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(54) Title: REFRIGERATION LOAD REDUCTION SYSTEM AND METHODS

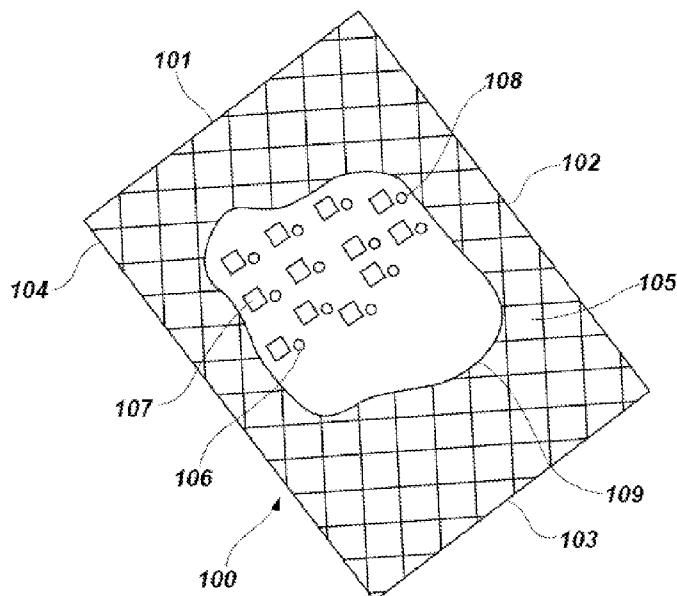


FIG. 2

(57) Abstract: A refrigeration load reduction system can include a primary container (100) having gas permeable openings therein. A granular composition is retained within the container. The granular composition is a granular mixture (106) of a sodium carbonate mineral (107) and a mono-, di- or tricarboxylic acid (108). Typically, the sodium carbonate mineral (107) is a trona mineral, although other minerals can be used singly or in combination with trona. A method of reducing refrigeration load can include orienting the refrigeration load reduction system within a fluid circulation path of a refrigeration unit adapted to cool a refrigeration chamber.

REFRIGERATION LOAD REDUCTION SYSTEM AND METHODS

5 RELATED APPLICATIONS

This application claims priority to U.S. Provisional Application No. 62/043,933, filed August 29, 2014 and which is incorporated herein by reference.

FIELD OF THE INVENTION

10 The present invention relates to systems and specific compositions which reduce refrigeration load. Accordingly, the present invention relates generally to refrigeration technologies and chemistry.

BACKGROUND OF THE INVENTION

15 Distribution, storage and transport of perishable consumer products and other perishable items presents unique challenges in terms of preserving such items to the point of sale or use. Exposure to oxygen is one factor that leads to spoilage of perishable items. Oxygen perishable items from the time of gathering or production, whether by reaping, picking, digging, cutting, collecting, butchering, processing, cooking, displaying, packaging or any other means, where
20 such items are present in an open environment for a period of time, are subject to being exposed to oxygen. Surrounding environments are those present when gathering perishables by any of the above methods as well as loading, transporting, warehousing, manufacturing or processing, packaging in crates or other shipping containers for overland or sea transport, packaging or sealing in containers for sale, refrigerated shipping or storage, cooling and sectioning of
25 butchered animals and the like. An open environment is also inclusive of enclosed or semi-enclosed spaces such as found in display counters holding fruits, meats or vegetable in retail outlets. Temperature conditions also affect rates of spoilage. The subjecting of perishable items to an open atmosphere in the presence of oxygen and particularly when at ambient or elevated temperatures causes the perishable items to lose freshness and texture, decay, produce
30 objectionable odors, and become inedible, unsalable or unusable. To rectify this, means and methods have been sought to lessen the objectionable results and extend the useful life of

perishable items. Most decay or spoilage of perishable items is the result of growth of aerobic microorganisms or pathogens including bacteria, fungi, viruses, which are of animal or vegetable origin.

5 Currently perishable items are routinely kept at low temperatures in order to slow decay and/or spoilage of items in order to meet or exceed times needed for processing, distribution, and ultimate use of such perishable items. Refrigeration systems in warehouses, tractor trailers, retail locations, and consumer locations account for a significant portion of product costs due to the quantity of energy required to sufficiently cool perishable items to safe temperatures. Further, refrigeration systems frequently require maintenance and specific defrost cycling in order to
10 maintain performance and heat transfer away from refrigerated locations. Accordingly, systems and methods which reduce costs associated with refrigeration systems are desirable and continue to be sought.

SUMMARY OF THE INVENTION

15 The present invention relates generally to a refrigeration load reduction system which includes a primary container having gas permeable openings therein. Further, a granular composition is retained within the container. The granular composition is a granular mixture of a sodium carbonate mineral and a mono-, di- or tricarboxylic acid. Typically, the sodium carbonate mineral is a trona mineral, although other minerals can be used singly or in combination with
20 trona. Non-limiting examples of other suitable minerals can include gaylussite, natron, prissonite, northupite, nahcolite, thermonatrite, and combinations thereof.

 A method of reducing refrigeration load can include orienting the refrigeration load reduction system within a fluid circulation path of a refrigeration unit adapted to cool a refrigeration chamber.

25

BRIEF DESCRIPTION OF THE DRAWINGS

 In order that the manner in which the invention, including methods, uses, apparatus, devices or any other means recited, are to be carried out to obtain the desired advantages and results set forth herein, a more particular description of the invention is illustrated in the
30 attached drawing and the written description which follows. It is to be understood that these drawings depict only representative embodiments of the invention and are not to be considered

as limiting the scope which is limited only by the attached claims and functional equivalents thereof.

Fig. 1 is a perspective view of a liquid or gas permeable woven packet of the invention containing a mixture of trona and one or more mon-, di- or tri-carboxylic acids.

5 Fig. 2 is a partial breakaway view of the packet of Fig. 1 showing the trona and carboxylic acid particles in the interior of the packet.

Fig. 3 is a perspective view of a gas permeable package of the invention containing a mixture of trona and one or more mono-, di- or tri-carboxylic acids.

10 Fig. 4 is a partial breakaway view of the packet of Fig. 3 showing the trona and carboxylic acid particles in the interior of the packet.

Fig. 5 is a perspective view of a gas permeable tube containing, in partial breakaway, a packet as shown in Fig. 3.

Fig. 6 is a perspective view of a liquid container for holding pieces of oxygen perishable goods, pieces of ice and packets of gas and liquid permeable packets as shown in Fig. 1.

15 Fig. 7 is a perspective view of a container or crate holding oxygen perishable goods for shipment and also containing one or more packets as shown in Fig. 3.

Fig. 8 is a perspective view of a display stand holding oxygen perishable goods adapted for water spray means and showing packets of Fig. 3 strategically placed within an aperture tube 130 as in Fig. 5.

20 Fig. 9 is a perspective view of a refrigerated display case containing oxygen perishable goods and containing a gas permeable tube containing trona/carboxylic acid packets as shown in Fig. 5.

Fig. 10 is a representation of a storage unit showing shelving, air flow arrows, oxygen absorber packet storage for placing in a warehouse or other storage areas.

25 Fig. 11 is a partial breakaway view of a cargo shipping container having placed therein containers or crates filled with oxygen perishable goods such as shown in Fig. 7 for shipment in trucks, railway cars, cargo ships, and as air freight.

Fig. 12 is a perspective view of a container having either no lid or a clear lid and holding oxygen perishable goods for display or shipment and containing gas permeable packets of 30 trona/carboxylic acid to adsorb/absorb oxygen and produce carbon dioxide.

Fig 13 is a view of a plastic reclosable bag marketing jerky strips and containing gas permeable trona/carboxylic acid packet(s).

Fig 14 is a view of a tray for marketing fresh meat products placed on absorbent pads for absorbing liquids and also containing gas permeable packets of trona/carboxylic acid placed on
5 the tray.

Fig. 15 is a view of an absorbent pad for displaying fresh meat products and absorbing liquids, such a blood, and, in a partial breakaway view, showing granules of trona and mono-, di- or tricarboxylic embedded in the pad.

Fig. 16 illustrates a sealed No. 10 can for holding grain kernels or other particulate matter
10 and also containing packets of trona/carboxylic acid for absorbing/adsorbing oxygen and forming a carbon dioxide atmosphere within the can.

Fig. 17 illustrates a bottle with a replaceable cap containing pharmaceutical tablets or capsules and also a packet of trona/carboxylic acid to absorb/adsorb oxygen and promote the formation of carbon dioxide within the bottle.

Fig. 18 is a schematic illustration of a refrigeration unit including a refrigeration load
15 reduction system.

Fig. 19 is a picture of a secondary container as a rigid box for containment of loose granular mixture or within primary packets.

Fig. 20 is a partial cutaway view of an aperture tube having at least one packet of
20 granular mixture oriented within the tube.

DETAILED DESCRIPTION OF THE INVENTION

A refrigeration load reduction system can include a primary container having gas permeable openings therein. A granular composition is retained within the container which
25 contributes to reduction in cooling loads of a corresponding refrigeration unit. The granular composition is a granular mixture of a sodium carbonate mineral and a mono-, di- or tricarboxylic acid. Typically, the sodium carbonate mineral is a trona mineral, although other minerals can be used singly or in combination with trona. Non-limiting examples of other suitable minerals can include gaylussite, natron, prissonite, northupite, nahcolite, thermonatrite,
30 and combinations thereof. A method of reducing refrigeration load can include orienting the

refrigeration load reduction system within a fluid circulation path of a refrigeration unit adapted to cool a refrigeration chamber as outlined in more detail herein.

Trona is a natural mineral composed mainly of sodium carbonate and sodium bicarbonate and is chemically referred to as trisodium hydrogendicarbonate dehydrate or sodium
5 sesquicarbonate, having the formula: $\text{Na}_3(\text{CO}_3)(\text{HCO}_3) \cdot 2\text{H}_2\text{O}$. Trona is generally mined from salt lake deposits which may be found in the United States, Africa, China, Turkey, and Mexico. Large stratified deposits are mined in Sweetwater County, Wyoming. Other trona deposits are also found in the states of Nevada and California in the United States. Mined trona may be found
10 in, or processed into, various degrees of purification. Some trona may contain minute amounts of potassium carbonate and potassium bicarbonate with even lesser amounts of magnesium and calcium salts and other trace minerals.

Other sodium carbonate minerals, somewhat similar to trona, include gaylussite, natron, prissonite, northupite, nahcolite and thermonatrite. To the extent these sodium carbonate
15 containing minerals may be functionally used in place of, or as a substitute for trona, they are deemed to be within the scope of this invention. Therefore, the term “sodium carbonate mineral or minerals” as used herein generically will be inclusive of trona, gaylussite, natron, prissonite, northupite, nahcolite and thermonatrite. These sodium carbonate minerals all have an oxygen
adsorbing and/or absorbing capability.

Trona is the preferred sodium carbonate mineral having oxygen adsorbing, or absorbing
20 characteristics and is made up primarily of trisodium hydrogendicarbonate dihydrate, $[\text{Na}_3(\text{CO}_3)(\text{HCO}_3) \cdot 2\text{H}_2\text{O}]$ as the primary active ingredients. The only limitation in defining trona is that of functionality including oxygen uptake, i.e. adsorption and/or absorption. To that extent, for purposes of this disclosure, trona and hydrogendicarbonate dihydrate may be used
interchangeably.

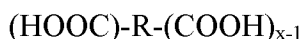
25 Although not required, the sodium carbonate mineral can be recovered and used directly, e.g. without calcining, recrystallization, purification, etc. In some cases, the sodium carbonate mineral can be separated from rock or other debris, however can typically be used without substantive modification of the native mineral other than crushing to a suitable size.

Trona may sometimes be referred to in older literature as *urao* or *nitrum*. Trona is
30 generally processed or purified by calcination to obtain soda ash or sodium carbonate (Na_2CO_3)

and is used primarily in glass manufacture. Trona is also used in many other applications ranging from animal feed, chemical manufacture, and medicine.

The mono-, di- or tricarboxylic acids that may be utilized may contain from two to twenty carbon atoms and may be formed of straight, branched, saturated or unsaturated carbon chains and, aromatic moieties and be substituted or unsubstituted.

The carboxylic acids may be any of a wide variety of mono-, di- and tricarboxylic acids. These carboxylic acids may be comprised of mono-, di- or tricarboxylic acids having the general formula:



Where x is an integer of 1, 2 or 3, and R is a saturated or unsaturated, straight, or branched carbon chain having one to eighteen carbon atoms, or an aromatic moiety having six to eighteen carbon atoms which may be substituted or unsubstituted by OH, COOH, COOM, COOR', -OR' substituents, where M can be an alkali or alkaline earth metal, and where R' can be saturated or unsaturated, straight, or branched carbon chain having from one to eight carbons, an aromatic moiety having six to eighteen carbon atoms which may be substituted by alkyl groups having one to eight carbons, OH, COOH, COOM, COOR', -OR' substituents, and M can be an alkali or alkaline earth metal. For purposes described herein salicylic acid and citric acid are particularly useful carboxylic acids with citric acid providing exceptional results, although other carboxylic acids can also be used. Suitable carboxylic acids can be used singly or in combination with multiple carboxylic acids. Representative, but not inclusive, of such carboxylic acids are found in the following listings.

Representative of monocarboxylic saturated and unsaturated acids are:

25	CH ₃ CO ₂ H	acetic acid
	CH ₃ CH ₂ CO ₂ H	propionic acid
	CH ₃ (CH ₂) ₂ CO ₂ H	butyric acid
	CH ₃ (CH ₂) ₃ CO ₂ H	valeric acid
	CH ₃ (CH ₂) ₄ CO ₂ H	caproic acid
30	CH ₃ (CH ₂) ₆ CO ₂ H	caprylic acid
	CH ₃ (CH ₂) ₈ CO ₂ H	capric acid

	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	Lauric acid
	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	Myristic acid
	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	Palmitic acid
	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	Stearic Acid
5	$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	Myristoleic acid
	$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	Palmitoleic acid
	$\text{CH}_3(\text{CH}_2)_8\text{CH}=\text{CH}(\text{CH}_2)_4\text{COOH}$	Sapienic acid
	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	Oleic acid
	$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	α -Linolenic acid

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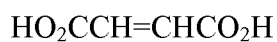
Representative of mono- and di-carboxylic aromatic acids are:

	$\text{C}_6\text{H}_4(\text{COOH})_2$	[benzene-1,2-dicarboxylic acid] <i>o</i> -phthalic acid	<i>o</i> -phthalic acid
15	$\text{C}_6\text{H}_4(\text{COOH})_2$	[benzene-1,3-dicarboxylic acid]	isophthalic acid or <i>m</i> -phthalic acid
20	$\text{C}_6\text{H}_4(\text{COOH})_2$	[benzene-1,4-dicarboxylic acid]	terephthalic acid or <i>p</i> -phthalic acid
	<i>o</i> - $\text{HOC}_6\text{H}_4\text{COOH}$	[<i>o</i> -hydroxybenzoic acid]	salicylic acid
25	<i>o</i> - $\text{CH OOC}_6\text{H}_4\text{COOH}$	[<i>o</i> -acetylsalicylic acid]	aspirin

25

Representative of dicarboxylic saturated and unsaturated acids are:

	HOOC-COOH	Oxalic acid
	$\text{HOOC-(CH}_2\text{)-COOH}$	Malonic acid
30	$\text{HOOC-(CH}_2\text{)}_2\text{-COOH}$	Succinic acid
	$\text{HOOC-(CH}_2\text{)}_3\text{-COOH}$	Glutaric acid
	$\text{HOOC-(CH}_2\text{)}_4\text{-COOH}$	Adipic acid
	$\text{HOOC-(CH}_2\text{)}_5\text{-COOH}$	Pimelic acid
	$\text{HOOC-(CH}_2\text{)}_6\text{-COOH}$	Suberic acid
35	$\text{HOOC-(CH}_2\text{)}_7\text{-COOH}$	Azelaic acid
	$\text{HOOC-(CH}_2\text{)}_8\text{-COOH}$	Sebacic acid



Maleic acid (cis form)



Fumaric acid (trans form)

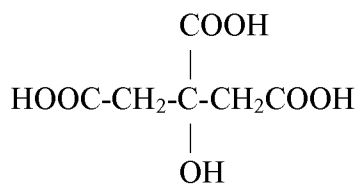


Glutaconic acid

Traumatic acid

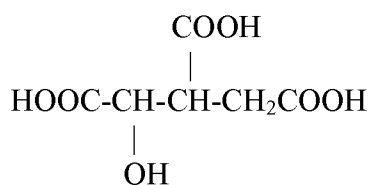
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Representative of tricarboxylic acids are:



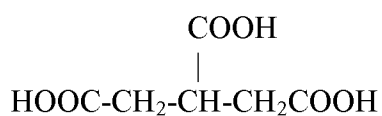
Citric acid

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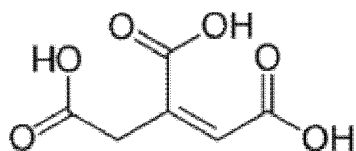
Isocitric acid

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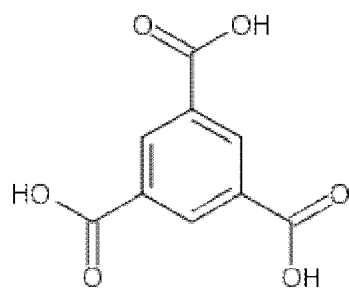
Propane-1,2,3-tricarboxylic acid

20



Aconitic acid

25

Trimesic acid
benzene-1,3,5-tricarboxylic acid

30

The chemical compositions comprise a novel combination of the sodium carbonate mineral and one or more mono-, di- or tri-carboxylic acids in appropriate proportions. Trona contains, as primary ingredients, a mixture of sodium carbonate and sodium bicarbonate along with minor amounts of other minerals or mineral salts as noted above. When the combination of trona and the carboxylic acid are brought together an acid/base reaction occurs and carbon dioxide is produced. Also, testing has shown that when trona and a carboxylic acid are brought together in an oxygen containing environment, oxygen is taken up by the reaction and the concentration of oxygen is diminished or essentially eliminated. This is particularly relevant when the reaction takes place in the presence of oxygen perishable goods. By what mechanism this works is not fully understood. It is postulated that the solid trona/carboxylic acid composition not only reacts in the presence of moisture but also serves as an oxygen adsorber or absorber with oxygen being adsorbed on the surface of the trona crystals by chemical adsorption and/or absorbed into the trona/carboxylic acid combination where it chemically interacts with some or all of the components in the mixture to cause the oxygen to be converted into carbon dioxide. Presumably the carbonates present in the trona/acid mixture provide the carbon necessary for the oxygen conversion into carbon dioxide but how the reaction takes place is not presently understood.

What is known is that laboratory tests, as well as testing in the presence of oxygen perishable goods, shows diminished oxygen content, preservation of oxygen perishable goods as will be delineated in this disclosure.

The ratio of trona to carboxylic acid may vary on a w/w basis. Although other ratios may be useful, as a general guideline, the ratio can often range from 200:1 to 5:1, and in some cases can be from 30:0.5 to 5:1. For example, in the case of citric acid, ratios of about 9:1 are particularly preferred. The ratio can depend on the particular carboxylic acid, the number of acid groups and other functional groups, the molecular weight and other factors that can be determined systematically.

The amount of trona/carboxylic acid will generally be contained in a pouch or packet that is permeable to oxygen or oxygen and water or other liquid depending upon the intended use. Packets may contain measured weight amounts of this mixture ranging from 0.1 to 50 grams per packet to be used to treat 50 to 500 cubic feet of air surrounding the oxygen perishable goods being treated or protected. When used in a liquid environment, such as the cooling of cooked

meat segments in a water reservoir the trona/carboxylic acid packets may also contain from 0.1 to 50 grams, in single or multiple packets and used to treat up to 500 gallons of water.

Preliminary tests have shown two packets containing about 36 grams each of a 9:1 (w/w) trona/citric acid mixture is sufficient to treat 450 gallons of water in order to reduce the temperature of 900 lbs beef shanks cooked to a temperature of about 150⁰ F. to a marketable temperature in about half the time it took to cool similar shanks cooled only by being immersed in water.

The trona and carboxylic acid can often be provided in a dry particulate form. Although particle size can vary, sizes from about 0.01 mm to about 5 mm can be useful, and in many cases ranges from about 0.05 mm to about 1.5 mm. Particle size can affect exposed surface area of the dry mixture and rates of oxygen uptake. Additional materials can optionally be added to the trona/carboxylic acid mixture such as, but not limited to, stabilizers, colorants, fillers, and the like.

The trona and carboxylic acid compositions can often be enveloped in a packet which holds a predetermined amount of the composition within a packet volume. The packet can be formed to allow oxygen and air to permeate from surrounding environment into the packet volume to contact the oxygen capturing composition. Packet sides and walls can be perforated or be formed of porous material. Perforations can optionally be formed by laser lines. Alternatively, a non-porous material can be used which is then opened immediately prior to use. For example, packets can be formed of plastic film, perforated plastic film, fabric, paper, or the like. Non-limiting examples of suitable materials include polyester films, polyester terephthalate (PET) films, paper, and the like. The packets can range in size depending on the application, and often range in dimensions of about 1 cm² to 100 cm².

Packets may be replaced as necessary. Generally, spent or used packets can be determined by noting a rise in temperature within the monitored environment, oxygen sensors, or other similar approaches. Optionally, one or more packets can be sealed in a transport package which isolates the packet(s) from exposure to oxygen until ready for use.

The invention also relates to methods for using packets of the combined trona and mono-, di- and tri-carboxylic acids compositions in moist or humid environments to absorb oxygen from and prolong the useable life of a variety of perishable products, which may include foods, fresh vegetables and fruits, grains and other plant products, animal products and the like. For instance, a moist or humid atmosphere can be obtained by humidifying or spraying with water vegetables,

fruits or other produce in grocery stores, restaurants, refrigerated trucks, or other locations, where packets containing the trona/acids compositions are strategically placed thereby maintaining the freshness of the produce for a period longer than is otherwise possible.

Another method for applying the aqueous composition is to immerse a perishable product within a water bath or other aqueous environment. For example, freshly cooked meat under USDA guidelines requires a drop in temperature from cooking temperature, i.e. $\sim 145^{\circ}\text{C}$ to $\sim 45^{\circ}$ in six hours or less. Upon the trona/carboxylic acid coming into contact with water an endothermic reaction is produced and the temperature within the immediate surrounding environment is lowered.

Still another method according to the implementations of the invention, the trona and di- or tri-carboxylic acid combination can be formulated as a dry mixture and packaged in moisture absorbent devices such as permeable packets of various sizes that encase the combined materials. These packets can be strategically placed in vicinities appropriate to contact with the perishable products or otherwise be placed in sufficiently close proximity to affect atmosphere as described herein. For example, the such packets may be constructed and used to introduce carbon dioxide into and absorb oxygen from produce bins, produce loaded into trucks, railway cars and ships, refrigerators, frozen food lockers, butchered meat storage lockers and directly to produce to extend the useable life or shelf life of produce beyond what has been previously possible. The invention can also be used to prevent exposed, refrigerated meats, fish, seafood, cheeses, and other similar foods from prematurely discoloring and spoiling. The shelf life of cookies, breads, cakes, brown sugar, tortillas, and other dry or non-refrigerated foods can also be extended according to the present invention. When used in transportation or storage in bins, crates, or the like the transportation means, trucks, train cars, ships etc. will be refrigerated. The same holds true for display in grocery stores, stands, or other display units where ambient temperatures would hasten product degradation. Further, packets of trona and carboxylic acids may be placed in perforated pipes or other ventilating devices that release carbon dioxide and absorb oxygen when activated. Once it has been determined how many packets of trona and carboxylic acid are required for any enclosed environment they can be place in any desired space and packet size relative to the material to be treated. It is advantageous that this material is non-toxic, releases carbon dioxide and, in some manner not fully understood also absorbs oxygen.

While not known for a certainty, as previously noted, it appears plausible that the atoms of an adsorbed gas, such as oxygen, are in direct chemical combination with the atoms in the surface of the solid trona carboxylic acid mixture or combinations. These surface oxygen atoms, by reason of their position, may be in a chemical state which is somewhat different from that of the atoms within the body of the solid trona/carboxylic acid combination. The oxygen atoms adsorbed on the surface of the trona and/or carboxylic acid mixture may, therefore, be considered as chemically combined, and their chemical environment is not essentially different from that of the oxygen atoms just within the bonding "surface" of the trona carboxylic acids combination itself. It is believed that it is the trona that provides the surface for the oxygen absorption and not the di- or tri-carboxylic acid but ongoing tests are being conducted to verify this belief. Where on the surface of the trona molecule the bonding takes place is not known. What is known is that it functions in the uptake of oxygen as will be demonstrated below

As in the preceding paragraph, it is not known for a certainty how the solid trona carboxylic acid mixture or combinations serve as an oxygen absorber. The interaction of the carbonates or bicarbonates in trona, reacting with the carboxylic acid certainly function, at least in part, as an acid and base releasing carbon dioxide and water. However, there are additional reactions or interactions that take place when trona, a carboxylic acid and optionally moisture come together that are unexplained in that, oxygen, in addition to that present in the carbonates, is taken up such that the oxygen in the surrounding atmosphere is reduced or minimized.

Just how the interaction of trona with the carboxylic acid functions is not readily explained and hence the term oxygen uptake composition is used over terms oxygen absorber (as used in the prior art) or oxygen adsorber. However, as used in this disclosure, the terms oxygen uptake and oxygen absorber/oxygen adsorber and the like may be used interchangeably. Various theories may be postulated but what is known through repeated demonstrations is that the combination of trona and carboxylic acids within the confines as described herein, and optionally in the presence of moisture, will reduce, minimize or eliminate the presence of oxygen in the immediate atmosphere surrounding oxygen perishable goods.

Although not required, application of moisture to strategically placed packets of powdered trona and carboxylic acids can be accomplished by the introduction of an aqueous spray or fogging in of mist into the enclosure containing the packets and perishable product to be treated. For enclosed structures such as display cases, crates, trucks, railway cars, ships,

refrigerated containers for meats and other food products, and the like this can be readily accomplished. One distinct advantage of the trona carboxylic acid mixture is that it produces an endothermic reaction in addition to providing carbon dioxide and absorbing oxygen and therefore has an additional cooling effect.

5 When the combined cooling and oxygen absorption effect of items in bunched or clumped form is required, such as the cooling of large pieces of cooked meat is required, the trona/carboxylic acid composition of the invention is also preferably contained in a water and gas permeable packaged form which is added to a water container holding the meat to be cooled. Chunks of ice plus the endothermic action of the trona carboxylic acid packets in the container
10 accelerates the cooling time. Monitoring the temperature drop and adding additional packets of trona carboxylic acid packets and ice makes it possible to reduce the cooling time of such cooked meat from the required six hours to less than three hours. As used herein "meat" may be inclusive of flesh from all forms of animal life, preferably used for human consumption. Animal life is broadly deemed to be inclusive of four- legged animals such as cattle, sheep, swine, deer,
15 elk, moose and the like which are slaughtered and used or preserved for human consumption. Animals are also inclusive of birds of all kinds and primarily those used for human consumption and lake, stream or sea life including fish, shell fish and the like.

 Oxygen perishable products *per se* are not limited to any specific category of class so long as such product is perishable in the presence of oxygen and can be passivated or preserved
20 by an oxygen uptake composition and in the presence of carbon dioxide, preferably under refrigerated conditions. Therefore, any product or item such as those mentioned above including products from plants and animals are inclusive and are exemplified by fruits, vegetables, grains, meats, dairy products, processed fruits, and any of the above which have been processed and/or combined into mixtures such as casseroles, soups, baked goods, or any other processed form fit
25 within the definition of oxygen perishable goods. In addition to oxygen perishable goods, it may also be possible to utilize the trona/carboxylic acid compositions to stabilize or extend shelf life of oxygen scavenging or absorbing chemicals such as functioning as an anti-caking agent.

 Applying the trona carboxylic acid packets in the environment of perishable products also has significant advantages over conventional humidifying devices. The absorption devices are
30 self-contained units that do not require electrical power or other external energy sources. Accordingly, the packets described herein can be used in many environments where

conventional humidifying devices have been impractical or impossible. The cost of manufacturing and operating the packets disclosed herein are less than those associated with conventional humidifying systems, due to the simple design of the packets, their lack of moving parts, and their ability to operate without electricity. Another advantages of using the trona carboxylic acid packets disclosed herein, include portability, reusability of the packets in different locations, and ease of use.

Figure 1 is a perspective view of a liquid or gas permeable woven packet 100 having a front 105 a back (not shown) and sealed at the perimeters 101, 102, 103 and 104 enveloping a particulate mixture of trona and one or more mono-, di- or tri-carboxylic acids.

Figure 2 is a perspective view of the packet 100 as shown in Figure 2 with a cut away - 109 in the front 105 exposing the particulate mixture 106 consisting of particles of trona 107 and a mono-, di- or tricarboxylic acid 108.

Figure 3 is a perspective view of a gas permeable only folded plastic packet 120 having a front 121 a back (not shown) and sealed at the perimeters 123, 124, and 125 enveloping a particulate mixture of trona and one or more mono-, di- or tri-carboxylic acids (not shown).

Optional perforations 126 can be formed in the plastic film of the packet 120 to allow gases to permeate into and out of the packet. The plastic packet can be formed of any suitable material such as plastic film, rigid plastic, porous fabric, and the like. Non-limiting examples of suitable packet material can include polyethylene film, woven or non-woven fabric, cloth, and the like.

The perforations can be patterned along lines, along a grid, or oriented random positions across one or more surfaces of the packet.

Figure 4 is a perspective view of the packet 120 as shown in Figure 3 with a cut away 127 in the front 121 exposing the particulate mixture 106 consisting of particles of trona 107 and a mono-, di- or tricarboxylic acid 108. The packet can optionally be folded along fold 122.

Figure 5 is a perspective view of an elongated gas permeable tube 130 having open ends 131 and 132 and containing in partial breakaway 133, at least one gas permeable packet 120 containing, in granular form, trona and a mono-, di- or tricarboxylic acid mixture 106 as shown in Fig. 1. Tube 130 can be formed of a material which is apertured such as a metal mesh 134, grid, perforated sheet, or the like.

Figure 6 is a perspective view of a liquid container 140 filled with water 141 holding segments of oxygen perishable goods 142, such as chunks of cooked meat, in need of rapid

cooling, pieces of ice 143 and one or more liquid and gas permeable packets 100 as shown in Fig. 1 enveloping a particulate mixture 106 of trona 107 and one or more mono-, di- or tri-carboxylic acids 108.

Figure 7 is a cut away view of an enclosed shipping crate 145 containing oxygen perishable fruit 146 and having gas permeable packets 120 of the trona carboxylic acid mixture 106, as shown in Fig. 2, distributed throughout the crate 145 as needed to adsorb/absorb oxygen and produce an atmosphere of carbon dioxide surrounding the fruit.

Figure 8 is a perspective view of a produce display 150 containing oxygen degradable produce such as tomatoes 151, lettuce 152, celery 153 and broccoli 154 and retained in a moist environment by mean of an aqueous spray 156 fed through a supply line 157 to spray nozzles 155. Also in the environment is a gas permeable elongated tube 130, as shown in Figure 5, containing strategically located gas permeable packets of granulated trona and a mono-, di- or tri-carboxylic acid (not shown) to absorb/adsorb oxygen from the immediate environment and enhance a presence of carbon dioxide.

Figure 9 is a perspective view of yet another enclosed refrigerated display container 160 showing oxygen perishable deli vegetables such as olives 161, cauliflower tips 162, carrot sticks 163, and mushrooms 164 and having inserted into the interior environment of the container an elongated gas permeable tube 130 as shown in Figure 5 containing in one or more gas permeable packets (not shown) containing, in granular form, trona and a mono-, di- or tricarboxylic acid mixture as shown in Fig. 3.

Figure 10 is a perspective view of a warehouse storage unit 170 containing shelving 171 and ventilated throughout as shown by directional arrows 172. The warehouse is maintained in a moisture or humidity controlled environment for the storage of oxygen perishable goods 173. Packets 120 of trona and carboxylic acid as shown in Figure 3 may be strategically placed on the shelving 171 to absorb/adsorb oxygen from environment surrounding the perishable goods 173 and replace it with a carbon dioxide environment.

Figure 11 is a partially cut away view of a shipping container 180 for transporting prepackaged oxygen perishable goods represented by 181. Goods 181 may be enclosed in containers or crates which may be sealed or in slatted type crates to promote air circulation. The container 180 and prepackaged goods 181 within may be loaded as cargo on a train, truck, ship, airplane or other means of transportation. Packaged within the goods 181 or in container 180

may be placed any number of trona/acid packets 120 based on the projected oxygen absorption/adsorption from within the environment of the goods and also bringing about an enhanced presence of carbon dioxide within the environment of the oxygen perishable goods. The moisture present within the cargo space or hold during shipping and the determination of how much trona/acid should be present and the size of the packets containing the same can be determined by one skilled in the art depending on numerous factors, distance of shipping, humidity of the outside environment, volume of perishable goods being transported, size of the containers, etc.

Figure 12 is a perspective view of a display or shipping container 185 having a transparent or open top 186 and filled with oxygen perishable produce such as asparagus 187, grapes 188, apples 189 and cucumbers 190, preferably stored in a humidity controlled environment and containing gas permeable packets 120 of trona/carboxylic acid mixtures as shown in Figures 3 and 4 wherein the trona/carboxylic acid mixtures are activated by contact with environment within the container and the surrounding environment to absorb/adsorb oxygen and enhance the presence of carbon dioxide.

Figure 13 is a front view of a reclosable plastic envelope or bag 200 that can be resealed at the top 201 by a zipper type action 202. Inserted into the bag 200 are strips of jerky 203 or other oxygen perishable produce having limited moisture content. Also contained within the bag are gas permeable packets 120 of a granular mixture of trona and mono-, di- or tri-carboxylic acids such as shown in Figures 3 and 4. The trona/carboxylic acid mixture is designed to lessen the oxygen content and result in an increase in carbon dioxide in the bag interior. The amount of trona/carboxylic acid is determined so as not to dehydrate the jerky strips such that they become friable. In other words a minimal amount of moisture is to be tolerated in the jerky strips. However, the carbon dioxide content is sufficient to prevent the strips from being contaminated by bacteria, mold, etc. Even with repeated opening and closing of the bag, the jerky remains free of such contamination.

Figure 14 is a perspective view of a tray 210 or similar type container having placed thereon absorbed pads 211 on which oxygen degradable produce such as fresh meat 212 can be placed. Exemplary of fresh meat 212 is beef, pork, fish and poultry. Illustrated as the meat 212 in Figure 14 is a beef steak. The moisture from the steak will be absorbed by the pads 211. Also on the tray are one or more gas permeable packets 120 of a granular mixture of trona and mono-, di-

or tri-carboxylic acids such as shown in Figures 3 and 4. The tray 210 may be placed in an enclosed display case (not shown) where oxygen in the environment surrounding the meat is adsorbed/absorbed by the trona/carboxylic acid mixture in the packets 120 thereby lessening the oxygen content in this atmosphere and also resulting in an increase in carbon dioxide in the surrounding environment.

Figure 15 is a top plan view of a gaseous and moisture absorbent pad 220 for holding meat or other oxygen perishable produce in an enclosed environment (not shown). In partial break away is shown a granular mixture of trona 107 and mono-, di- or tri-carboxylic acids particles 108 embedded in this pad 220 for absorbing/adsorbing oxygen from the environment surrounding the pad 220 thereby lessening the oxygen content and also resulting in an increase in carbon dioxide in such environment.

Figure 16 is a perspective view of a round storage can or container 225, such as a No. 10 can, having a closable top or lid 226 and a sealed bottom 227. The interior 228 of the container may contain oxygen degradable grain kernels 229 such as corn, wheat, barley, rice, and the like, and also gaseous permeable packets 120 of a granular mixture of trona and mono-, di- or tri-carboxylic acids. The container 225 may be opened and closed as warranted and some of the grain kernels 229 removed. Oxygen in the gaseous space within the container 225 is adsorbed/absorbed by the granular mixture of trona and carboxylic acid which prevents spoilage from occurring. Carbon dioxide formed within the container prevents oxidation of the grain kernels and spoilage from occurring.

Figure 17 is a perspective view of a see through storage container 235 having a sealed bottom 236 and a closable top 237 for holding dosage units of medication 238 such as pills, tablets, capsules, lozenges, and the like. Within the container 235, in addition to the medication 238, is a gas permeable packet or packets 120 of a granular mixture 106 of trona and mono-, di- or tri-carboxylic acid particles for absorbing/adsorbing oxygen from the environment within the container and surrounding the medication. The container 235 may be opened and closed repeatedly by removing the top 237 to remove units of medication 238 thereby allowing for the entrance of oxygen containing outside air. Even with repeated opening and closing, the oxygen within the interior of the container 235 will be absorbed by the trona/carboxylic acid granules for an extended period of time and the carbon dioxide content within the container will be enhanced preventing the medication from being oxidized and degraded.

In one alternative aspect, the granular mixture can be packaged with cooked foods or other perishable items. For example, a cooked food can be vacuum sealed with an amount of the granular mixture resulting in substantially extended shelf life even without refrigeration. Furthermore, the granular mixture can be heated in a microwave along with the food upon use by a consumer.

As mentioned previously, the granular mixture further reduces chilling loads in refrigerated environments, can reduce humidity and condensation, and can operate to reduce defrost times. More specifically, refrigerated environments can include stationary refrigeration rooms, refrigerated trailers, and the like. The granular mixture can be oriented adjacent to one or more components of a refrigeration system to obtain varied benefits as explained below. Typically, the granular mixture can be retained within a primary container having gas permeable openings therein to form a refrigeration load reduction system. Reduced humidity can also improve adherence of stickers (e.g. compliance, safety and maintenance stickers). In addition, introduction of the refrigeration load reduction system can allow for control of the refrigeration chamber within tighter temperature tolerances. For example, typical temperature tolerances for walk-in freezers and refrigerated trailers can be +/- about 10 °F. Using the systems of the present invention can allow for tolerances that are 10% to 50% reduced over conventional tolerances.

One class of refrigeration units utilizes a refrigerant fluid (e.g. glycol) which is circulated through pipes (e.g. copper) which are cooled by the fluid. Fans are used to circulate air across chilled pipes and into a refrigeration chamber. The chamber can optionally be a marlite lined room with sealed concrete floors, although other chambers can be used. A control panel can be used to adjust target temperatures through varying fluid circulation rates and optionally fan speed. Over time the cooling pipes and some other equipment can become encrusted in frost deposits. Such frost can reduce cooling efficiencies and may damage equipment. Conventional refrigeration units include a defrost cycle which removes frost from chilled pipes by heating. Accordingly, multiple refrigeration units may be used to provide continued cooling during a defrost cycle of one unit while other unit(s) continue cooling. In many systems, the defrost cycle is repeated 3-4 times each day, running up to 35 minutes per cycle. Placement of the refrigeration load reduction system of the present invention within cooling fluid circulation paths can dramatically reduce defrost cycle times and in some cases completely eliminate defrost cycles. In one aspect, the refrigeration load reduction system can reduce defrost cycle times by up to 80%,

and in some cases about 70%. Similarly, the refrigeration load reduction system can also reduce moisture which collects on floors which can reduce potential accidents.

In another optional aspect, the granular composition can be mixed with a suitable liquid carrier to form a liquid composition having superior cooling properties. Although other liquid carriers may be used, water can be particularly useful. As a general guideline, about 0.1 to about 15 wt% of granular composition can be mixed into the liquid carrier. Further, the granular composition will typically dissolve to form a solution, although in some cases at least a portion of the granular composition does not dissolve so as to form a solution and slurry. The liquid composition can be used as a heat transfer fluid within cooling and refrigeration units. For example, the liquid composition can be suitable as an ethylene glycol replacement.

In yet another optional aspect, the granular composition can be used as an ice melt. In this case, the granular composition can be directly applied to areas having undesirable accumulation of ice such as, but not limited to, conduit surfaces, floors, and the like. Thus, the granular composition can be applied to an iced surface in sufficient amounts to reduce or eliminate icing of the surface.

Referring generally to Figure 18, refrigeration load of a refrigeration unit 300 can be reduced by orienting the refrigeration load reduction system 302 within a fluid circulation path 304 of the refrigeration unit which is adapted to cool a refrigeration chamber 306. The refrigeration unit can be any refrigeration unit such as a walk-in chiller, refrigerator or freezer, a commercial display refrigerator or freezer, a residential refrigerator, a trailer refer, or the like. Figure 18 illustrates the refrigeration load reduction system oriented at an intake 308 of the refrigeration unit. Typically, the refrigeration unit can include a compressor, condenser, evaporator, and a defrost system (e.g. reversing valve, heater and/or controllers). In one optional aspect, the refrigeration unit is a compressor driven heat exchanger. In another aspect, the refrigeration load reduction system can be oriented adjacent perishable food products 309 within the refrigeration chamber 306.

Figure 19 illustrates one example of a refrigeration load reduction system which includes a rigid box 310 as the primary container. The rigid box includes a closeable access opening 312 adapted to allow replacement of the granular composition. The rigid box can also include openings 314 which allow gases to migrate into and out of the rigid box to contact the granular composition. The rigid box can be shaped to fit within a refrigeration intake unit or attached to

an exterior surface of an intake vent. In another alternative, the rigid box can be shaped to be oriented within a refrigeration chamber adjacent a refrigeration unit. The rigid box can be sized to accommodate a particular application. In some cases a box having dimensions of about several inches in each dimension can be useful, while in some cases a box having up to 2-3 feet in one or more dimensions can be used.

In one example, the refrigeration load reduction system can be oriented within a refrigeration unit of a tractor trailer (e.g. with a cooling system sometimes referred to as a “reefer”). As mentioned, the granular composition reduces chilling loads and produces CO₂ during use. As a result, perishable products such as, but not limited to, produce can benefit from extended freshness. For example, in one product shipment route approximately 40% of romaine lettuce is lost and unusable due to transit times. Introduction of the refrigeration load reductions system can substantially increase retained product extending freshness of romaine lettuce up to about fifteen days. This can often result in less than 10%, and in some cases less than 5%, loss of product within an expected transit time. Typically, in the absence of such approaches, transit times in excess of 16 hours can result in up to 30% losses.

Furthermore, the refrigeration load reduction system can also reduce humidity and condensation buildup. Accordingly, in one example the refrigeration load reduction system can be oriented adjacent a circuit board of the refrigeration unit. Examples of such an approach can result in substantial reduction in condensation around circuit boards and can increase replacement intervals from about 3 months to about a year or longer.

Depending on the use conditions and amount of granular composition, replacement of the granular composition can often become desirable after a period of time as the granular composition become depleted and the described advantages begin to taper. The period of time may vary but is often from about 30 to 90 days. Therefore, in one optional variation, a secondary container can be adapted to receive and retain one or more primary containers. For example, Figure 20 illustrates an apertured tube 320 having apertures distributed throughout the tube. A plurality of primary containers such as packets 322 are oriented within the apertured tube. These packets were previously described as gas permeable and contain the granular composition. Optional hangers 324 can be attached to ends of the tube to allow the apertured tube to be secured within the fluid circulation path of the refrigeration unit. In one specific embodiment the apertured tube can be formed of a mesh material, although any tube having openings therein can

be suitable such as, but not limited to, perforated tubes, solid tubes with one or more windows or openings, and the like.

Although the fluid circulation path and refrigeration system can often be a gas environment, in some cases the refrigeration system can utilize a liquid circulation path. In such cases, the refrigeration chamber is filled with a refrigerated liquid which is circulated past an evaporator or other chilled unit. In one liquid path example, the refrigeration unit is a chiller tank. In one specific alternative example, the fluid circulation path is liquid blood work and the refrigeration unit is a blood cooler. In another example, the granular mixture can be introduced into a chiller tank. For example, cooked meats and products can be cooled in a water or liquid bath. Introduction of the granular mixture can reduce chilling times by about 30-50%. As a non-limiting example, 72 grams of granular mixture can be introduced for every 400 gallons of chilling liquid. As a general guideline, from about 3 to about 10 grams (and often about 5 grams) of granular mixture can be used for each gallon of chilling liquid depending on the desired chilling effects.

EXAMPLES

EXAMPLE 1:

This example demonstrates oxygen absorption with trona/citric acid mixtures.

In order to test the oxygen removing capacity of the present invention, an oxygen permeable packet containing trona with citric acid powder, at a weight ratio of 9:1, was placed in a one inch diameter by three inch long test tube. In an identical tube a one-gram sample of a commercial iron/iron oxide powder, also in an oxygen permeable packet, was tested to compare the oxygen absorbing results of the present invention to a product that is presently used commercially. These tubes were sealed for 20 minutes after the introduction of the packets. A gas chromatograph-mass spectrometer (GC-MS) was used to analyze the oxygen content of the air in the tube. Ambient air contains greater than 200,000 ppm (parts per million) by weight oxygen. After twenty minutes exposure of the air in the respective tubes, the tube containing the trona/citric acid sample registered 11.06 ppm of oxygen and tube containing the iron/iron oxide sample registered 15.85 ppm oxygen. The caps were removed and the tubes were exposed to ambient air for 30 minutes with the respective samples remaining in the tubes. The tubes were then sealed for another 20 minutes and the air in the tubes was again analyzed for oxygen using a GC-MS. The trona/citric acid tube registered 8.96 ppm oxygen and the iron/iron oxide tube

registered 15.23 ppm oxygen. Interestingly, the second test showed better oxygen removal results than the first test particularly for the trona/citric acid. Presumably this is due to the trona/citric acid sample in the tube continuing to absorb oxygen even while the tube was open to the atmosphere. These tests demonstrate that the trona/citric acid packet absorbed oxygen significantly better than the iron/iron oxide packet.

EXAMPLE 2

This example confirms the results of Example 1.

It was calculated that 11.6 mg of the trona/citric acid product of Example 1 would be comparable, on a w/v basis, to a two gram packet of the same product in a #10 tin can used for food storage. To further compare the oxygen removing capacity of the present invention with the commercial oxygen absorbing iron/iron oxide product, 11.6 mg of each of these products, in a sealed oxygen permeable packet, were placed in a one inch by three inch tube as in Example 1. When the 11.6 mg trona/citric acid packet was placed in the tube and analyzed after the tube was sealed for 20 minutes as in Example 1, the GC-MS analysis showed the oxygen content in the tube had been lowered to 43.7 ppm. When the 11.6 mg of iron/iron oxide packet was sealed in the tube for 20 minutes, it had reduced the oxygen content to 43.1 ppm. As in Example 1, these tubes were exposed to air for 30 minutes and after the tubes were again sealed for 20 minutes, the trona/ citric acid tube contained 35.8 ppm oxygen and the iron/iron oxide tube contained 40.2 ppm oxygen. These tests again demonstrate that the present invention of trona/citric acid removed oxygen as well as, or better than, the commercially used iron/iron oxide oxygen-absorbing product.

EXAMPLE 3:

This example shows lengthened shelf life of packaged jerky at ambient temperatures.

To demonstrate how well the present invention inhibits bacterial growth, an accelerated 12 month test was conducted on a 4 oz. packet of beef jerky. To this sample of beef jerky a one-gram packet of trona/citric acid (9:1 w/w) was added. The beef jerky was contained in a moisture and gas impermeable plastic envelope, and at the conclusion of the accelerated test, the jerky was removed and analyzed using the AOAC 966.23 method and the standard plate count was less than 10 CFU/g. The coliform count was determined using the AOAC 991.14 method, and it was

also found to be less than 10 CFU/g. When the E. Coli count was determined using the same method, it was also found to be less than 10 CFU/g. Using AOAC 2003.07 method the Staphylococcus count was also found to be less than 10 CFU/g. To analyze for Salmonella a modified AOAC 998.09 method was used and it was negative in a 25 gram sample. The yeast and mold were less than 10 CFU/g when the FDA BAM method was used. The moisture content was found to be 15.89 wt. % when it was analyzed using a Denver IR-200.

Generally, after an accelerated 12 month test, the jerky would be dry and brittle and the bacterial count would be greatly increased. In this test the moisture content of the jerky packet was essentially the same as when first packaged. The jerky was not hard but pliable.

Furthermore, the bacterial counts were comparable, if not less than, when the jerky was first packaged. These tests clearly demonstrate that the oxygen removing capacity of the trona/citric acid prevents the drying out of and controls the bacterial growth on packaged beef jerky.

EXAMPLE 4

Jerky

To demonstrate how well the present invention inhibits bacterial growth, an accelerated 12 month test was conducted on a 6 oz. packet of beef jerky in a plastic envelope as in Example 3. The only difference was the size of the beef jerky (6 oz.) in the packet. To this sample of beef jerky a one-gram gas permeable packet of trona/citric acid (9:1 w/w) was added. The beef jerky packet was sealed, and at the conclusion of the accelerated test, the jerky was analyzed using the AOAC 966.23 method and the standard plate count was 5500 CFU/g. The coliform count was determined using the AOAC 991.14 method, and it was found to be less than 10 CFU/g. When the E. Coli count was determined using the same method it was also found to be less than 10 CFU/g. Using AOAC 2003.07 method the Staphylococcus count was also found to be less than 10 CFU/g. To analyze for Salmonella a modified AOAC 998.09 method was used and it was negative in a 25 gram sample. The yeast and mold were less than 10 CFU/g when the FDA BAM method was used. The moisture content was found to be 9.82 wt. % when it was analyzed using a Denver IR-200.

As in Example 3 the moisture content of the jerky packet was essentially the same as when first packaged. The jerky was not hard but pliable. Furthermore, the bacterial counts were comparable, if not less than, when the jerky was first packaged. These tests again clearly

demonstrate that the oxygen removing capacity of the trona/citric acid prevents the drying out of and controls the bacterial growth on packaged beef jerky.

EXAMPLE 5

5 Jerky

To further confirm the results of Examples 3 and 4 on bacterial growth and moisture content of jerky following an accelerated 12 month test, a third test was conducted on a 4 oz. packet of beef jerky. The trona/citric acid content was the same as in Examples 3 and 4. At the conclusion of the tests the bacterial, yeast and mold counts were as reported in Examples 3 and 10 4. The moisture content of the jerky was found to be 16.46 wt. % when it was analyzed using a Denver IR-200. All of these tests confirm the results of Examples 3 and 4. In other words the oxygen removing capacity of the trona/citric acid prevents the drying out of and controls the bacterial growth on packaged beef jerky.

15 EXAMPLE 6:

This example shows rapid cooling of cooked chunks of meat by means of trona/citric acid mixtures.

When large pieces or chunks of meat are cooked, the existing regulations require that such cooked meats are to be cooled from the cooking temperature, about 150⁰ F., to about 45⁰F 20 in not more than six hours. In this example, to four tanks, 4'x 4'x 4', was added 450 gallons of water and 13 blocks of ice (each block weighing about 10 lbs.). To two of the tanks was added two 36 gram packets of trona/citric acid, (9:1 w/w) powder encased in plastic packets permeable to both liquid and gas. Approximately 900 lbs of cooked beef shanks, each shank being about 12 to 15 lbs in weight, and which had been cooked at about 150⁰F for about 1.5 hours, was added to 25 each tank. Temperature probes monitored selected pieces of beef shank at 30 minute intervals at the top, center and bottom of each tested shank until an average temperature of 80⁰F was reached. The shanks in the tubs containing the trona/citric acid packet reach the 80⁰F temperature in an average time of about 1.5 hours whereas the tanks not containing the trona/citric acid the packet took about 2 hours. When the meat reached a temperature of about 30 60⁰F the shanks were removed and placed in a cooler room maintained at 30-35⁰F. The shanks

from the trona/citric acid tank reached the desired temperature of about 45⁰ F in the cooler room in about 3 hours whereas the meat from the untreated tanks took between 5 and 6 hours.

The difference in time between the trona/citric acid cooled shanks and the plain water cooled shanks results in a significant labor and time savings and also accelerates the efficiency and throughput of meat from cooking to final cooling temperature significantly. The financial gain resulting from increased productivity in a shorter period of time is a major factor in cooked meat production.

EXAMPLE 7

Perishable Products

In reference to Figures 5 and 9, tubes containing packets of trona/acid (9:1 w/w) will enhance the chilling and preservation of perishable products within an oxygen containing environment. The oxygen absorbing capabilities of the trona/acid and the production of carbon dioxide gas stops or slows the growth of spoilage pathogens within such enclosed environment. Susceptible spoilage pathogens are inclusive of bacteria, fungi, viruses, and other microorganisms of animal or vegetable origin. Susceptible environments include, but are not limited to, warehouses or similar storage facilities to keep perishable products fresh and enhance cooling properties; manufacturing plants to absorb heat from ovens, machinery, outside environment; transportation environments to preserve perishable products for extended periods, i.e. days or weeks; crates or containers for shipping overland or overseas to preserve perishable products; refrigerated trucks or reefers to enhance energy efficiency and save on transportation fuel costs while simultaneously chilling and preserving perishable products; maintaining moisture in meats, and produce such as fruits and vegetables.

In general the tubes containing trona/acid packets will extend the life of perishable products such that they maintain freshness, moisture and reduce or eliminate spoilage depending upon the number of packets and the amount of trona/acid within the packets.

EXAMPLE 8

Perishable Goods

Packets as shown in Figures 3 and 4 situated in open and closable containers containing oxygen perishable goods may be used to extend the life of such goods even though there are repeated openings and closings of the containers. This lengthens storage or shelf life even after repeated opening/closing of the package or container for days or
5 weeks and also will permit the container to be made of thinner packaging materials thus reducing costs.

EXAMPLE 9

Jerky and Dried Fruit

10 Into a container as shown in Figure 13 is placed freshly cured jerky and/ or dried fruit (e.g. pears, apples, peaches, etc.) along with a packet of trona/acid as shown in Figures 3 and 4. The oxygen in the container is absorbed by the trona/acid and replaced by carbon dioxide as a result of the interaction of the trona/acid with the oxygen. The jerky or fruit, when placed in the container, will maintain freshness for about 18 months, or even longer if not subjected to the
15 open atmosphere. The amount of trona/acid will depend upon the volume of the fruit to be treated.

Even with continuous opening and closing, the jerky or dried fruit in the container will remain fresh, i.e. not lose its moisture content, for 30 days or longer due to the presence of the trona/acid packets.

EXAMPLE 10

Produce

The trona/acid packets in the presence of produce, fruits and vegetables slows the natural decay process which allows such produce to maintain better color, texture and smell for up to 30
25 days from harvest to point of sale. Even additional days of freshness from the fields to the retailer and in the store may be obtained when produce is properly handled and refrigerated. The trona/acid packets removes oxygen and enhances the production of carbon dioxide (CO₂) providing an atmosphere having bacteriostatic properties that helps to retard the growth of spoilage bacteria present on fruits and vegetables.

Particularly when the produce is refrigerated, the endothermic properties of the trona/acid packets will provide an atmosphere which chills harvested food quickly and naturally and extends the freshness of the produce from the fields to the retailer and in the store; extends refrigerated shelf life of the produce; reduces the risk of cross contamination and related liability of the produce; improves the air quality inside refrigerated storage and display cases (See Figure 9); reduces offensive odors thereby in fewer discards, markdowns and spoilage.

EXAMPLE 11

Meat

The trona/acid mixture contained in packets comprise a natural, non-toxic product. What is beneficial is that this product, when exposed to the oxygen present on the surface of meat or in the atmosphere surrounding the meat somehow aids in the production of carbon dioxide (CO₂), an inert gas known to have bacteriostatic properties. CO₂ gas is believed to wrap itself around meat creating an envelope that helps retard the growth of spoilage bacteria present on meats.

By slowing the natural decay process; meats (including red meat, poultry and fish) maintain better color, texture and smell consistent with freshness. This property leads to Consumer takeaway, satisfaction and repeat sales are increased.

Moreover, growers, producers, wholesalers, shippers, manufacturers, processors and retailers will realize immediate benefits when using the combined trona/acid combinations which will (a) extend the freshness from processing and shipping to the warehouse and in the store; (b) extend refrigerated shelf life of red meat, poultry and fish; (c) reduce the risk of cross contamination and related liability of oxygen degradable products; (d) improve the air quality inside refrigerated storage and display cases; (e) reduce offensive odors; and (f) result in the reduction of discards, markdowns and spoilage of oxygen perishable meat products.

EXAMPLE 12

Warehousing and Storage

When used in refrigerated warehouses and storage units, the combined trona/carboxylic acid mixture can change the atmospheric conditions within the enclosed environment to improve efficiencies in cooling. Temperatures are lowered not only on the oxygen degradable produce and meats but within the entire warehouse. This cooling results in enhanced preservation of products along with the ability for products to retain their moisture content thereby keeping the produce fresh over a longer period of time.

The trona/carboxylic acid mixture is a natural and safe product which not only reduces oxygen content within an enclosed atmosphere but also somehow, not fully understood, results in the production of carbon dioxide (CO₂), which, when removing oxygen from within the immediate vicinity of oxygen perishable products, may serve as an inert gas having bacteriostatic properties. The carbon dioxide gas settles around the oxygen perishable produce creating an envelope that helps retard the growth of spoilage bacteria present on produce such as red meat, poultry, fish, fruits and vegetables.

By slowing the natural oxidation or decay process in produce; fruits and vegetables there will be maintained a better color, texture and smell of such produce. Some of the advantage attributable to the presence of trona/carboxylic acid packets in sufficient number and strategically located are: (a) extending product freshness in the warehouse; (b) increasing the storage days of products while maintaining fresh meat, fish, produce and dry goods: (c) reducing the risk of cross contamination and related liability: (d) improving the air flow, air quality and circulation inside refrigerated storage and display cases: (e) reducing offensive odors: (e) minimizing discards, markdowns and spoilage: (f) lowering the temperature of food naturally: (g) chilling harvested food products quickly and naturally: and (h) improving the efficiencies of cooling systems thus reducing power costs.

EXAMPLE 13

Transportation

Packets containing trona/carboxylic acid mixtures, in appropriate amounts and strategically spaced within a cargo space will protect oxygen perishable goods shipped long distances, i.e. from one country to another, cross country, and by various means of transportation, such as air cargo, ships, railway, trucks and any other means. If

appropriately utilized and spaced the trona/carboxylic acid packets will increase the sustainability of such oxygen perishable products and add additional days or even weeks of freshness. By placing trona/carboxylic acid packets in pallets with product or in the shipping area, it will keep the product cool, maintain moisture in products, minimize or
5 remove oxygen in the environment and surround products with carbon dioxide which, in such an environment possesses bacteriostatic properties.

When shipping produce under such conditions the shipper can add extra days of freshness when transporting produce, meats and fish, increase geographical coverage with additional days while keeping perishables fresh. By slowing the natural decay
10 process in meats, fish and produce during shipping and transportation, foods stay fresher longer and arrive in the stores with longer shelf life and less spoilage. As a result the moisture content of the produce will be maintained, the risk of cross contamination and related liability will be reduced, the air quality inside the storage area will be improved and offensive odors reduced. The result will be to extend the sustainability and freshness
15 of perishable products from the fields to the retailer and to the stores, the produce will arrive at the final destination with less spoilage and fewer discards, and there will be an increased area of geographical coverage with additional days while keeping perishables fresh.

20 EXAMPLE 14

Growers

Growers and producers of fruits and vegetables have found that they may preserve their products immediately upon being picked and/or harvested by the use of the trona/carboxylic acid filled packets of this invention. As previously stated this trona/acid
25 combination protects oxygen perishable produce and also results in enhancing an environment of carbon dioxide (CO₂), which has been shown to have bacteriostatic properties. Fruits and vegetables are cocooned or enclosed in the stable environment protected by the trona/acid combination which allows this such produce to retain its moisture content and remain in a picked or harvested state.

By slowing the natural decaying process in produce during harvesting, storage and shipping, which is attributed to the presence of oxygen, foods stay fresh longer and arrive at stores with increased shelf life and reduced spoilage.

5 EXAMPLE 15

Home Storage/Refrigeration

Within an enclosed atmosphere, such as a refrigerator or pantry, the trona/carboxylic acid, when appropriately placed in oxygen permeable packets will extend the freshness of oxygen perishable products for up to about one month. In this regard it will extend the shelf life and retard the growth of bacteria that may be present on meats, jerky, dried fruit, and produce.

By slowing the natural decay process in produce; fruits and vegetables maintain better color, texture and smell. Other advantages to be found are that it will (a) extend the freshness of opened food in enclosed areas up to 30 days; (b) improve the air quality inside home refrigerators and pantries; (c) be ideal for home food storage and long term emergency preparedness; (d) reduce the risk of cross contamination or various produce items; (e) reduce offensive odors; and (f) result in less produce spoilage and discards.

EXAMPLE 16

20 Pharmaceuticals

Pharmaceuticals, particularly tablets or capsules, are usually packaged in larger containers for shipment from the manufacturer to a pharmacy or other intermediary. From there the pharmaceuticals may be dispensed as is or divided into smaller containers to pharmacies, hospitals, nursing homes, extended care facilities. Any pharmaceutical that has a limited shelf-life of less than a few weeks can particularly benefit from this invention. Such pharmaceuticals can include, but are not limited to, flu shots, antibiotics, and the like. If a prescription item, the pharmaceuticals may be further dispensed in smaller containers. If marketed without a prescription and are placed on a shelf in the pharmacy, supermarket, or other retail outlet for the consumer to purchase they are still considered to be pharmaceuticals for purposes of this invention. In each of these events the tablets or capsules are subjected to an open environment numerous times

which may be detrimental to the viability and stability of the pharmaceutical. This allows the pharmaceutical to be subjected to an oxygen atmosphere. It is not unusual to have a silica gel or similar packet present in the container to absorb moisture but the oxygen content in the surrounding atmosphere is not reduced.

5 By placing an appropriate amount of trona/carboxylic acid packets in the container the oxygen present within the container will be absorbed and the stability of the pharmaceuticals will be enhanced. The container having the trona/carboxylic acid packets will provide an oxygen free environment within its confines and will continue to absorb oxygen and provide a carbon dioxide (CO₂), environment within the pharmaceutical
10 container for days and even weeks although the container may be repeatedly opened and closed as the tablets or capsules within are dispensed. Furthermore, the packets additionally reduce moisture content and can function as a desiccant which can further extend shelf-life of sensitive pharmaceutical products.

15 EXAMPLE 17

Red Blood Cell Transfusions

Although transfusions can be lifesaving, they are not without risk. In critically ill patients, red blood cell (RBC) transfusions are associated with increased morbidity and mortality, which may increase with prolonged RBC storage before transfusion. Red blood
20 cells can be stored from 21 to 42 days if kept refrigerated at 33.8 to 42.8 °F (1 to 6 °C) and an approved preservative is added. The mean storage time before transfusion in the United States is 17 days. This shelf life can be extended if packets of these red blood cells are kept in the presence of trona/acid packets (as shown in Figure 3). The oxygen absorbing capabilities and the production of carbon dioxide gas stops or slows the growth
25 of pathogens, which help prevent storage lesion - a set of biochemical and biomechanical changes which occur during storage within such enclosed environment. Current regulatory measures are in place to minimize red blood cell, RBC, storage lesion - including a maximum shelf life (currently 42 days), a maximum auto-hemolysis threshold (currently 1% in the US), together with an average 24-hour post-transfusion RBC
30 survival *in vivo* of more than 75%. These regulatory measures are exceeded when red blood cells are stored in the usual manor in the presence of trona/acid mixture.

EXAMPLE 18

Whole Blood Transfusions

Whole blood, unseparated venous blood, can be stored for up to 35 days if kept
5 refrigerated at 33.8 to 42.8 °F (1 to 6 °C) and an approved preservative is added. This
shelf life can be extended if packets of this whole blood are kept in the presence of
trona/acid packets (as shown in Figure 3). The oxygen absorbing capabilities and the
production of carbon dioxide gas stops or slows the growth of pathogens, which help
prevent storage lesion - a set of biochemical and biomechanical changes which occur
10 during storage within such enclosed environment. The storage lesions are reduced by the
presence of trona/acid and the transfusion efficacy in a patient is improved. In general the
presence of trona/acid packets will extend the shelf life of whole blood so that it can be
used in blood transfusions, and these blood transfusions will have greater efficacy.

15 EXAMPLE 19

Plasma Transfusions

Plasma and fractionated plasma products benefit by storage in the presence of
trona/acid packets (as shown in Figure 3). The oxygen absorbing capabilities and the
production of carbon dioxide gas stops or slows the growth of pathogens. These
20 conditions increase the shelf life, and improve the transfusion efficacy in a patient.

EXAMPLE 20

Organ Transplants

Because most transplanted organs are from deceased donors, the organ must
25 inevitably be stored after its removal from the donor until it can be transplanted into a
suitable recipient. The donor and recipient are often in different locations, and time is
needed to transport the donor organ to the hospital where the recipient is being prepared
for transplantation. Effective, safe, and reliable methods are needed to preserve the organ
ex vivo until transplantation can be performed. Acceptable preservation times vary with
30 the organ. Most surgeons prefer to transplant the heart within 5 hours of its removal; the
kidney can safely be stored for 40-50 hours, but earlier transplantation is preferred. Most

pancreas transplants are performed after 5-15 hours of preservation. Liver transplantations usually are performed within 6-12 hours. Hypothermia is the preferred technique of organ preservation because it is simple, does not require sophisticated expensive equipment, and allows ease of transport. Hypothermia is beneficial because it slows metabolism. Organs exposed to normothermic ischemia remain viable for relatively short periods, usually less than 1 hour. However, biodegradable reactions continue; these include the accumulation of lactic acid, a decrease in intracellular pH, proteolysis, lipolysis, and lipid peroxidation. The oxygen absorbing capabilities and the production of carbon dioxide gas as disclosed herein stops or slows the growth of pathogens, which help prevent storage lesion - a set of biochemical and biomechanical changes which occur during storage within such enclosed environment. In the presence of trona/acid (Figure 3) the conditions are improved, and the preservation of organs ex vivo can be extended until transplantation can be performed.

EXAMPLE 21

Containers of granular mixture were distributed throughout a 90,000 square foot meat plant as outlined in Table 1 below.

Table 1

Location	Containers	Time without	Time with Containers	KWH (with/without)
Holding Cooler		4:30	1:20	876/21.9
Meat Cooler		3:30	2:20	657/43.8
Shipping Dock		4:30	3:20	876/43.8
Packaging Area		4:30	3:20	1076/538
Distribution Cooler		5:30	2:20	1095/43.8
Production Area		3:30	3:20	798/538
Meat Cutting Area		4:30	3:20	1076/538
Total		30:30	19:20	6454/1767.3
Savings			11.1 Hours	4786.7

Data obtained from Paksense Temp Loggers. Notably, the observed reduction in energy was just over 25%.

5 EXAMPLE 22

Containers as described in Example 21 were placed in a standard refrigerated trailer using a reefer unit. An amount of diesel fuel was used as fuel for the reefer unit. This amounts to a savings of about 22 gallons/day for this unit without using the containers of granular composition.

10

EXAMPLE 23

A stationary reefer unit having a refrigeration trailer was operated for one day as described in Example 21. An amount of 0.5 gallons of fuel was used, as opposed to 2.2 gallons for the same unit without the containers of granular composition.

15

EXAMPLE 24

Side-by-side reefer units were operated simultaneously under common conditions with and without the containers of granular composition. The reefer unit without the granular composition used 11.4 gallons of fuel, while the reefer unit with the granular composition used 8.4 gallons of fuel.

20

EXAMPLE 25

The reefer unit of Example 24 was again tested with a refrigeration temperature of 55 °F (outside temperature of 90 °F) and including containers of the granular composition. An amount of 2.5 gallons of fuel was used over 24 hours. The reefer unit and trailer was aired-out for 3 days and the test repeated without the containers. The reefer unit used 5 gallons of fuel.

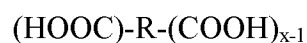
25

It should be understood that the foregoing disclosure relates to exemplary embodiments of the invention and that modifications may be made without departing from the spirit and scope of the invention as set forth in the claims that follow.

CLAIMS

What is claimed is:

1. A refrigeration load reduction system, comprising:
 - a. a primary container having gas permeable openings therein; and
 - b. a granular composition retained within the container, said granular composition comprising a granular mixture of a sodium carbonate mineral and a mono-, di- or tricarboxylic acid, wherein the sodium carbonate mineral is a member selected from the group consisting of trona, gaylussite, natron, prissonite, northupite, nahcolite, thermonatrite, and combinations thereof.
2. The system of claim 1, wherein the primary container is a flexible packet.
3. The system of claim 2, wherein the flexible packet is formed of a plastic film having perforations therein or is formed of a porous fabric.
4. The system of claim 1, wherein the primary container is a rigid box which includes a closeable access opening adapted to allow replacement of the granular composition.
5. The system of claim 4, wherein the rigid box is shaped to fit within a refrigeration intake unit or shaped to be oriented within a refrigeration chamber adjacent a refrigeration unit.
6. The system of claim 1, further comprising a secondary container adapted to receive and retain at least one primary container, wherein the secondary container is optionally an apertured tube.
7. The system of claim 1, wherein the mono-, di- or tricarboxylic acids have the general formula:



where x is an integer of 1, 2 or 3, and R is a saturated or unsaturated, straight, or branched carbon chain having one to eighteen carbon atoms, or an aromatic moiety

having six to eighteen carbon atoms which may be substituted or unsubstituted by OH, COOH, COOM, COOR', -OR' substituents, where M can be an alkali or alkaline earth metal, and where R' can be saturated or unsaturated, straight, or branched carbon chain having from one to eight carbons, an aromatic moiety having six to eighteen carbon atoms which may be substituted by alkyl groups having one to eight carbons, OH, COOH, COOM, COOR', -OR' substituents, and M can be an alkali or alkaline earth metal.

8. The system of claim 1, wherein the mono-, di- or tricarboxylic acid is a member selected from the group consisting of citric acid and salicylic acid.
9. The system of claim 1, wherein the granular mixture has a w/w ratio of mineral to acid of 200:1 to 5:1.
10. A method of reducing refrigeration load, comprising orienting a refrigeration load reduction system within a fluid circulation path of a refrigeration unit adapted to cool a refrigeration chamber, said refrigeration load reduction system including:
 - a. a primary container having gas permeable openings therein; and
 - b. a granular composition retained within the container, said granular composition comprising a granular mixture of a sodium carbonate mineral and a mono-, di- or tricarboxylic acid.
11. The method of claim 10, wherein the refrigeration load reduction system is oriented within the refrigeration chamber adjacent the refrigeration unit or within an air intake of the refrigeration unit.
12. The method of claim 10, wherein the fluid circulation path is air and the refrigeration unit is a compressor driven heat exchanger.
13. The method of claim 12, wherein the refrigeration load reduction system is oriented adjacent perishable food products within the refrigeration chamber.

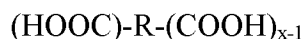
14. The method of claim 10, wherein the fluid circulation path is liquid and the refrigeration unit is a chiller tank.

5 15. The method of claim 10, wherein the refrigeration load reduction system is oriented adjacent a circuit board of the refrigeration unit.

16. The method of claim 10, wherein the fluid circulation path is liquid blood work and the refrigeration unit is a blood cooler.

10 17. The method of claim 10, wherein the sodium carbonate mineral is a member selected from the group consisting of trona, gaylussite, natron, prissonite, northupite, nahcolite, thermonatrite, and combinations thereof.

15 18. The method of claim 10, wherein the mono-, di- or tricarboxylic acids have the general formula:



where x is an integer of 1, 2 or 3, and R is a saturated or unsaturated, straight, or branched carbon chain having one to eighteen carbon atoms, or an aromatic moiety having six to eighteen carbon atoms which may be substituted or unsubstituted by OH, COOH, COOM, COOR', -OR' substituents, where M can be an alkali or alkaline earth metal, and where R' can be saturated or unsaturated, straight, or branched carbon chain having from one to eight carbons, an aromatic moiety having six to eighteen carbon atoms which may be substituted by alkyl groups having one to eight carbons, OH, COOH, COOM, COOR', -OR' substituents, and M can be an alkali or alkaline earth metal.

19. The method of claim 10, wherein the mono-, di- or tricarboxylic acid is a member selected from the group consisting of citric acid and salicylic acid.

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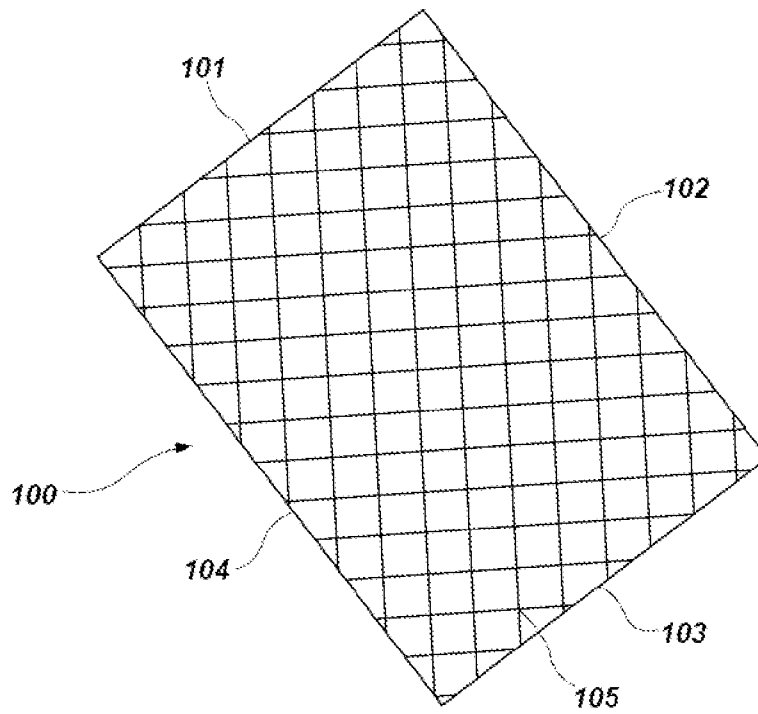


FIG. 1

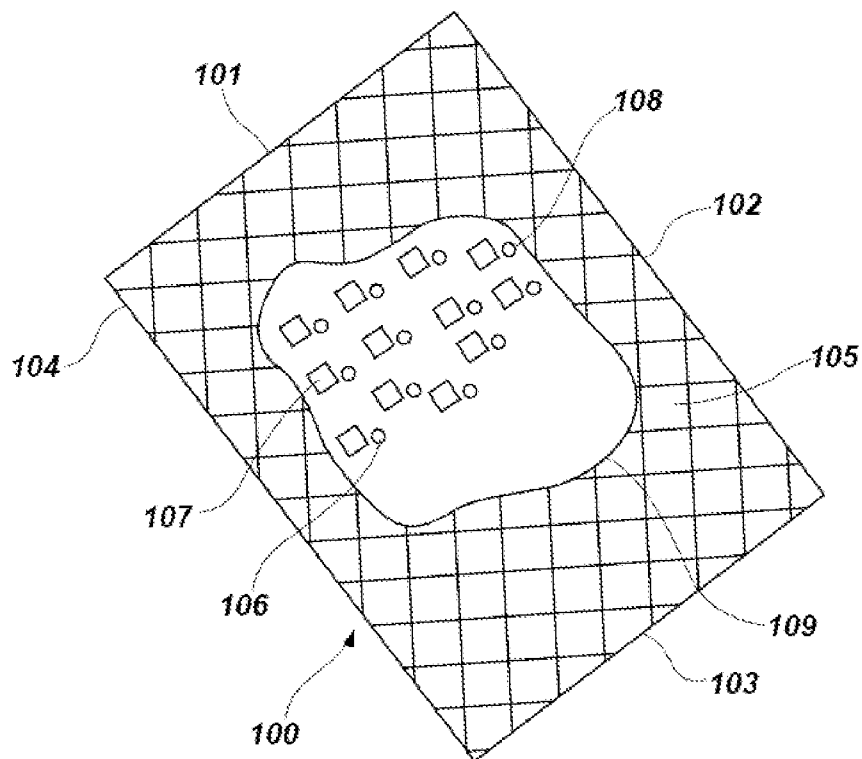


FIG. 2

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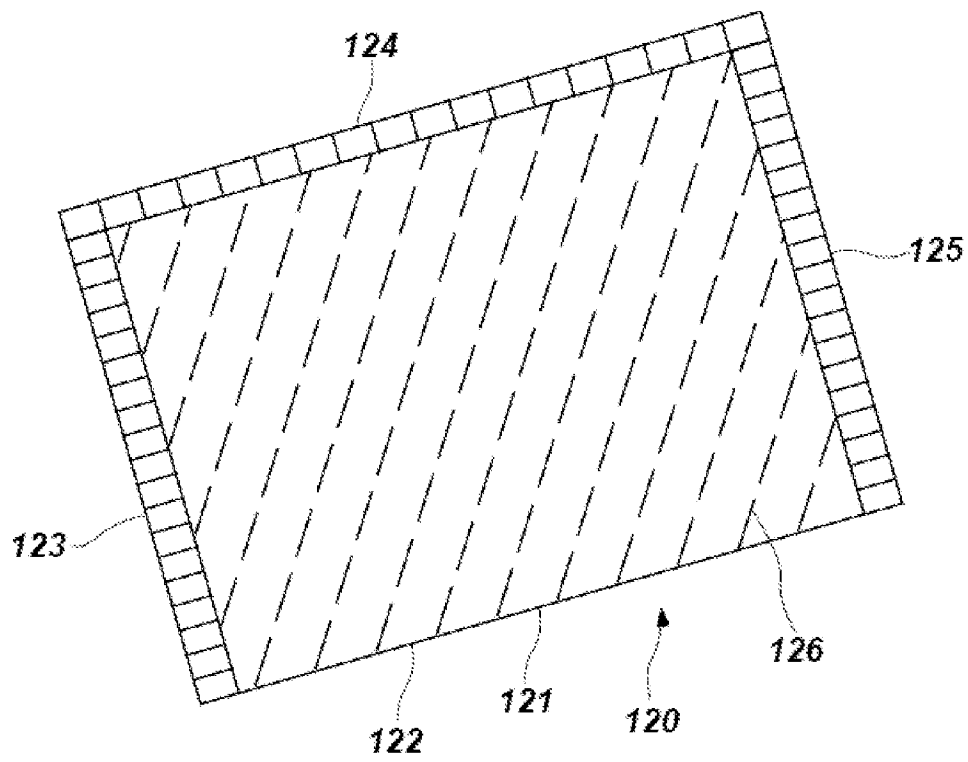


FIG. 3

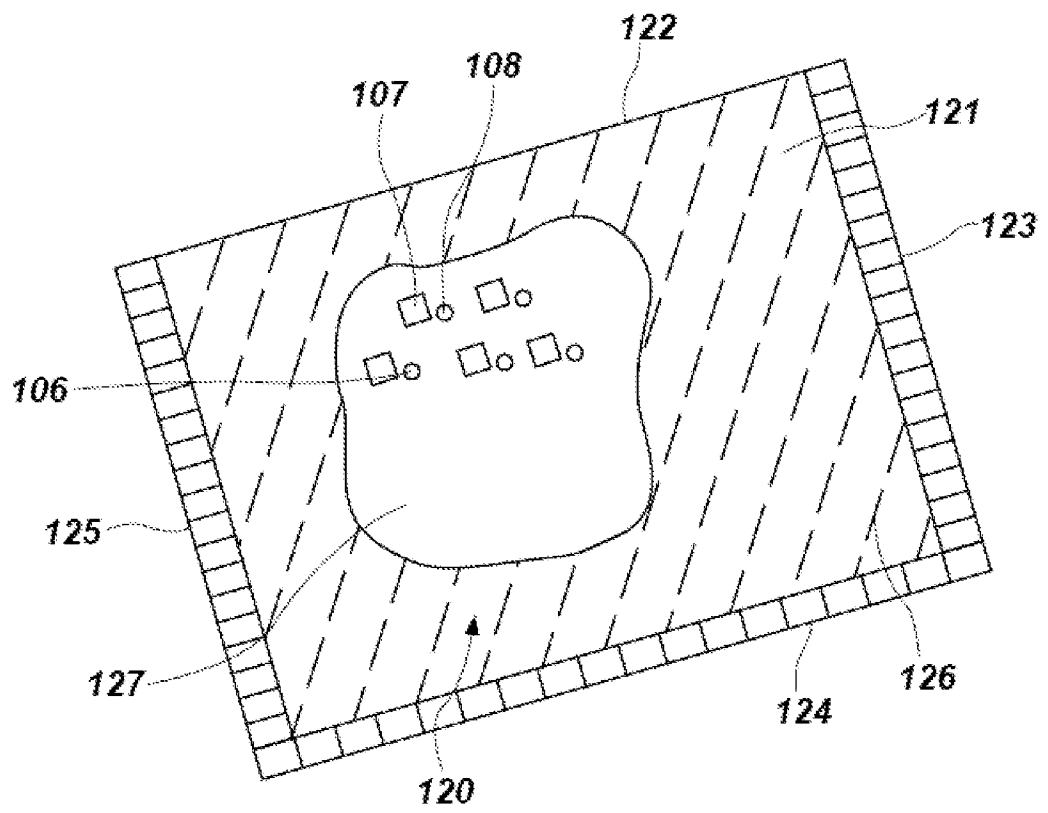


FIG. 4

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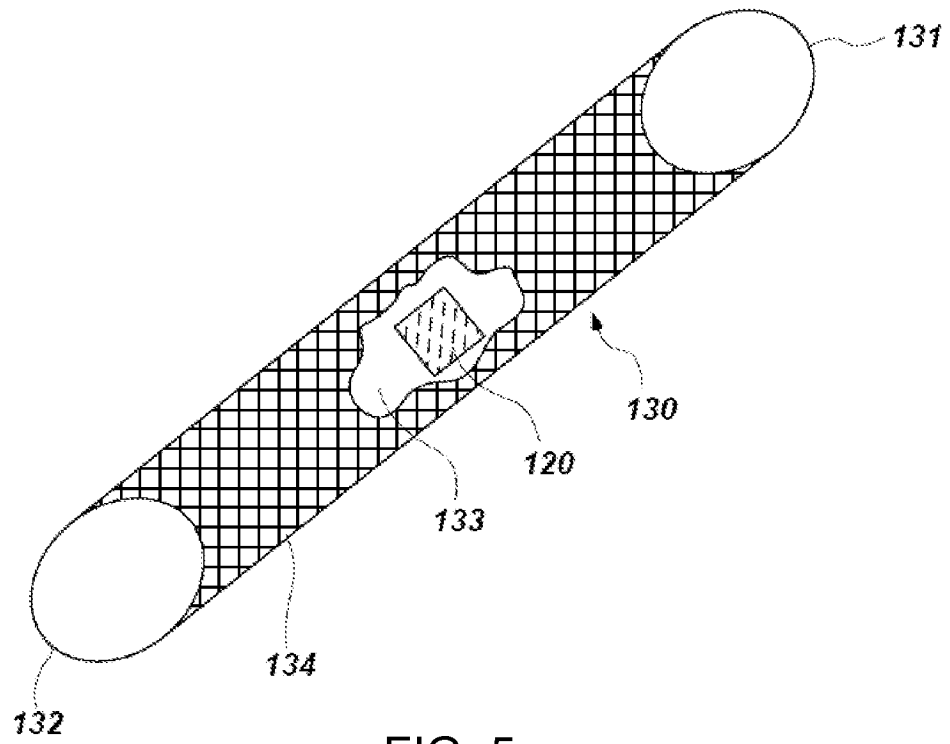


FIG. 5

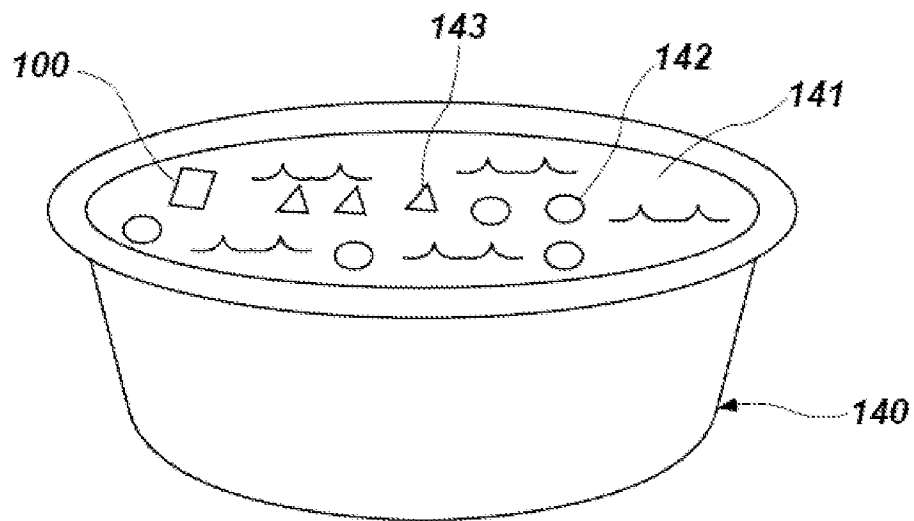


FIG. 6

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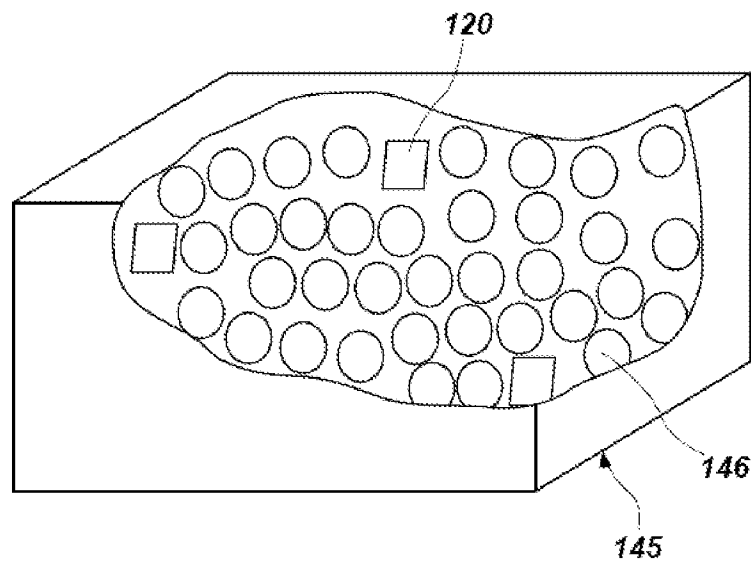


FIG. 7

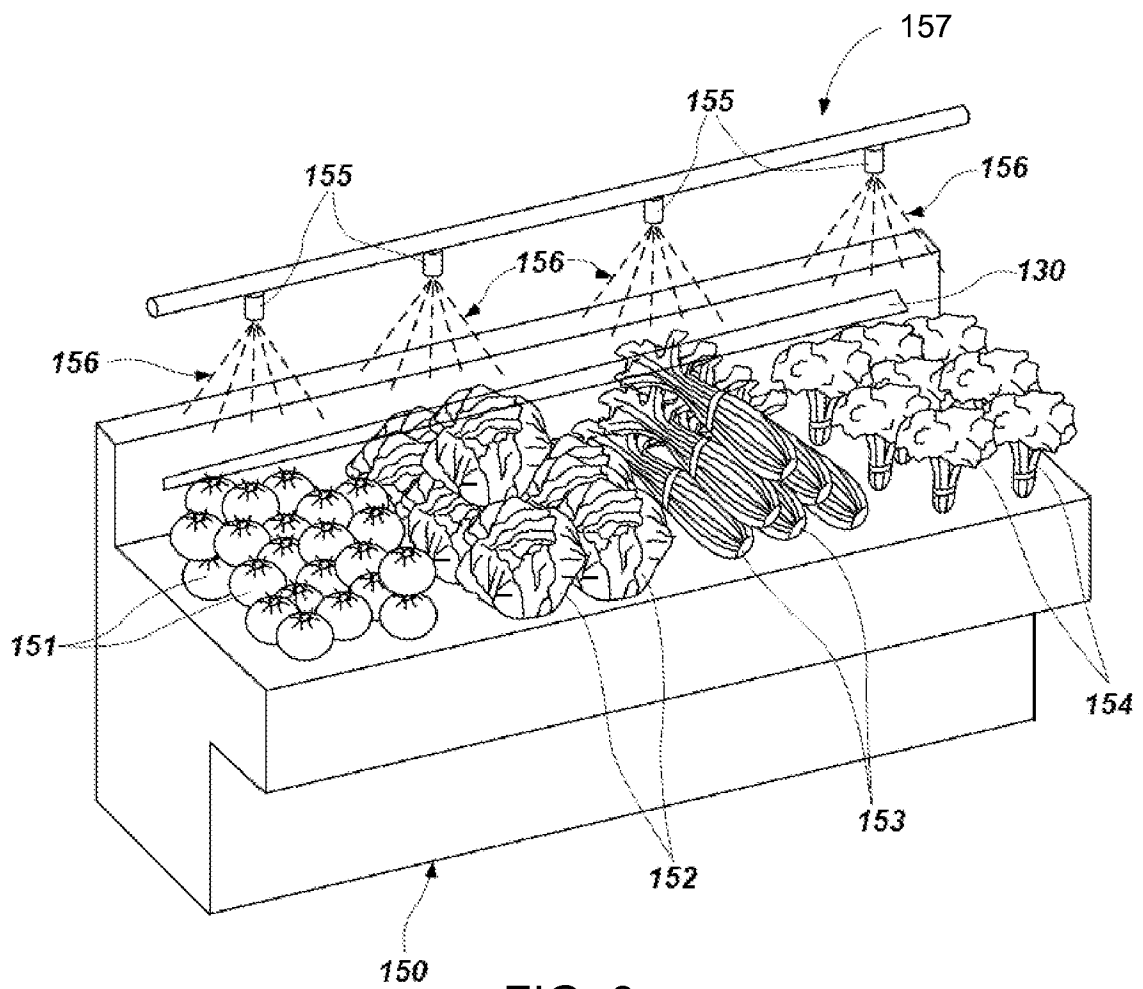


FIG. 8

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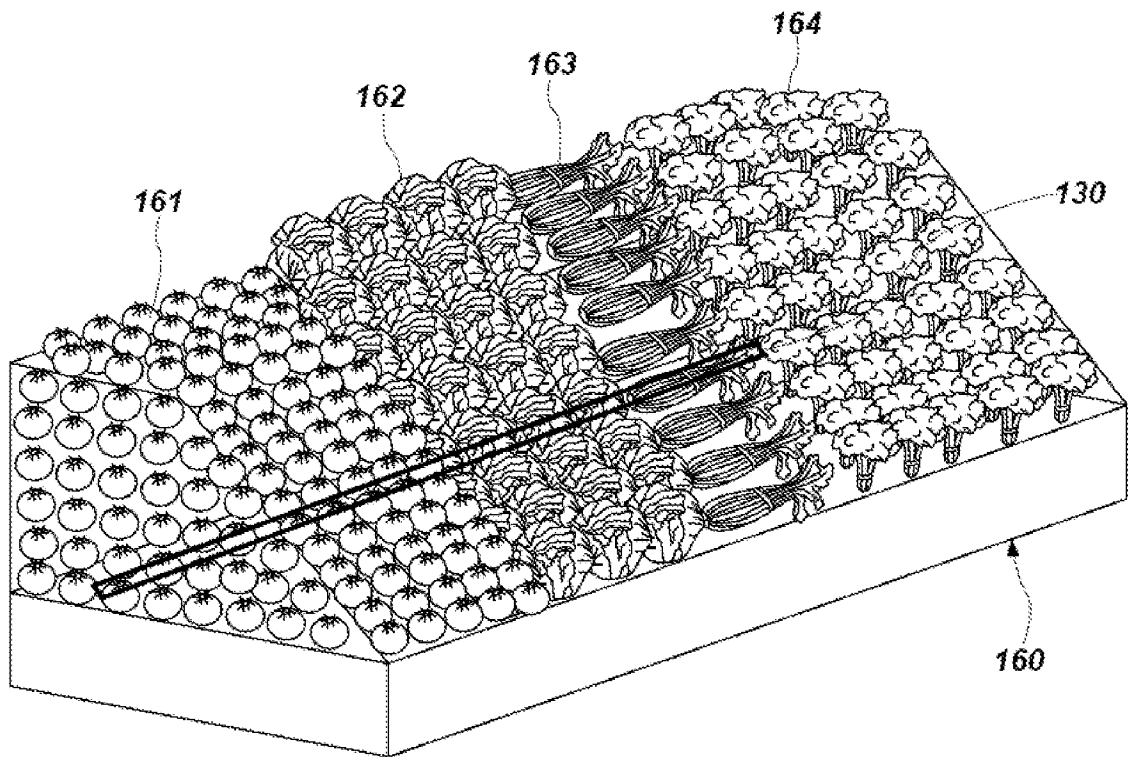


FIG. 9

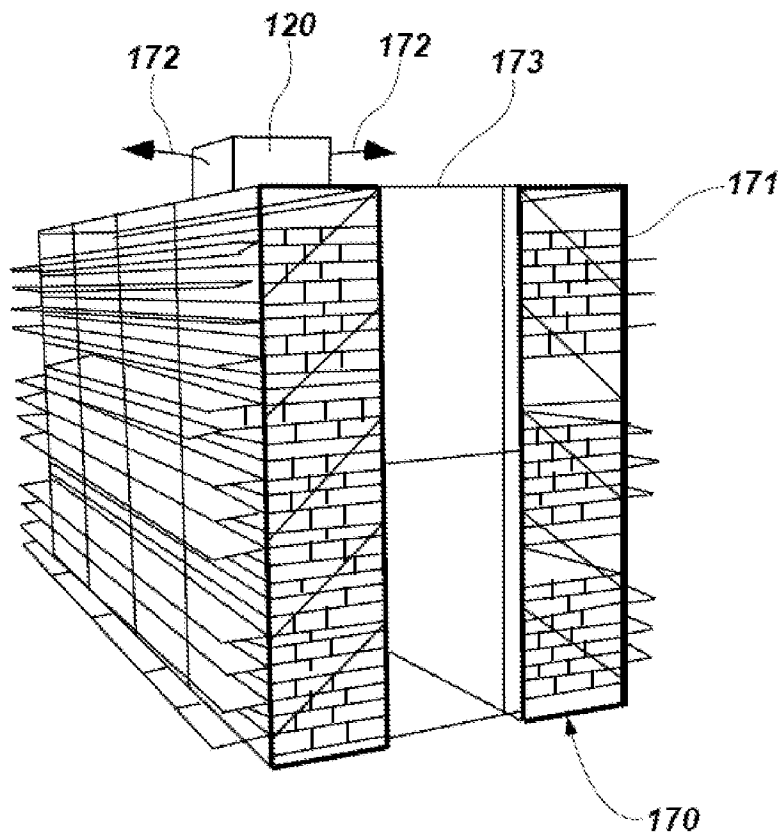


FIG. 10

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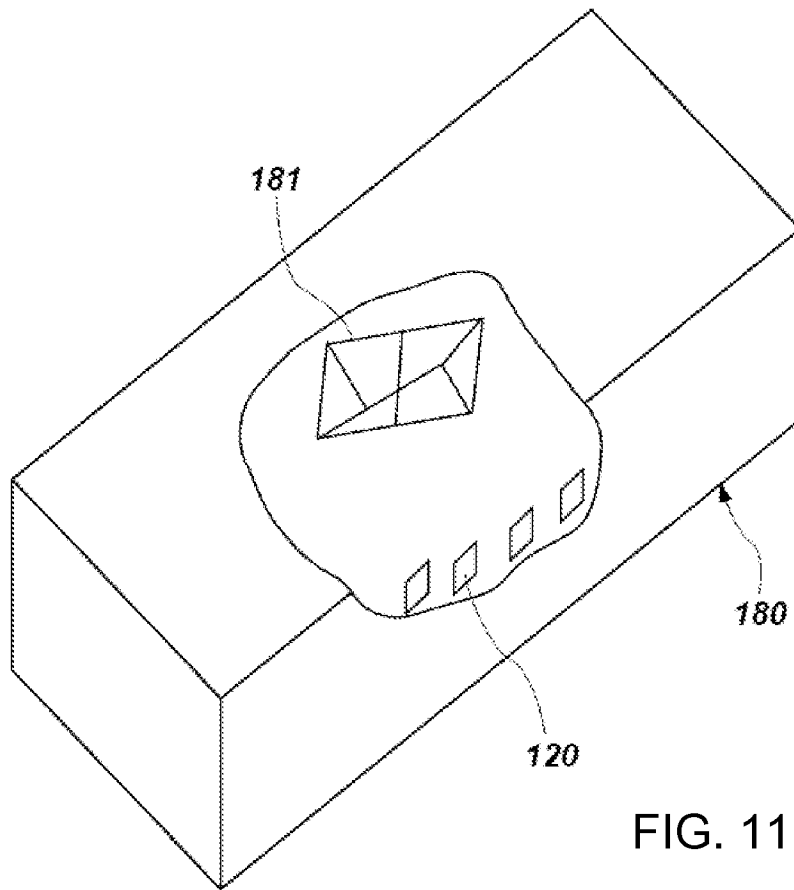


FIG. 11

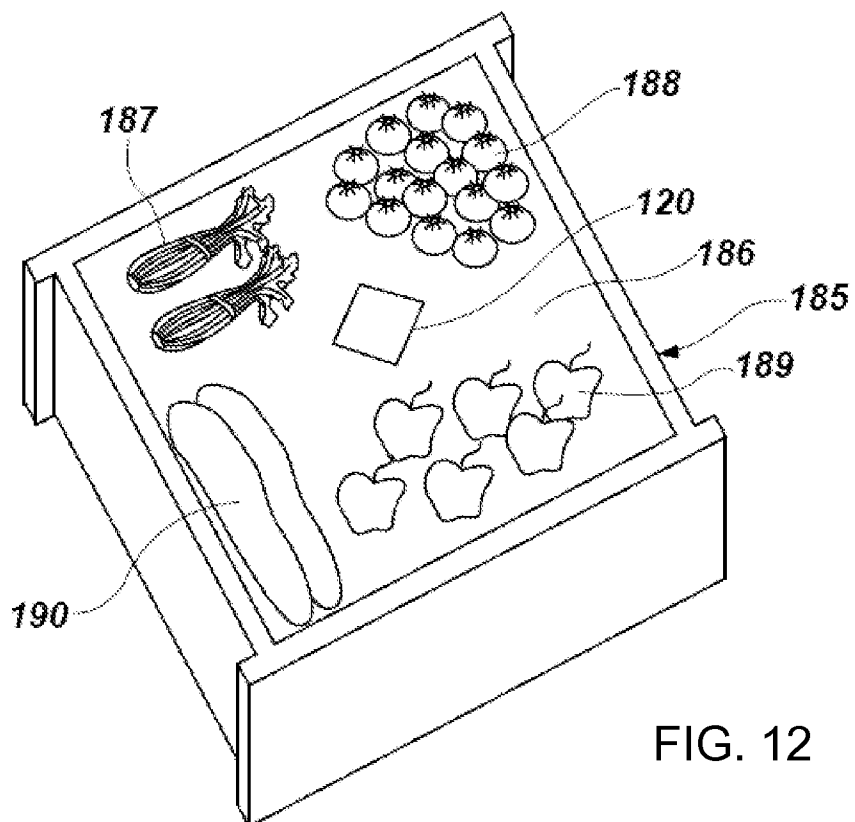


FIG. 12

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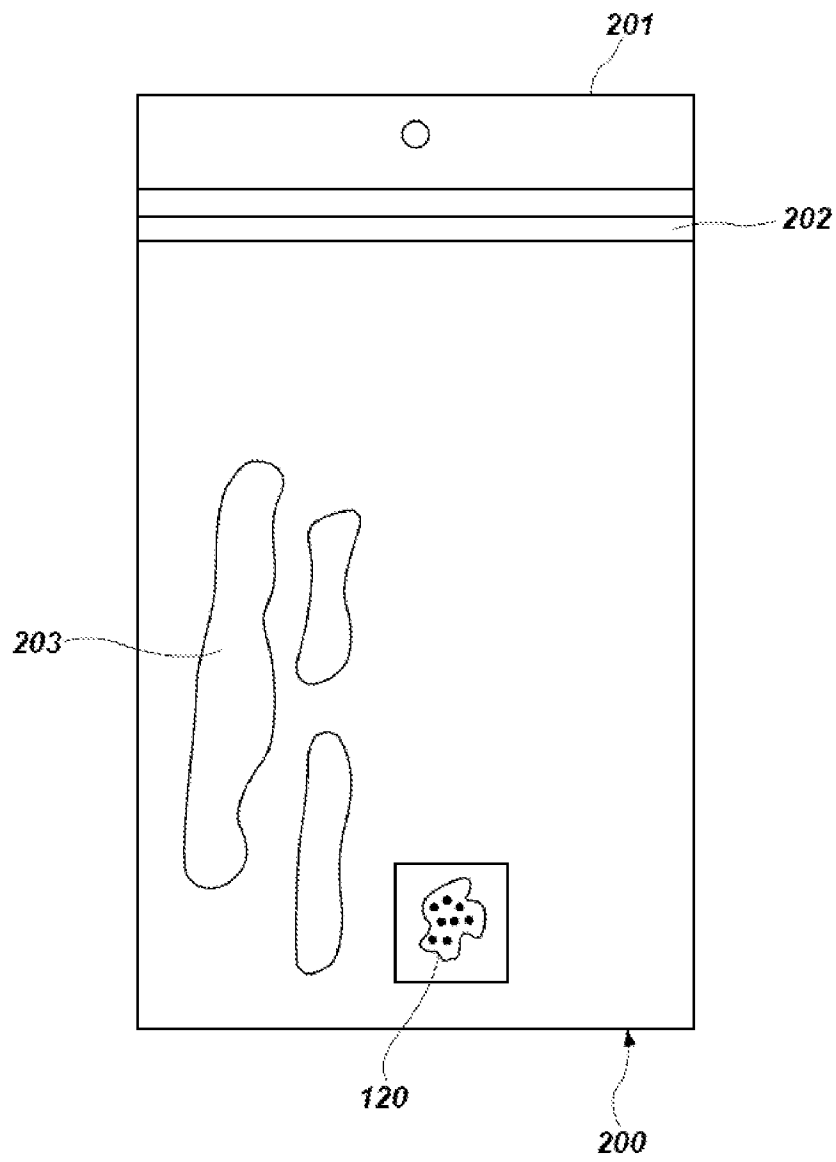
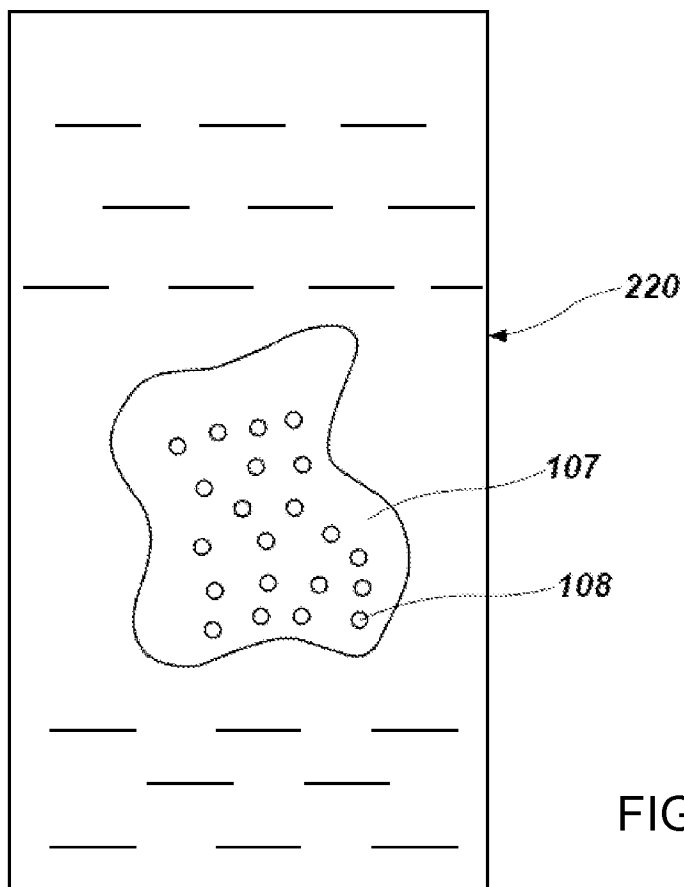
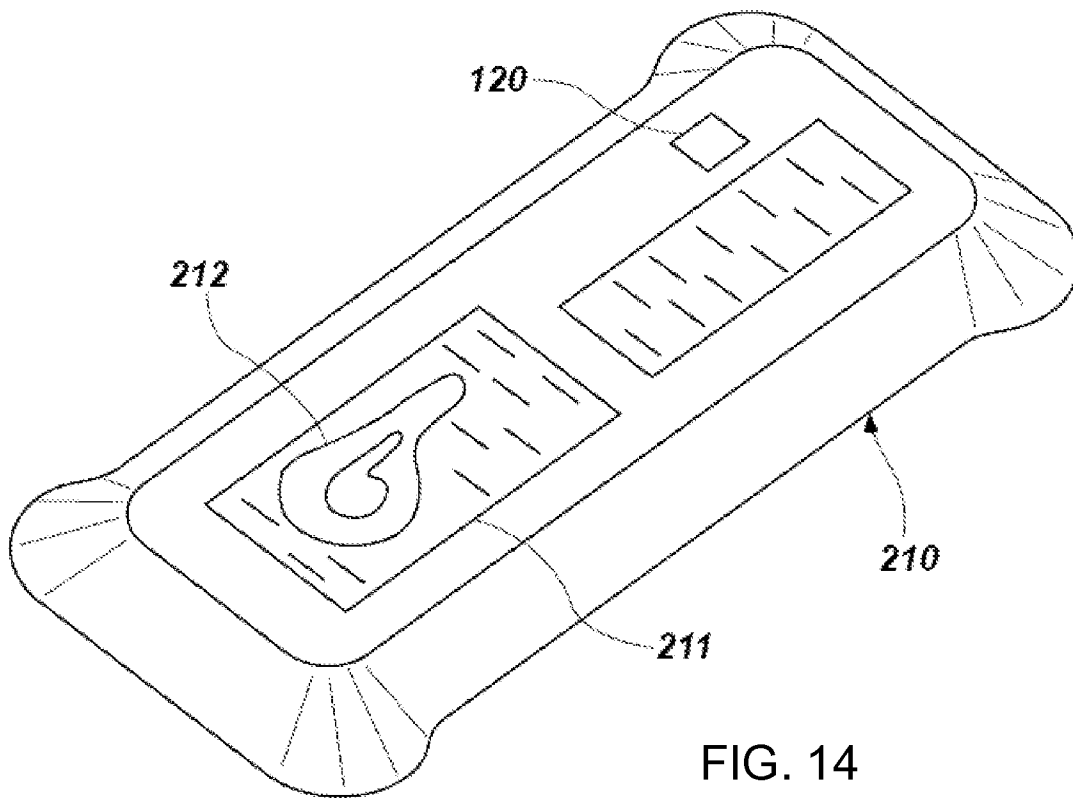


FIG. 13

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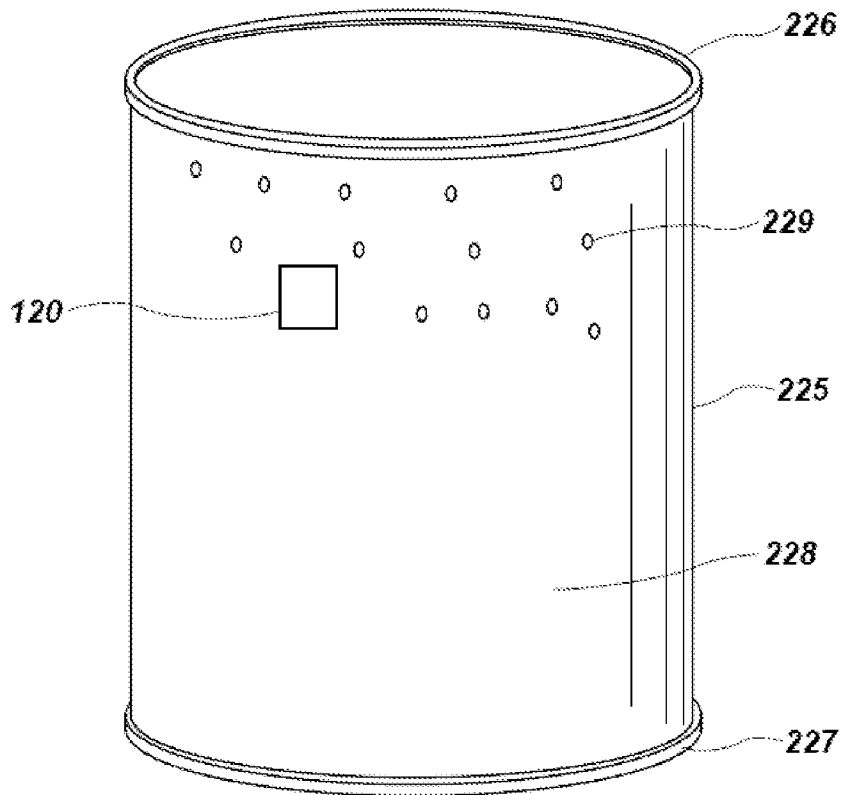


FIG. 16

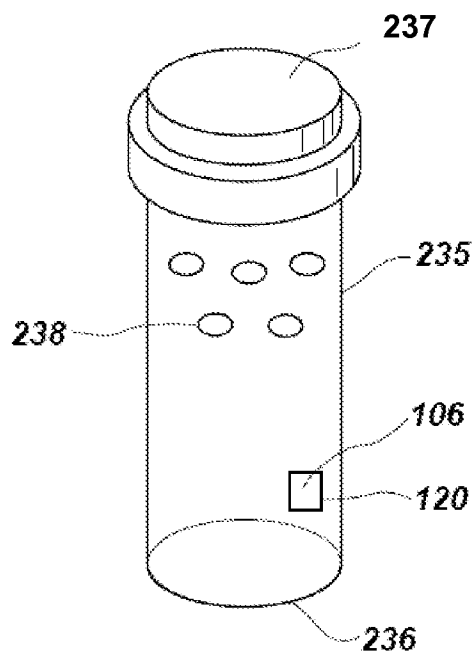


FIG. 17

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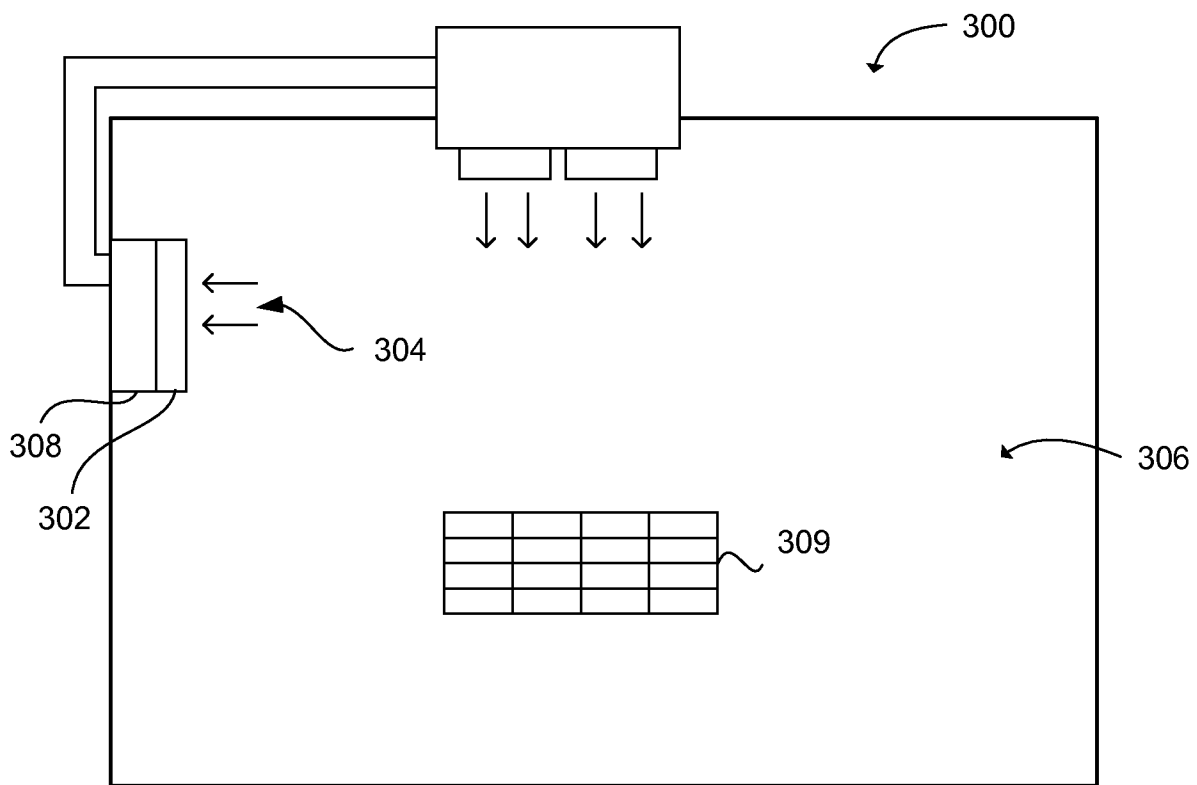


FIG. 18

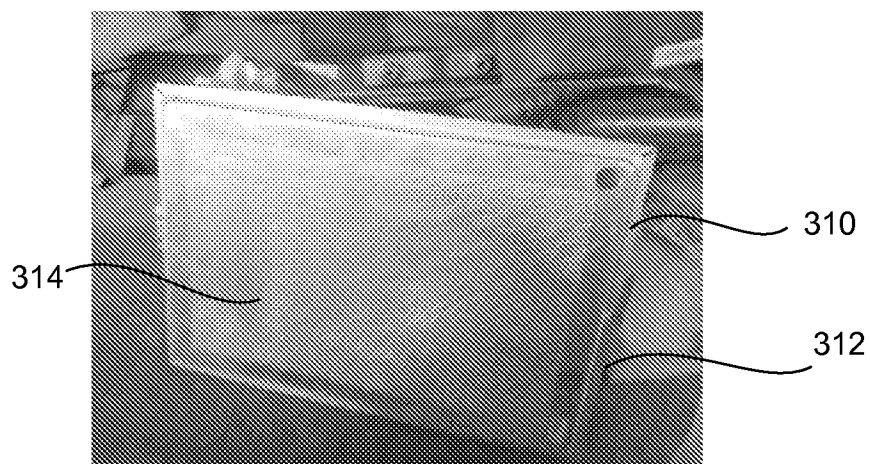
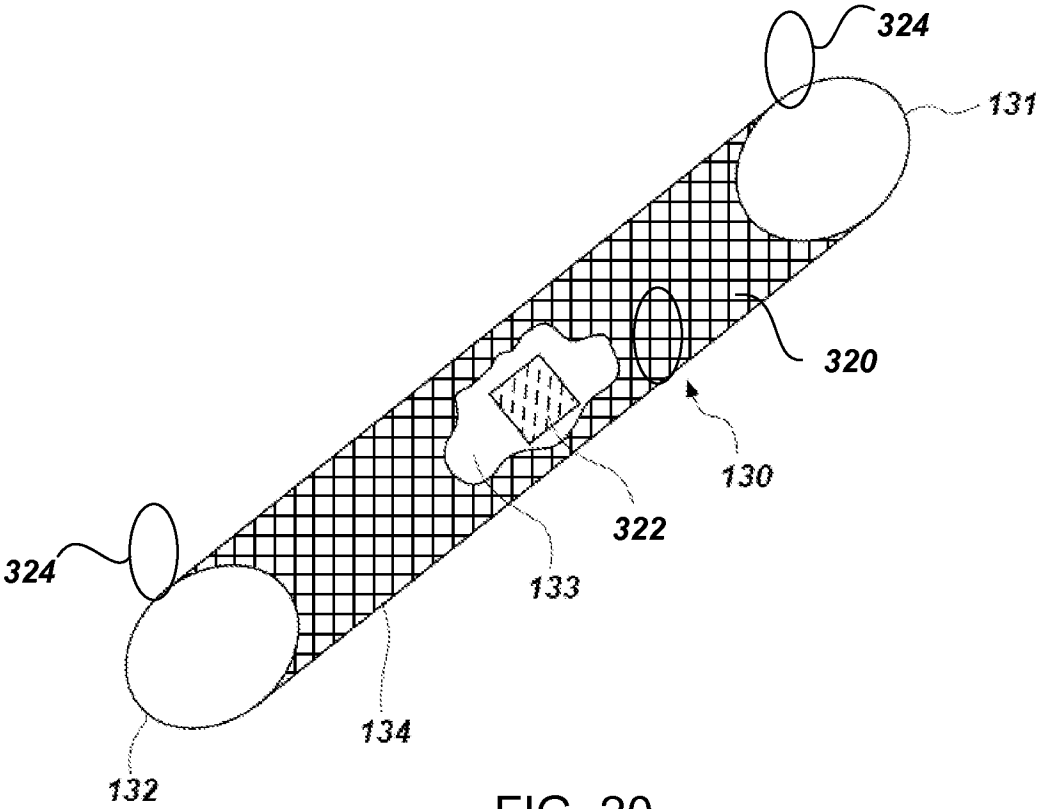


FIG. 19



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US15/47790

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - A23L 3/34; B01D 53/14; F25D 3/06 (2015.01)

CPC - A23L 3/3427; B60H 1/32; F25D 11/003

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8): A23L 3/34; B01D 53/14; F25D 3/06 (2015.01)

CPC: A23L 3/3427; B60H 1/32; F25D 11/003

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, Other Countries (INPADOC), RU, AT, CH, TH, BR, PH), ProQuest, PatentsGoogle, Google Scholar, sciencedirect.com: refrigeration load reduction system, sodium carbonate, carboxylic acid, Trona, gaylussite, natron, prissonite, northupite, nahcolite, thermonatrite, grains, granular, heat exchanger, compressor, circuit board, blood

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,913,942 (JICK, JJ) 3 April 1990; abstract; figure 1; column 2, lines 50-55; claim 1;	1-19
Y	US 6,264,740 B1 (MCNULTY, JR, WJ) 24 July 2001; abstract; column 2, lines 5-35; claims 1, 19, 21	1-19
Y	US 4,708,886 (NELSON, LA) 24 November 1987; figures 1, 5; column 1, lines 1-45, 50-60; column 3, lines 5-15; column 4, lines 20-35; column 7, lines 5-25;	6, 12-16, 18
Y	US 2010/0031853 A1 (VISOCEKAS, F et al.) 11 February 2010; paragraphs [107], [109], [0133]-[0137]	7, 18

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search

30 October 2015 (30.10.2015)

Date of mailing of the international search report

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