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## (54) HYBRID NANOREINFORCED LINER FOR MICROWAVE OVEN

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#### (56) References Cited

#### U.S. PATENT DOCUMENTS

3,941,967	A	3/1976	Sumi et al.	
4,542,271	Α	9/1985	Tanonis et al.	
5,268,546	A *	12/1993	Berg	H05B 6/6494
			-	426/243
5,523,549	Α	6/1996	Tenzer	
5,853,632	A	12/1998	Bunke et al.	
6,420,293		7/2002		
6,858,173	B2	2/2005	Zhan et al.	
(Continued)				

#### FOREIGN PATENT DOCUMENTS

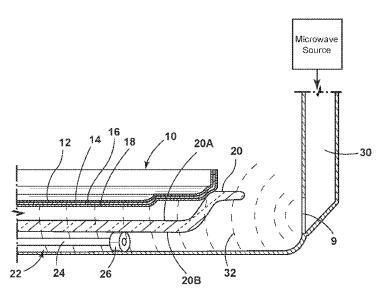
EP	0240235 A1	10/1987
EP	3654736 A1	5/2020
	(Cont	inued)

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#### (57) ABSTRACT

A liner for a crisp plate includes ceramic nanoparticles and a polymer material combined with the ceramic nanoparticles to provide a mixture. A network of carbon nanotubes is embedded within the mixture to form a composite matrix, wherein the carbon nanotubes are unidirectionally aligned within the composite matrix.

#### 18 Claims, 3 Drawing Sheets



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#### (56) References Cited

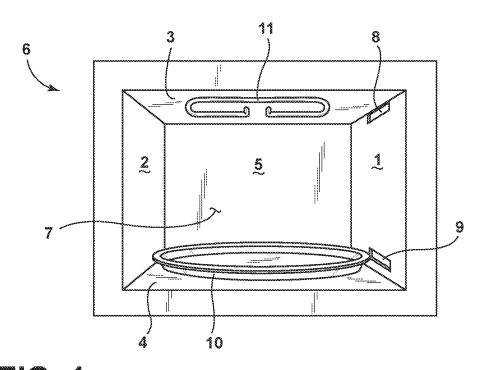
## U.S. PATENT DOCUMENTS

6,986,942 B1	1/2006	Mayes
7,306,828 B2	12/2007	Barrera et al.
8,269,154 B2	9/2012	Samuels et al.
9,232,618 B2	1/2016	Bourke, Jr. et al.
9,249,528 B2	2/2016	Mitra et al.
9,725,809 B2	8/2017	Perillon et al.
2005/0236407 A1	10/2005	Aisenbrey
2007/0062936 A1	3/2007	Young et al.
2007/0243124 A1	10/2007	Baughman
2008/0210473 A1	9/2008	Zhang et al.
2009/0045374 A1	2/2009	Lawrenz et al.
2011/0245378 A1	10/2011	Russ
2011/0297672 A1	* 12/2011	Niklasson H05B 6/6447
		219/702
2012/0213896 A1	* 8/2012	Owensby B32B 27/34
		523/100
2014/0097917 A1	4/2014	Shah
2014/0238250 A1	8/2014	Gephart et al.
2016/0015207 A1	* 1/2016	
		219/730
2016/0360920 A1	12/2016	Park
2018/0220500 A1		Staton A47J 37/0623
2020/0163172 A1		Khizar et al.

## FOREIGN PATENT DOCUMENTS

KR	101967112 B1	4/2019
WO	2007015710 A1	2/2007
WO	2011127148 A1	10/2011
WO	2016118151 A1	7/2016

<sup>\*</sup> cited by examiner



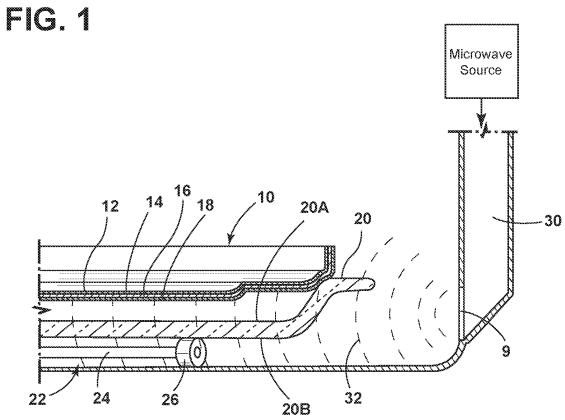


FIG. 2A

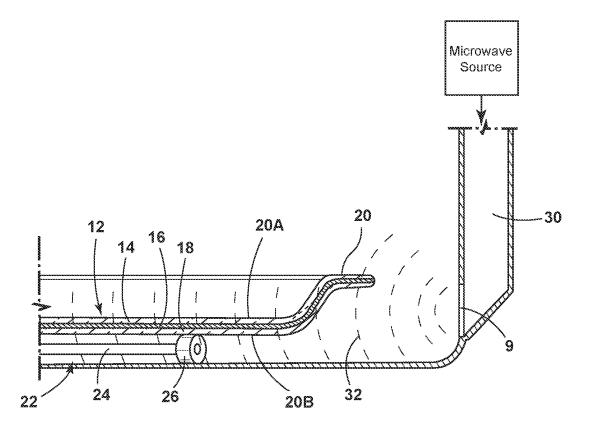


FIG. 2B

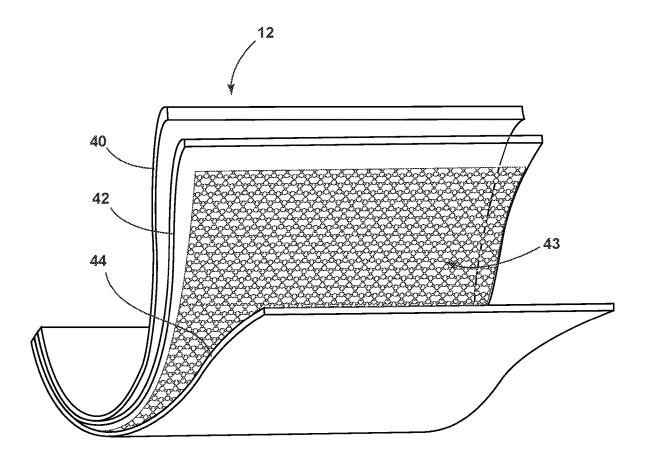


FIG. 3

# HYBRID NANOREINFORCED LINER FOR MICROWAVE OVEN

## CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation of U.S. patent application Ser. No. 16/192,235, now U.S. Pat. No. 11,234,298, filed on Nov. 15, 2018, entitled HYBRID NANOREIN-FORCED LINER FOR MICROWAVE OVEN, the entire disclosure of which is hereby incorporated by reference.

#### BACKGROUND

The present device generally relates to a liner material, and more specifically, to a liner for use with a microwave oven, wherein the liner is comprised of materials suitable for improving the overall performance of a microwave oven, improving cooking times and cooking thoroughness, and making the microwave oven more energy efficient.

Microwave oven cooking has always been problematic in 20 terms of the excessive power required to generate the appropriate heat for cooking. This is mainly due to excessive wastage of the produced heat caused by heat dissipation. Therefore, significant efforts are needed to reduce cavity generated heat losses which can be utilized in cooking to improve the process and the quality of the cooked food.

In current microwave ovens, the supporting parts and assemblies, along with the turn-table or crisp plate, acts as non-conductive materials (dielectric) which absorb microwave radiations as a dielectric loss. Dielectric loss quantifies a dielectric material's inherent dissipation of electromagnetic energy. Such properties are frequency dependent for frequencies in the range of 2.4 GHz, as used in a microwave oven. As a result, ferrite particles embedded within silicon have been used to control the heat within current backing plates and trays. This measure helped to improve the crisp plate performance to a certain extent, but due to their microwave frequencies activation limitation and Curie temperature Tc limitation of used ferrite, targeted benefits were not achieved. Realizing the conductive nature of the current crisp plate materials (such as aluminum) which heat up for 40 various reasons such as antenna effects and ohmic loss, and the heavy loads imposed on the microwave generating device, it is important to use an excellent electromagnetic radiation absorbing material as compared to the existing ferrite and silicon coated crisp plates. For a typical microwave oven, an existing crisp plate may contain up to 90% micro-powder by weight under ~110 bar forming pressure fired at 1050° C. to 1150° C. in air. The shrinkage rate of such a crisp plate largely depends on the micro-powder used in forming the crisp plate. When such plates are used in a microwave oven without an efficient electromagnetic radiations absorbing coating/film attached, the crisp plate draws significant radiation (energy) from a microwave generator. This issue is compounded in larger microwave ovens. This imposes serious restrictions on the utilization of functional heat sources and tends to introduce issues linked to the 55 quality of the cooked food.

Thus, a nano-reinforced liner system is desired that uses a hybridization of carbon nanotubes to proprietary ceramic materials and selected elastomeric materials to provide a ferriteless liner. Unique about this hybrid material system is 60 the tuning properties under the exposure of microwave frequencies.

### SUMMARY

In at least one aspect, a crisp plate, includes a plate and a liner disposed on a surface of the plate. The liner includes a 2

network of carbon nanotubes combined with aluminum nanoparticles and ceramic alumina material. The network of carbon nanotubes is embedded within a polymer matrix, and are unidirectionally aligned within the matrix.

In at least another aspect, a liner for a crisp plate includes aluminum and ceramic nanoparticles and a polymer combined with the ceramic nanoparticles to provide a mixture. A network of carbon nanotubes is embedded within the mixture to form a composite matrix, wherein the carbon nanotubes are unidirectionally aligned within the composite matrix.

In at least another aspect, a method of forming a liner for a crisp plate includes the steps of 1) providing a polymer matrix; 2) embedding a network of unidirectionally aligned carbon nanotubes along with aluminum nanoparticles within the polymer matrix to provide a composite matrix; and 3) providing a ceramic alumina component to the composite matrix to form a nanoreinforced liner.

These and other features, advantages, and objects of the present device will be further understood and appreciated by those skilled in the art upon studying the following specification, claims, and appended drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings:

FIG. 1 is a front perspective view of a microwave oven having a crisp plate disposed in a cavity thereof;

FIG. 2A is a fragmentary cross-sectional view of a microwave oven having a support plate with a crisp plate supported thereon, wherein the crisp plate includes a liner;

FIG. **2**B is a fragmentary cross-sectional view of a microwave oven having a crisp plate with a liner disposed thereon; and

FIG. 3 is a front perspective view of a liner illustrating components of the liner in a partially exploded view.

#### DETAILED DESCRIPTION OF EMBODIMENTS

For purposes of description herein the terms "upper," "lower," "right," "left," "rear," "front," "vertical," "horizontal," and derivatives thereof shall relate to the device as oriented in FIG. 1. However, it is to be understood that the device may assume various alternative orientations and step sequences, except where expressly specified to the contrary. It is also to be understood that the specific devices and processes illustrated in the attached drawings, and described in the following specification are simply exemplary embodiments of the inventive concepts defined in the appended claims. Hence, specific dimensions and other physical characteristics relating to the embodiments disclosed herein are not to be considered as limiting, unless the claims expressly state otherwise.

Proposed is a hybrid nanoreinforced liner developed with carbon nanotubes embedded in a select material matrices. The liner is configured for enhanced electromagnetic radiation absorbing properties, so that the liner offers excellent self-heating performance, especially when exposed to microwave radiations. For this, a proposed liner includes a matrix of fully dense nanocomposites of carbon nanotubes with aluminum nanoparticles and nanocrystalline ceramic nanoparticles, such as aluminum nanoparticles (Al, 99.9%, 30-50 nm) and alumina (Al<sub>2</sub>O<sub>3</sub>), blended with a two-part pre-polymerized polymer with a fracture toughness of approximately 10 MPa. This hybrid nanoreinforced liner provides enhanced electromagnetic radiation absorbing

capabilities without dissipation of the generated heat when the liner is provided on a surface of a crisp plate in a microwave oven.

In developing the hybrid nanoreinforced liner, chemical vapor deposition grown carbon nanotubes are mixed with 5 aluminum nanoparticles (Al, 99.9%, 30-50 nm) and aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) nanoparticles at sintering temperatures as low as 1150° C. by spark-plasma sintering. This hybrid matrix of carbon nanotubes and aluminum oxide nanoparticles may then be blended with a two-part pre-polymerized 10 polymer. The carbon nanotubes are contemplated to have a diameter of approximately 3 nm. It has been found that the exceptionally large surface area and nanopits of the carbon nanotubes helps to strengthen interface connections with aluminum nanoparticles and aluminum oxide nanoparticles, 15 especially when blended with a two-part pre-polymerized polymer. More so, the incorporation of carbon nanotubes and aluminum nanoparticles into the liner helps to enhance the electrical conductivity and toughness of the liner, while reducing the brittleness of the aluminum oxide by convert- 20 ing the hybrid material system into an electromagnetic radiation absorbing liner. Unique about this hybrid liner is that it offers exceptionally high mechanical strength, improved resistance against corrosion and high sensitivity to electromagnetic radiation absorption. More on, the liner 25 presents remarkably high improvements to its inter-laminar fracture toughness, de-lamination resistance, in-plane mechanical and thermal performance, damping, and thermoelastic behavior, which makes this hybrid liner system an ideal liner for a crisp plate application.

Referring now to FIG. 1, a microwave oven 6 is shown, in which a door for closing a cavity 7 of the microwave oven 6 has been omitted. The cavity 7 is defined by sidewalls 1 and 2, a top wall 3, a bottom wall 4, and a rear wall 5. Disposed along the right sidewall 1, upper and lower input 35 fine ceramic material. It has the same sintered crystal body openings 8 and 9 are configured to supply of microwaves 32 (see FIG. 2A) into the cavity 7 from a microwave source via a waveguide device 30 (see FIG. 2A). The input openings 8, 9 and the waveguide device 30 are arranged to supply microwaves 32 to the cavity 7 for cooking a food substrate. 40 In the embodiment shown in FIG. 1, an electric browning element 11 is positioned along the top wall 3 of the cavity 7 and is configured for browning the upper side of a food substrate by electric heating means.

As further shown in FIG. 1, a crisp plate 10 is positioned 45 on the bottom wall 4 of the cavity 7. The crisp plate 10 may be a removable plate that is positioned directly on the bottom wall 4 of the cavity 7. The crisp plate 10 may also be situated on a support plate, such as support plate 20 shown in FIG. 2A. In FIG. 2A, the crisp plate 10 is supported on an upper 50 surface 20A of the support plate 20, and the support plate 20 is further supported from an undersurface 20B of the support plate 20 by a rotation mechanism 22 having an arm 24 and wheel 26.

In FIG. 2A, the crisp plate 10 includes a liner 12, 55 according to the present concept. The liner 12 may include one or more layers 14, 18 which are designed to enhance the browning features of the crisp plate 10. Specifically, the liner 12 of the present concept is configured to offer uniform heating of a food substrate, provide improved heating times, 60 consume less energy in a cooking procedure, and include upper temperature limits to avoid overcooking or burning of food substrates. In FIG. 2A, the layers 14, 18 of the liner 12 are shown disposed on upper and lower sides or surfaces of a plate 16. It is contemplated that the plate 16 may be a metal 65 plate comprised of a metal material, such as ceramic or aluminum. Further, it is contemplated that the liner 12 may

be applied on both the upper and lower sides of the plate 16, the upper side alone, or the lower side alone.

As used herein, the term "crisp plate" is meant to refer to a plate that aids in the browning or crisping of a food substrate when exposed to microwave radiation. The crisp plate 10 may also be referred to herein as a browning plate, a crisper pan, or a susceptor plate. Further, as used therein, the term "liner" is meant to refer to a coating or film that is provided on a surface of a crisp plate to improve the performance of the same. The proposed liner 12 of the present concept may be referred to herein as a coating, a film, a layer, a hybrid nanoreinforced liner, a matrix or a composite material. The liner 12 may be provided on a crisp plate using various techniques, such as spraying, hot stamping, injection molding, and other like techniques further described below. In this way, the crisp plate is coated with the liner 12.

The present concept relates to forming a composite coating that may include carbon nanotubes embedded into a polymer. Specifically, the composite may include the application of a polymer onto carbon nanotubes to form a composite of unidirectionally aligned carbon nanotubes embedded in the polymer matrix. The polymer material is contemplated to include a polymer suitable to form a polymer matrix in which a controlled loading concentration of carbon nanotubes and aluminum nanoparticles are unidirectionally aligned can be embedded. A ceramic material, such as alumina, is also contemplated for use with the composite coating. As used herein, the term "unidirectionally aligned" refers to the alignment of carbon nanotubes (with or without aluminum nanoparticles) in a composite, wherein the carbon nanotubes are generally horizontally aligned or parallel to a substrate, such as a crisp plate.

Alumina or aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) is a commonly used as sapphire and ruby. It is often used in in electrical components for its high electrical insulation, and is widely used in mechanical parts for its high strength, and corrosionresistance and wear-resistance. The ceramic component of the present concept may be referred to herein as ceramic alumina, alumina, aluminum oxide or ceramic nanocrystalline particles.

Several types of polymers have been considered as suitable matrices for highly conductive carbon nanotube/polymer composites. Selection of a particular polymer heavily depends on a multitude of factors that must be considered in order to meet certain selection criteria. Electrical conductivity heavily depends on the ease of electron transfer throughout a material. While most polymer materials are insulators with very low electrical conductivity properties, the addition of carbon nanotubes and aluminum nanoparticles to the polymer matrix improves the electrical conductivity of the composite material due to the carbon nanotube network formation within the composite material. Using carbon nanotube-to-carbon nanotube contacts with the composite material, electron transfer throughout the polymer matrix is enabled by providing conductive pathways through the carbon nanotube and aluminum nanoparticles network. Thus, the carbon surface of the carbon nanotubes is used as a medium for ballistic transport of electrons from one carbon nanotube to another. Further, it has been found that disrupting carbon nanotube network formation plays a critical role in reducing the electrical resistivity of the carbon nanotubepolymer composite by either forming a resistive material barrier between carbon nanotubes or by limiting direct carbon nanotube interconnection. As such, the polymer matrix blended with aluminum nanoparticles alone is con-

templated to have an electrical conductivity level that is less than an electrical conductivity level of the composite matrix of the polymer matrix combined with the network of carbon nanotubes. As used herein, the term "network" is contemplated to describe a formation of carbon nanotubes (with or without aluminum nanoparticles) that provides unbroken connections across a substrate, such as a crisp plate.

Referring now to FIG. 2B, the support plate 20 itself has been coated with the liner 12 of the present concept at upper and lower layers 14, 18, such that the support plate defines 10 a crisp plate as used in the microwave 6.

Referring now to FIG. 3, the liner 12 is shown in a graphic illustration wherein component parts of the liner 12 are portrayed in an exploded view. The component parts of the liner 12 are contemplated to be intermixed components that 15 may or may not be aligned in specific layers as represented in FIG. 3, but may be blended in the liner system. The liner 12 shown in FIG. 3 includes a ceramic component 40 as described above. A network 43 of unidirectionally aligned carbon nanotubes and aluminum nanoparticles 42 is also 20 illustrated in FIG. 3. The network 43 of unidirectionally aligned carbon nanotubes along with aluminum nanoparticles 42 is contemplated to be dispersed throughout the liner 12, such that microwave absorption is consistent throughout the liner 12 as applied to a crisp plate. A polymer component 25 44 is also shown in FIG. 3 and is contemplated to have the carbon nanotubes along with aluminum nanoparticles 42 and alumina embedded within a matrix provided by the polymer component 44.

It is further an object of the present concept to develop 30 certain upper temperature limits of the liner when applied to select surfaces. As noted above, the liner is to be used to create a coating for a browning plate or crisp plate disposed within a microwave, such as crisp plate 10 disposed within microwave 6 (FIG. 2A). Thus, the liner 12, as applied to the 35 crisp plate 10 and positioned within the cavity 7 of the microwave 6, is exposed to microwaves 32. The liner 12 of the present concept is configured to rapidly heat up to a suitable cooking temperature during a cooking procedure. Specifically, the liner 12 of the present concept is configured 40 to heat up to a cooking temperature of approximately 200° C. in approximately 2 minutes under electromagnetic radiation exposure. The liner 12 of the present concept is further configured to include an upper heat limit of approximately 250° C. The novel compilation of component parts of the 45 liner 12 has been specifically formulated to ensure that the upper heat limit will not be exceeded regardless of the exposure time of the liner 12 to microwaves during a cooking procedure. In this way, the liner 12 provides for a crisp plate 10 that avoids over cooking or burning of food 50 substrates by controlling the upper heat limit.

Further, the liner 12 is contemplated to provide a hybrid nano-reinforced liner system. The liner system includes a nanocoating formulation which comprises a nanostructure provided by carbon nanowires and aluminum nanoparticles. 55 A liquid two-part pre-polymerized polymer having one or more functional groups is configured to graft to the nanostructure of the nanoparticles. A final component of the liner 12 includes alumina. The combined components of the liner 12 result in a liner having an enhanced response to microwave radiation absorption, as compared to other known liner systems.

In another embodiment of the present concept, the liner 12 includes carbon nanotubes that are dispersed in a liquid polymer, and an effective amount of a synthetic additive, 65 such as aluminum nanoparticles and ceramic alumina, that form a strong interaction with the carbon nanotube and

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liquid polymer blend. It is contemplated that this ceramic alumina is provided in solution, such that the effective amount of carbon nanotubes suspended in the liquid polymer can be mixed with the effective amount of the aluminum nanoparticles and ceramic alumina dissolved in a solvent to create a coating of the present concept. The aluminum nanoparticles may include metallic aluminum dissolved in a solvent, and the ceramic alumina may include ceramic alumina nanoparticles dissolved in a solvent. A substrate, such as the metal crisp plate 16, may be coated with the intermixed coating using one of the techniques noted below. After the substrate is coated, it is allowed to air cure to provide a thin liner coating having a thickness of about 150 microns to about 200 microns on the crisp plate substrate.

The coating of the present concept provides for a hybrid nano-reinforced liner system that is comprised of a composite matrix created by combining a polymer, aluminum nanoparticles, ceramic alumina, and carbon nanotubes which are unidirectionally aligned. By incorporating a controlled loading concentration of carbon nanotubes into a specialty polymer matrix with aluminum nanoparticles and ceramic alumina, the electrical conductivity of the polymer is increased and mechanical stability is reinforced.

Among the key contributing factors in the conductivity enhancement of carbon nanotube-polymer composites are the dispersion of the carbon nanotubes throughout the polymer matrix. This dispersion of the carbon nanotubes throughout the polymer matrix increases carbon nanotube-to-carbon nanotube interconnection and network formation, thereby further increasing electrical conductivity of the composite material.

Structural alignment of carbon nanotubes in a uniform direction has been ensured to achieve higher electrical conductivity values by controlling carbon nanotubes loading concentrations and their random dispersion. This is important to provide direct, unidirectional conductive pathways which allows for unobstructed electron transport throughout the composite material, thereby helping to increase electrical conductivity throughout a polymer matrix. Through a parallel plate's setup, a high voltage electric field is applied across a mixture of carbon nanotubes and a low viscosity medium resulting in the unidirectional alignment of the carbon nanotubes. To ensure the carbon nanotubes effectively align within a high viscosity polymer, an electric field vacuum system technique is used. The highly viscous twopart pre-polymerized polymer acts as a barrier to carbon nanotube movement. The electric field vacuum system technique helps for uniform dispersion and alignment of the carbon nanotubes when spraying a mixture of carbon nanotubes blended with aluminum nanoparticles and ceramic alumina within an electric field to ensure rapid dispersion of the carbon nanotubes.

The electric field vacuum system technique noted above comprises a vacuum, a filter chamber, a high voltage power supply, a filter, an electrical wiring, and a spray system. Ceramic alumina, used as one of the additives, plays an important role in improving hardness, chemical inertness and higher melting point of the matrix and can retain up to 90% of its strength even at 1100° C. Furthermore, use of a ceramic alumina component is important for any spray coating process because any such coatings are attacked by voids which could compromise the corrosion resistance of the coating. Controlled loading of ceramic alumina can play a pivotal role in improving the impact strength of the liner 12, reducing the generation of voids, and improving the high temperature resistance of the hybrid liner system.

To be more specific, the application of the polymer onto the carbon nanotubes forms composites that comprise unidirectionally aligned carbon nanotubes embedded within the polymer. In order to maintain unidirectional alignment of the carbon nanotubes used as active ingredients, conductive plates or adjustable conductive plates are used, such that parallel conductive plates of copper electrode material allow for adjusting a direction of the electric field in order to form unidirectionally aligned carbon nanotubes at various desired angles. Technically, such desired angles may range from about 0° to about 135° from the direction of an electric field having strengths of 115 V/cm, and 220 V/cm.

One type of polymer considered to be suitable for the coating of the present concept is RBL-9050-50P Liquid Silicone Rubber. Two-part, 10 to 1 mix, clear, fabric coating 15 grade liquid silicone rubber offers unique homogeneous mixing. This two-part pre-polymerized polymer composite is the 10 to 1 mix, clear, fabric coating grade liquid silicone rubber which has an extremely low viscosity, no post-curing requirements, and excellent electrical insulating properties. Further, this two-part pre-polymerized polymer composite is equally suitable for spray-on and dip coating applications. The 10 to 1 mix of this polymer refers to the 10 to 1 base to catalyst 87-RC ratio of the polymer.

Different forms of carbon nanotubes may be utilized with 25 the methods, systems and composites of the present concept. For example, the carbon nanotubes utilized with the proposed coating system could be single-wall carbon nanotubes, double-wall carbon nanotubes, few-wall carbon nanotubes, multi-wall carbon nanotubes, ultra-short carbon 30 nanotubes, and combinations thereof. In some cases, the carbon nanotubes are functionalized, metal-coated and pristine carbon nanotubes. Carbon nanotubes that are to be applied to various systems of the present invention may be provided in a solution, such as a dispersant. Such solutions 35 may also comprise surfactants to aid in the dispersion. Non-limiting examples of suitable surfactants include LDS, SDS, Zwitterionic surfactants, cationic surfactants, anionic surfactants, and the like. In more specific embodiments, the carbon nanotubes may be dispersed in N-methylpyrrolidone 40 (NMP).

#### Example 1

For Example 1, the hybrid liner matrix is prepared using 45 purified few-wall carbon nanotubes of controlled loading concentration of 1.5 wt % mixed with liquid silicone rubber and ceramic alumina. The process of creating the hybrid liner starts with the dispersion of the carbon nanotubes into a liquid polymer by using a 900 W ultrasonic probesonicator 50 for approximately 45 minutes to create a composite matrix of the polymer and carbon nanotubes. The composite matrix is then decanted using a centrifuge set at approximately 10,000 rpm to settle out larger carbon agglomerates followed by mixing the composite matrix with ceramic alumina 55 (15 wt %). This combination is then heated to approximately 120° C. The polymer along with aluminum nanoparticles and ceramic alumina forms a matrix which enables ease of its handling, cross-linking networking, and minimizes all those issues linked with the abrupt shrinkage strain upon 60 polymerization via the progressive substitution of the pelletized silicon by the pre-polymerized liquid polymer. Specifically, the polymer has a low viscosity, doesn't require post-curing, offers excellent electrical insulating properties, is easily pigmented, and is suitable for spray-on and dip 65 coating applications. In order to avoid the entrapment of any air bubbles during the mixing process, the mixture was

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thoroughly de-gassed under vacuum to avoid the build-up of voids which may eventually effect the overall performance, especially when used as a blending agent.

As another option, the present invention matrix can also be incorporated as more than one layer as a result of the repetition of the above-described methods of the present concept. For this, each layer comprises unidirectionally aligned carbon nanotubes that are embedded in a polymer matrix to form a multilayer structure that includes a liner, as described above, coated with a same liner composition. The highly aligned carbon nanotubes in polymer matrices significantly improve the electrical, mechanical and thermal properties of the composites of the present coating. Various spraying techniques may be utilized. For example, the spraying may involve electro-spraying, mechanical or manual spraying options can be used. Additional methods may include, without limitation, spincoating, drop-casting, dip coating, physical application, sublimation, blading, inkjet printing, screen printing, injection molding, hot stamping, and direct placement. The overall thickness of proposed hybrid reinforced liner coating is approximately 1 mm to 1.2 mm depending on the flatness requirements of the substrates to be coated.

As noted above, in some cases, the carbon nanotubes are functionalized. The Functionalization of carbon nanotubes is mainly to modify surface properties of the carbon nanotubes. Two separate approaches, such as chemical and physical functionalization approaches, have been exploited as interactions between active materials and carbon nanotubes. Briefly, chemical functionalization is based on the covalent bond of functional groups onto carbon form of carbon nanotubes. It can be performed at the end caps of nanotubes or at their sidewalls which have many defects. Direct covalent sidewall functionalization is associated with a change of hybridization from sp2 to sp3 and a simultaneous loss of p-conjugation system on graphene layer. This process can be made by reaction with some molecules of a high chemical reactivity. In the first approach, fluorination of carbon nanotubes has been used mainly because the sidewalls of the carbon nanotubes are expected to be inert. The fluorinated carbon nanotubes have C-F bonds that are weaker than those in alkyl fluorides and thus provides substitution sites for additional functionalization. In one embodiment, replacements of the fluorine atoms by amino, alkyl and hydroxyl functional groups have been used for the functionalization of carbon nanotubes. However, cycloaddition, such as Diels-Alder reaction, carbene and nitrene addition, chlorination, bromination, hydrogenation, azomethineylides can also be exploited for this purpose.

For a broader scope of the functionalization technique used, a defect functionalization of carbon nanotubes has also been reported. Certain intrinsic defects are supplemented by oxidative damage to the nanotube framework by strong acids which leave holes functionalized with oxygenated functional groups. Certain treatments of carbon nanotubes with strong acids such as nitric acid (HNO3), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), or mixtures thereof, or treatments with strong oxidants such as potassium permanganate (KMnO4), ozone (O3), or reactive plasma tend to open these carbon nanotubes and subsequently generate oxygenated functional groups, such as carboxylic acid, ketone, alcohol and ester groups, that serve to tether many different types of chemical moieties onto the ends and defect sites of these carbon nanotubes. These functional groups have rich chemistry and the carbon nanotubes have been used as precursors for further chemical reactions, such as salinization, polymer grafting, esterification, and thiolation. The technique of

carbon nanotube functionalization offers an additive advantage mainly because carbon nanotubes possess many functional groups, such as polar or non-polar groups, that play a critical role in activating such features effectively.

However, serious care should be used such as during the 5 functionalization reaction, a large number of defects are inevitably created on the carbon nanotube sidewalls. In some extreme cases, carbon nanotubes are fragmented into smaller pieces. For example, the carbon hybridization of carbon nanotubes can change from sp2 to sp3. These dam- 10 aging effects can result in severe degradation in mechanical properties of carbon nanotubes as well as disruption of Pi electron systems in nanotubes. This is important because the disruption of p-electrons is detrimental to the transport properties of carbon nanotubes, because defect sites scatter 15 electrons and phonons that are responsible for the electrical and thermal conductions of carbon nanotubes. Also, concentrated acids or strong oxidants are often used for carbon nanotube functionalization. Therefore, special care should be exercised when handling any such acid baths and treating 20 carbon nanotubes in these baths to avoid unnecessary damage to the carbon nanotubes during their functionalization.

As noted above, the liner of the present concept may be provided as a monolayer on a plate. As used herein, the term "monolayer" is used to describe a liner that is a single 25 continuous layer or film that is one cell, molecule, or atom in thickness.

In summary, the methods and systems of the present invention can be tailored to various sizes and shapes, along with the use of different carbon nanotubes or polymers based 30 on the multifunctional composite requirements. The formed composite coating or thin film along with spray coating option, can also be cut in several ways to produce a cylindrical shape and other such geometries. In short, a hybrid composite liner system is developed by utilizing 35 different sizes carbon nanotubes, a selected liquid polymer, aluminum nanoparticles, and ceramic alumina in a single reaction to achieve highly uniform surfaces with fast heating rate and provided an access to tune nanotubes through irradiated microwave radiations, such that an upper tem- 40 perature limit is provided by exploiting a controlled loading concentration of carbon nanotubes embedded into its blending agents. As noted above, the present concept is able to provide the composite coating or thin film liner without ferrites in the composition, such that the liner can be said to 45 be ferriteless, ferrite-free or free from ferrites in composi-

In at least one aspect, a crisp plate includes a plate with a liner is disposed on a surface of the plate. The liner includes functionalized carbon nanotubes combined with 50 aluminum nanoparticles and ceramic alumina. A polymer is provided that is suitable to form a matrix. The functionalized carbon nanotubes are embedded within the matrix.

According to another aspect of the disclosure, the plate is comprised of an aluminum material.

According to another aspect of the disclosure, the functionalized carbon nanotubes include carbon nanotubes treated with an acid selected from the group consisting of nitric acid, sulfuric acid, and mixtures thereof to provide oxygenated functional groups.

According to another aspect of the disclosure, the functionalized carbon nanotubes include carbon nanotubes treated with an oxidant selected from the group consisting of potassium permanganate, ozone, and reactive plasma to provide oxygenated functional groups.

According to another aspect of the disclosure, the functionalized carbon nanotubes include fluorinated carbon **10** 

nanotubes that have been functionalized to provide amino, alkyl and hydroxyl functional groups.

According to another aspect of the disclosure, the functionalized carbon nanotubes are selected from the group consisting of single-wall carbon nanotubes, double-wall carbon nanotubes, few-wall carbon nanotubes, multi-wall carbon nanotubes, ultra-short carbon nanotubes, and combinations thereof.

According to another aspect of the disclosure, the functionalized carbon nanotubes are unidirectionally aligned within the matrix.

According to another aspect of the disclosure, the liner is free from ferrites.

According to another aspect of the disclosure, the liner includes 1.5% by weight of the polymer material, and further includes 15% by weight of the ceramic alumina.

According to another aspect of the disclosure, a liner for a crisp plate includes aluminum nanoparticles and ceramic nanoparticles. A polymer material is combined with the ceramic nanoparticles to provide a mixture. A network of functionalized carbon nanotubes are embedded within the mixture to form a monolayer matrix. The functionalized carbon nanotubes are unidirectionally aligned within the monolayer matrix.

According to another aspect of the disclosure, the liner heats up to 200° C. within two minutes or less when exposed to microwaves.

According to another aspect of the disclosure, the liner includes an upper heat limit of 250° C. when exposed to microwaves.

According to yet another aspect of the disclosure, a method of forming a crisp plate includes: (1) providing a polymer matrix, (2) providing carbon nanotubes, (3) functionalizing the carbon nanotubes to provide functionalized carbon nanotubes, (4) embedding the functionalized carbon nanotubes within the polymer matrix to provide a composite matrix, (5) providing aluminum nanoparticles and ceramic alumina to the composite matrix to form a nanoreinforced liner, (6) providing a plate, and (7) applying the nanoreinforced liner to a surface of the plate.

According to another aspect of the disclosure, the step of applying the nanoreinforced liner to a surface of the plate further includes hot stamping the nanoreinforced liner to the surface of the plate.

According to another aspect of the disclosure, the step of applying the nanoreinforced liner to a surface of the plate further includes injection molding the nanoreinforced liner on the surface of the plate.

According to another aspect of the disclosure, the step of applying the nanoreinforced liner to a surface of the plate further includes spraying the nanoreinforced liner on the surface of the plate.

According to another aspect of the disclosure, the step of functionalizing the carbon nanotubes to provide functionalized carbon nanotubes further includes treating the carbon nanotubes with an acid to provide oxygenated functional groups.

According to another aspect of the disclosure, the step of functionalizing the carbon nanotubes to provide functionalized carbon nanotubes further includes treating the carbon nanotubes with an oxidant to provide oxygenated functional groups.

According to another aspect of the disclosure, the step of functionalizing the carbon nanotubes to provide functionalized carbon nanotubes further includes fluorinating the carbon nanotubes to provide fluorinated carbon nanotubes.

According to another aspect of the disclosure, fluorine atoms of the fluorinated carbon nanotubes are replaced with functional groups selected from the group of functional groups consisting of amino, alkyl and hydroxyl functional groups.

It will be understood by one having ordinary skill in the art that construction of the described device and other components is not limited to any specific material. Other exemplary embodiments of the device disclosed herein may be formed from a wide variety of materials, unless described 10 otherwise herein.

For purposes of this disclosure, the term "coupled" (in all of its forms, couple, coupling, coupled, etc.) generally means the joining of two components (electrical or mechanical) directly or indirectly to one another. Such joining may 15 be stationary in nature or movable in nature. Such joining may be achieved with the two components (electrical or mechanical) and any additional intermediate members being integrally formed as a single unitary body with one another or with the two components. Such joining may be permanent 20 in nature or may be removable or releasable in nature unless otherwise stated.

It is also important to note that the construction and arrangement of the elements of the device as shown in the exemplary embodiments is illustrative only. Although only 25 a few embodiments of the present innovations have been described in detail in this disclosure, those skilled in the art who review this disclosure will readily appreciate that many modifications are possible (e.g., variations in sizes, dimensions, structures, shapes and proportions of the various 30 elements, values of parameters, mounting arrangements, use of materials, colors, orientations, etc.) without materially departing from the novel teachings and advantages of the subject matter recited. For example, elements shown as integrally formed may be constructed of multiple parts or 35 elements shown as multiple parts may be integrally formed, the operation of the interfaces may be reversed or otherwise varied, the length or width of the structures and/or members or connector or other elements of the system may be varied, the nature or number of adjustment positions provided 40 between the elements may be varied. It should be noted that the elements and/or assemblies of the system may be constructed from any of a wide variety of materials that provide sufficient strength or durability, in any of a wide variety of colors, textures, and combinations. Accordingly, all such 45 modifications are intended to be included within the scope of the present innovations. Other substitutions, modifications, changes, and omissions may be made in the design, operating conditions, and arrangement of the desired and other exemplary embodiments without departing from the spirit of 50 the present innovations.

It will be understood that any described processes or steps within described processes may be combined with other disclosed processes or steps to form structures within the scope of the present device. The exemplary structures and 55 processes disclosed herein are for illustrative purposes and are not to be construed as limiting.

It is also to be understood that variations and modifications can be made on the aforementioned structures and methods without departing from the concepts of the present 60 device, and further it is to be understood that such concepts are intended to be covered by the following claims unless these claims by their language expressly state otherwise.

The above description is considered that of the illustrated embodiments only. Modifications of the device will occur to 65 those skilled in the art and to those who make or use the device. Therefore, it is understood that the embodiments

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shown in the drawings and described above is merely for illustrative purposes and not intended to limit the scope of the device, which is defined by the following claims as interpreted according to the principles of patent law, including the Doctrine of Equivalents.

What is claimed is:

- 1. A crisp plate, comprising:
- a plate;
- a liner disposed on a surface of the plate, wherein the liner includes:
  - carbon nanotubes combined with aluminum nanoparticles and ceramic alumina; and
  - a polymer suitable to form a matrix, wherein the carbon nanotubes are embedded within the matrix.
- 2. The crisp plate of claim 1, wherein the plate is comprised of an aluminum material.
- 3. The crisp plate of claim 1, wherein the carbon nanotubes include carbon nanotubes treated with an acid selected from the group consisting of nitric acid, sulfuric acid, and mixtures thereof to provide functionalized carbon nanotubes having oxygenated functional groups.
- 4. The crisp plate of claim 1, wherein the carbon nanotubes include carbon nanotubes treated with an oxidant selected from the group consisting of potassium permanganate, ozone, and reactive plasma to provide functionalized carbon nanotubes having oxygenated functional groups.
- 5. The crisp plate of claim 1, wherein the carbon nanotubes include fluorinated carbon nanotubes that have been functionalized to provide amino, alkyl and hydroxyl functional groups.
- 6. The crisp plate of claim 1, wherein the carbon nanotubes are selected from the group consisting of single-wall carbon nanotubes, double-wall carbon nanotubes, few-wall carbon nanotubes, multi-wall carbon nanotubes, ultra-short carbon nanotubes, and combinations thereof.
- 7. The crisp plate of claim 1, wherein the carbon nanotubes are unidirectionally aligned within the matrix.
- 8. The crisp plate of claim 2, wherein the liner is free from
- 9. The crisp plate of claim 8, wherein the liner includes 1.5% by weight of the polymer material, and further includes 15% by weight of the ceramic alumina.
- 10. A liner for a crisp plate, comprising: aluminum nanoparticles; ceramic nanoparticles;
- a polymer material combined with the ceramic nanoparticles to provide a mixture; and
- a network of carbon nanotubes embedded within the mixture to form a monolayer matrix, wherein the carbon nanotubes are unidirectionally aligned within the monolayer matrix.
- 11. The liner of claim 10, wherein the liner heats up to 200° C. within two minutes or less when exposed to micro-
- 12. The liner of claim 10, wherein the liner includes an upper heat limit of 250° C. when exposed to microwaves.
  - **13**. A method of forming a crisp plate, comprising: providing a polymer matrix;

providing carbon nanotubes;

functionalizing the carbon nanotubes to provide functionalized carbon nanotubes, wherein the step of functionalizing the carbon nanotubes to provide functionalized carbon nanotubes includes one of treating the carbon nanotubes with an acid to provide oxygenated functional groups, and treating the carbon nanotubes with an oxidant to provide oxygenated functional groups;

embedding the functionalized carbon nanotubes within the polymer matrix to provide a composite matrix; providing aluminum nanoparticles and ceramic alumina to the composite matrix to form a nanoreinforced liner; providing a plate; and

applying the nanoreinforced liner to a surface of the plate.

14. The method of claim 13, wherein the step of applying the nanoreinforced liner to a surface of the plate further includes:

hot stamping the nanoreinforced liner to the surface of the 10 plate.

15. The method of claim 13, wherein the step of applying the nanoreinforced liner to a surface of the plate further includes:

injection molding the nanoreinforced liner on the surface 15 of the plate.

16. The method of claim 13, wherein the step of applying the nanoreinforced liner to a surface of the plate further includes:

spraying the nanoreinforced liner on the surface of the 20 plate.

17. The method of claim 13, wherein the step of functionalizing the carbon nanotubes to provide functionalized carbon nanotubes further includes:

fluorinating the carbon nanotubes to provide fluorinated 25 carbon nanotubes.

18. The method of claim 17, wherein fluorine atoms of the fluorinated carbon nanotubes are replaced with functional groups selected from the group of functional groups consisting of amino, alkyl and hydroxyl functional groups.

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