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(54) **LIGHTWEIGHT PLASTIC LAMINATE
SUITABLE FOR GAS AND MOISTURE
RESISTANT ENVIRONMENTAL HOUSINGS**

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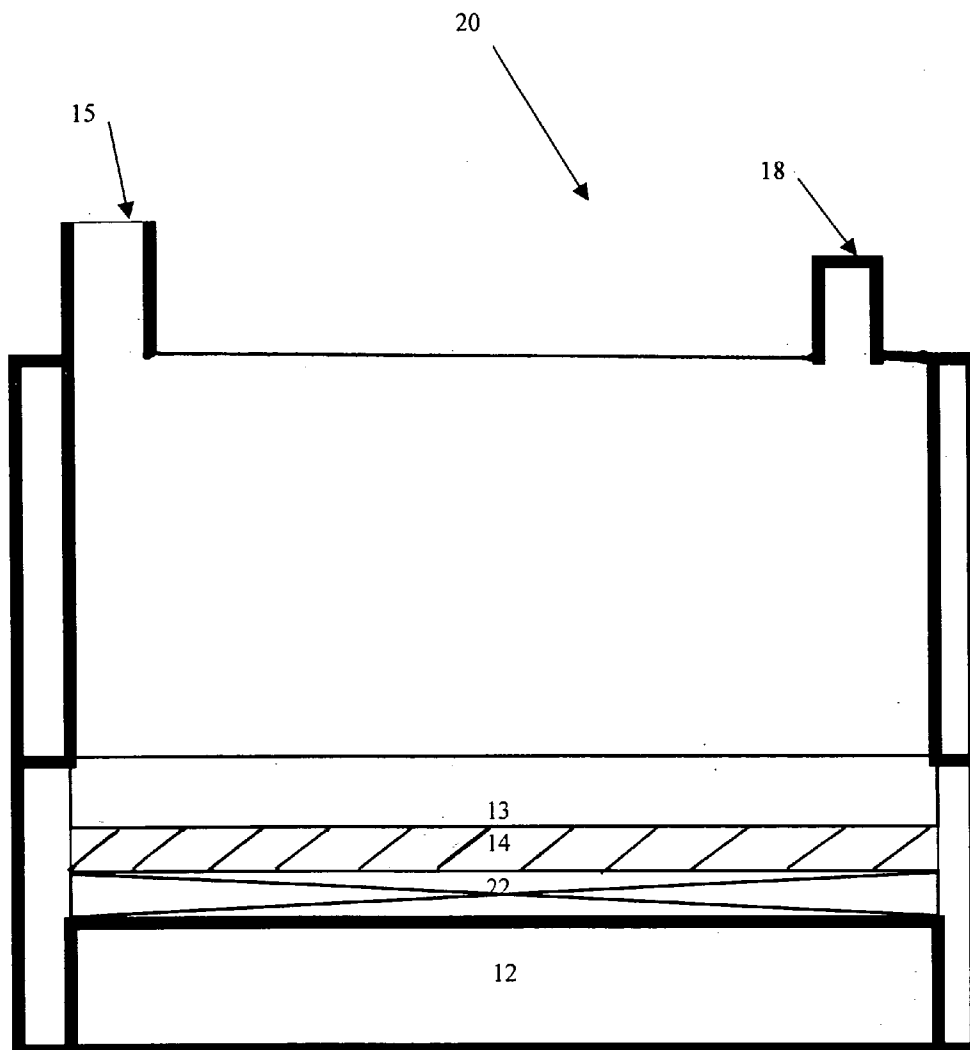
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(57) **ABSTRACT**

The instant invention relates to a housing structure for replacement of glass or metal housings currently in use in applications where high gas or water impermeability is desired. Herein is described a combination of structural polymers based on LCP with an additional layer or layers or barrier films of organic, inorganic or combinations thereof which enhance the barrier properties of the overall structure. These films may be located inside the structural polymeric substrate, outside of the structural polymeric substrate, or on both sides of the structural polymeric substrate. In an additional embodiment, an additional structural layer may also be present. In addition, various getter materials may also be used to further enhance the barrier properties.



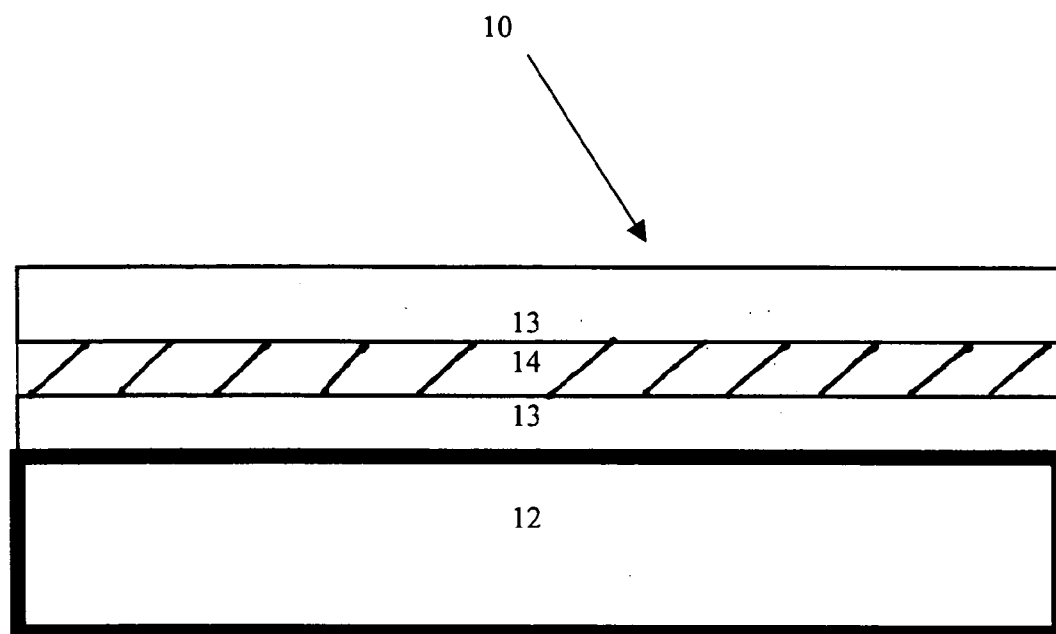


FIG. 1

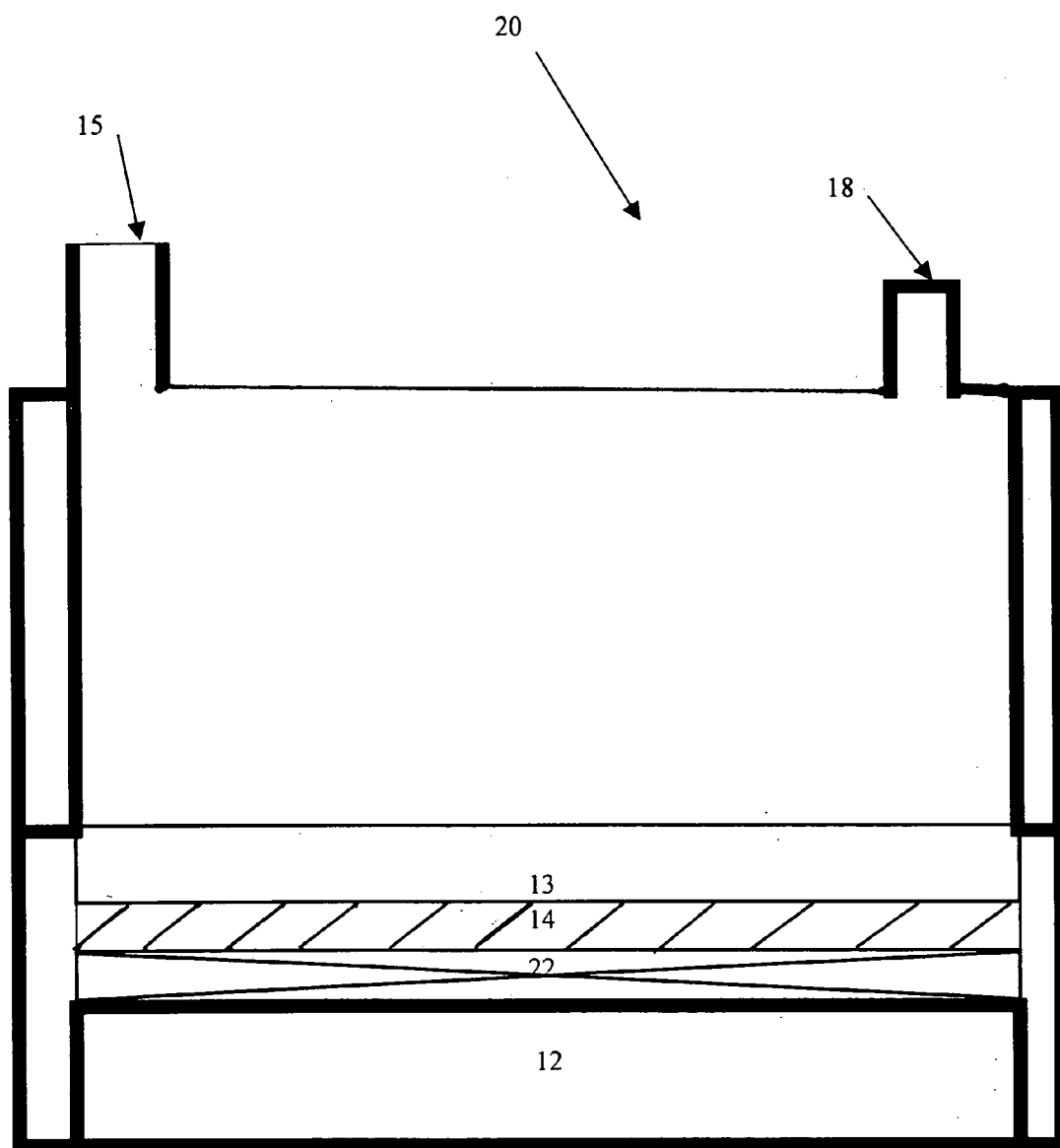


FIG. 2

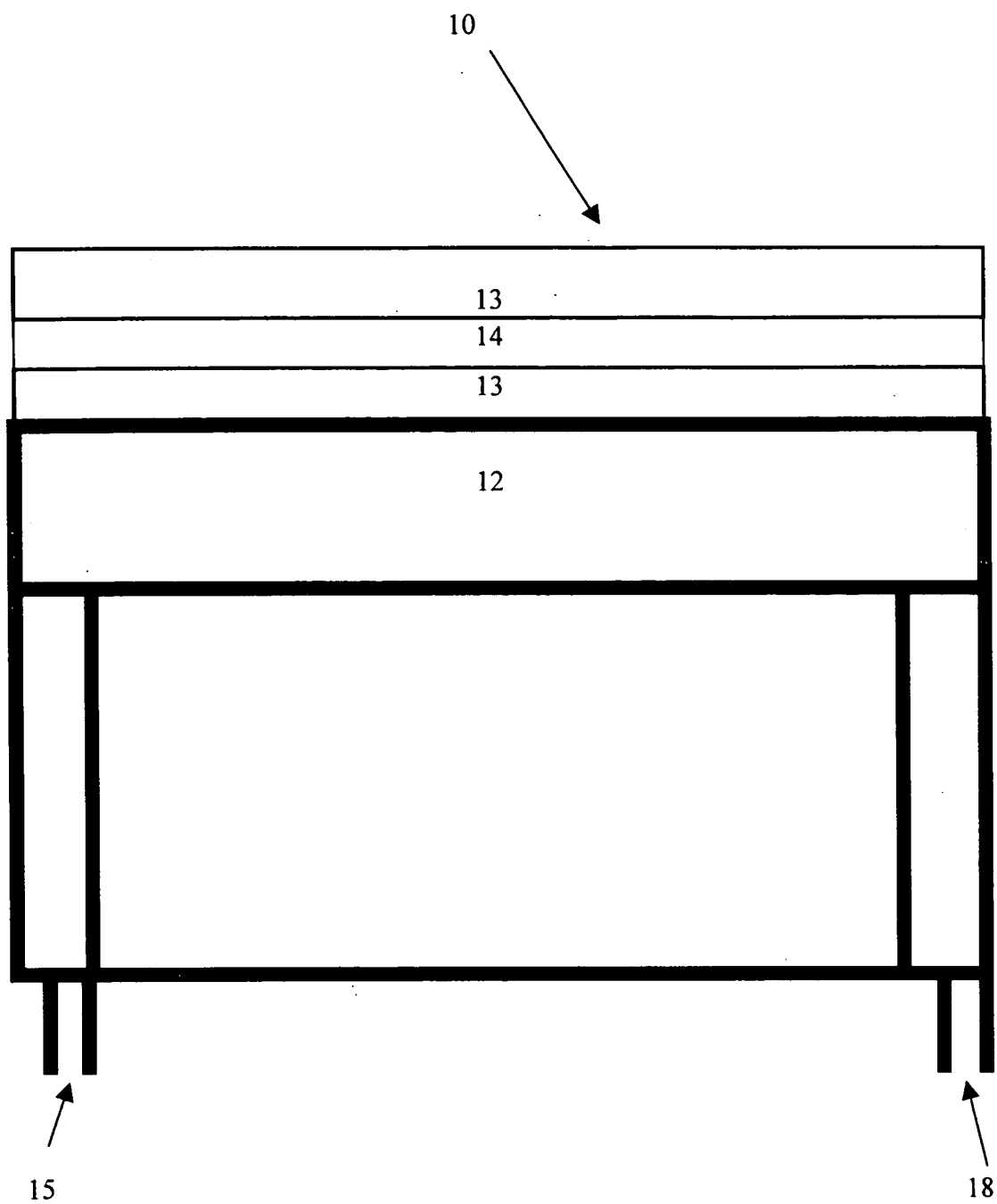


FIG. 3

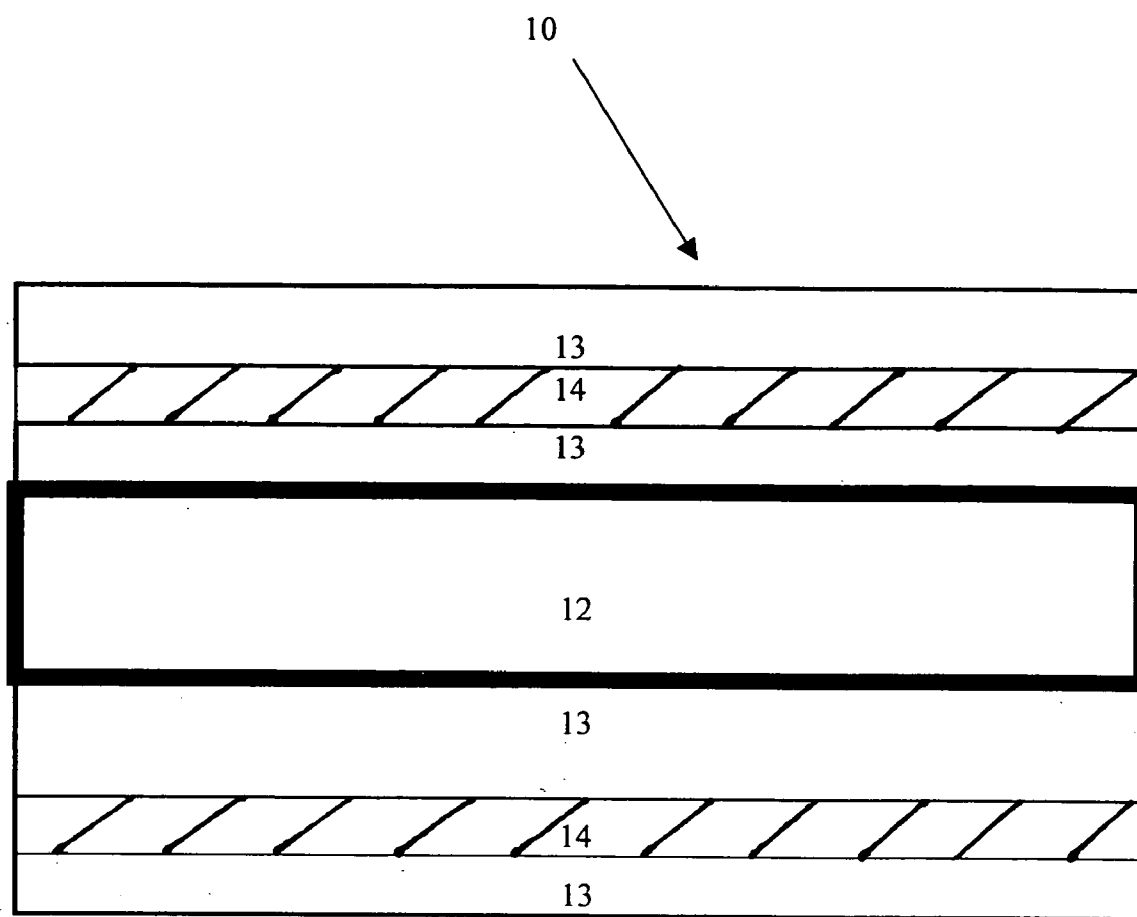


FIG. 4

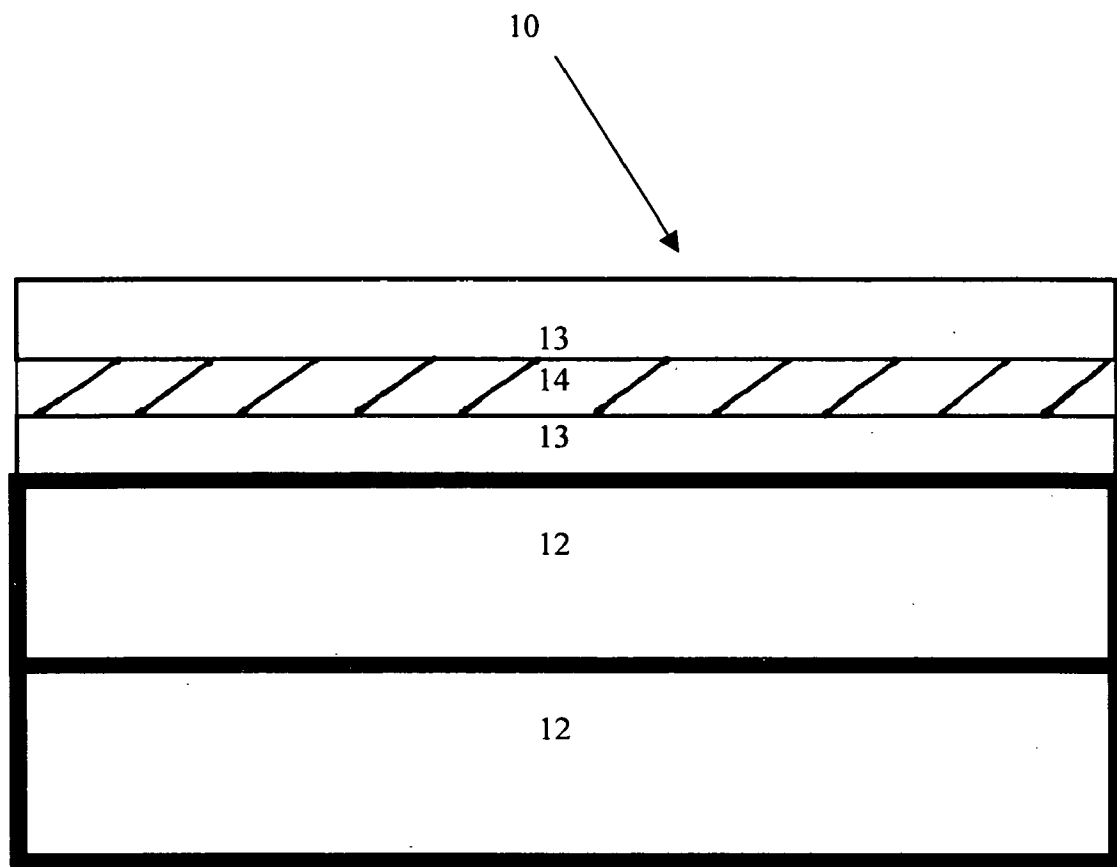


FIG. 5

LIGHTWEIGHT PLASTIC LAMINATE SUITABLE FOR GAS AND MOISTURE RESISTANT ENVIRONMENTAL HOUSINGS

FIELD OF THE INVENTION

[0001] This invention relates to the field of structural members for use in areas where high gas impermeability is desirable. This type of structure is highly desirable in applications where, to date, glass vacuum and metal housings have been employed such as in the protection of environmentally sensitive optical, opto-electric, electronic devices, in vacuum and in underwater applications in which machines, instruments and other pieces of sensitive equipment are used.

BACKGROUND OF THE INVENTION

[0002] The early 1990's saw single layer coatings of metals, such as Al, or ceramic oxides, including SiO_2 - Al_2O_3 , applied to food packages to reduce oxygen and water permeation by two orders of magnitude. In the mid 1990's multilayer polymer/inorganic barrier coatings for flexible plastic substrates were developed. These polymer/inorganic coatings become very complicated in some instances, with as many as 10 alternating layers of acrylate polymers alternating with inorganic materials such as SiO_2 or Al_2O_3 becoming widespread in the art. These coating proved to be extremely effective in preventing oxygen and water penetration to the underlying materials protected by them. The inorganic layer provides the barrier properties in these laminates, while the polymer seals and decouples the inorganic layers. A tortuous path through the adjoining and alternating layers limits the diffusion of gases and water.

[0003] One type of polymer system that became of great interest was the use of liquid crystal polymers in the context of barrier film structures. This class of polymers proved to be excellent in promoting the desired characteristics of providing impermeability necessary in packaging and in other industries.

[0004] One such film is described in Jester, U.S. Pat. No. 5,654,045 and Jester et al U.S. Pat. No. 5,248,530. Here a multi-axially oriented film of liquid crystal polymer (LCP) is used alone or in combination with metals or other laminating films in the electronic industry. Here the properties, however, are the rigidity of the LCP sheet and the excellent thermal coefficient properties of the films. No mention of increased barrier properties is made.

[0005] Another example of a multi-layered barrier film for oxygen sensitive packaging is described in McKnight, U.S. Patent Publication No. 2002/0155233. Here, the use of LCP films is equated with metal foil layers, metallized films, silicon and aluminum oxide coated films.

[0006] Food packaging films based on LCP's are described in Suokas et al, U.S. Pat. No. 6,146,764. Here the barrier properties of the LCP film material is described as well as the ability of the polymers to be used in combination with other materials. These laminate structures, however, are taught as being bags, wrappers, moisture-proof papers and similar products, and not in rigid structures.

[0007] Another food packaging film is described in Sumida et al, U.S. Pat. No. 5,364,669. Again the use of LCP in combination with other film materials is disclosed and the

teaching of barrier properties in the flexible packaging industry is maintained. Sumida teaches, however, that the LCP barrier films are weak in strength in various orientations, thus leading to limitations in use of the LCP's in various applications.

[0008] This problem is further addressed in Ora et al, U.S. Pat. No. 6,333,086. To remedy the problems faced in the packaging industry, Ora adds a second polymer to form a blend with the LCP and then making a laminate with other films. Ora adds that his laminate is additionally useful for structural articles such as gasoline tanks, barrier containers, chemical containers, and the like. However, Oda requires the use of a paperboard component to provide structural stability to the final article.

[0009] Jud et al, U.S. Pat. No. 6,405,896, describes a similar type of article with again equating the LCP as a substitute for metal or metallized or ceramic coated films to provide barrier properties.

[0010] Another example of a blend polymer incorporating LCP is found in Percec et al, U.S. Pat. No. 5,084,352. Here, the barrier properties are desired for packaging and the limitations of processing the barrier materials is overcome by co-extrusion and co-polymer blends.

[0011] Yageta et al, U.S. Patent Publication No. 2002/0146621 describes the use of LCP films for protective sealing of an article such as a battery element. Thus, the use of a LCP film is shown to be used in the context of a corrosive environment protection element, however structural properties are lacking, so the LCP is a protective film and not a structural member as well.

[0012] The use of LCP's in containment systems is further shown in Meyer et al, U.S. Pat. Nos. 5,950,450 and 5,943,876, and Salyer et al, U.S. Pat. No. 6,192,703. Here the LCP's are used in the manufacture of insulated vacuum panels. Again, the barrier properties of the LCP are noted.

[0013] Other thermal insulation panels incorporating LCP films for barrier purposes are disclosed in Hunter, U.S. Pat. Nos. 5,792,539 and 6,037,033. Again the polymers are used in combination with other structures to give rigidity to the final article.

[0014] Various structural types of applications have also been disclosed in the prior art. These have been used to make various different types of articles and include:

[0015] Bachner, Jr., U.S. Pat. No. 6,266,819, who makes a ballistic resistant garment with fibers of LCP material. This patent is directed to a physical characteristic based on the fibers formed and not a gas barrier property.

[0016] Another similar fiber material based on LCP fibers is described in Isayev, U.S. Pat. No. 5,238,638.

[0017] Rudy, U.S. Pat. No. 5,042,176 uses the LCP to trap nitrogen gas in a shoe structure, making it a reverse barrier situation.

[0018] Wu et al, U.S. Pat. Nos. 6,379,631 and 6,572,819 makes a sterilization container from LCP. Here, the choice of material is related to chemical resistance to hydrogen peroxide in vapor form when it is used in the sterilization process. This, therefore, relates to chemical inertness of the material and not barrier properties.

[0019] Ide, U.S. Pat. No. 4,332,759 describes the extrusion of LCP to form shaped articles. He reports that the structural integrity of these articles is acceptable due to the rigid nature of the LCP.

[0020] Similar molded articles formed of LCP are shown in Furuta et al, U.S. Pat. No. 5,612,101, Valyi, U.S. Pat. No. 5,939,153 and Minami et al, U.S. Pat. No. 6,544,610. These are all examples of structural articles made by various blow molding processes and incorporating LCP's into the final structures as barrier films.

[0021] Kimmel et al, U.S. Pat. No. 6,426,128 is another example of a laminate formed with LCP as a barrier. Here, a high strength article is formed for foodstuffs by blow-molding.

[0022] The use of LCP as a barrier layer in tubular products is shown in Bernstein et al, U.S. Pat. No. 6,064,007 and Ide et al, U.S. Pat. No. 4,772,089. Here the use is for protection of fiber optic cable members from moisture in various usage environments.

[0023] LCP in combination with getter materials is disclosed in Hunter et al, U.S. Pat. No. 6,001,449. The LCP here is the film type and this film is an outer skin over a structure including the getter material. The films here actually shield the getter from outside gas intrusion and allow the getter to perform its function within the enclosed space it occupies.

[0024] Even though LCP film structures are known in the prior art for use in barrier applications, there is no teaching of a combination of LCP with other barrier layers to form a structurally stable laminate, which is lightweight and possesses the barrier properties of glass and metal structures.

SUMMARY OF THE INVENTION

[0025] It is therefore an object of the invention to provide a lightweight structurally sound vacuum vessel which is impervious to gas or liquid intrusion.

[0026] It is another object of the invention to provide a system for protection of electronic components, which has high structural integrity as well as high resistance to gases and liquids which is formed of a liquid crystal polymer.

[0027] It is yet an additional object of the invention to provide an additional laminate for housing electronic components having a substrate layer with a barrier layer of LCP affixed to it to provide excellent impermeability.

[0028] It is another object of the invention to provide a barrier laminate with an intermediate layer of LCP in combination with a substrate and other barrier layers overlying the LCP layer.

[0029] It is a further object of the invention to provide a vacuum housing that is lightweight yet possesses the properties of heavier glass or metal-based housings.

[0030] Still additional objects will become apparent as the invention is further described.

BRIEF DESCRIPTION OF THE DRAWINGS

[0031] FIG. 1 shows the basic laminate housing of the present invention.

[0032] FIG. 2 shows another embodiment of the instant invention wherein the laminate contains an intermediate layer of LCP.

[0033] FIG. 3 shows the basic laminate structure of the present invention with the laminate layers affixed to the exterior of the substrate.

[0034] FIG. 4 depicts a third embodiment of the invention with the laminate layers affixed to both sides of the substrate.

[0035] FIG. 5 shows a fourth embodiment of the invention which employs an additional substrate layer for dimensional integrity.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0036] The instant invention is the creation of a lightweight, heterogeneous plastic based vacuum vessel, which is particularly suitable for gas and liquid resistant applications, such as hermetic housings. The invention is the incorporation of three key features, which in combination yield non-expected results in the retardation of gases and moisture. The three features include the use of liquid crystal polymers in combination with organic films affixed thereto, and in the preferred embodiment, includes the use of inorganic coatings on the organic films.

[0037] Referring to FIG. 1, the first feature of the instant laminate 10 is the use of a base layer 12 formed of any suitable polymeric material such as a polyolefin, polycarbonate, polyester, polyimide, polyamide, other known engineering plastics, liquid crystal polymer (LCP), or any other known polymeric substrate material as known to those of ordinary skill in the art. In the preferred embodiment, the base layer 12 is formed of a liquid crystal polymer and is characterized as being a highly rigid as well as impervious base layer. This desired base layer 12, in the preferred embodiment, forms the substrate layer for the subsequent layers in the laminate structure.

[0038] Because of its generally rigid nature, the base layer 12 is made sufficiently thick enough to afford structural integrity to the laminate and thus any housing thereby formed. Thus, this base layer 12 may range in thickness from micron to centimeter scale and beyond, to provide structural rigidity for subsequent barrier layer adhesions. In addition, the polymer comprising the base layer 12 may contain any known filler, such as fibers, to improve the rigid nature of this base layer. The actual thickness of the base layer 12 is again a matter of choice and is dependent on the degree of rigidity desired and the actual polymeric material chosen. Indeed, even a partial degree of flexibility is considered within the scope of the invention as well as totally rigid laminate structures.

[0039] In addition to the base layer 12, additional of layers of barrier coatings of both inorganic, organic thin films and combinations thereof are added to the base layer 12 to give further impermeability. In the preferred embodiment, a structural polymeric base is covered with a thin LCP barrier film and then, further covered with multilayers of inorganic/organic coatings, such as SiO₂-acrylate layers. In addition, the use of various getter materials may also be included within or next to the structure to enhance the sequestering effects. The preferred LCP layer is a biaxially oriented film layer, which provides excellent barrier properties.

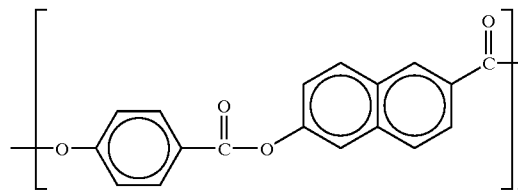
[0040] The application of vacuum technology and hermetic packaging is well known in the vacuum science and technology fields and microelectronic industry. A new and emerging area in vacuum sciences is in portable vacuum houses for analytical instruments and in better plastic over-molded materials for microchip protection. The ability to protect electronic devices and to create artificial vacuum volumes has in the past been accomplished with moisture resistant plastics in the electronic applications and glass and metal packages for the vacuum vessel applications, which have proven to be either not impermeable enough or heavy and cumbersome. Thus, using complex heterogeneous materials in thin film multi-layers enables another route to retard the transmission of gases across an interface, but solves the problems of the heretofore known systems as to the amount of gas blocked by a lightweight system.

[0041] The application of organic and inorganic thin films using vacuum based processes is a common practice for creating barrier coatings and is known in the art, but the use of these coatings in combination with thin LCP, both as a substrate or as an overlay on top of polymeric structural substrates is not. Therefore, the instant invention addresses the use of polymeric substrates with a LCP overlay for its rigidity characteristics and to a certain extent for its gas barrier properties, but it overcomes the problems of material incompatibility with respect to other film layers by use of deposition techniques or by inclusion of a multi-layer composite film adhered to the LCP covered substrate. It is anticipated that an adhesion promotion layer may be incorporated between the substrate and the LCP film and inorganic-organic multiplayer, this being used to promote bonding and increase interfacial adhesion. In addition, the film layer structure may be formed by extrusion techniques, sputtering techniques and other known processing methods known to those of ordinary skill in the art.

[0042] As shown in FIG. 2, the instant housing 10 is comprised of a base layer 12 of a structural polymer, such as LCP, having a LCP overlay 22 and one or more layers of polymers, such as acrylate, affixed to at least a portion of the LCP layer. This polymer layer may be metallized or non-metallized and the actual polymer may be chosen from any other known polymers known to those of ordinary skill in the art of packaging materials. Thus it is contemplated, again, that polyolefins, polyamides, polyesters, and any other suitable polymeric layers may be used in this structure.

[0043] In addition to the walls of the final housing structure, various other features such as an evacuation port 15, may be present, this enabling the evacuation of gases after the housing is in place surrounding the intended device to be protected. In addition, inlet ports, such as shown by 18 may be present so that gases or even getter materials may be introduced into the system after the initial sealing of the housing. The ports are designed to contain the appropriate septa to insure that the desired internal environment is maintained. In practice, the outlet port may be used to evacuate gases from the interior of the housing and if then, if desired, another gaseous environment may be introduced or even getter materials may be introduced via the inlet port. In practice, it is also possible to forego the evacuation with the introduction of getters solely.

[0044] Examples of LCP polymers especially useful for the base layer for creation of the barrier property are:



Vectra A950

[0045] One representative polymer of this type is known as Vectra A950, manufactured and distributed by Foster Miller, Roger Corp. and Gore Electronics. Other similar LCP polymers may also be used in this structure, and indeed, any LCP that is known in the art to possess barrier properties, as widely known to those of ordinary skill in the art may be used in the instant laminate.

[0046] Thermoplastic adhesive layers may also be present to adhere the layers of polymeric films to each other or to the base layer. These include, but are not limited to: polyalkylene terephthalates, olefin polymers, nylons, polycarbonates and the like. When the LCP has the polymeric film layer laminated or extruded directly it, the addition of a polymer having adhesive properties may also be used.

[0047] Typical examples of the adhesive thermoplastic polymer layer include modified polyolefins and polyesters. The polyesters contained in the adhesive thermoplastic polymer layer are other polyesters than polyalkylene terephthalates and liquid crystal polyesters, and are actually polyesters known by those of ordinary skill in the art to be adhesive with respect to the LCP. The typical adhesive thermoplastic polymer useful in this application has heat sealing or hot-melt adhesive properties.

[0048] In addition to metallization, the polymeric layer or layers may also be coated with gas impervious inorganic coatings such as silicates, ceramic oxides, etc. and combinations of metals and ceramic coatings.

[0049] In addition to a single polymeric layer, a plurality of layers may be used in the structure, and these may be chosen to all be of the same polymer or may be of a variety of differing polymers and may have selective metallizations also thereupon. Incorporation of various getter materials is also considered within the scope of the invention, and these may be embedded within a polymer matrix or found loose between the rigid substrate and any polymer film in the structure.

[0050] The getter materials, when incorporated, are used to absorb any gasses which remain in the voids the housing 20 contains even after being evacuated or for any gases which might permeate the outer skin of the housing 20 after exposure for an extended period of time. These getter materials are solids, which work by physical adsorption, chemical adsorption or absorption to trap or "get" the gases in the evacuated space. Typical thermally conductive gases, which remain or permeate the housing 20 over time include water vapor, hydrogen, nitrogen, oxygen, carbon monoxide or dioxide and other gases found in the atmosphere or

released during the fabrication process. Typical getter materials are alloys of zirconium and iron (eg. St 707, a trademark of SAE#S Getters/USA, Inc.) designed to sorb hydrogen, oxygen, water, carbon monoxide or dioxide and nitrogen. Other preferred getter materials include COMBO SUPERGETTER or SUPERGETTER, products of SAES Getters/USA, Inc, which are barium lithium alloys alone or in combination with barium oxide and either palladium or cobalt oxide. These are herein disclosed as representative getter materials and other getters, as known to those of ordinary skill in the art are also applicable for incorporation into the instant structure.

[0051] The degree of attachment of the polymeric layer to the LCP is also considered a matter of choice to the ordinary skilled artisan and is dictated by the final use of the end product. It is important to note that in certain applications if it is desirable to be able to vacuum and or heat press the polymer overlay (LCP) film to the item being encased, then the polymer film has to be affixed to the polymeric structural substrate in such a fashion that permits this to be done.

[0052] FIG. 3 shows another embodiment of the invention with the polymeric layers affixed to the outer sides of the base layer 12 substrate. This alternate allows for the vacuum sealing of the base layer substrate itself within the walls established now by the polymeric layers.

[0053] FIG. 4 is another embodiment wherein the polymeric layers, such as an LCP plus an inorganic-organic multilayer barrier film, are located both inside and outside of the LCP substrate. The layers used in this embodiment may be the same composition on both sides of the base layer substrate or may have different compositions.

[0054] Indeed, the films may even differ in one side being formed of inorganic materials and the other side being formed of organic materials or any combinations of materials

[0055] FIG. 5 is an additional embodiment of the invention in which an additional layer is added for dimensional integrity. This layer may be of any composition, but for the lightweight effect, it is preferred that a polymeric substrate layer be used. The polymer may be chosen from any known polymeric composition and includes poliolefins, polyimides, polycarbonates, polyamides, polyacrylates, and other engineering plastics used for rigid substrates as readily available to those of ordinary skill in the art.

[0056] The unexpected result so obtained by the instant laminate 10 is that the newly formed housing is as resistant to gas and liquid intrusion as metal or glass housing with a significant decrease in the weight of the housing.

[0057] The instant structure far exceeds the expectations derived from the use of polymeric layer barriers and LCP layers alone. Indeed, the instant combination far exceeds the expected results projected for the combination based on LCP data and polymeric film laminate data combined. In fact, the laminate of the invention actually has the barrier properties of metal or glass without the weight characteristics that make such housing undesirable. The instant combination thus yields an unexpected result over the expected compilation of the prior art. Indeed, the multiplicative benefit of combining polymers of minimal gas transport yield a barrier that permits for the first time structurally sound plastic

material to have gas impermeability that is in the regime of glass and metal such that practical lightweight vacuum vessels may be generated.

[0058] Modification and variation can be made to the disclosed embodiment of the instant invention without departing from the scope of the invention as described. Those skilled in the art will appreciate that the applications of the present invention herein are varied, and that the invention is described in the preferred embodiment. Accordingly, additions and modifications can be made without departing from the principles of the invention. Particularly with respect to the claims it should be understood that changes may be made without departing from the essence of this invention. In this regard it is intended that such changes would still fall within the scope of the present invention. Therefore, this invention is not limited to the particular embodiments disclosed, but is intended to cover modifications within the spirit and scope of the present invention as defined in the appended claims.

What is claimed is:

1. A laminate for use in structures such as housings comprising:

- a. a substantially rigid polymeric base layer substrate, and
- b. a film layer affixed to the base layer substrate, wherein at least one of the base and film layers are of liquid crystal polymer.
2. The laminate of claim 1, wherein both layers are of liquid crystal polymer.
3. The laminate of claim 1, wherein the film layer is biaxially oriented.
4. The laminate of claim 1, wherein the base layer is a polymer material with fillers incorporated therein.
5. The laminate of claim 1, wherein there is an intermediate layer of liquid crystal polymer between the base and film layers.
6. The laminate of claim 5, wherein at least one of the intermediate and film layers is biaxially oriented.
7. The laminate of claim 1, wherein the film layer is a single layer.
8. The laminate of claim 1, wherein the film layer is characterized by being formed of an acrylate.
9. The laminate of claim 1, wherein the film layer has an inorganic component.
10. The laminate of claim 1, wherein the film layer has multiple layers.
11. The laminate of claim 10, wherein the film layer is a laminate of polymer layers bonded to each other via a processing technique.
12. The laminate of claim 10, wherein the film layer is a laminate of polymer layers bonded together using one or more adhesive layers.
13. The laminate of claim 1, wherein the film layer is characterized by having an additional coating applied to it.
14. The laminate of claim 13, wherein the coating is selected from the group consisting of ceramic compounds, other inorganic compounds, metals, and combinations thereof.
15. The laminate of claim 1, wherein the substrate defines a structure with a defined interior region.
16. The laminate of claim 15, wherein the structure is a housing.

17. The laminate of claim 16, wherein an outlet port is incorporated into the housing structure.

18. The laminate of claim 16, wherein an inlet port is incorporated into the housing structure.

19. The laminate of claim 16, wherein both an inlet and out port are incorporated into the housing structure.

20. The laminate of claim 1, wherein the film layer is affixed to the substrate in the region defined as inside a final structure.

21. The laminate of claim 1, wherein the film layer is affixed to the region defined by the substrate as outside of a final structure.

22. The laminate of claim 1, wherein there are two film layers, located on both the inside and outside regions of a final structure.

23. The laminate of claim 1, wherein there further included a getter material incorporated into the housing structure.

24. The laminate of claim 1, wherein the films located on the outside of the substrate are the same composition as those on the inside of the substrate.

25. The laminate of claim 1, wherein the films located on the outside of the substrate are different in composition from those of the inside of the substrate.

26. The laminate of claim 1, wherein there is an additional layer in the structure to supply rigidity to the laminate.

27. The laminate of claim 26, wherein the additional layer is polymeric in nature.

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