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(54) Title: SYNTHETIC CLOSURE

(57) Abstract: By achieving an extruded, foamed core formed from plastic material peripherally surrounded and integrally bonded with a plurality of cooperating synthetic, plastic, extruded, outer layers, a unique, multi-component, multi-layer synthetic closure is provided which may be employed as a bottle closure or stopper for any desired product, whether the product is a liquid, a viscous material, or a solid distributed in a bottle or container and dispensed through the open portal of the container neck. The present invention achieves a mass producible, resilient, synthetic bottle closure which is employable for any desired bottle, including wine. By employing the present invention, a multi-component or multi-layer synthetic closure is attained which possesses physical properties substantially equal to or better than the physical properties found in cork material, which has caused such cork material to be the principal closure material for wine bottles.

SYNTHETIC CLOSURE

This invention relates to closures or stoppers for containers containing liquids, low viscosity substrates, and small solids, and more particularly, to closures or stoppers formed from synthetic materials and employable as a bottle stopper for a
5 container.

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BACKGROUND ART

In view of the wide variety of products that are sold for being dispensed from containers, particularly containers with round necks which define the dispensing portal, numerous constructions have evolved for container stoppers or closure means for the portals. Generally, products such as vinegar, vegetable oils, laboratory liquids, detergents, honey, condiments, spices, alcoholic beverages, and the like, impose similar requirements on the type and construction of the closure means used for containers for these products. However, wine sold in bottles represents the most demanding product for bottle closure means, due to the numerous and burdensome requirements placed upon the closure means used for wine bottles. In view of these demands, most wine bottle closures or stoppers have been produced from a natural material known as "cork".

Although synthetic materials have been proposed for use as wine bottle stoppers or closures, such products have been unable to satisfy all of the stringent requirements. As a result, cork has remained the dominant material for wine closures, in spite of the numerous inherent problems that exist with cork.

Cork represents the bark of a particular variety of cork oak, *quercus suber*, a tree of the oak family characteristic of western Mediterranean countries, such as Portugal, Spain, Algeria, Morocco, France, Italy, and Tunisia, that has the ability to renew its bark indefinitely. Cork is a vegetable plant comprising tissue made up of dead microcells, generally 14-sided polyhedrons, slotting in one against the other, with the intercell space filled with a gaseous mixture, essentially atmospheric air but without the carbon dioxide. It is estimated that 1 cm³ of cork numbers 15 to 40 million hexagonal cells with the thickness of the cellular membranes varying between 1 and 2.5 microns.

The suberose texture is not arranged in a uniform fashion. It is crisscrossed within its thickness by pores or ducts with walls more or less lignified, forming the lenticels. These are filled with powder of a reddish-brown color, rich in tannin.

The lenticels are permeable to gases and liquids and they are often invaded by molds and other microorganisms.

The unevenness, both in membrane thickness and in the height and diameter of the cell forming the suberose parenchyma, can affect some of the cork's mechanical and physical properties, namely its compressibility and elasticity. The cork oak being able to keep its physiological process active at all times, the difference in cell size and the thickness of the cellular membrane between cork produced in spring and the succeeding autumn leave discernible rings showing the extent of each year's growth.

The contents of newly formed cells disappear during growth and the subsequent process of suberization of the membranes, on completion of which all communication with the plant's living tissues ceases. The uniqueness of quercus suber is the achieved thickness of cork bark, up to several centimeters, which insulates the tree from heat and loss of moisture and protects it from damage by animals.

In order to harvest the thick cork bark for the first time, the growth cycle takes between 20 and 30 years, depending on location, weather conditions etc. yielding the so-called virgin cork. Afterwards, some 10 years are needed between each harvest of cork boards or reproduction cork in order to gain the necessary length for some corks. Due to this process, the cork used for the manufacture of bottle closures is a reproduction of cork that is formed again after several barking phases.

The properties of cork derive naturally from the structure and chemical composition of the membranes. Because 89.7% of the tissue consists of gaseous matter, the density of cork is extremely low, about 120 to 200 kg/m³, which makes the cork light and a good insulator. Density differences can be explained by the humidity differences, the age and quality of the cork bark and the cork tree and its growth differences. The cellular membranes are very flexible, rendering the cork both compressible and elastic. Elasticity enables it to rapidly recover to its original dimensions after any deformation. Its chemical composition gives the cork the

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property of repelling moisture. The walls of the cells are crusted with suberin, a complex mixture of fatty acids and heavy organic alcohols.

The value of cork is further increased by its low conductivity of heat, sound and vibration due to the gaseous elements sealed in tiny, impervious compartments. 5 Cork is also remarkably resistant to wear and has a high friction coefficient, thanks to the honeycomb structure of the suberose surface. Cork does not absorb dust and consequently does not cause allergies nor pose a risk to asthma sufferers. It is fire resistant, recyclable, environmentally friendly and a renewable product.

These advantages have made natural cork the preferred bottle closure for 10 wine storage, particularly for medium and high quality wines where tradition, the wine mystique and the bottle opening ritual with a corkscrew, are a very important, though intangible, aspect of the wine consumption. However, numerous disadvantages of natural cork also exists and derive naturally from the structure and chemical composition of the membranes.

15 Because cork is a natural product, it is a limited resource. Its limitations become even more obvious with the following facts: the natural growing of cork is geographically limited to the western Mediterranean countries; the world wide annual harvest of cork oak bark is 500,000 tons and can barely be increased, because of climatic and ecological reasons; and ten-year cycles are needed between 20 each harvest of cork boards. In order to meet the rising worldwide cork demand, the pare cycles of cork have been shortened, leading to inferior qualities and constantly rising raw material prices.

The irregularities of the cork's structure due to geographic, climatic and ecological reasons causes many quality variances. This creates a complex categoriza- 25 tion of qualities and standards. Through different types of washing processes, various chemical agents are combined in order to decontaminate the cork and to treat the appearance of the cork. High quality corks do not need washing. The cork quality is graded, based on the number of lenticels, horizontal and vertical cracks, their sizes, and other cork specific characteristics. The grading process is a subjec-

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tive task based on statistically significant populations which is difficult to perform due to its natural origin, since every cork looks, feels, functions and smells different.

Wine market experts estimate that 1% to 5% of all bottled wine is spoiled by cork taint. At least six chemical compounds have been associated with cork taint in
5 wines. Most frequently, 2,4,6-trichloranisole (TCA) is the major culprit responsible for the offensive off-odor and impact on the flavor of the wine. TCA has an extremely low threshold for odor detection. It is detectable at concentrations as low as 1 ppt or 1.0 nanogram per liter.

In most cases, cork taint does not involve the wine-making process. Typi-
10 cally, the tainting chemical is not found in vineyards or in parts of the winery where the wine is produced. After the wine is bottled, the defect shows itself, thus spoiling the wine. It is almost exclusively associated with corks.

Also, there is evidence that once the corks have been treated with chlorine, and are brought into interaction with mold fungus through humidity, chloranisole is
15 created. Other types of wine spoilage are caused by oxidation, hydrogen sulfide, volatile acidity, sulfur dioxide, brettanomyces, and mercaptans.

Another problem commonly found with natural cork is leaking bottles. Typically, the lack of tightness between the cork and the neck of the bottle causes
20 10% to 20% of bottle leakage. However, the majority of wine leakage is caused by passage of the wine through the cork body. These problems are most often found with lower quality cork material, which is typically porous, too soft, out of round, or out of the predetermined specifications.

In view of the fact that wine spoilage is caused by oxidation of the wine, any
25 gas exchange between ambient conditions and the interior of the wine bottle must be avoided. However, many corks are deformed by the chops or jaws of the bottle corking equipment, which enables air exchange and oxidation to occur. Furthermore, when bottles are stored in an environment where ideal humidity is not maintained, optimum functionality of the cork is not achieved and the cork loses its efficiency as a sealing medium by drying out, becoming brittle and/or losing its

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mechanical properties. These problems often cause the cork to break when pulled out of the bottle or enable wine spoilage to occur. In addition, natural cork absorbs liquids, depending on its structure and quality. This also results in breakage, while the cork is pulled out of the bottle.

5 Further problems or deficiencies found with natural cork is the propensity of cork worms to store or lay their eggs on the cork material, enabling the larvae to dig gullies into the cork. Consequently, enlarged apertures or channels are formed in the cork, unknown to the bottler, producing unwanted contamination. In addition to these drawbacks, cork powder and other cork impurities are often able to fall into the
10 wine during the corking process, causing further problems for wine bottlers and unwanted surprises for the wine consumer.

In order to avoid some of the difficulties, bottlers have developed various spray coatings, such as paraffins, silicones and polymer materials, in an attempt to ease the movement of the cork into and out of the bottle, as well as to improve the
15 permeability of the cork and fill imperfections in the cork surface. However, no ideal cork spray coating product has been developed to protect a wine corking member from all of the inherent difficulties or drawbacks of the material.

The vast majority of wine-containing bottles are currently being sold with natural cork stoppers. However, due to the inherent problems existing with natural
20 cork, various other products have been developed to close liquid bearing containers, such as wine bottles. These other closures principally comprise structural synthetic plastics, crown cap metal stoppers, aluminum caps, plastic caps and combinations thereof.

In spite of these prior art efforts, a universally applicable closure has not been
25 developed which satisfies all bottlers and consumer requirements. Particularly, the substantially burdensome requirements imposed upon closure means used in the wine industry have generally been employed as the standard that must be attained by a bottle closure that will be accepted by the industry. As a result of these stringent

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requirements, these prior art products have been incapable of satisfying the requisite needs of the industry.

In particular, one of the principal difficulties to which any bottle closure is subjected in the wine industry is the manner in which the closure is inserted into the bottle. Typically, the closure is placed in a jaw clamping member positioned above
5 the bottle portal. The clamping member incorporates a plurality of separate and independent jaw members which peripherally surround the closure member and are movable relative to each other to compress the closure member to a diameter substantially less than its original diameter. Once the closure member has been fully
10 compressed, a plunger moves the closure means from the jaws directly into the neck of the bottle, where the closure member is capable of expanding into engagement with the interior diameter of the bottle neck and portal, thereby sealing the bottle and the contents thereof.

In view of the fact that the jaw members must be independent of each other
15 and separately movable in order to enable the closure member to be compressed to the substantially reduced diameter, each jaw member comprises a sharp edge which is brought into direct engagement with the closure member when the closure member is fully compressed. Depending upon the composition of the closure member, score lines are frequently formed on the outer surface of the closure member, which
20 prevents a complete, leak-free seal from being created when the closure member expands into engagement with the bottle neck.

As a result of this sealing system, closure members other than cork have not been accepted by the wine industry, due to their inability to withstand this conventional bottling and sealing method. Furthermore, many cork sealing members also
25 incur damage during the bottling process, resulting in leakage or tainted wine.

Another problem inherent in the wine industry is the requirement that the wine stopper must be capable of withstanding a substantial pressure build up that occurs during the storage of the wine product after it has been bottled and sealed. Due to natural expansion of the wine during hotter months, pressure builds up,

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imposing a burden upon the bottle stopper that must be resisted without allowing the stopper to be displaced from the bottle. As a result, the bottle stopper employed for wine products must be capable of secure, intimate, frictional engagement with the bottle neck in order to resist any such pressure build up.

5 A further problem inherent in the wine industry is the requirement that secure, sealed engagement of the stopper with the neck of the bottle must be achieved virtually immediately after the stopper is inserted into the neck of the bottle. During normal wine processing, the stopper is compressed, as detailed above, and inserted into the neck of the bottle to enable the stopper to expand in place and seal the bottle.
10 However, such expansion must occur immediately upon insertion into the bottle since many processors tip the bottle onto its side or neck down after the stopper is inserted into the bottle neck, allowing the bottle to remain stored in this position for extended periods of time. If the stopper is unable to rapidly expand into secure, intimate, frictional contact and engagement with the walls of the neck of the bottle, wine
15 leakage will occur.

 A further requirement imposed upon closures or stoppers for wine bottles is the requirement that the closure be removable from the bottle using a reasonable extraction force. Although actual extraction forces extend over a wide range, the generally accepted, conventional extraction force is typically below 100 pounds.

20 In achieving a commercially viable stopper or closure, a careful balance must be made between secure sealing and providing a reasonable extraction force for removal of the closure from the bottle. Since the requirements for these two characteristics are in direct opposition to each other, a careful balance must be achieved so that the stopper or closure is capable of securely sealing the wine in the bottle,
25 preventing both leakage and gas transmission, while also being removable from the bottle without requiring an excessive extraction force.

 Another requirement for commercially viable wine stoppers or closures is the ability for printed material to be placed on the outer surface of the wine closure or stopper in order to allow the wine company to display any desired names, logos, and

the like directly on the wine stopper. Depending upon the particular composition of the wine stopper, the requirement for enabling printed material to be placed thereon often imposes difficult conditions and limitations on the construction and functioning of the stopper for its intended purpose.

5 It has been found with many prior art closures that the process required for enabling the synthetic closure to receive and retain the ink for displaying printed indicia and/or logos also interferes with maintaining a reasonable extraction force for the synthetic closure. In this regard, synthetic closures are required to be specially treated, in order to enable the surface of the synthetic closure to accept the printing
10 ink. Typically, this treatment requires the outer surface of the synthetic closure to be exposed to a high-intensity corona, plasma, or flame.

 Although the exposure of the synthetic closure to a high-intensity beam of corona, plasma, or flame typically enables the surface of the closure to receive and retain printing inks, the treatment has been found to have a deleterious effect on the
15 outer surface of the synthetic closure. In this regard, it has been found that extraction forces required to remove the treated synthetic closure from a bottle or container continuously increase with the passage of time. As a result, one of the principal requirements for an effective synthetic closure is not attainable by such prior art products.

20 Therefore, it is a principal object of the present invention to provide closure means for containers which is manufacturable from synthetic materials and effectively closes and seals any desired bottle, container, package and the like.

 Another object of the present invention is to provide a synthetic closure having the characteristic features described above which is manufacturable on a
25 continuing production basis, thus providing lower manufacturing costs compared to natural or synthetic (structured) closures and satisfying industry requirements for a removable bottle stopper which is producible substantially more economically than cork closure/stoppers.

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Another object of the present invention is to provide a synthetic closure having the characteristic features described above which meets or exceeds all of the requisite physical characteristics found in natural closures or stoppers such as cork.

5 A further object of the present invention is to provide a synthetic closure or stopper having the characteristic features described above which is capable of simulating all of the visually aesthetic and tactile characteristics found in natural stoppers, such as cork, so as to be effectively a substitute for cork stoppers or closures for the wine industry, particularly its ends users in both appearance and feel.

10 Another object of the present invention is to provide a synthetic closure or stopper having the characteristic features described above which is capable of being employed in conventional bottling equipment for being inserted into a bottle container without experiencing any unwanted physical damage.

15 Another object of the present invention is to provide a synthetic closure or stopper having the characteristic features described above that can be substituted for a cork stopper in wine bottles, providing all of the desirable characteristics of conventional cork stoppers while also being removable from the bottle in the conventional manner without breaking.

20 Another object of the present invention is to provide a synthetic closure or stopper having the characteristic features described above, which is physiologically neutral, capable of being sterilized, as well as capable of being formed to visually simulate any desired classification of natural cork.

A further object of the present invention is to provide a synthetic closure or stopper having the characteristic features described above which is odorless, remains odorless in position, is tasteless, and only absorbs limited amounts of water.

25 Another object of the present invention is to provide a synthetic closure or stopper having the characteristic features described above which is unaffected by diluted acids and bases as well as unaffected by most oils.

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Another object of the present invention is to provide a synthetic closure or stopper having the characteristic features described above which does not shrink, does not age, does not absorb mold or fungus, and resists damage from insects.

5 Another object of the present invention is to provide a synthetic closure or stopper having the characteristic features described above which can be mass produced on a continuing basis and eliminates any spoilage of wine due to cork taint.

10 Another object of the present invention is to provide a synthetic closure or stopper having the characteristic features described above which is capable of being removed from the container using conventional extraction forces, which forces remain reasonably constant regardless of the period of time over which the stopper has been in the bottle.

15 Another object of the present invention is to provide a synthetic closure or stopper having the characteristic features described above which is capable of receiving printed material thereon without requiring special treatment to the outer surface thereof.

Another object of the present invention is to provide a synthetic closure or stopper having the characteristic features described above which is capable of being easily inserted into any desired bottle container, as well as being removed from the bottle or container without requiring excessive force.

20 Another object of the present invention is to provide a synthetic closure or stopper having the characteristic features described above which is capable of providing a wide variety of alternate surface treatments or visual appearances.

25 Another object of the present invention is to provide a synthetic closure or stopper having the characteristic features described above which consistently and uniformly provides all required physical attributes for a closure without requiring any special treatments or surface coatings to be applied to the outer surface thereof.

Other and more specific objects will in part be obvious and will in part appear hereinafter.

SUMMARY OF THE INVENTION

By employing the present invention, all of the difficulties and drawbacks found in the prior art have been completely overcome and a mass producible, resilient, synthetic bottle closure is realized by achieving a synthetic, extruded, foamed polymer core peripherally surrounded and integrally bonded with a plurality of cooperating, synthetic, separate, independent, extruded, outer layers or skin members. The present invention can be employed on any desired product, whether the product is a liquid, a viscous material, or a solid distributed in a bottle or container and dispensed through the open portal of the container neck.

As will become evident from the following detailed disclosure, the multi-component, multi-layer synthetic closure of the present invention may be employed as a bottle closure or stopper for any desired product. However, for the reasons detailed above, wine products impose the most burdensome standards and requirements on a bottle closure. Consequently, in order to clearly demonstrate the universal applicability of the multi-component/multi-layer synthetic closure of the present invention, the following disclosure focuses on the applicability and usability of the multi-component/multi-layer synthetic closure of the present invention as a closure or stopper for wine containing bottles. However, this discussion is for exemplary purposes only and is not intended as a limitation of the present invention.

As discussed above, a bottle closure or stopper for wine must be capable of performing numerous separate and distinct functions. One principal function is the ability to withstand the pressure build up due to temperature variations during storage, as well as prevent any seepage or leakage of the wine from the bottle. Furthermore, a tight seal must also be established to prevent unwanted gas exchange between ambient conditions and the bottle interior, so as to prevent any unwanted oxidation or permeation of gases from the wine to the atmosphere. In addition, the unique corking procedures employed in the wine industry also impart substantial restrictions on the bottle closure, requiring a bottle closure which is highly compress-

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ible, has high immediate compression recovery capabilities and can resist any deleterious effects caused by the clamping jaws of the bottle closure equipment. Finally, the bottle stopper or closure must be removable using normal extraction forces and must also be capable of accepting printed material thereon.

5 Although prior art synthetic products have been produced in an attempt to satisfy the need for alternate bottle closures employable in the wine industry, such prior art systems have been incapable of meeting all of the stringent requirements and demands imposed upon a bottle closure for wine products. However, by employing the present invention, all of the prior art inabilities have been obviated and an
10 effective, easily employed, mass-produced synthetic closure has been realized.

The present invention overcomes all of the prior art problems by achieving a multi-component, multi-layer synthetic closure which possesses physical properties substantially equal to or better than the physical properties found in cork material, which has caused such cork material to be the principal closure material for wine
15 bottles. In the present invention, the prior art failings have been overcome by achieving a multi-component, multi-layer synthetic bottle closure which incorporates a central core member peripherally surrounded by and integrally bonded to a plurality of separate, independent outer peripheral layers or skin members, each of which impart additional, desirable physical characteristics to the effective outer surface of
20 the synthetic bottle closure. By employing multi-components and multi-layers to form the synthetic bottle closure of the present invention, all of the prior art difficulties and drawbacks have been eliminated and an effective, multi-purpose, easily employed and economically mass produced synthetic closure is realized.

The multi-component/multi-layer synthetic bottle closure of the present
25 invention comprises, as its principal component, the core member which is formed from extruded, foamed, plastic polymers, copolymers, or homopolymers. Although any known foamable plastic material can be employed in the extrusion process for developing the bottle closure of the present invention, the plastic material must be selected for producing physical properties similar to natural cork, so as to be capable

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of providing a synthetic closure for replacing natural cork as a closure for wine bottles.

By employing the present invention, a synthetic bottle closure is produced in a highly automated, high-tech extrusion or molding process with product tolerances being closely maintained. As a result, various prior art difficulties encountered with
5 cork products being out of round or having improper diameters are completely eliminated.

In the present invention, one aspect of the unique synthetic bottle closure is realized by forming a first outer layer or skin member peripherally surrounding the
10 core member in intimate, bonded, interengagement therewith. The first outer, peripheral layer/skin member of the synthetic closure is formed from plastic material which is integrally bonded to the cylindrical surface of the core member by applying the first outer layer/skin member to the core member by extrusion or molding. However, the first outer, peripherally surrounding layer/skin member is formed with
15 a substantially greater density in order to impart desired physical characteristics to the synthetic bottle closure of the present invention.

Although many desirable physical characteristics are achieved by the combination of the core member and the first, outer, peripherally surrounding layer/skin member, all of the requirements imposed upon a synthetic closure are not fully
20 realized. However, it has been found that all requirements desired by the industry for a synthetic closure or stopper are fully satisfied by forming a second, outer layer or skin member which peripherally surrounds the first outer layer or first skin member, with said second outer layer/skin member being in intimate bonded engagement with the first layer/skin member. In addition, if desired, a third outer layer or
25 skin member is intimately bonded to the second layer/skin member to assure that all desired attributes are attained.

In the preferred construction, the second, outer layer/skin member is formed from plastic material which is integrally bonded to the cylindrical surface of the first layer/skin member by applying the second layer/skin member to the first layer/skin

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member by extrusion or molding. Furthermore, the second outer layer/skin member comprises a construction and a composition which imparts all of the desired physical characteristics and attributes to the synthetic closure which were sought by the industry and not provided by prior art constructions.

5 In order to provide this desirable, and heretofore unattainable result, the second outer layer/skin member employed in the present invention comprises a material which easily receives and retains printed indicia thereon without requiring post-production treatments for enhancing ink adhesion. In addition, the second outer layer/skin member also comprises a material which controls the extraction forces
10 required for removal of the closure from the container, as well as assures ease of entry of the closure into the container during the corking process.

 In order to attain these desirable results, it has been found that the second outer layer/skin member preferably comprises one or more materials or blends of materials selected from plastic polymers, copolymers or homopolymers. If desired,
15 the materials employed for the second outer layer/skin member can be substantially identical to the materials employed for the core member and/or the materials employed for the first outer layer. However, in forming the second outer layer/skin member as well as the first outer layer/skin member, it has been found that these layers may comprise a foamed plastic or a non-foamed plastic.

20 If employed, the third outer layer/skin member is constructed substantially identically to the second layer/skin member, while being bonded to the outer surface of the second layer/skin member. In addition, the third layer/skin member would incorporate additives and physical properties to enhance and complement the properties provided by the first and second layers/skin members.

25 As fully detailed below, the composition of the second and third outer layers/skin members incorporate a base material and required additives or blends which assure that the desired, controlled, frictional engagement with the container surface is realized. In addition, the compositions employed are also formulated for receiving and retaining printing ink in order to fully display any desired name or logo on the

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surfaces thereof without degradation or interference with other properties. Alternatively, the second or third out layer/skin member may be formulated to protect indicia printed on the adjacent, underlying layer.

In addition, by incorporating selected additives, colors, pigments, and the like
5 into the second and third outer layers/skin members, the multi-component/
multi-layer synthetic bottle closure of the present invention is manufacturable in any
desired color or with any desired markings, or indicia placed on the outer surface
thereof. Furthermore, special effect constructions are also capable of being
achieved, such as three-dimensional effects, textured appearances, and colors or
10 indicia which glow or are responsive to special lighting, such as black light or ultra-
violet light.

Consequently, if desired, the synthetic bottle closure of the present invention
may be manufactured with a visual appearance substantially identical to the visual
appearance of a cork stopper or with virtually any other desired appearance. In
15 addition to the natural, wood-grain cork appearance, the synthetic closure of the
present invention may also be produced with any desired indicia, colors, stripes,
logos, etc. formed on the surfaces thereof. These desired indicia can be formed on
either the surface of the synthetic closure of the present invention using conventional
printing techniques, embossing techniques, laser printing, laser etching, etc. as
20 known in the printing industry.

Furthermore, depending upon the sealing process employed for inserting the
synthetic closure of the present invention in a desired bottle, additives, such as slip
additives, may be incorporated into the second or third, outer, peripherally surround-
ing layers/skin members of the synthetic closure of the present invention to provide
25 lubrication of the synthetic closure during the insertion process. In addition, other
additives may also be incorporated into the synthetic closure of the present invention
for improving the sealing engagement of the synthetic closure with the bottle as well
as reducing the extraction forces necessary to remove the synthetic closure from the
bottle for opening the bottle. If desired, a unique combination of additives selected

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from the group consisting of antimicrobial agents, antibacterial compounds, and oxygen scavenging materials can be incorporated into the second outer layer/skin member of the present invention in order to impart unique, heretofore unattainable desirable attributes .

5 By achieving a multi-component, multi-layer synthetic bottle closure in accordance with the present invention, a bottle closure is realized which is capable of satisfying all requirements imposed thereon by the wine industry, as well as any other bottle closure/packaging industry. As a result, a synthetic bottle closure is attained that can be employed for completely sealing and closing any desired bottle
10 for securely and safely storing the product retained therein.

The invention accordingly comprises an article of manufacture possessing the features, properties, and relation of elements which will be exemplified in the article hereinafter described, and the scope of the invention will be indicated in the claims.

THE DRAWINGS

For a fuller understanding of the nature and objects of the invention, reference should be made to the following detailed description taken in connection with the accompanying drawings, in which:

5 FIGURE 1 is a perspective view of one embodiment of the multi-component or multi-layer synthetic bottle closure of the present invention;

 FIGURE 2 is a cross-sectional side elevation view of the multi-component or multi-layer synthetic bottle closure of FIGURE 1;

 FIGURE 3 is a cross-sectional side elevation view of an alternate embodiment of
10 the multi-component, multi-layer synthetic bottle closure of this invention;

 FIGURE 4 is a side elevation view, partially broken away, of an alternate embodiment of the multi-component, multi-layer synthetic bottle closure of this invention wherein the outer surface thereof has been formed with a fish scale appearance;

 FIGURE 5 is a cross-sectional side elevation view, partially broken away, of the
15 synthetic bottle closure of FIGURE 4 taken along line 5-5;

 FIGURE 6 is a front elevation view of an embossing system constructed for embossing any desired patterns onto the outer surface of the synthetic closure of the present invention;

 FIGURE 7 is a side elevation view of the embossing system of FIGURE 6;

20 FIGURE 8 is a test data diagram depicting the effect of temperature on oxygen absorption over time;

 FIGURE 9 is a test data diagram depicting the effect of humidity on oxygen adsorption over time; and

 FIGURE 10 is a test data diagram depicting the change in oxygen content in the
25 wine bottle headspace over time with and without oxygen scavengers.

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DETAILED DISCLOSURE

By referring to FIGURES 1-5, along with the following detailed disclosure, the construction of several alternate embodiments of the multi-component, multi-layer synthetic bottle closure of the present invention can best be understood. In FIGURES 5 1-5, as well as in the following detailed disclosure, the multi-component, multi-layer synthetic closure of the present invention is depicted and discussed as a bottle closure for wine products. However, as detailed above, the present invention is applicable as a synthetic closure for use in sealing and retaining any desired product in any desired closure system. Due to the stringent and difficult demands and requirements placed 10 upon a closure for wine products, the following detailed disclosure focuses on the applicability of the synthetic bottle closure of the present invention as a closure for wine bottles. However, it is to be understood that this detailed discussion is provided merely for exemplary purposes and is not intended to limit the present invention to this particular application and embodiment.

15 As shown in FIGURE 1, multi-component, multi-layer synthetic bottle closure 20 comprises a generally cylindrical shape having an outer diameter larger than the diameter of the portal-forming neck of the bottle into which the closure is to be inserted. In general, the overall diameter of multi-component, multi-layer synthetic closure 20 is slightly greater than the diameter of the portal into which bottle closure 20 20 is to be inserted. In this way, assurance is provided that secure sealed contacting interengagement is attained between synthetic closure 20 and the portal within which it is employed.

In the embodiment depicted in FIGURES 1 and 2, multi-component/multi-layer synthetic bottle closure 20 comprises core member 22, a first peripheral layer or skin 25 member 24, which peripherally surrounds and is integrally bonded to core 22, and a second peripheral layer or skin member 25, which peripherally surrounds first layer/

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skin member 24. In addition, as shown in FIGURE 3, if desired, a third peripheral layer or skin member 26 may also be employed to provide additional desired attributes and physical characteristics to synthetic closure 20. As depicted, when employed, third peripheral layer/skin member 26 peripherally surrounds and is bonded to second layer/skin member 25.

In the preferred embodiment, core member 22 is formed comprising a substantially cylindrically shaped surface 21, terminating with substantially flat end surfaces 27 and 28. In addition, first peripherally surrounding layer/skin member 24 is intimately bonded directly to core member 22, peripherally surrounding and enveloping surface 21 of core member 22. Furthermore, second layer/skin member 25 is intimately bonded directly to first layer/skin member 24, peripherally surrounding and enveloping first layer/skin member 24 along cylindrical surface 23. Similarly, if employed, third layer/skin member 26 is intimately bonded directly to second layer/skin member 25, peripherally surrounding and enveloping second layer/skin member 25 on cylindrical surface 30.

If desired, as shown in FIGURE 2, in order to assist in assuring entry of synthetic bottle closure 20 into the portal of the bottle into which closure 20 is inserted, terminating edges 31 of peripheral layers/skin members 24 and 25 may be beveled or chamfered. Similarly, terminating edges 32 of peripheral layers/skin members 24 and 25 also may comprise a similar bevel or chamfer. Although any desired bevel or chamfered configuration can be employed, such as a radius, curve, or flat surface, it has been found that merely cutting ends 31 and 32 with an angle of about 45, the desired reduced diameter area is provided for achieving the desired effect.

By incorporating chamfered or beveled ends 31 and 32 on synthetic bottle closure 20, automatic self-centering is attained. As a result, when synthetic bottle closure 20 is compressed and ejected from the compression jaws into the open bottle for forming the closure thereof, synthetic bottle closure 20 is automatically guided into the bottle opening, even if the clamping jaws are slightly misaligned with the portal of the bottle. By employing this configuration, unwanted difficulties in inserting bottle

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closure 20 into any desired bottle are obviated. However, in applications which employ alternate stopper insertion techniques, chamfering of ends 31 and 32 may not be needed.

Furthermore, in certain applications, chamfering or beveling of ends 31 and 32 are not desired. In these instances, as shown in FIGURE 3, first peripheral layer/skin member 24, second peripheral layer/skin member 25, and third peripheral layer/skin member 26 extend the entire length of closure 20, terminating as an integral part of end surfaces 27 and 28.

In order to produce the attributes required for use in the wine industry, core 22 is formed from foam plastic material using a continuous extrusion process. Although other prior art systems have employed molded foamed plastic material, these processes have proven to be more costly and incapable of providing a final product with the attributes of the present invention.

In the preferred embodiment, core member 22 is formed as an extruded, medium or low density closed cell foamed plastic comprising one or more plastics selected from the group consisting of inert polymers, homopolymers, and copolymers. The preferred plastic material is preferably selected from the group consisting of polyethylenes, metallocene catalyst polyethylenes, polybutanes, polybutylenes, polyurethanes, silicones, vinyl based resins, thermoplastic elastomer, polyesters, ethylene acrylic copolymers, ethylene-vinyl- acetate copolymers, ethylene-methyl acrylate copolymers, ethylene-butyl-acrylate copolymers, ethylene-propylene-rubber, styrene butadiene rubber, ethylene-ethyl-acrylic copolymers, ionomers, polypropylenes, and copolymers of polypropylene and copolymerizable ethylenically unsaturated commoners, as well as ethylenic acrylic copolymers, ethylene-vinyl-acetate copolymers, ethylene-methyl-acrylate copolymers, thermoplastic polyurethanes, thermoplastic olefins, thermoplastic vulcanizates, flexible polyolefins, fluorelastomers, fluoropolymers, polyethylenes, teflons, ethylene-butyl-acrylate copolymers, ethylene-propylene-rubber, styrene butadiene rubber, ethylene-ethyl-acrylic copolymers and blends thereof. Furthermore, if a polyethylene is employed, it has been found that the polyethylene may comprise one or

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more polyethylenes selected from the group consisting of high density, medium density, low density, linear low density, ultra high density, and medium low density.

Regardless of the foamable plastic material selected for forming core member 22, the resulting extruded foam product must have a density ranging between about 100 kg/m³ to 500 kg/m³. Although this density range has been found to provide an effective core member, the density of the extruded foam core member 20 preferably ranges between about 200 kg/m³ to 350 kg/m³.

Since core member 22 is substantially closed cell in structure, additives are intermixed with the plastic material to form a closed cell foam with minute cells. The resulting core member 22 of the present invention has average cell sizes ranging from between about .02 millimeters to 0.50 millimeters and a cell density ranging between about 25,000,000 cells/cm³ to 8,000 cells/cm³. Although this cell configuration has been found to produce a highly effective product, it has been found that the most desirable product possesses an average cell size ranging between about .05 and 0.1 millimeters with a cell density ranging between about 8,000,000 cells/cm³ to 1,000,000 cells/cm³. Furthermore, in order to assure that core member 22 possesses inherent consistency, stability, functionality and capability of providing long-term performance, the cell size of core member 22 is homogeneous throughout its entire length and diameter.

In order to control the cell size of core member 22 and attain the desired cell size detailed above, a nucleating agent is employed. In the preferred embodiment, it has been found that by employing a nucleating agent selected from the group consisting of calcium silicate, talc, clay, titanium oxide, silica, barium sulfate, diamatious earth, and mixtures of citric acid and sodium bicarbonate, the desired cell density and cell size is achieved.

In this regard, it has been found that cell size and cell density is most advantageously realized in the formation of core member 22 by employing between about 0.1 and 5 parts by weight of the nucleating agent for every 100 parts by weight of the plastic foam. In this way, the desired physical characteristics of core member 22 are

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realized along with the desired control of the cell size and cell density. This leads to product consistency currently not available with natural and synthetic materials.

As is well known in the industry, a blowing agent is employed in forming extruded foam plastic material. In the present invention, a variety of blowing agents can be employed during the extruded foaming process whereby core member 22 is produced. Typically, either physical blowing agents or chemical blowing agents are employed. Suitable blowing agents that have been found to be efficacious in producing the core member of the present invention comprise one or more selected from the group consisting of: Aliphatic Hydrocarbons having 1-9 carbon atoms, Halogenated Aliphatic Hydrocarbons having 1-9 carbon atoms and Aliphatic alcohols having 1-3 carbon atoms. Aliphatic Hydrocarbons include Methane, Ethane, Propane, n-Butane, Isobutane, n-Pentane, Isopentane, Neopentane, and the like. Among Halogenated Hydrocarbons and Fluorinated Hydrocarbons they include Methylfluoride, Perfluoro-methane, ethyl Fluoride, 1,1-Difluoroethane (HFC-152a), 1,1,1-Trifluoroethane (HFC 430a), 1,1,1,2-Tetrafluoroethane (HFC 134a), Pentafluoroethane, Perfluoroethane, 2,2-Difluoropropane, 1,1,1-Trifluoropropane, Perfluoropropane, Perfluorobutane, Perfluorocyclobutane. Partially Hydrogenated Chlorocarbon and Chlorofluorocarbons for use in this invention include Methyl Chloride, Methylene Chloride, Ethyl Chloride, 1,1,1-Trichlorethane, 1,1-Dichloro1-Fluoroethane (HCFC-141b), 1-Chloro1, 1-Difluoroethane (HCFC142b), 1,1-Dichloro-2,2,2-Trifluoroethane (HCFC-123) and 1-Chloro-1,2,2,2-Tetra-fluoroethane (HCFC124). Fully Halogenated Chloro-fluorocarbons include Trichloromonofluoromethane (CFC11), Dichlorodifluoromethane (CFC12), Trichlorotrifluoroethane (CFC113), Dichlorotetrafluoroethane (CFC114), Chloroheptafluoropropane, and Dichlorohexafluoropropane. Fully Halogenated Chlorofluorocarbons are not preferred due to their ozone depletion potential. Aliphatic alcohols include Methanol, Ethanol, n-Propanol and Isopropanol. Suitable inorganic blowing agent is useful in making the foam of the present invention include carbon dioxide, nitrogen, carbon, water, air, nitrogen, helium, and argon.

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Chemical blowing agents include Azodicarbonamic, Azodiisobutyro-Nitride, Benzenesulfonhydrazide, 4,4-Oxybenzene Sulfonylsemicarbazide, p-Toluene Sulfonylsemicarbazide, Barium Azodicarboxlyate, N,N'-Dimethyl-N,N'-Dinitrosoterephthalamide and Trihydrazinotriazine. Preferably, in order to produce the desired product, the blowing agent is incorporated into the plastic melt in a quantity ranging between about .005% to 10% by weight of the weight of the plastic material.

As detailed above, either a physical blowing agent or a chemical blowing agent can be employed as part of the extrusion process for forming core member 22 of the present invention. However, it has been found that the selection of a physical blowing agent is preferred since physical blowing agents allow core member 22 of synthetic bottle closure 20 to be achieved with a lower density, which is closer to natural cork.

In this regard, a blowing agent which is inert is preferred. Although any desired inert blowing agent may be employed, the blowing agent is preferably selected from the group consisting of nitrogen, carbon dioxides, sulphur dioxide, water, air, nitrogen, helium, and argon. In addition, hydrocarbons can be employed as the blowing agent which are preferably selected from the group consisting of butane, isobutene, pentane, isopentane and propane.

In addition to attaining core member 22 which possesses a construction with physical characteristics similar to nature cork, multi-component, multi-layer synthetic bottle closure 20 of the present invention also comprises first peripheral layer/skin member 24 and, at least, second peripheral layer/skin member 25. Peripheral layers/skin members 24 and 25 are of particular importance in attaining synthetic bottle closure 20 which is capable of meeting and exceeding all of the difficult requirements imposed upon a closure or stopper for the wine industry.

As discussed above, the wine industry incorporates corking machines which incorporate a plurality of cooperating, movable jaws which move simultaneously to compress the bottle stopper to a diameter substantially smaller than the diameter of the portal into which the stopper is inserted. Then, once fully compressed, the stopper is

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forced out of the jaws directly into the bottle, for expanding and immediately closing and sealing the bottle.

Due to the operation of the cooperating jaws which are employed to compress the stopper for insertion into the bottle, sharp edges of the jaw members are forced into intimate contact with the outer surface of the stopper. Although cork material has been successful in resisting permanent damage from the jaw edges in most instances, other prior art synthetic stoppers have been incapable of resisting these cutting forces. As a result, longitudinal cuts, score lines or slits are formed in the outer surface of the stopper, enabling liquid to seep from the interior to the exterior of the bottle.

Multi-component/multi-layer synthetic bottle closure 20 of the present invention eliminates this inherent problem, existing with prior art cork and synthetic closures, by incorporating first peripheral layer/skin member 24 which surrounds and envelopes substantially the entire outer surface 21 of core member 22. In addition, by forming first peripheral layer/skin member 24 from high density, rugged, score-resistant material, synthetic bottle closure 20 overcomes all of the prior art difficulties and achieves a bottle closure having physical properties equal to or superior to conventional cork material.

In the preferred embodiment, first peripheral layer/skin member 24 is formed from plastic material identical or similar to the plastic material employed for core member 22. However, as detailed below, the physical characteristics imparted to first peripheral layer/skin member 24 differ substantially from the physical characteristics of core member 22.

In the preferred construction, first peripheral layer/skin member 24 comprises a thickness ranging between about 0.05 and 5 millimeters and, more preferably, between about 0.1 and 2 millimeters. Although these ranges have been found to be efficacious to producing synthetic bottle closure 20 which is completely functional and achieves all of the desired goals, the preferred embodiment for wine bottles comprises a thickness of between about 0.1 and 1 millimeter.

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In producing first peripheral layer/skin member 24 and achieving the desired tough, score and mar-resistant surface for core member 22, first peripheral layer/skin member 24 preferably comprises a density ranging between about 300 kg/m³ to 1,500 kg/m³. Most ideally, it has been found that the density of first peripheral layer/skin member 24 ranges between about 750 kg/m³ to 1,000 kg/m³.

In addition, as fully discussed above, other difficulties encountered with prior art synthetic closures include an inability for printed indicia to be received and/or retained on the surface of the closure, unless the closure is treated for improved ink adhesion. Typically, the required post treatments employed include corona, flame, or plasma exposures. Since these application processes are only able to be used after the synthetic closure has been fully produced, substantial additional expense is incurred. Furthermore, in many instances, it has been found that these post treatments cause the surface of the synthetic closure to be degraded.

Another problem detailed above in regard to prior art synthetic closures is the inability of many of these prior art closures to be removable from a bottle or container, such as a wine bottle, without requiring excessive extraction forces. In addition, the smooth insertion of the closure in a bottle has been a further area of difficulty, with many synthetic closures adhering to the interior surface of the bottle prior to the closure being fully engaged with the bottle.

In order to overcome these prior art difficulties and provide multi-component/multi-layer synthetic closure 20, which fully and completely eliminates all prior art shortcomings and difficulties, second, peripheral layer/skin member 25 is incorporated thereon, peripherally surrounding and enveloping substantially the entire outer surface 23 of first peripheral layer/skin member 24. In addition, by forming second peripheral layer/skin member 25 from specially selected plastic material or blends, all of the desired attributes of ink reception and adhesion, as well as controlled frictional engagement with the surface of the bottle or container, are attained. As a result, synthetic bottle closure 20 possesses all of the physical attributes required for an effective closure

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for wine bottles and, as a result, a bottle closure is achieved which has physical properties equal to or superior to conventional cork material.

In the preferred embodiment, second peripheral layer/skin member 25 is formed from plastic material identical or similar to the plastic material employed for core member 22 and/or first peripheral layer/skin member 24. However, as detailed below, specific additives or blends of materials are incorporated into second peripheral layer/skin member 25 in order to provide the precisely desired physical characteristics being sought.

In the preferred construction, second peripheral layer/skin member 25 comprises a thickness ranging between about 0.0001 and 0.1 inches (0.002 and 2.5 mm). In addition, second peripheral layer/skin member 25 preferably comprises a density ranging between about 100 kg/m³ and 1000 kg/m³. By employing these ranges, in combination with the ranges detailed above for core member 22 and first peripheral layer/skin member 24, a highly effective, completely functional synthetic bottle closure is realized which possesses all of the desired physical attributes sought in the industry and, heretofore, incapable of being fully provided.

If desired, multi-component/multi-layer synthetic bottle closure 20 of the present invention may also incorporate third peripheral layer/skin member 26 formed in peripherally surrounding, bonded interengagement with second peripheral layer/skin member 25. If all of the desired physical attributes being sought are not capable of being provided by second peripheral layer/skin member 25, or if special, unique characteristics, pigments, colors, and the like are desired, third peripheral layer/skin member 26 may be employed. In this way, assurance is provided that the resulting multi-component/multi-layer synthetic bottle closure 20 attained is capable of providing all physical attributes and inherent characteristics being sought.

In those instances in which third peripheral layer/skin member 26 is employed, third peripheral layer/skin member 26 is preferably formed from plastic material substantially identical to or similar to the plastic material employed for first peripheral

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layer 25. However, as is more fully detailed below, special additives and/or blends of materials would be incorporated into second peripheral layer/skin member 26 in order to attain the precisely desired performance characteristics and/or physical appearance sought.

5 In most applications, in order to impart the desired characteristics and attributes to synthetic closure 20, third peripheral layer/skin member 26 comprises a thickness ranging between about 0.0001 and 0.1 inches (about 0.002 and 2.5 mm). In addition, third peripheral layer/skin member 26 preferably comprises a density ranging between about 100 kg/m³ and 1000 kg/m³.

10 In accordance with the present invention, multi-component, multi-layer synthetic bottle closure 20 must be formed with first peripheral layer/skin member 24 intimately bonded to substantially the entire surface 21 of core member 22 and with second peripheral layer/skin member 25 intimately bonded to substantially the entire surface 23 of first peripheral layer/skin surface 24. Furthermore, if employed, third peripheral
15 layer/skin member 26 must be intimately bonded to substantially the entire surface 30 of second peripheral layer 25. If any large unbonded areas exist, flow paths for gas and liquid could result. Consequently, secure, intimate, bonded interengagement of first peripheral layer/skin member 24 with core member 22 is required for attaining a bottle closure for the wine industry.

20 In order to achieve this integral bonded interconnection between peripheral layers/skin members 24, 25, and 26 and core member 22, peripheral layers/skin members 24, 25, and 26 are formed about core member 22 in a manner which assures intimate bonded engagement. Preferably, the desired secure, intimate, bonded, inter-
25 engagement is attained by employing one or two alternate extrusion methods. In the first extrusion method, core member 22, first peripheral layer/skin member 24, second peripheral layer/skin member 25 and, if desired, third peripheral layer/skin member 26 are simultaneously co-extruded using well known extrusion equipment. In the second extrusion process, core member 22 is formed and, preferably cooled. Then, first

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peripheral layer/skin member 24 is extruded onto the surface of core member 22 while the preformed core member 22 is fed through the extrusion equipment. Thereafter, second peripheral layer/skin member 25 is extruded onto first peripheral layer/skin member 24 as the pre-formed component is fed through the extrusion equipment. Using
5 a similar procedure, the third peripheral layer/skin member 26 is extruded onto second peripheral layer/skin member 25. By employing either process, intimate bonded inter-engagement of peripheral layer/skin members 24, 25, and 26 to core member 22 is attained, with all layers being integrally engaged with each other.

By employing the teaching of this invention, multi-component/multi-layer
10 synthetic bottle closure 20 of the present invention and shown in FIGURE 2 can be produced by co-extruding core member 22 simultaneously with first peripheral layer/skin member 24 and second peripheral layer/skin member 25 to provide a final product wherein peripheral layers/skin members 24 and 25 are intimately bonded to each other and to core member 22 in a single, continuous operation. Using this three component
15 co-extrusion process, the continuous, elongated, co-extruded layers forming synthetic bottle closure 20 are completely formed in a single, multiple component extrusion process and, once completed, are ready for final processing. At that time, the elongated multiple component material produced is merely cut to the precise length desired for forming synthetic bottle closures 20, thereby completing the required production steps.

20 After each bottle closure 20 has been formed with the desired length, the chamfer, if needed, is formed at each end of peripheral layers/skin members 24 and 25 in order to provide the benefits detailed above. Once the chamfer or radius has been achieved, synthetic bottle closure 20 is ready for distribution to the desired consumer, other than printing if desired.

25 In the alternate construction, core member 22 is formed as an elongated, continuous, extruded foam product and is cooled or allowed to cool until ready for subsequent processing. Then, whenever desired, the continuous elongated length forming core member 22 is fed through a cross-head machine which enables first

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peripheral layer/skin member 24 to be extruded onto core member 22 and positioned in the desired location peripherally surrounding core member 22 in intimate bonded interengagement therewith. In addition, simultaneously with the extrusion of first peripheral layer/skin member 24 onto core member 22, second peripheral layer 25 is
5 extruded and separately applied to the outer surface 23 of first peripheral layer/skin member 24. By employing this extrusion process, second peripheral layer/skin member 25 is intimately bonded and integrally affixed in its entirety to the entire surface 23 of first peripheral layer/skin member 24.

Alternatively if desired, first peripheral layer/skin member 24 is extruded onto
10 core member 22 as detailed above and either cooled or allowed to cool. Then, when desired, the pre-formed core member 22 with first peripheral layer/skin member 24 is fed through a cross-head machine which enables second peripheral layer/skin member 25 to be extruded onto first layer/skin member 24 in intimate bonded engagement with surface 23 thereof.

15 Using these identical production methods, bottle closure 20 shown in FIGURE 3 is also manufactured, when desired, with third outer layer/skin member 26. As detailed above, if all desired attributes are not incorporated into second outer layer/skin member 25, a third layer/skin member 26 is formed, peripherally surrounding and fully enveloping second outer layer/skin member 25.

20 By employing either of the two alternate extrusion methods fully detailed above, third outer layer/skin member 26 is extruded onto surface 30 of first outer layer/skin member 25 in complete peripheral surrounding engagement therewith, and secured thereto in bonded interengagement with the entire surface 30. As a result, open zones or voids are eliminated, and securely affixed, bonded engagement of third peripheral
25 layer/skin member 26 with second peripheral layer/skin member 25 is provided.

Once the multiple component product has been completed, the elongated length of material is cut to the desired length for forming bottle closure 20. As detailed above,

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if desired, a chamfer or radius is formed in the outer peripheral layers to attain the chamfered final product.

In a further alternate embodiment, synthetic bottle closure 20 of the present invention is formed by employing generally conventional injection molding techniques.

5 As is well known, injection molding is a manufacturing process where plastic is forced into a mold cavity under pressure. The mold cavity is essentially a negative of the part being produced, and the cavity is filled with plastic, and the plastic changes phase to a solid, resulting in a positive. Typically, injection pressures range from 5,000 to 20,000 psi. Because of the high pressures involved, the mold must be clamped shut during
10 injection and cooling.

By employing this process, a plurality of separate and independent bottle closures 20 are simultaneously formed in a multi-cavity mold having the precisely desired shape and configuration. Consequently, if beveled or chamfered edges are desired, the desired configuration is incorporated into the mold, thereby producing a
15 product with the final shaped desired.

Typically, injection molding is employed to produce products having a single composition. However, if desired core member 22 may be formed with first outer peripheral layer/skin member 24, second outer peripheral layer/skin member 25, and if desired, third outer peripheral layer/skin member 26 surrounding and intimately bonded
20 thereto using alternate techniques such as multi-step molding and multi-component molds. By employing these procedures, synthetic bottle closures 20 of the present invention are formed in an injection molding process, as desired, achieving the unique, multi-layer, multi-component synthetic bottle closure of the present invention.

As discussed above, intimate bonded interengagement of peripheral layers/skin
25 members 24, 25, and 26 to core member 22 and to each other is required for providing a synthetic bottle closure 20 capable of being used in the wine industry. In this regard, although it has been found that the processes detailed above provide secure intimate bonded interengagement of peripheral layers/skin members 24, 25, and 26 to core

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member 22 and to each other, alternate layers or bonding chemicals can be employed, depending upon the particular materials used for forming core member 22 and peripheral layers/skin members 24, 25, and 26.

If desired, well known bonding agents or tie layers can be employed on the outer surface of core member 22, and/or the outer surface of peripheral layers/skin members 24 and 25, in order to assure secure intimate bonded interengagement of each peripheral layer/skin member 24, 25, and 26. If a tie layer is employed, the tie layer would effectively be interposed between core member 22 and first peripheral layer/skin member 24 as well as between first peripheral layer/skin member 24 and second peripheral layer/skin member 25, and, if desired, second peripheral layer/skin member 25 and third peripheral layer/skin member 26 to provide intimate bonded interengagement by effectively bonding each peripheral layer and core member 22 to the intermediately positioned tie layer. However, regardless of which process or bonding procedure is employed, all of these alternate embodiments are within the scope of the present invention, providing a synthetic bottle closure capable of overcoming all of the prior art difficulties and drawbacks.

As detailed above, a wide variety of plastic materials can be employed to produce the extruded multi-component, multi-layer synthetic bottle closure 20 of the present invention. Although each of the plastic materials detailed herein can be employed for both core member 22 and peripheral layers/skin members 24, 25, and 26, the preferred plastic material for forming both core member 22 and peripheral layers/skin members 24, 25, and 26, comprises one or more selected from the group consisting of medium density polyethylenes, low density polyethylenes, metallocene catalyst polyethylenes, polypropylenes, polyesters, ethylene-butyl-acrylate copolymers, vinyl-acetate copolymers, ethylene-methyl acrylate copolymers, and blends of these compounds.

It has also been discovered that the outer peripheral layers/skin members 24, 25, 26 may comprise a thermoplastic composition which differs from the thermoplastic

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composition employed for core member 22. In this regard, outer peripheral layers/skin members 24, 25, and 26 may comprise one or more selected from the group consisting of foamable or non-foamable thermoplastic polyurethanes, thermoplastic olefins, thermoplastic vulcanizates, flexible polyolefins, fluoroelastomers, fluoro-polymers, polyethylenes, teflons, and blends thereof. In addition, peripheral layers/skin members 24, 25, and 26 may be formed from thermoplastic olefinic elastomers such as petrothene TPOE, thermoplastic urethanes thermoplastic polyesters, and other similar product formulas.

If desired, the outer, exposed surface of synthetic bottle closure 20 can be manufactured incorporating a particular configuration, design, or surface structure. In particular, outer surface 35 of peripheral layer/skin member 26, if the embodiment of FIGURE 3 is employed, or outer surface 30 of peripheral layer/skin member 25, if the embodiment of FIGURE 2 is employed, can be formed incorporating the precisely desired configuration, design, or structure being sought.

Typically, in order to employ this aspect of the present invention, outer surface 30 or outer surface 35 is embossed with a particular design or configuration during the extrusion process or after formation of synthetic closure 20. In this way, any desired pattern, design, or other visually distinctive elements are formed directly on the outer exposed surface of synthetic bottle closure 20 in order to provide a unique, readily distinguish configuration and/or to establish desired physical attributes.

As shown in FIGURES 4 and 5, synthetic closure 20 is depicted incorporating peripheral layer/skin member 26 on which a visually distinctive fish scale type pattern has been formed on surface 35. In addition to providing a visually distinctive outer surface, the fish scale pattern, as clearly shown in FIGURE 5, incorporates a plurality of overlapping sloping surfaces wherein each individual "scale" comprises a thick upper end which slopes downwardly to a thin lower end. As a result, by properly orienting synthetic closure 20 during the insertion process into a bottle, this configuration promotes insertion ease into the bottle, while requiring additional force to withdraw

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closure 20 from the bottle, due to the increased frictional forces being exerted on the inside surface of the bottle after closure 20 has been inserted therein.

An additional surface pattern that is formable on the outer, exposed surface of synthetic closure 20 is a plurality of small holes or dimples. This is easily achieved by employing an embossing or forming system as disclosed in FIGURES 6 and 7.

As shown in FIGURES 6 and 7, a plurality of generally circular embossing or forming wheels 36 are rotationally mounted in juxtaposed, spaced, cooperating relationship with each other, defining a common forming zone 37. In addition, each embossing or forming wheel 36 incorporates a plurality of radially extending pins 38 formed on the outer surface thereof. In the preferred embodiment, forming zone 37 is dimensioned for receiving individually formed synthetic closures 20 and fully manufactured, elongated rod members prior to being cut into individual closure members.

By passing synthetic closure 20, either individually or in rod form, through forming zone 37, radially extending pins 38 of each forming wheel 36 penetrate the outer surface of closure 20, imparting the desired small, micro-holes into the surface thereof. In this way, the desired hole pattern is achieved. By forming a plurality of small, micro-holes in the outer surface of closure 20, printing inks are able to penetrate and be absorbed by the surface, thereby enhancing the retention of printing inks thereon.

Using this forming process, virtually any desired design, pattern, or surface construction can be formed on the outer surface of synthetic bottle closure 20. In order to achieve the desired visual presentation, each forming wheel 36 would incorporate the particular shape or surface element desired, which would then be applied to the outer surface of synthetic closure 20. As a result, any desired pattern, design, etc. can be quickly and easily formed or embossed onto the outer surface of closure 20.

In addition to forming a desired surface configuration by employing a plurality of embossing or forming wheels, a shark skin surface construction can be achieved on the outer surface of closure 20 by employing a melt fracture process. As is known in

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the art of film forming, if shear stress exceeds a critical value, an instability in the flow function occurs which can establish an unstable region in the vicinity of the die orifice. This causes the flowing melt to change from adhering to slipping with the coefficient of friction changing discontinuously. As a result, a melt fracture is manifested, producing
5 a rough and periodically deformed surface.

By employing this process, this rough and deformed surface, similar to a shark skin appearance, can be achieved. In addition to providing a visually distinctive appearance, this surface configuration also enhances the extraction forces required to remove synthetic bottle closure 20 from a container. As a result, substantial benefits
10 are achieved.

The particular composition employed for peripheral layer/skin member 24 is selected to withstand the compression forces imposed thereon by the jaws of the corking machine. However, many different polymers, as detailed above, are able to withstand these forces and, as a result, can be employed for peripheral layer/skin member 24. In
15 this regard, one principal feature of the present invention is the type of material used for peripheral layer/skin member 24, as well as the discovery that a substantially solid, non-foamed or foamed plastic-based peripheral layer/skin member 24 is securely affixed about and bonded to foamed plastic center core 22, to produce a multi-layer synthetic closure which is able to withstand the forces of a cork machine. The ability of the
20 present invention to withstand these forces, without product leakage, exists even if cork dust filler is present between the core and peripheral layer/skin member 24.

In order to form synthetic bottle closure 20 with all of the desirable inherent physical and chemical properties detailed above, one compound that has been found to be most advantageous to employ for peripheral layer/skin member 24 is metallocene
25 catalyst polyethylene. As detailed below, peripheral layer/skin member 24 may comprise 100% metallocene catalyst polyethylene or, if desired, the metallocene catalyst polyethylene may be intermixed with a polyethylene. In this regard, it has been found that peripheral layer/skin member 24 preferably comprises between about 25%

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and 100% by weight based upon the weight of the entire composition of one or more poly-ethylenes selected from the group consisting of medium density polyethylenes, medium low density polyethylenes, and low density polyethylenes.

In order to demonstrate the efficacy of this embodiment of the present invention, a supply of synthetic closures 20 were produced employing 100% by weight of metallocene catalyst polyethylene for peripheral layer/skin member 24. This supply of synthetic bottle closures 20 were identified as Synthetic Closure A and were tested in combination with natural cork bottle closures and synthetic bottle closures 20 in accordance with the present invention, using alternative formulations for peripheral layer/skin member 24. The formulations employed for these comparative samples are detailed below, along with the test data demonstrating the efficacy of all of the alternate embodiments of the present invention.

Another formulation which has been found to be highly effective in providing an peripheral layer/skin member 24 which meets all of the required physical and chemical attributes to attain a commercially viable synthetic bottle closure 20 is a polyether-type thermoplastic polyurethane.

By employing this material and forming the material in peripheral, surrounding, bonded engagement with any desired foamed core member 22, a highly effective, multi-layer synthetic closure is attained which is able to meet and exceed all requirements for a wine bottle closure.

In the preferred construction of this embodiment, the particular polyether-type thermoplastic polyurethane employed for forming peripheral layer/skin member 24 comprises Elastollan LP9162, manufactured by BASF Corporation of Wyandotte, Michigan. As detailed below in the test data provided, this compound, referred to as Synthetic Closure B, has been found to produce peripheral layer/skin member 24 in combination with core member 22 which provides all of the physical and chemical characteristics required for attaining a highly effective synthetic closure 20 for the wine industry.

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In addition to employing the polyether-type thermoplastic polyurethane detailed above, another compound that has been found to be highly effective in providing all of the desirable attributes required for peripheral layer/skin member 24 is a blend of thermoplastic olefins and thermoplastic vulcanizates. In the preferred embodiment, the
5 blend of thermoplastic olefins and thermoplastic vulcanizates comprises between about 10% and 90% by weight based upon the weight of the entire composition of the thermoplastic olefin and between about 10% and 90% by weight based upon the weight of the entire composition of the thermoplastic vulcanizate. As detailed below in the test data, the construction of synthetic closure 20 using peripheral layer/skin member 24 formed
10 from this blend, referred to below as Synthetic Closure C, provides a wine bottle closure which exceeds all requirements imposed thereon.

Another compound that has also been found to provide a highly effective peripheral layer/skin member 24 for synthetic closure 20 of the present invention comprises flexible polyolefins manufactured by Huntsman Corporation of Salt Lake
15 City, Utah. These compounds are sold under the trademark REXflex FPO, and comprise homogeneous reactor-synthesized polymers, produced under proprietary technology which attains polymers having unique combinations of properties.

In a further alternate embodiment, a highly effective synthetic bottle closure 20 is attained by employing metallocene catalyst polyethylenes, either independently or in
20 combination with one selected from the group consisting of low density polyethylenes, medium density polyethylenes, and medium low density polyethylenes. In this embodiment, these materials are preferably employed for both core member 22 and peripheral layer/skin member 24.

In order to provide bottle closure 20 with a construction which provides all of
25 the desired attributes for a wine bottle closure, closure 20 incorporates second peripheral layer/skin member 25 which is specifically formulated to provide secure, leak-free sealing engagement with the interior walls of the bottle, while also assuring that closure 20 is removable, when desired, using normal extraction forces. In addition, second

layer/skin member 25 also comprises a construction which either receives and retains printing ink, without requiring special surface treatments, such as corona, plasma, or flame exposures, or is formulated for protecting the ink printed on surface 23 of layer 24.

5 In addition to being formulated from one or more of the thermoplastic materials detailed above, second layer/skin member 25 preferably comprises pure or neat thermoplastic polyurethane or thermoplastic polyurethane blended with high molecular weight silicones or polyolefins. Alternatively, if desired, in order to optimize the removability of closure 20 from a bottle, second layer/skin member 25 may comprise one or more
10 selected from the group consisting of teflon-based compounds and ultra high molecular weight polyethylenes (OHMWPE). Furthermore, if desired, second layer/skin member 25 may comprise a polyurethane material, such as Elastollen LP 9162, manufactured by BASF Corporation of Wyandotte, Michigan, due to the low coefficient of friction provided by this product.

15 Further additional compounds which have been found to provide highly effective peripheral layers/skin members 25 for forming synthetic bottle closures 20, in accordance with the present invention, comprise Teflon, fluoro-elastomeric compounds and fluoropolymers. These compounds, whether employed individually or in combination with each other or with the other compounds detailed above have been found to be
20 highly effective in producing an outer peripheral layer/skin member 25 which is capable of satisfying all of the inherent requirements for synthetic bottle closure 20.

 In addition, it has also been found that additives may be incorporated into outer peripheral layer/skin member 25 in order to further enhance the performance of the resulting synthetic bottle closure 20. As detailed above, these additional additives
25 include slip resistant additives, lubricating agents, and sealing compounds.

 In addition to establishing a formulation for peripheral layer/skin member 25 which satisfies the requirements for sealing and extraction, the preferred synthetic closure 20 also is capable of receiving and retaining printing inks to enable any designs,

logos, names, etc. to be printed thereon, without requiring post production treatments. In this regard, in addition to employing the material formulations detailed above, peripheral layer/skin member 25 may incorporate additional additives, such as diatomaceous earth in order to adsorb the printing ink, or may comprise a formulation for protecting the printing ink placed on peripheral layer/skin member 24.

As detailed above, synthetic closure 20 may incorporate third peripheral layer/skin member 26. In general, it has been found that third peripheral layer/skin member 26 is employed when all desired attributes cannot be incorporated into second peripheral layer/skin member 25.

Preferably, third peripheral layer/skin member 26 is formed from a thermoplastic polyurethane, which is either pure or is blended with any desired plastic material and/or additives detailed above in reference to second peripheral layer/skin member 25. If employed, third layer/skin member 26 is formed from the materials detailed above which are required to attain the desired additional attributes.

In addition, peripheral layers/skin members 25 and 26 may also incorporate special additives such as pigments, dyes, colors, etc. in order to achieve special visual effects, a three-dimensional look, real textured appearance, or elements responsive to black light or ultra-violet light. Furthermore, special tracers or identifiers may also be incorporated in this manner in order to enable the resulting synthetic closure to be identifiable at any time during its distribution and sale.

If desired, peripheral layers/skin members 25 and 26 may comprise the desired plastic polymer, as detailed above, in blended combination with cork dust. The ratio of cork dust to the plastic polymer can range between about 10 to 90 parts of cork dust to 90 to 10 parts of the plastic polymer. By incorporating the cork dust, air dried inks can be employed, as is common in the nature cork industry.

Any of the compounds detailed herein for producing peripheral layer/skin members 24, 25, and 26 can be employed using the extrusion processes detailed above to produce a layer/skin member which is securely and integrally bonded to the adjacent

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member, either as a foamed outer layer or a non-foamed outer layer. In addition, these compounds may also be employed using the molding processes detailed above to produce the desired multi-component, multi-layer, synthetic bottle closure 20 of the present invention.

5 In addition, it has also been found that further additional additives may be incorporated into core member 22, and/or peripheral layers/skin members 24, 25, and 26 of synthetic closure 20 in order to provide further enhancements and desirable performance characteristics. These additional additives incorporate antimicrobial agents, antibacterial compounds, and or oxygen scavenging materials.

10 The antimicrobial and antibacterial additives are incorporated into the present invention to impart an additional degree of confidence that in the presence of a liquid the potential for microbial or bacterial growth is extremely remote. These additives have a long term time release ability and further increases the shelf life without further treatments by those involved with the bottling of wine. This technology has been shown
15 to produce short as well as long term results (microbial and bacterial kills in as little as ten minutes with the long term effectiveness lasting for tens of years) which cannot be achieved with a natural product. An additional additive employed in the present invention is an oxygen scavenging system. Since oxygen is the worst enemy for wine, this system will for all intent and purposes eliminate the possibility of wine oxidation.

20 Free diatomic oxygen has an antagonistic effect on still wine. Oxidation occurs over a period of time to render the beverage undrinkable. However, during the bottling process, there is a chance that oxygen is trapped in the headspace between the wine and the closure, oxygen is solublized and released from the wine, and/or oxygen is released from or permeates through the closure.

25 In order to reduce the possibility of this oxidation in wine, an oxygen scavenger is incorporated into the synthetic closure to extend and preserve the freshness and shelf life of the product. Oxygen scavenger concentrates such as sodium ascorbate, sodium sulfite, edetate dipotassium (dipotassium EDTA), hydroquinone, and similar substances

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are used to actively bind free oxygen unlike passive barrier layers such as glass and/or barrier polymers. Oxygen residing in the headspace after bottling and dissolved oxygen in the wine are unaffected by the passive barriers, but the concentration is reduced in the presence of the oxygen scavengers.

5 With an oxygen scavenger, the closure system can be designed with both active and passive protection from oxidation and result in a prolonged shelf life and an improved wine quality. The oxygen scavenging capability of the closure remains dormant throughout the bottling process until the mechanism is activated in the presence of moisture. One other major advantage of this oxygen scavenging capability is the
10 possibility to eliminate the need for vacuum in the headspace before closure insertion; therefore, eliminating one variable in the still wine bottling operation.

Oxidation in wine is also expedited by elevated temperatures. Because the kinetics of the reaction mechanism of the scavenging system also increase with temperature, closures containing oxygen scavengers provide heightened levels of protection
15 against oxidation. By referring to FIGURES 8, 9, and 10, the highly effective, advantageous results attained by employing an oxygen scavenger in the present invention are fully detailed.

By employing any desired combination of these agents or additives, a further enhanced synthetic closure is realized which is capable of providing a product performance which has heretofore been incapable of being provided by either cork closures or
20 conventional synthetic closures.

EXAMPLES

In order to demonstrate the efficacy of the present invention, a plurality of samples of multi-component/multi-layer synthetic bottle closures 20, manufactured in
25 accordance with the present invention, were produced and tested. These sample products were produced by employing metallocene catalyst polyethylene and low density polyethylene intermixed with each other in the ranges detailed above to form

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core member 22. In forming core member 22 of each sample product, the two compounds were intermixed and formed using conventional foam extrusion equipment. In forming peripheral layer/skin member 24, the various compounds detailed above were employed to produce alternate embodiments of synthetic closure 20 of this invention and identified as Synthetic Closure A, Synthetic Closure B, and Synthetic Closure C. These separate embodiments were each tested and the results thereof are detailed below.

In addition, in order to unequivocally demonstrate the substantially improved and enhanced synthetic closure 20 obtained by employing second peripheral layer/skin member 25, several additional sample products were manufactured and tested. The formulations employed and the test results obtained are detailed below.

In the forming process, peripheral layer/skin member 24 was foamed in the extrusion equipment peripherally surrounding core member 22 and being intimately bonded thereto. The resulting products were cut in lengths suitable for forming bottle closure 20, followed by a chamfer being formed in edges 31 and 32. The resulting closures were then employed in a plurality of tests to prove the ability of the present invention to overcome the prior art difficulties and provide a bottle closure which is equivalent to or better than the properties and performance characteristics provided by cork.

In producing synthetic closures 20 which incorporate peripheral layer/skin member 25, the identical process detailed above was employed, with second peripheral layer/skin member 25 being applied to peripheral layer/skin member 24 in a separate co-extrusion process. Other than this step, the identical procedures defined herein were used.

In producing the synthetic bottle closure 20 of the present invention in the manner detailed above, blowing agents and nucleating agents detailed above were employed as previously disclosed. These additives were employed using standard procedures well known in the foam extrusion process.

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In order to demonstrate the ability of the synthetic bottle closure 20 of the present invention to possess physical properties similar to or better than natural cork, a comparative analysis of natural cork and synthetic closure 20 of the present invention with peripheral layer/skin member 24 was made using the sample products produced as detailed above. By referring to Table I, the ability of the synthetic bottle closure 20 of the present invention with peripheral layer/skin member 24 to achieve physical properties that are equivalent to or better than natural cork is clearly demonstrated.

TABLE I

<u>Property</u>	<u>Natural Cork</u>	<u>Synthetic Closure</u>
10 Compressive strength to 15.5 mm radial Max load (LBF)	591	581
15 Compressive strength to 15.5 mm Radial Max stress (psi)	113.6	126.4
Compressive strength (36%) rectangular Max stress (psi)	280.4	300.4
20 Compressive recovery instantaneous (%)	94.79	94.12
Compressive recovery 1 hour (%)	98.33	97.88
25 Compressive recovery 24 hours (%)	99.58	98.35

In order to demonstrate the ability of the multi-component/multi-layer, synthetic bottle closure of the present invention to meet or exceed the physical qualities possessed

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by natural cork when employed as a bottle closure or stopper for wine, numerous tests were conducted directly comparing the synthetic bottle closure of the present invention to natural cork stoppers. However, natural cork varies in quality from an ultra low quality to an ultra high quality. Typically, the quality of the cork is determined by price
5 in accordance with the following schedule:

ultra low quality corks are below \$90 per 1,000 pieces

low quality natural corks range from \$95 to \$120 per 1,000 pieces

medium quality natural corks range from \$125 to \$180 per 1,000 pieces

10 high quality natural corks range from \$175 to \$250 per 1,000 pieces

ultra high quality natural corks are above \$250 per 1,000 pieces

As detailed below, most test comparisons were made using medium quality natural cork. In this regard, since the price for medium quality natural cork ranges between about \$125 to \$180 per 1,000 pieces, the samples tested in the following
15 comparisons were made using medium quality natural cork found in the highest price range for this category.

Before being used as a test sample, each of the natural cork stoppers were inspected to assure high quality and eliminate obvious flaws that might exist. As a result, all of the natural cork stoppers employed in these tests met the following standards.

20 Each natural cork stopper was 45mm in length, 24mm in diameter and, upon visual inspection, had no visual or functional flaws. Furthermore, natural cork stoppers tested to possess a maximum of three very shallow or narrow lenticels, and were free of dust particles. In addition, the stoppers had no holes or pores in excess of 2mm, possessed a maximum of one crack, which was classified as being very tight and less
25 than 8% of the cork length. Furthermore, no worm activity was visible, as well as no bellspots or greenwood. The ends of each cork were relatively clean and possessed

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very little chance of chipping on the edges. Finally, no cracks originated from the ends, and growth rings were uniform and substantially equidistant.

In conducting the following tests, a supply of synthetic bottle closure of the present invention were manufactured in the manner detailed above. In addition, a
5 separate supply of each different type of natural cork stoppers was established. In conducting each test, a plurality of samples were randomly selected from each supply and tested in accordance with the procedures detailed herein. The results for each test were computed and are provided in Tables II, III, IV, and V.

Compression Tests

10 In this test, the force required to compress each closure or stopper from its original diameter to a diameter of 15.5mm was determined. In conducting this test, 6 random samples were selected from the supply of medium quality natural cork stoppers and six random samples were selected from the supply of synthetic bottle closures of the present invention manufactured in the manner detailed above.

15 Each sample was separately positioned on a radial compression device, which was installed onto an Instron 1011 Material Tester. When positioned on the radial compression device, each sample was compressed from its normal diameter, typically 24.0mm, to a compressed diameter of 15.5mm. The force value required for compress-
20 ing each test sample was recorded. The overall average resulting force values for each sample type were computed and are reported in Table II as the maximum compression force in pounds.

TABLE II

Compression Tests

Sample	Test	Max. Radial Compression Force to 15/5 mm (LBF)	Compression Recovery Instantaneous	Compression Recovery After 15 min.	Compression Recovery After 1 Hour	Compression Recovery After 24 Hrs.	Compression Set
Synthetic Closure A		481.7	94.90%	97.45%	97.77%	98.09%	17.49%
Natural Cork Medium Quality		483.75	93.86%	96.44%	96.72%	97%	28.78%
Synthetic Closure B		398.00	93.5%	97.1%	97.5%	97.7%	
Synthetic Closure C		329.42	92.2%	95.4%	95.9%	96.3%	

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Another compression test was conducted to determine the recovery rate for the closures or stoppers at different time intervals. In conducting this test, six random samples were selected from the supply of synthetic bottle closures of the present invention, manufactured in the manner detailed above, and six random samples were selected from the supply of medium quality natural cork closures. This test was designed to determine the recovery rate for each of the closures after compression to 13.0mm and release therefrom.

In conducting this test, each of the selected samples was positioned in a commercially available hand corker having a capability to compress the closures from their original diameter to a diameter of 13.0mm, and then allow each of the stoppers to be released by pushing them out of the compression jaws with a plunger. In each case, the original diameter of each sample was recorded.

Thereafter, the diameter of each test sample was recorded immediately after being ejected from the compression jaws, fifteen minutes after ejection, one hour after ejection, and twenty-four hours after ejection. The percent recovery for each measurement was calculated by employing the following formula:

$$\% \text{ Recovery} = \frac{D_m}{D_o} \times 100$$

where D_m is the measured diameter at the different time interval and D_o is the original diameter. The average percent recovers was computed for each sample type and the results are shown in Table II.

The final compression test conducted was a determination of the compression set, which is a determination of the ability of each stopper to recover after being exposed to a prolonged 50% linear compression. In conducting this test, three random samples were selected from the supply of medium quality natural cork stoppers and three random samples were selected from the supply of synthetic bottle closures of the present invention manufactured in the manner detailed above.

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The diameter of each sample was recorded. Then, following the method detailed in ASTM Method D-3575 Suffix B, each sample was linearly compressed to 50% of its original diameter and maintained at this compression for 22 hours. The test device consisted of two flat, surface ground plates capable of securing the samples at the desired 50% compression. At the end of the 22 hours, the samples were allowed to recover for 2 hours, after which the diameter of each sample was measured in the compression direction and the measurements recorded.

The compression set was determined for each sample using the following formula: Percent Compression Set = $100 - [(diameter\ after\ compression) \div (original\ diameter) \times 100]$. The overall average percent compression set for each sample type was determined by averaging the individual values calculated for each test sample. This overall average result is provided in Table II.

Extraction Force

Another comparative test which was conducted was an extraction force test to determine the amount of force required to extract each type of closure from a properly corked bottle. In conducting this test, six random samples were selected from the supply of medium quality natural corks, and six random samples selected from the supply of synthetic bottle closures of the present invention manufactured in the manner detailed above. The device used for testing was an Instron Model 1011 Material Tester, which was outfitted with a corkscrew fixture to perform the extraction and measure the forces.

In conducting this test, each of the test samples were inserted into a 750 ml bottle filled with water to the 55mm fill level, using the procedure described in Practical Aspects of Wine Corkage by Jean Michel Riboulet and Christian Alegoet, Bourgogne Publications, Chaintre, France, pages 148-157. The corkscrew was inserted into the corked bottle and the cork removed, while recording the forces required to extract the cork. For each sample, both the maximum force and the average force required for its extraction was recorded. In Table III, the overall average for both the

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maximum extraction force and the average extraction force for each sample type is detailed.

TABLE III
Extraction Force

Sample Type	Maximum Extraction Force (lbs)	Average Extraction Force (lbs)
Synthetic Closure A	44.50	25.89
Natural Cork - Medium Quality	39.80	23.05
Synthetic Closure B	51.5	25.32
Synthetic Closure C	45.083	24.76

Sealing Behavior

The next performance test conducted was a sealing behavior test which determines the ability of the closure or stopper to resist compromising the integrity of the seal when the closure is subjected to elevated pressures inside the bottle. In conducting this test, six random samples were selected from the supply of high quality natural corks, six random samples were selected from the supply of medium quality natural corks, six random samples were selected from the supply of low quality natural corks, and six random samples were selected from the supply of the synthetic bottle closure of the present invention, manufactured in the manner detailed above. The device used for testing each of the the samples was a conventional 750 ml bottle, which was modified to allow the pressure in the bottle to be regulated from 0 psi to 30 psi.

In conducting this test, each sample closure was inserted into a bottle and allowed to recover in the bottle for one hour prior to testing. Thereafter, the samples

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were inverted and connected to the pressure device. The samples were subjected to four elevated pressure levels for two-minutes at each level. The pressure levels were 10 psi, 15 psi, 22.5 psi and 30 psi. At the end of the two-minute interval at each pressure level, each sample was individually observed and rated on the following scale:

- | | | | | |
|----|---|-----|---|--|
| 5 | • | 10 | = | closure did not move from its original location and no dampness detected |
| | • | 8 | = | closure moved from its original location without popping out of the bottle and no dampness detected |
| 10 | • | 6 | = | closure did not move from its original location and dampness was detected, but no dripping |
| | • | 4 | = | closure moved from its original location without popping out of the bottle and no dampness detected, but no dripping |
| | • | 2 | = | closure did not move from its original location and drips |
| 15 | • | 1 | = | closure moved from its original location without popping out of the bottle and drips |
| | • | 0 | = | closure popped out of bottle |
| | • | -40 | = | test pressure is lost |

The evaluations for each sample were recorded at each interval and the results for each sample at the four different test intervals were totaled. Any sample receiving a total score less than 40 was considered a failure. With six closures being tested of each sample type, a total score of 240 represented the maximum score attainable and was employed as the standard for passing this test. When fully evaluated, the synthetic bottle closure A of the present invention, the high quality natural cork stoppers, and the medium quality natural cork stoppers all scored 240 points, synthetic bottle closure B

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and C both scored 260 points thereby passing this test. The low quality natural cork stoppers received a total point score of 224, resulting in a failure of this test.

Temperature Test

The next performance test was a temperature test to compare the ability of the closures to resist any compromising sealing integrity at elevated temperatures. In
 5 conducting this test, two random samples were selected from the supply of medium quality natural cork and two random samples were selected from the synthetic bottle closure of the present invention manufactured in the manner detailed above. 750 ml
 10 bottles were filled with water to a level of 55mm from the bottle lip and 63mm from the bottle lip. This filling was done in accordance with the disclosure found in Practical Aspects of Wine Corkage, as detailed above.

Each sample type was inserted into both the 55mm and 63mm fill levels and when sealed in position, the bottle was placed horizontally in an oven at 38 C for
 15 twenty-four hours. The samples were observed after twenty-four hours for leakage and movement of the closure. Any leakage or movement was considered a failure. The results of this test are shown in Table IV.

TABLE IV

Sample	55mm Fill Level		63mm Fill Level	
	Leaking	Movement	Leaking	Movement
20 Natural Cork - Medium Quality - 1	Fail	Pass	Fail	Pass
Natural Cork - Medium Quality - 2	Fail	Pass	Fail	Pass
Synthetic Closure - A	Pass	Fail	Pass	Pass
Synthetic Closure - B	Pass	Fail	Pass	Pass
25 Synthetic Closure - C	Pass	Fail	Pass	Pass

Aroma Absorption

In the next performance test, the ability of the closures to resist absorption of aromas were performed. In this test, eighteen random samples were selected from the supply of medium quality natural corks and eighteen random samples were selected
5 from the supply of synthetic bottle closures of the present invention manufactured in the manner detailed above. Each of the closures were individually soaked in a white wine solution for a period of 24 hours. After soaking, each wine solution sample was analyzed for retained odors. The overall results revealed the synthetic closures of the present invention had an aroma which was described as very consistent, neutral, and
10 light woody. The medium quality natural cork closures had aromas which were described as vanilla, woody, cardboardy, and papery.

Capillarity

Another test performed on the closures was a capillarity test, which is designed to determine the ability of the materials tested to resist the absorption of red wine above
15 the level of the hydrostatic head of the liquid. In conducting this test, three random samples were selected from the supply of medium quality natural cork stoppers and three random samples were selected from the supply of synthetic bottle closures of the present invention manufactured in the manner detailed above. The device used for testing was a flat-bottom vessel capable of holding red wine at a constant level of 5mm.

20 Each of the samples were vertically positioned on the flat-bottom vessel submerged in 5mm of wine for twenty-four hours. Thereafter, the samples were removed from the holding tank and blotted dry. Then, the length of the wine stain on the exterior of each of the closures was measured and recorded in millimeters. Due to variations in the rate of absorbency over the cross-section of the closures, particularly
25 the natural cork closures, the maximum capillarity or maximum length of the wine stain was measured as well as the overall average capillarity or wine stain length. The

overall average of each of these results for each of the sample types tested is shown in Table V.

TABLE V
Capillarity

Sample	Maximum Capillarity	Average Capillarity
Synthetic Closure A	0.00	0.00
Natural Cork - Medium Quality	20.03	6.60
Synthetic Closure B	0.00	0.00
Synthetic Closure C	8.0	7.7

10 Water Absorption

Another test conducted was a water absorption test to compare the amount of water absorbed by each of the sample types. In conducting this test, three random samples were selected from the supply of medium quality natural cork stoppers and three random samples were selected from the synthetic bottle closures of the present invention manufactured in the manner detailed above. The water absorption test conducted was in compliance with ASTM Method D-570. In conducting this test, the device used was a water-tight vessel capable of holding enough water to completely submerge each sample. The vessel also contained a screen with enough weight to submerge all of the samples simultaneously.

20 Each sample was weighed to the nearest 1/10,000 of a gram and submerged in the tank for 24 hours. Thereafter, the samples were removed from the tank and blotted dry. Then, the samples were weighed to the nearest 1/10,000 of a gram and the amount of water absorbed determined as the difference between the weight of the

sample before and after submersion. The water absorption for each sample was computed in accordance with the following formula:

$$\text{Water Absorption} = \frac{\text{Weight of Water}}{\text{Original Weight of Sample}} \times 100$$

- 5 The resulting average absorbency for the synthetic bottle closure A. of the present invention was 0.27%, for synthetic closure B. 0.215%, and for synthetic closure C 0.491%, while the average of water absorbency for the medium quality natural cork stopper was 13.06%.

Second Peripheral Layer/Skin Member

- 10 In order to clearly demonstrate the substantially enhanced synthetic bottle closure obtained by incorporating second peripheral layer/skin member 25, a supply of synthetic closures were manufactured using the process detailed above with foam core member 22 comprising metallocene catalyst polyethylene and low density polyethylene intermixed with each other as herein provided. In each of these test closures, peripheral layer/skin member 24 was formed about foam core member 22 by employing
15 styrene-ethylene-butylene-styrene, with peripheral layer/skin member 25 comprising a blend of thermoplastic olefins and thermoplastic vulcanizates (TPO/TPV).

- In conducting this test, two separate batches of synthetic bottle closures 20 were formed with peripheral layer/skin member 25 formed thereon. In this regard, both
20 batches of synthetic closures 20 employed a thermoplastic olefin and thermoplastic vulcanizate blend which incorporated between about 0.2 percent and 0.5 percent by weight based upon the weight of the entire peripheral layer/skin member 25 of polytetrafluoroethylene (PTFE). The polytetra-fluoroethylene employed comprises a micronized powder which is manufactured by Lawter International, Inc of Northbrook
25 IL and functions as a built-in lubricant. In addition, the blend of thermoplastic olefins and thermoplastic vulcanizates (TPO/TPV) employed herein was manufactured by Ampacet Corp. of Tarrytown NY.

In addition, in forming peripheral layer/skin member 25, an ultra high molecular weight (UHMW) silicone was incorporated therein. In this regard, the closures designated as "Batch 1" incorporated 5% by weight based upon the weight of the entire peripheral layer/skin member 25 of the UHMW silicone, while the closure designated as "Batch 2" comprised 7.5% by weight based upon the weight of the entire peripheral layer/skin member 20 of the UHMW silicone.

In order to determine the improvement in controlling extraction forces which is realized by incorporating peripheral layer/skin member 25, several closures were selected from each batch and inserted into wine bottles using normal corking procedures. In order to compare the results with a representative control product, a batch of synthetic closures were manufactured incorporating the identical foam core 22 and peripheral layer/skin member 24, which was treated with silicone after its formation. Representative samples of these control closures were selected from this batch and inserted into wine bottles in the same manner.

Wine bottles were randomly selected from each test group at specific intervals and the extraction force required to remove the closure from the wine bottle was determined and recorded. By referring to the Table VI, the results of these tests are clearly evident.

TABLE VI

Extraction Force (Lbs)

Closure	1 Day	14 Days	23 Days
Control	63.2	103.4	115.8
Batch 1	60.1	76.4	83.2
Batch 2	64.3	81.5	79

As detailed in Table VI, the incorporation of peripheral layer/skin member 25 produces a synthetic closure 20 which is capable of achieving a synthetic bottle closure

wherein the extraction force after 23 days is well below the maximum preferred limit of 90 pounds. In addition, by employing peripheral layer/skin member 25, the rate of increase of the extraction force appears to reach equilibrium, thereby assuring that excessive extraction forces over longer time periods will not be realized.

5 As a result, these examples clearly demonstrate that the incorporation of peripheral layer/skin member 25 provides a synthetic bottle closure 20 wherein extraction forces are controlled and maintained at optimal levels. In addition, if desired, additional additives, as detailed above, can be incorporated into peripheral layer/skin member 25 in order to further increase or decrease the extraction forces.

10 As is evident from a review of the test results detailed above, the multi-component/multi-layer synthetic bottle closure of the present invention has been clearly demonstrated as possessing physical characteristics which are either equivalent to or better than the physical characteristics possessed by bottle stoppers formed from natural cork. As a result of these test procedures, as well as the foregoing detailed disclosure
15 regarding the synthetic bottle closure of the present invention, it is immediately apparent that all of the inherent problems, difficulties, and drawbacks existing with natural cork stoppers have been completely overcome by the present invention, and a uniform, consistent, easily manufactured and comparatively inexpensive synthetic bottle closure has been achieved which can be employed for sealing products in bottles, such as wine,
20 without incurring any loss or unwanted change in the physical characteristics of the product.

 It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in the above article without departing from the scope of the invention, it is
25 intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

 It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of

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the scope of the invention which, as a matter of language, might be said to fall therebetween.

Particularly, it is to be understood that the in said claims, ingredients or compounds recited in the singular are intended to include compatible mixtures of such ingredients wherever the sense permits.

Having described my invention, what I claim is new and desire to secure by Letters Patent is:

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THE CLAIMS

1. A stopper or closure for a product retaining container constructed for being inserted and securely retained in a portal forming neck of the container, said stopper/closure comprising:
- 5 stopper/closure comprising:
- A. an elongated, cylindrically shaped core member formed from foamed plastic material;
- B. at first layer or skin member
- 10 a. peripherally surrounding and intimately bonded to the cylindrical surface of the core member, and
- b. comprising at least one plastic material selected from the group consisting of polyethylenes, metallocene catalyst polyethylenes, polybutanes, polybutylenes, polyurethanes, silicones, vinyl-based resins, thermoplastic elastomers, polyesters, ethylenic acrylic copolymers, ethylene-vinyl-acetate copolymers, ethylene-methyl-acrylate copolymers, thermoplastic polyurethanes, thermoplastic olefins, thermoplastic vulcanizates, flexible polyolefins, fluorelastomers, fluoropolymers, poly-ethylenes, teflons, and blends thereof, ethylene-butyl-acrylate copolymers,
- 15 ethylene-propylene-rubber, styrene butadiene rubber, ethylene-ethyl-acrylic copolymers, ionomers, polypropylenes, and copolymers of polypropylene and copolymerizable ethylenically unsaturated comonomers, foamable or non-foamable thermoplastic polyurethanes, thermoplastic olefins, thermoplastic vulcanizates, flexible polyolefins, fluoroelastomers, fluoropolymers, polyethylenes, teflons, and blends thereof ; and
- 20
- 25
- C. a second layer or skin member

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- a. peripherally surrounding and intimately bonded to the cylindrical surface of the first layer/skin member, and
- b. comprising at least one plastic material selected from the group consisting of polyethylenes, metallocene catalyst polyethylenes, polybutanes, polybutylenes, polyurethanes, silicones, vinyl-based resins, thermoplastic elastomers, polyesters, ethylenic acrylic copolymers, ethylene-vinyl-acetate copolymers, ethylene-methyl-acrylate copolymers, thermoplastic polyurethanes, thermoplastic olefins, thermoplastic vulcanizates, flexible polyolefins, fluorelastomers, fluoropolymers, polyethylenes, teflons, and blends thereof, ethylene-butyl-acrylate copolymers, ethylene-propylene-rubber, styrene butadiene rubber, ethylene-ethyl-acrylic copolymers, ionomers, polypropylenes, and copolymers of polypropylene and copolymerizable ethylenically unsaturated comonomers, foamable or non-foamable thermoplastic polyurethanes, thermoplastic olefins, thermoplastic vulcanizates, flexible polyolefins, fluoroelastomers, fluoropolymers, polyethylenes, teflons, and blends thereof ;

whereby a multi-layer/multi-component synthetic closure is attained which is capable of completely sealing any desired product in a container, retaining the product in the container for any desired length of time without any degradation of the product or degradation of the closure.

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2. The synthetic closure/stopper defined in Claim 1, wherein the cylindri-
cally shaped core member is further defined as comprising substantially flat terminating
surfaces forming the opposed ends of said cylindrically shaped core member, said first
layer/skin member is further defined as enveloping substantially the entire cylindrical
5 surface of the core member, and the second layer/skin member is further defined as
enveloping substantially the entire cylindrical surface of the first layer/skin member.

3. The synthetic closure/stopper defined in Claim 1, wherein the plastic
material forming the core member is further defined as comprising medium density or
low density, closed cell, foamed plastic comprising one or more selected from the
10 group consisting of inert polymers, homopolymers, and copolymers.

4. The synthetic closure/stopper defined in Claim 3, wherein said closed
cell foam plastic material is further defined as comprising at least one selected from the
group consisting of polyethylenes, metallocene catalyst polyethylenes, polybutanes,
polybutylenes, polyurethanes, silicones, vinyl-based resins, thermoplastic elastomers,
15 polyesters, ethylenic acrylic copolymers, ethylene-vinyl-acetate copolymers, ethylene-
methyl-acrylate copolymers, ethylene-butyl-acrylate copolymers, ethylene-propylene-
rubber, styrene butadiene rubber, ethylene-ethyl-acrylic copolymers, ionomers, poly-
propylenes, and copolymers of polypropylene and copolymerizable ethylenically
unsaturated comonomers, as well as ethylenic acrylic copolymers, ethylene-vinyl-
20 acetate copolymers, ethylene-methyl-acrylate copolymers, thermoplastic polyurethanes,
thermoplastic olefins, thermoplastic vulcanizates, flexible polyolefins, fluorelastomers,
fluoropolymers, polyethylenes, teflons, and blends thereof, ethylene-butyl-acrylate
copolymers, ethylene-propylene-rubber, styrene butadiene rubber, ethylene-ethyl-
acrylic copolymers.

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5. The synthetic closure/stopper defined in Claim 3, wherein said closed cell, foamed plastic material is further defined as comprising one or more polyethylenes selected from the group consisting of high density, medium density, low density, linear low density, ultra high density, and medium low density.

5 6. The synthetic closure/stopper defined in Claim 1, wherein said core member is further defined as comprising a density ranging between about 100 kg/m³ to 500 kg/m³.

7. The synthetic closure/stopper defined in Claim 6, wherein said core member further comprises a density ranging between about 200 kg/m³ to 350 kg/m³.

10 8. The synthetic closure/stopper defined in Claim 6, wherein said core member is further defined as comprising closed cells having an average cell size ranging from between about .02 millimeters to 0.50 millimeters and a cell density ranging between about 8,000 cells/cm³ to 25,000,000 cells/cm³.

15 9. The synthetic closure/stopper defined in Claim 8, wherein said core member is further defined as comprising cell size ranging between about 0.05mm and 0.1mm and a cell density ranging between about 1,000,000 cells/cm³ to 8,000,000 cells/cm³.

20 10. The synthetic closure/stopper defined in Claim 1, wherein said first layer/skin member and said second layer/skin member are further defined as comprising one selected from the group consisting of foamed plastics and non-foamed plastics.

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11. The synthetic closure/stopper defined in Claim 10, wherein said first layer/skin member and said second layer/skin member each comprise one selected from the group consisting of polyether-type polyurethanes, thermoplastic polyolefins, thermoplastic polyvulcanizates, flexible polyolefins, and blends thereof.

5 12. The synthetic closure/stopper defined in Claim 11, wherein said first layer/skin member and said second layer/skin member each further comprise between about 10% and 90% by weight based upon the weight of the entire composition of a thermoplastic olefin and between about 10% and 90% by weight based upon the weight of the entire composition of a thermoplastic vulcanizate.

10 13. The synthetic closure/stopper defined in Claim 1, wherein said core member is formed by injection molding.

14. The synthetic closure/stopper defined in Claim 13, wherein said first layer/skin member and said second layer/skin member are formed in an injection molding die during the formation process for the core member.

15 15. The synthetic closure/stopper defined in Claim 1, wherein said second layer/skin member further comprises at least one additive selected from the group consisting of lubricating agents, slip-enhancing compounds, antimicrobial agents, antibacterial agents, and oxygen scavenging compounds.

20 16. The synthetic closure/stopper defined in Claim 1, wherein said first layer/skin member is further defined as comprising a thickness ranging between about 0.05mm and 5mm.

17. The synthetic closure/stopper defined in Claim 16, wherein said first layer/skin member is further defined as comprising a thickness ranging between about 0.1mm and 2mm.

5 18. The synthetic closure/stopper defined in Claim 1, wherein said first layer/skin member is further defined as comprising a tough, score and mar resistant surface and a density ranging between about 300 kg/m³ and 1,500 kg/m³.

19. The synthetic closure/stopper defined in Claim 18, wherein the density of the first layer/skin member is further defined as comprising between about 750
10 kg/m³ and 1,000 kg/m³.

20. The synthetic closure/stopper defined in Claim 1, wherein said second layer/skin member is further defined as comprising a thickness ranging between about 0.002mm and 2.5 mm.

21. The synthetic closure/stopper defined in Claim 1, wherein said second
15 layer/skin member comprises a density ranging between about 100 kg/m³ and 1,000 kg/m³.

22. The synthetic closure/stopper defined in Claim 1 wherein said core member and said first layer/skin member and said second layer/skin member are further defined as being formed by extrusion.

20 23. The synthetic closure/stopper defined in Claim 22, wherein said core member, said first layer/skin member and said second layer/skin member are further defined as being extruded simultaneously.

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24. The synthetic closure/stopper defined in Claim 22, wherein said core member is further defined as being extruded separately and subsequent thereto said first layer/skin member is formed in extrusion equipment peripherally surrounding and enveloping the preformed core member, and said second layer/skin member is formed
5 in extrusion equipment peripherally surrounding and enveloping the preformed first layer/skin member.

25. The synthetic closure/stopper defined in Claim 22, wherein said extrusion process is further defined as incorporating one or more blowing agents selected from the group consisting of carbon dioxide, sulphur dioxide, nitrogen, carbon, water,
10 air nitrogen, helium, and argon, Azodicarbonamic Azodiiso-butyro-Nitride, Benzenesulfonylhydrazide, 4,4-Oxybenzene Sulfonylsemicarbazide, p-Toluene Sulfonylsemi-carbazide, Barium Azodicarboxylate, N,N'-Dimethyl-N,N'-Dinitrosoterephthalamide, Trihydrazinotriazine, Aliphatic Hydrocarbons having 1-9 carbon atoms, Halogenated Aliphatic Hydrocarbons having 1-9 carbon atoms, Aliphatic
15 Hydrocarbons having 1-9 carbon atoms, Aliphatic alcohols having 1-3 carbon atoms and partially Hydrogenated Chlorocarbon and Chlorofluorocarbons.

26. The synthetic closure/stopper defined in Claim 25, wherein said blowing agent is further defined as comprising between about .005% and 10% by weight of the weight of the plastic material and comprises an inert blowing agent selected from the
20 group consisting of nitrogen, carbon dioxide, sulphur dioxide, water, air, nitrogen, helium, and argon.

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27. The synthetic closure/stopper defined in Claim 23, wherein a nucleating agent is employed in the extrusion process and said nucleating agent is selected from the group consisting of calcium silicate, talc, clay, titanium oxide, silica, barium sulfate, diamatious earth, and mixtures of citric acid and sodium bicarbonate.

5 28. The synthetic closure/stopper defined in Claim 27, wherein said nucleating agent is further defined as comprising between about 0.1 and 5 parts by weight for every 100 parts by weight of the plastic material.

29. The synthetic closure/stopper defined in Claim 1, wherein one selected from the group consisting of said first layer/skin member and said second layer/skin member is further defined as comprising indicia formed on the outer surface thereof.

10

30. The synthetic closure/stopper defined in Claim 29, wherein said indicia comprises one or more selected from the group consisting of letters, symbols, colors, graphics, and wood tones.

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31. A stopper or closure for a product retaining container constructed for being inserted and securely retained in a portal forming neck of the container, said stopper/closure comprising:

- 5
- A. an elongated, solid cylindrically shaped member dimensioned for insertion in the neck of the fluid product retaining container for closing and sealing the fluid product in the container;
 - B. comprising at least four components concentrically mounted to each other and integrally bonded together in the manner which prevents passage of the fluid therebetween;
 - 10 C. said first component comprising an elongated, solid, cylindrically shaped core member formed from extruded foamed plastic material comprising a density ranging between about 100 kg/m³ to 500 kg/m³ and constructed for sealing the fluid product retained in the container and preventing transfer of the fluid product from the container prior to removal;
 - 15 D. said second component
 - a. peripherally surrounding the cylindrical surface of the first component, and
 - b. comprising a plastic material in peripheral surrounding, intimate, bonded engagement with the cylindrical surface of the first component and comprising at least one selected from the group consisting of polyethylenes, metallocene catalyst polyethylenes, polybutanes, polybutylenes, polyurethanes, silicones, vinyl-based
 - 20 resins, thermoplastic elastomers, polyesters, ethylenic acrylic copolymers, ethylene-vinyl-acetate copolymers, ethylene-methyl-
 - 25 acrylate copolymers, thermoplastic polyurethanes, thermoplastic olefins, thermoplastic vulcanizates, flexible polyolefins,

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- 5 fluorelastomers, fluoropolymers, polyethylenes, teflons, and blends thereof, ethylene-butyl-acrylate copolymers, ethylene-propylene-rubber, styrene butadiene rubber, ethylene-ethyl-acrylic copolymers, ionomers, poly-propylenes, and copolymers of polypropylene and copolymerizable ethylenically unsaturated comonomers, foamable or non-foamable thermoplastic polyurethanes, thermoplastic olefins, thermoplastic vulcanizates, flexible polyolefins, fluoroelastomers, fluoropolymers, polyethylenes, teflons, and blends thereof;
- 10 E. a third component
- a. peripherally surrounding the cylindrical surface of the second component, and
- b. comprising a plastic material in peripheral surrounding, intimate, bonded engagement with the cylindrical surface of the second component and comprising at least one selected from the group
- 15 consisting of polyethylenes, metallocene catalyst polyethylenes, polybutanes, polybutylenes, polyurethanes, silicones, vinyl-based resins, thermoplastic elastomers, polyesters, ethylenic acrylic copolymers, ethylene-vinyl-acetate copolymers, ethylene-methyl-acrylate copolymers, thermoplastic polyurethanes, thermoplastic olefins, thermoplastic vulcanizates, flexible polyolefins,
- 20 fluorelastomers, fluoropolymers, polyethylenes, teflons, and blends thereof, ethylene-butyl-acrylate copolymers, ethylene-propylene-rubber, styrene butadiene rubber, ethylene-ethyl-acrylic copolymers, ionomers, polypropylenes, and copolymers of polypropylene and copolymerizable ethylenically unsaturated comonomers, foamable or non-foamable thermoplastic
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polyurethanes, thermoplastic olefins, thermoplastic vulcanizates, flexible polyolefins, fluoroelastomers, fluoropolymers, polyethylenes, teflons, and blends thereof; and

F. a fourth component

- 5 a. peripherally surrounding the cylindrical surface of the third component,
- b. comprising a plastic material in peripheral surrounding intimate bonded engagement with the cylindrical surface of the third component and comprising at least one selected from the group consisting of polyethylenes, metallocene catalyst polyethylenes, 10 polybutanes, polybutylenes, polyurethanes, silicones, vinyl-based resins, thermoplastic elastomers, polyesters, ethylenic acrylic copolymers, ethylene-vinyl-acetate copolymers, ethylene-methyl-acrylate copolymers, thermoplastic polyurethanes, thermoplastic olefins, thermoplastic vulcanizates, flexible polyolefins, 15 fluorelastomers, fluoropolymers, polyethylenes, teflons, and blends thereof, ethylene-butyl-acrylate copolymers, ethylene-propylene-rubber, styrene butadiene rubber, ethylene-ethyl-acrylic copolymers, ionomers, polypropylenes, and copolymers of polypropylene and copolymerizable ethylenically unsaturated comonomers, foamable or non-foamable thermoplastic polyurethanes, thermoplastic olefins, thermoplastic vulcanizates, flexible polyolefins, fluoroelastomers, fluoropolymers, polyethylenes, teflons, and blends thereof; and
- 20 c. having an exposed surface constructed for frictionally engaging a surface of the portal formed in the neck of the container and being securely engaged therewith until forcibly removed there-
- 25

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from, sealing the fluid product in the container and resisting all forces generated by the fluid product when retained in said container;

whereby a multi-layer/multi-component synthetic closure is attained which is capable of completely sealing any desired fluid product in a container, retaining the product in the container for any desired length of time without any degradation of the fluid product or degradation of the closure.

32. The synthetic closure/stopper defined in Claim 31, wherein the plastic material forming the core member is defined as comprising medium density or low density, closed cell, foamed plastic comprising one or more selected from the group consisting of inert polymers, homopolymers, and copolymers.

33. The synthetic closure/stopper defined in Claim 32, wherein said closed cell foam plastic material is further defined as comprising at least one selected from the group consisting of polyethylenes, metallocene catalyst polyethylenes, polybutanes, polybutylenes, polyurethanes, silicones, vinyl-based resins, thermoplastic elastomers, polyesters, ethylenic acrylic copolymers, ethylene-vinyl-acetate copolymers, ethylene-methyl-acrylate copolymers, ethylene-butyl-acrylate copolymers, ethylene-propylene-rubber, styrene butadiene rubber, ethylene-ethyl-acrylic copolymers, ionomers, polypropylenes, and copolymers of polypropylene and copolymerizable ethylenically unsaturated comonomers as well as ethylenic acrylic copolymers, ethylene-vinyl-acetate copolymers, ethylene-methyl-acrylate copolymers, thermoplastic polyurethanes, thermoplastic olefins, thermoplastic vulcanizates, flexible polyolefins, fluorelastomers, fluoropolymers, polyethylenes, teflons, ethylene-butyl-acrylate copolymers, ethylene-propylene-rubber, styrene butadiene rubber, ethylene-ethyl-acrylic copolymers and blends thereof.

34. The synthetic closure/stopper defined in Claim 32, wherein said closed cell, foamed plastic material is further defined as comprising one or more polyethylenes selected from the group consisting of high density, medium density, low density, linear low density, ultra high density, and medium low density.

5 35. The synthetic closure/stopper defined in Claim 31, wherein each of said second, third, and fourth components are further defined as comprising one selected from the group consisting of foamed plastics and non-foamed plastics.

36. The synthetic closure/stopper defined in Claim 35, wherein said second, third, and fourth components each comprise one selected from the group consisting of
10 polyether-type polyurethanes, thermoplastic polyolefins, thermoplastic polyvulcanizates, flexible polyolefins, and blends thereof.

37. The synthetic closure/stopper defined in Claim 36, wherein said second, third and fourth components are each comprises between about 10% and 90% by weight based upon the weight of the entire composition of a thermoplastic olefin and
15 between about 10% and 90% by weight based upon the weight of the entire composition of a thermoplastic vulcanizate.

38. The synthetic closure/stopper defined in Claim 31, wherein said third and fourth components are each further defined as comprising a thickness ranging between about 0.002mm and 2.5mm.

20 39. The synthetic closure/stopper defined in Claim 31, wherein said third and fourth components are each further defined as comprising a density ranging between about 100 kg/m³ and 1,000 kg/m³.

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40. The synthetic closure/stopper defined in Claim 31, wherein said fourth component comprises an outer layer surface consisting of at least one selected from the group consisting of holes, dimples, fish scales, and shark skin appearance.

5 41. The synthetic closure defined in Claim 40, wherein said fourth component is further defined as being formed by one surface treatment selected from the group consisting of embossing and melt fracture.

42. The synthetic closure defined in Claim 31, wherein the outer surface of the fourth component is embossed by passing the synthetic closure through a plurality of rotating wheels having a desired surface configuration to be formed on the closure.

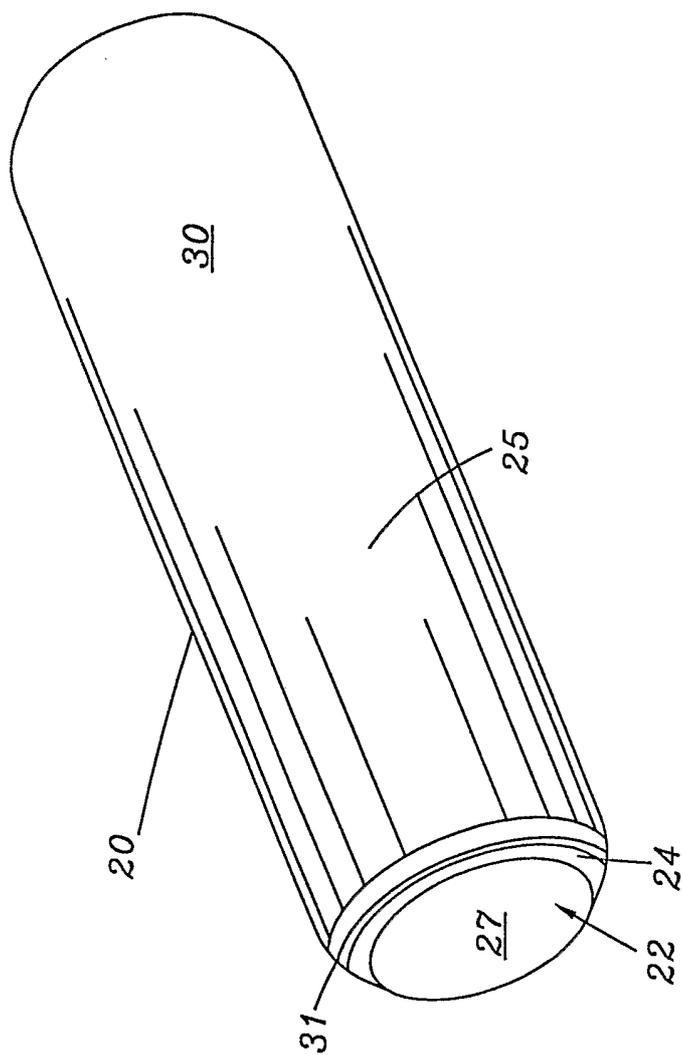


FIG. 1

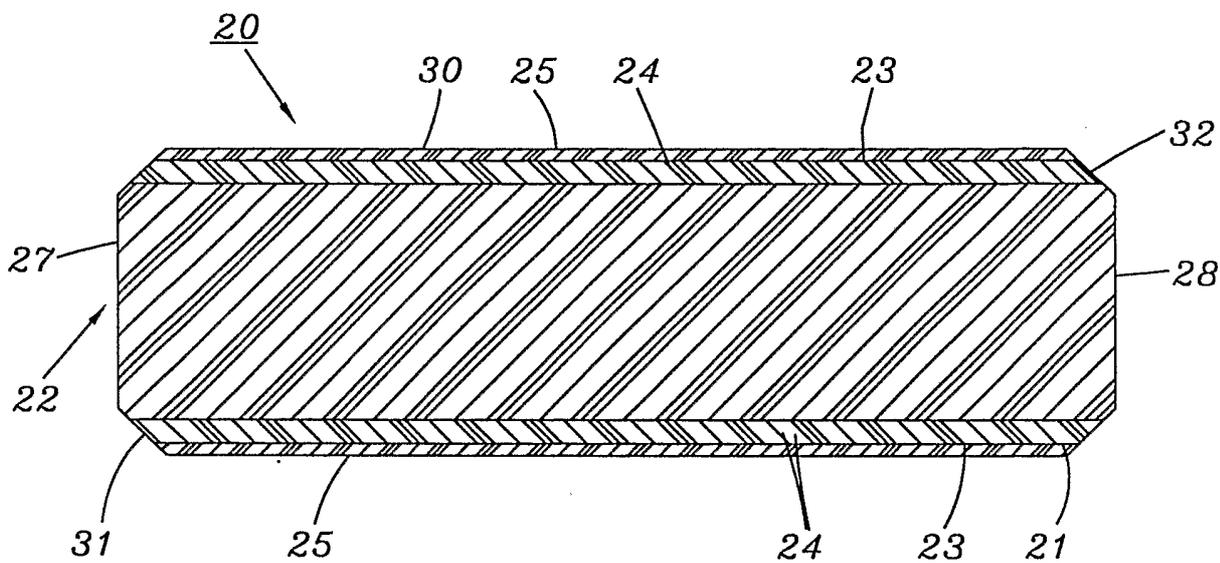


FIG. 2

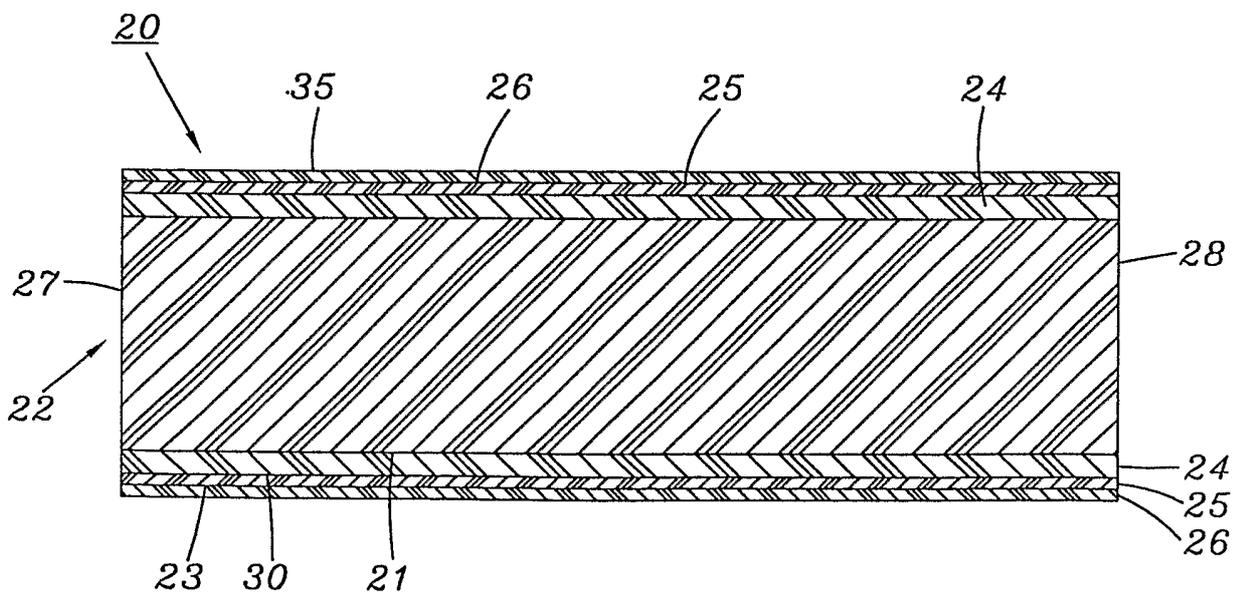


FIG. 3

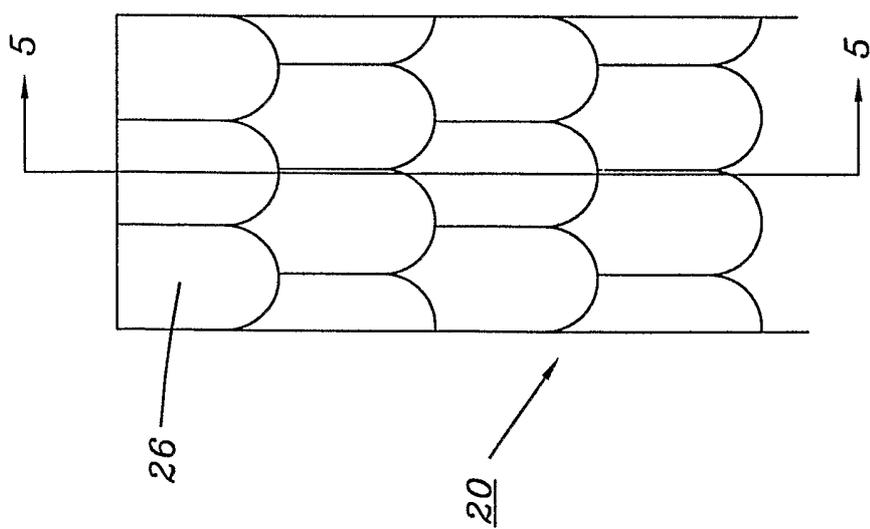


FIG. 4

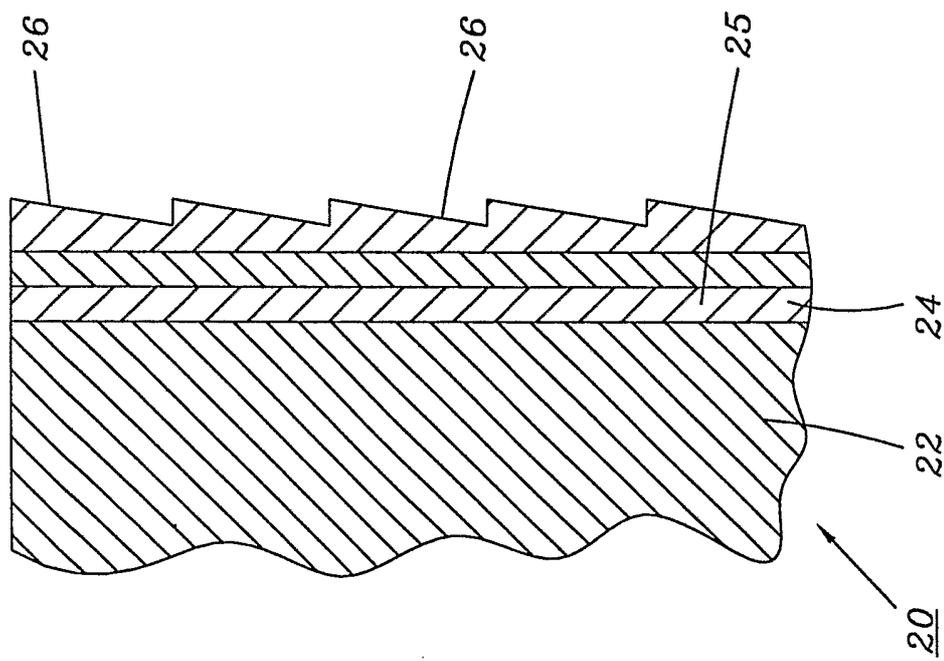


FIG. 5

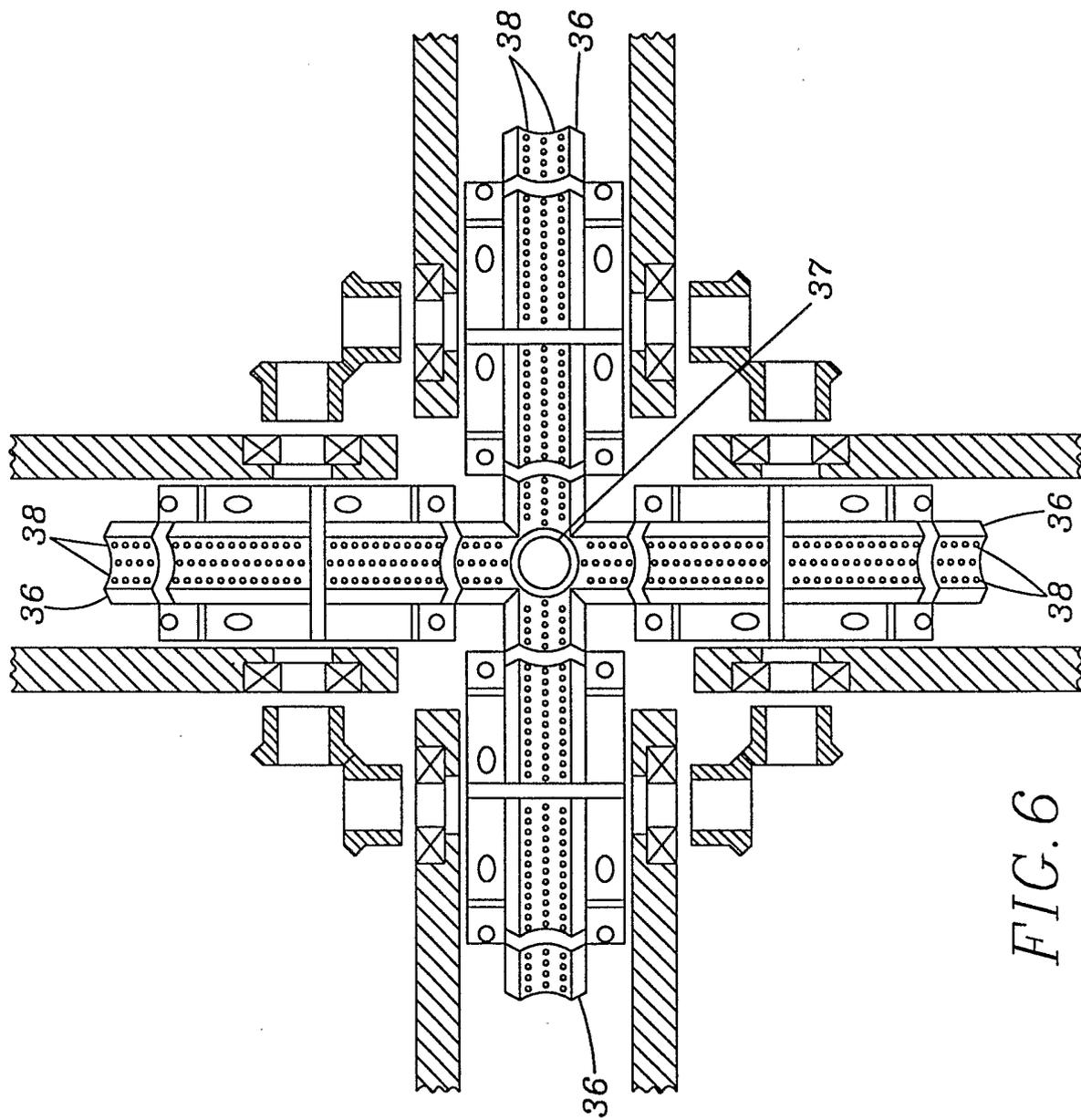


FIG. 6

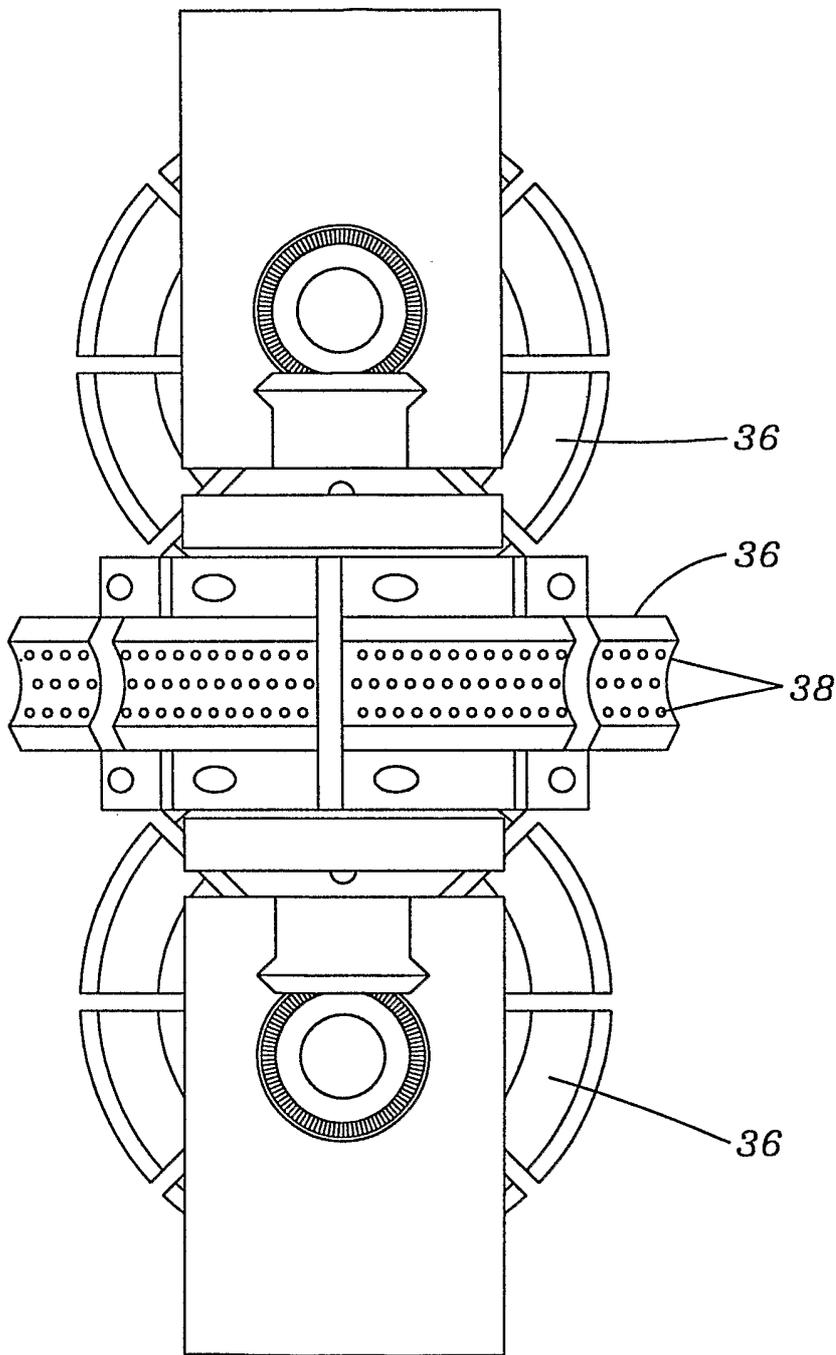


FIG. 7

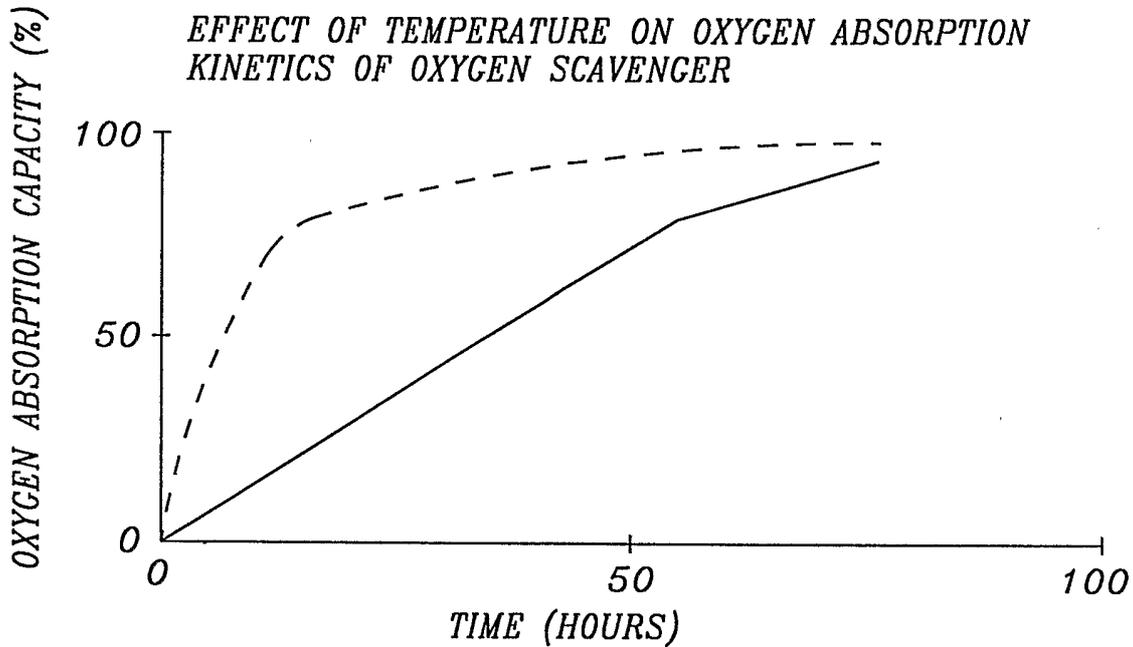


FIG. 8

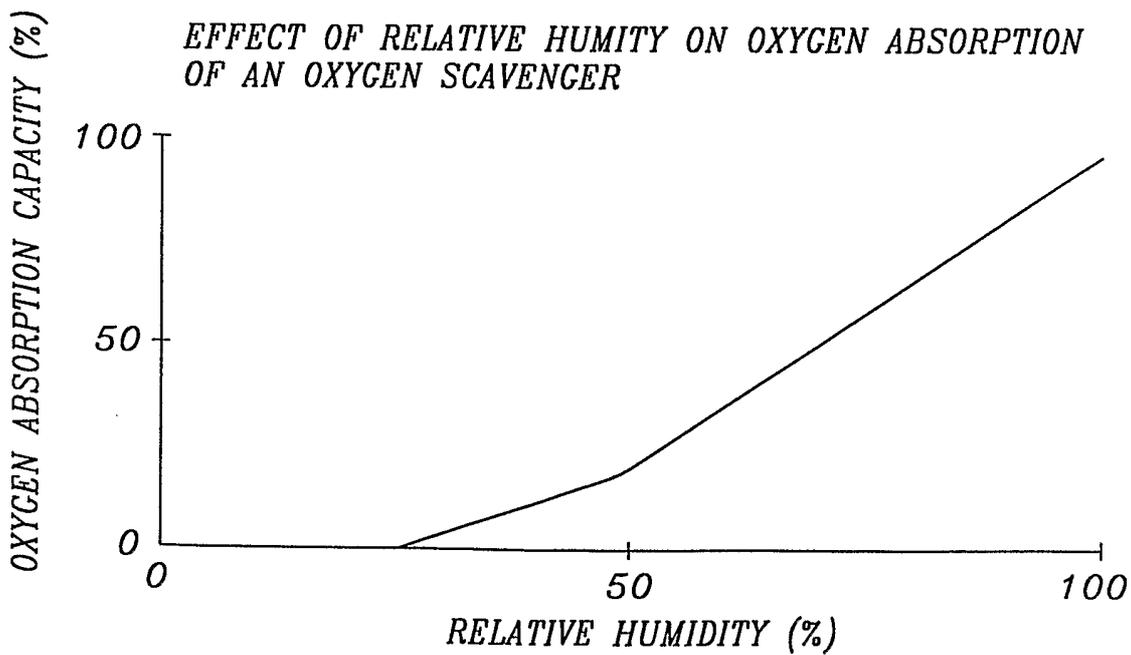


FIG. 9

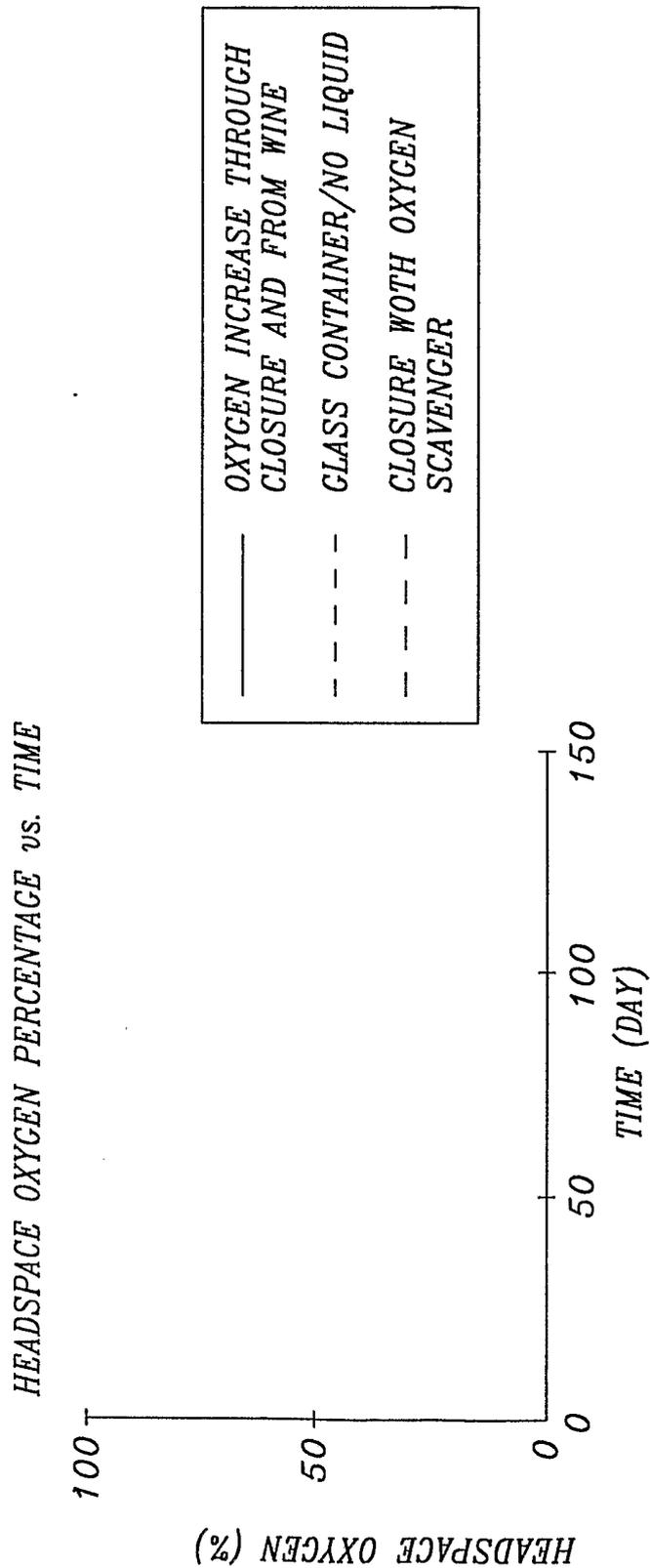


FIG. 10

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/22605

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B32B 1/08, 3/02; B65D 39/00
 US CL : 428/36.5, 66.3, 66.4; 215/230, 296, 364

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)
 U.S. : 428/36.5, 66.3, 66.4; 215/230, 296, 364

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ✓	US 6,153,275 A (YANIGER) 28 November 2000 (28.11.2000), whole document	1-30
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Y	whole document	31-42
Y ✓	US 3,900,124 A (MARCEL) 19 August 1975 (19.08.1975), Fig. 1, Columns 1 and 7	31-39
Y ✓	US 4,363,416 A (LOUGHMILLER) 14 December 1982 (14.12.1982), column 1, lines 57-59	40-42
A ✓	US 5,480,915 A (BURNS) 2 January 1996 (02.01.1996), whole document	1-42

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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

"P" document published prior to the international filing date but later than the priority date claimed

"T"

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X"

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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

"&"

document member of the same patent family

Date of the actual completion of the international search

01 October 2002 (01.10.2002)

Date of mailing of the international search report

03 JAN 2003

Name and mailing address of the ISA/US

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