Title: THERMOPLASTIC COMPOSITION COMPRISING AN ETHYLENE RESPONSE INHIBITOR RELEASING MATERIAL

Abstract: A method of inhibiting an ethylene response in flowers, fruits, vegetables and plants comprising the steps of applying to the plant an effective amount of an ethylene response inhibitor releasing composition comprising: a thermoplastic base, a filler, an ethylene response inhibitor releasing material and a moisture transmitting material that concentrates moisture at the ethylene response inhibitor releasing material, and activating the composition at humidity of at least about 80% Rh at 5°C.
THERMOPLASTIC COMPOSITION COMPRISING AN ETHYLENE RESPONSE INHIBITOR RELEASING MATERIAL

Detailed Description Of The Present Invention

The present invention relates to an ethylene response inhibitor releasing composition comprising a combination of an ethylene response inhibitor releasing material that is incorporated within a thermoplastic. In the presence of water, the ethylene response inhibitor releasing material reacts to release a gas, which is composed of an ethylene response inhibitor compound, through the thermoplastic into the surrounding environment.

Suitable thermoplastic materials include, but are not limited to, polyolefins such as polypropylene and polyethylene (linear low density), polycarbonates, polyamides, ethylene-vinyl acetate copolymers, ethylene-methacrylate copolymer, polyacrylanitrile, polysulfones, polycrylic ester, acrylic, polyurethane and polyacetal, or copolymers or mixtures thereof. It is understood that the desired thermoplastic is selected based on the end-use. For example, the specific thermoplastic selected may be based on the activation relative humidity of the active agent so as to allow the desired level of moisture into the thermoplastic and/or the desired amount of the ethylene response inhibitor gas out of the thermoplastic. In another example, the desired thermoplastic may be selected that has the desired end-use properties of the shaped article (e.g. tensile strength, moldability, elasticity, cost).

In yet a further embodiment, suitable ethylene response inhibitor releasing compounds include, but are not limited to, cyclopropene derivatives, 1-methylcyclopropene, and 1.1.1 propellane or derivatives thereof. In another example, mixtures of ethylene response inhibitor releasing compounds may be combined. In one example, the ethylene response inhibiting compounds may be produced by one or more of the methods that are disclosed in U.S. Patent Nos. 5,518,988; 6,194,350; or 6,365,549, incorporated by reference herein. For example, the ethylene response inhibiting compound is selected from the group consisting of 3,3-dipentyl-cyclopropene, 1-pent-2-enyl-2-pentyl-cyclopropene, 1-pent-2-enyl-3,3-dipentyl-cyclopropene, 4-(1-cyclopropenyl)-2-methylbutan-2-ol, 1-(n-amyl)-cyclopropene, 1-(5,5,5-trifluoropentyl)-cyclopropene, and 1,2-dipentyl-cyclopropene. In an embodiment, the ethylene response inhibitor releasing compound loading level can range from about 0.5% to about 15%, more specifically about 5% to about 10%, more specifically about .5% to about 1%, more specifically about 0.5% to about 2%, more specifically about 1% to about 3% more specifically about .5% to about 5% by weight with respect to the overall composition. In
another embodiment, the operating temperature is between about 3C to about 40C, in a further the range is about 3C to about 7C.

In another embodiment, to reduce the possibility of the reaction initiating prematurely, the ethylene response inhibitor releasing compound is in its solid granular form and/or in its salt form and is substantially free of moisture.

The present invention can be employed to modify a variety of different ethylene responses. Ethylene responses may be initiated by either exogenous or endogenous sources of ethylene. For example, ethylene responses include, for example, the ripening and/or senescence of flowers, fruits and vegetables, abscission of foliage, flowers and fruit, the shortening of life of ornamentals such as potted plants, cut flowers, shrubbery, seeds, and dormant seedlings, in some plants (e.g., pea) the inhibition of growth, and in other plants (e.g., rice) the stimulation of growth. Additional ethylene responses or ethylene-type responses that may be inhibited by active compounds of the present invention include, but are not limited to, auxin activity, inhibition of terminal growth, control of apical dominance, increase in branching, increase in tillering, changing bio-chemical compositions of plants (such as increasing leaf area relative to stem area), abortion or inhibition of flowering and seed development, lodging effects, stimulation of seed germination and breaking of dormancy, and hormone or epinasty effects.

In another embodiment, methods according to embodiments of the present invention inhibit the ripening and/or senescence of vegetables. As used herein, "vegetable ripening" includes the ripening of the vegetable while still on the vegetable-bearing plant and the ripening of the vegetable after having been harvested from the vegetable-bearing plant. Vegetables which may be treated by the method of the present invention to inhibit ripening and/or senescence include leafy green vegetables such as lettuce (e.g., Lactuca sativa), spinach (Spinacea oleracea), and cabbage (Brassica oleracea), various roots, such as potatoes (Solanum tuberosum) and carrots (Daucus), bulbs, such as onions (Allium sp.), herbs, such as basil (Ocimum basilicum), oregano (Origanum vulgare), dill (Anethum graveolens), as well as soybean (Glycine max), lima beans (Phaseolus limensis), peas (Lathyrus spp.), corn (Zea mays), broccoli (Brassica oleracea italica), cauliflower (Brassica oleracea botrytis), and asparagus (Asparagus officinalis).

In yet another embodiment, methods according to embodiments of the present invention inhibit the ripening of fruits. As used herein, "fruit ripening" includes the ripening of fruit while still on the fruit-bearing plant as well as the ripening of fruit after having been
harvested from the fruit-bearing plant. Fruits which may be treated by the method of the present invention to inhibit ripening include tomatoes (Lycopersicon esculentum), apples (Malus domestica), bananas (Musa sapientum), pears (Pyrus communis), papaya (Carica papaya), mangoes (Mangifera indica), peaches (Prunus persica), apricots (Prunus armeniaca), nectarines (Prunus persica nectarina), oranges (Citrus sp.), lemons (Citrus limonia), limes (Citrus aurantifolia), grapefruit (Citrus paradisi), tangerines (Citrus nobilis deliciosa), kiwi (Actinidia chinenus), melons such as cantaloupe (C. cantalupensis) and musk melon (C. melo), pineapple (Ananas comosus), persimmon (Diospyros sp.), various small fruits including berries such as strawberries (Fragaria), blueberries (Vaccinium sp.) and raspberries (e.g., Rubus ursinus), green beans (Phaseolus vulgaris), members of the genus Cucumis such as cucumber (C. sativus), and avocados (Persea americana).

In a further embodiment, ornamental plants which may be treated by the method of the present invention to inhibit senescence and/or to prolong flower life and appearance (e.g., delay wilting), include potted ornamentals, and cut flowers. Potted ornamentals and cut flowers which may be treated with the present invention include azalea (Rhododendron spp.), hydrangea (Macrophylla hydrangea), hibiscus (Hibiscus rosasanensis), snapdragons (Antirrhinum sp.), poinsettia (Euphorbia pulcherrima), cactus (e.g. Cactaceae schlumbergera truncata), begonias (Begonia sp.), roses (Rosa spp.), tulips (Tulipa sp.), daffodils (Narcissus spp.), petunias (Petunia hybrida), carnation (Dianthus caryophyllus), lily (e.g., Lilium sp.), gladiolus (Gladiolus sp.), alstroemeria (Alstroemeria brasiliensis), anemone (e.g., Anemone blanda), columbine (Aquilegia sp.), aralia (e.g., Aralia chinensis), aster (e.g., Aster carolinianus), bougainvillea (Bougainvillea sp), camellia (Camellia sp.), bellflower (Campanula sp.), cockscomb (Celosia sp.), falsecypress (Chamaecyparis sp.), chrysanthemum (Chrysanthemum sp.), Clematis (Clematis sp.), cyclamen (Cyclamen sp.), freesia (e.g., Freesia refracta), and orchids of the family Orchidaceae.

In yet another embodiment, plants which may be treated by the method of the present invention to inhibit abscission of foliage, flowers and fruit include cotton (Gossypium spp.), apples, pears, cherries (Prunus avium), pecans (Carva illinoensis), grapes (Vitis vinifera), olives (e.g. Vitis vinifera and Olea europaea), coffee (Coffee arabica), snapbeans (Phaseolus vulgaris), and weeping fig (Ficus benjamina), as well as dormant seedlings such as various fruit trees including apple, ornamental plants, shrubbery, and tree seedlings. In addition, shrubbery which may be treated according to the present invention to inhibit abscission of foliage include privet (Ligustrum sp.), photinea (Photinia sp.), holly (Ilex sp.), ferns of the
family Polypodiaceae, schefflera (Schefflera sp.), aglaonema (Aglaonema sp.), cotoneaster (Cotoneaster sp.), barberry (Berberis sp.), waxmyrtle (Myrica sp.), abelia (Abelia sp.), acacia (Acacia sp.) and bromeliades of the family Bromeliaceae.

In the embodiment comprising a thermoplastic and an ethylene response inhibitor releasing material, the desired article may be produced by any conventional process of making a plastic article that includes, but is not limited to, extrusion, melt inflation (e.g. blown film, blow moulding, thermoforming) and/or injection molding. At some stage of the process, the ethylene response inhibitor releasing material is blended with the thermoplastic and the resulting blend is subsequently processed into the desired shape article. In one example where the ethylene response inhibitor releasing material is sensitive to high temperatures, the ethylene response inhibitor releasing material is blended at a downstream location (e.g. at a downstream point in the extruder) so the ethylene response inhibitor releasing material is subjected to a minimum amount of high temperature processing.

In one example, the plastic film composition is based on the particular requirements of the fruit and/or vegetable packaged. For example, the loading of active agent can range from 0.5 - 10% by weight of the total, more specifically 1-5%. In another example, the film thickness may be in the range of 0.2 mm – 1.4 mm, more specifically, 0.4 – 0.6 mm.

In one application, the film can be placed in a sealed container either. The activation relative humidity is controlled by at least the moisture vapor transmission of the composition (e.g. the thermoplastic blend) and the ability of the composition to direct moisture effectively to the active agent. The release rate of the active agent in the film is controlled by at least the following: (1) the loading of active agent in the plastic, (2) the thickness of the plastic, and (3) moisture vapor transmission properties of the thermoplastic.

The film may be manufactured in any conventional method. For example, the film is manufactured in an extrusion process packaged in a continuous master roll. Multi-layer film constructions are possible. An adhesive layer with a release liner may be applied to one side of the film. In another embodiment, a gas barrier layer may be applied to one side of the film.

The formulation of the ethylene response inhibitor releasing composition of the present invention is designed based on one or more of the following considerations: the ethylene response inhibitor releasing material within the ethylene response inhibitor releasing composition should not release below a specified relative humidity (i.e. shelf stability); the ethylene response inhibitor releasing material within the ethylene response inhibitor releasing
composition should release above a specified relative humidity; the ethylene response inhibitor releasing material within the ethylene response inhibitor releasing composition should release over a specified time (e.g. 12-36 hours); the amount of ethylene response inhibitor releasing material within the ethylene response inhibitor releasing composition should result in substantially no the ethylene response inhibitor releasing material after the release; the ethylene response inhibitor releasing material within the ethylene response inhibitor releasing composition should be designed to withstand processing conditions during the forming of the composition (e.g. 100 C).

In another embodiment, the ethylene response inhibitor releasing composition comprises one more moisture transmitting materials that are capable of surrounding (e.g. have a preferential affinity towards) the ethylene response inhibitor releasing material when incorporated within the thermoplastic. As such, these moisture transmitting materials act as an osmotic regulator (e.g. controls the Rh that the ethylene response inhibitor releasing material is exposed to) surrounding the ethylene response inhibitor releasing material. For example, it is believed that polyethylene glycol ("PEG") is effective at directing (or concentrating) moisture to the ethylene response inhibitor releasing material within the ethylene response inhibitor releasing composition. It is further believed that moisture transmitting materials, similar to PEG, have the ability to substantially surround the ethylene response inhibitor releasing material within the ethylene response inhibitor releasing composition and to transmit, rather than absorbs moisture. Other suitable materials may include, but are not limited to: (1) polyethylene oxide, (2) polyvinylpyrrolidone, vinyl-acetate ("PVP-VA"), (3) Pluronic, PEBAX and (4) EVA-copolymer (with higher VA content).

**Working Example**

The following illustrates one example of the present invention. It is understood that this is merely one example and is not meant to limit the invention to this illustration.

A film was composed of a thermoplastic blend having an active agent of the ethylene response inhibitor releasing material. Two active films were manufactured with different concentrations of the ethylene response inhibitor releasing material (e.g. SmartFresh 1-MCP complex): (1) a 1% concentration and (2) a 5% concentration. The film formulations had the following compositions:

**Sample 1:**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SmartFresh Complex</td>
<td>1%</td>
</tr>
<tr>
<td>Carbowax 1000</td>
<td>7%</td>
</tr>
</tbody>
</table>
Elvax 3174  50%
Calcium Carbonate  42%

**Sample 2:**

- SmartFresh Complex  5%
- Carbowax 1000  7%
- Elvax 3174  50%
- Calcium Carbonate  38%

**Sample 3:**

- SmartFresh Complex  5%
- Carbowax 1000  7%
- Elvax 3174  50%
- Calcium Carbonate  28%
- Sorbitol  10%

**Sample 4:**

- SmartFresh Complex  1%
- Carbowax 1000  7%
- Elvax 3174  50%
- Calcium Carbonate  32%
- Sorbitol  10%

where Elvax 3174 is an ethylene vinyl-acetate manufactured by Dupont (E.I.) de Nemours; “SmartFresh” is 1-methylcyclopropene (MCP) manufactured by AgroFresh, a division of Rohm & Haas; and Carbowax 1000 is a polyethylene glycol (PEG), manufactured by The Dow Chemical Company.

Each sample was produced by the following process. First, Carbowax 1000 was heated above its melt temperature ~60°C into a liquid form. Second, the Smart Fresh Complex was mixed into the Carbowax, using the proper weight ratio for the sample type. Finally, the calcium carbonate was added to the Carbowax/SmartFresh blend and hand mixed. The blended mixture was allowed to cool so that the material solidified. The resultant mixture was in a powdered form.

The resultant mixture was then formed into a film using a Leistritz twin screw extruder. The extruder had 11-independently controlled temperature zones. The Elvax 3174 was loaded into a K-Tron material feeder and side stuffed into the Leistritz extruder at the most upstream feed location. The blended powder of Carbowax/SmartFresh/Calcium
Carbonate was fed into the extruder in the most downstream feed location. The blended powder was then mixed with the Elvax in the extruder. The highest temperature recorded by the thermoplastic compositions was 92 C. The extruded material was fed into a three roll calendaring stack. The three roll stack was used to both form the film to its final thickness and to cool the molten material into a solid form. The material was passed through a nip between two rolls; traveled over the surface of the center roll, passed through a second nip, traveled under the bottom roll and then transported towards the winder. The nip pressures and the temperatures of each of the rolls were controlled independently. The film was then passed through an NDC thickness gauge. This gauge had a traversing head, which emitted and measured gamma rays, which were passed through the film. Cross machine direction and machine direction data were gathered and displayed on a touch screen. The film was then slit to the desired width and wound onto a core using a single shaft center drive winder. The resulting film was about 0.4 mm thick and was cut into rectangular shapes. The films were exposed to a moisture environment at 25C in a closed container. The headspace was sampled at regular intervals to determine the concentration of 1-MCP in the headspace. The headspace was sampled until all the 1-MCP had been released.

It is believed that the Carbowax (polyethylene glycol) is effective at directing (or concentrating) moisture to the ethylene response inhibitor releasing material within the ethylene response inhibitor releasing composition. In the examples that utilize sorbitol, it is believed that sorbitol may acts as a competitor for moisture to the ethylene response inhibitor releasing material within the ethylene response inhibitor releasing composition – thus have an undesirable effect.

It is further believed that materials, similar to PEG, appear to be suited to this application because of the PEG’s ability to bind with the ethylene response inhibitor releasing material within the ethylene response inhibitor releasing composition and because PEG transmits, rather than absorbs moisture. Once activated the ethylene response inhibitor releasing material within the ethylene response inhibitor releasing composition is released and is transmitted through the thermoplastic blend to the environment.

The release rate of the film can be controlled by at least one or more of the following: (1) the selection of the type of thermoplastic based on its specific gas transmission properties (specifically MVTR), (2) the amount of moisture concentrating thermoplastic, and (3) the geometry of the film (surface area to thickness ratio). It is further believed that, in another
embodiment, the calcium carbonate filler particle may assist in providing microscopic pathways throughout the thermoplastic composition.

Whereas particular embodiments of the present invention have been described above as examples, it will be appreciated that variations of the details may be made without departing from the scope of the invention. One skilled in the art will appreciate that the present invention can be practiced by other than the disclosed embodiments, all of which are presented in this description for purposes of illustration and not of limitation. It is noted that equivalents of the particular embodiments discussed in this description may practice the invention as well. Therefore, reference should be made to the appended claims rather than the foregoing discussion of examples when assessing the scope of the invention in which exclusive rights are claimed.
What is claimed is:

1. An ethylene response inhibitor releasing composition comprising: a thermoplastic base, a filler, an ethylene response inhibitor releasing material and a moisture transmitting material that concentrates moisture at the ethylene response inhibitor releasing material.

2. The ethylene response inhibitor releasing composition of claim 1 wherein the moisture transmitting material encapsulates the ethylene response inhibitor releasing material.

3. The ethylene response inhibitor releasing composition of claim 1 wherein the moisture transmitting material is distributed throughout the thermoplastic base.

4. The ethylene response inhibitor releasing composition of claim 1 wherein the moisture transmitting material has a preferential affinity to the ethylene response inhibitor releasing material.

5. The ethylene response inhibitor releasing composition of claim 1 wherein the ethylene response inhibitor releasing material is selected from the group consisting of cyclopropene derivatives, 1-methylcyclopropene, and 1.1.1 propellane or derivatives thereof.

6. The ethylene response inhibitor releasing composition of claim 1 wherein the moisture transmitting material polyethylene glycol.

7. The ethylene response inhibitor releasing composition of claim 1 wherein the thermoplastic base is EVA co-polymer.

8. The ethylene response inhibitor releasing composition of claim 1 wherein the composition is a shaped article.

9. The ethylene response inhibitor releasing composition of claim 8 wherein the shaped article is a film.

10. The ethylene response inhibitor releasing composition of claim 9 wherein the film is a multi-layer construction comprising a barrier layer.

11. A method of inhibiting an ethylene response in flowers, fruits, vegetables and plants comprising the steps of:

applying to the plant an effective amount of a an ethylene response inhibitor releasing composition comprising: a thermoplastic base, a filler, an ethylene response inhibitor releasing material and a moisture transmitting material that concentrates moisture at the ethylene response inhibitor releasing material; and

activating the composition at humidity of at least about 80% Rh at 5C.

12. The method of inhibiting an ethylene response in flowers, fruits, vegetables and plants of claim 11, further comprising the steps of:
releasing ethylene response inhibitor releasing compound for a period of about 12 to about 36 hours.

13. The method of inhibiting an ethylene response in flowers, fruits, vegetables and plants of claim 11, further comprising the steps of:

releasing ethylene response inhibitor releasing compound for a period of about 12 hours.