises a polymer selected from the group consisting of LDPE, VLDPE, polypropylene or other suitable polymeric material, adhered to said outermost layer by an adhesive such as EVOH, and wherein second bubble plastic layer bubbles are provided with an insecticide in powder form, such as diatomaceous earth or other cuticle desiccant.

35. A polymeric laminate comprising:

- a) an outermost layer comprising a thermoplastic polymeric material containing at least one ultraviolet blocking material;
- b) an innermost layer comprising a food grade polymer and an adhesive; and, interposed between said outermost layer and innermost layers, the following layers:
- c) a first bubble plastic thermoplastic polymeric material layer comprising bubbles containing at least one rodent repellent material;
- d) a second bubble plastic thermoplastic polymeric material layer comprising bubbles containing at least one pesticide and/or insecticide;
- e) a bio-composite absorbent layer comprising [super-absorbent polymers]; and
- f) a bio-composite compatibilizer layer comprising activated [bamboo] carbon and a compatibilizer.

A Polymeric Storage Container for Harvested Agricultural Products

36. A polymeric storage container for harvested agricultural products, said container comprising a polymeric laminate according to any of claims 1 through 21.

System for Storage of Harvested Agricultural Products

37. A system for storage of harvested agricultural products said system comprising a

container made from a polymeric laminate according to any of claims 1 through 21.

Bubble Plastic Material with Insecticide laminate

38. A polymeric laminate comprising adapted to contact an insect of a given dimensional shape with a dose of an insecticide:
an innermost layer comprising a bubble plastic thermoplastic polymeric material layer comprising bubbles containing at least one insecticide, said bubbles having a shape and an inter-bubble distance adapted to resist the movement of said insect thereabout.
39. A polymeric laminate according to claim 38 wherein said insecticide is in powder form.
40. A polymeric laminate according to claim 38 wherein said insecticide comprises a material selected from the group consisting of diatomaceous earth and cuticle desiccants.
41. A polymeric laminate according to claim 38 wherein the burst strength of the thermoplastic bubbles of said bubble plastic thermoplastic polymeric material allows said insect to burst said thermoplastic bubbles so as to expose said insect to said at least one insecticide.
42. A polymeric laminate according to claim 38 wherein said bubble plastic thermoplastic polymeric material comprises a polymer selected from the group consisting of LDPE, VLDPE and polypropylene.
43. A polymeric laminate according to claim 38 additionally comprising a mesh material layer disposed adjacent said thermoplastic bubble layer, having openings of sufficient size to permit the partial passage of said insect through said mesh material so as to hold an insect of said dimensional shape.

44. A polymeric laminate according to claim 39 wherein the inter-layer distance between said bubble layer and said mesh material layer is less than the length of said insect so as to permit only the partial passage of said insect through said mesh material so as to hold an insect of said dimensional shape between said innermost layer and said mesh material layer.

45. A polymeric laminate according to claim 38, additionally comprising an outermost layer comprising a thermoplastic polymeric material containing at least one ultraviolet blocking material.

46. A polymeric laminate according to claim 38, additionally comprising a bio-composite absorbent layer comprising super-absorbent polymers, and a bio-composite compatibilizer layer comprising activated [bamboo] carbon and a compatibilizer.

47. A polymeric laminate according to claim 38, additionally comprising a rodent repellent intermediate layer comprising a thermoplastic polymeric material, a rodent repellent material and ethyl vinyl acetate.

48. A polymeric laminate according to claim 38, additionally comprising an oxygen barrier intermediate layer comprising ethylene vinyl alcohol and EMMA inorganic/organic additives.

49. A polymeric laminate according to claim 38, additionally comprising:

- a) an outermost layer comprising a woven thermoplastic polymeric material containing at least one rodent repellent material and an ultraviolet blocking material, and a layer comprising at least one pesticide and/or insecticide;
- b) an innermost layer comprising a food grade polymer and an adhesive; and, interposed between said outermost layer and innermost layers, the following layers: a bio-

composite layer comprising a thermoplastic yarn mesh containing at least one super-absorbent polymer and activated carbon.

50. A polymeric laminate according to claim 49, wherein said bio-composite layer of an HDPE mesh containing at least one super-absorbent polymer, and a second layer comprising an HDPE mesh containing a biocomposite material and activated bamboo carbon.

51. A polymeric laminate polymeric laminate according to claim 49 comprising:

- a) an outermost layer comprising a thermoplastic polymeric material containing at least one rodent repellent material;
- b) an innermost layer comprising a food grade polymer and an adhesive; and, interposed between said outermost layer and innermost layers, the following layers:
- c) a woven thermoplastic polymeric material;
- d) a bubble plastic thermoplastic polymeric material layer comprising bubbles containing at least one insecticide; and
- e) a bio-composite layer comprising a thermoplastic yarn mesh containing at least one super-absorbent polymer and activated carbon.