A stopper for use in a substantially cylindrical bottle opening is disclosed. The stopper is made of a natural cork body with a polymeric portion to prevent flavor scalping and seal the bottle opening. The stopper of the present invention is designed to enhance traditional bark corks in wine bottles. The stopper of the present invention reduces flavor scalping, water and ethanol permeation, and TCA permeation associated with traditional corks, and results in excellent Wine Protection Factor ratings. The method of producing a stopper for use in a substantially cylindrical bottle opening is also disclosed.
FIG. 3a

FIG. 3b

FIG. 3c
FIG. 3d

Water/Ethanol Barrier

Stopper Surface

FIG. 3e

Water/Ethanol Barrier

Aroma Barrier

Stopper Surface
UNIQUE WINE FLAVOR PROTECTOR

BACKGROUND OF THE INVENTION

Many liquid products such as oils, honey, alcoholic beverages, and the like, are sold with stoppered closures, such as corks. Most wine bottle closures or stoppers have been produced from a natural material known as “cork”. Natural cork has high resiliency properties that make it an excellent closure for containers with an elasticity which enables rapid recovery to its original shape after any deformation. Thus, its natural closure properties and traditional appearance make cork the preferred bottle closure for wine storage, particularly for medium and high quality wines where adequate closure properties and traditional appearance are important. A suitable wine stopper must also be able to withstand pressure build-up, pressure fluctuations that naturally occur during storage, and extraction forces.

Natural corks pose a particular difficulty with wine sold in bottles due to inherent problems of flavor scalping and taint that sometimes occur in wine. A natural cork is made up of small cells which are configured to form intercellular spaces. The irregularities of cork cause quality variances which result in varying grades of cork based on density and other surface characteristics. Since the texture of cork is not uniform, ducts or openings which are permeable to gases and liquids are often invaded by molds and other microorganisms.

A significant percentage of bottled wine is spoiled by cork taint. Cork taint typically occurs after the wine is bottled, as chemicals or microorganisms present in the cork contact and leach into the wine. There are six main chemical compounds associated with cork taint in wines. The most common and readily detectable taint compound is known as 2,4,6-trichloroanisole (hereinafter referred to as “trichloroanisole” or “TCA”). TCA is responsible for the offensive malodor and bad flavor associated with “corked” wine. TCA is analytically detectable at concentrations as low as 0.5 parts per trillion (ppt) or 0.5 nanogram per liter. Another problem commonly found with natural cork is flavor scalping. Flavor scalping is caused by absorption of wine flavor compounds by the cork or closure. Many of the closure materials traditionally used to prevent cork taint also remove flavor compounds from the wine. Additionally, cork impurities and compounds associated with synthetic materials applied to the cork are often able to leach into the wine causing flavor problems for wine bottlers. Similarly, many closure materials that would not interact with the flavor compounds of the wine when combined with natural cork would not prevent cork taint.

The present invention provides a cork stopper suitable for wine closures, which eliminates the problems of flavor scalping and taint associated with cork and synthetic closures. Furthermore, the cork stopper retains the traditional appearance of a wine cork and is able to withstand forces applied during the bottling process, pressure build up that naturally occurs during storage, and extraction forces.

SUMMARY OF THE INVENTION

The present invention provides a stopper with a body having at least one end suited to close a container opening; and a polymer portion comprising a water and ethanol barrier disposed on said at least one end wherein the stopper is adapted to conform to and seal a container opening. The polymer portion may comprise a multi-layer barrier film comprising at least one fluoropolymer based water and ethanol barrier and at least one aroma barrier layer. The multi-layer barrier film may further comprise a fluoropolymer tie layer, bonding the fluoropolymer based barrier layer to the aroma barrier layer. An adhesive layer may be used to join the aroma barrier layer to the stopper body.

The stopper body may comprise cork and the polymer portion may have a flavor scalp factor of less than 2.0 and daily water permeation factors of less than 6.0 g/m² per mm thickness. The stopper may further provide a flavor scalp factor of less than 2.0 in conjunction with a TCA permeation factor of less than 4.0 percent.

In certain embodiments the stopper comprises a cork body having at least one end suited to close a container opening; and a multi-layered polymer portion comprising polytetrafluoroethylene (PTFE), polyethylene glycol (PEG) or other suitable fluoropolymer based layer disposed on said at least one end wherein the stopper is adapted to conform to and seal said container opening.

In other certain embodiments, the stopper comprises a cork body having at least one end suited to close a container opening; and a multi-layered polymer portion comprising PTFE and ethylene vinyl alcohol disposed on said at least one end, wherein the stopper is adapted to conform to and seal said container opening.

DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a stopper comprising a cylindrical body and a polymer portion covering both ends. FIG. 2 shows a cross section of the polymer portion. FIGS. 3A-3E show schematic representations of polymeric portions of the present invention and stopper surfaces.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a unique flavor protective stopper with a body having at least one end suited to close a container opening; and a polymer portion comprising a water and ethanol barrier, preferably fluoropolymer based, disposed on said at least one end, wherein the stopper is adapted to conform to and seal a container opening. The polymer portion may comprise a multi-layer barrier film with at least two layers. The multi-layer barrier film may comprise at least one fluoropolymer based water and ethanol barrier and at least one aroma barrier layer. The multi-layer barrier film may further comprise a fluoropolymer tie layer, bonding the water and ethanol barrier layer to the aroma barrier layer. An adhesive layer may be used to join the aroma barrier layer to the stopper body. Suitable water and ethanol barriers include: polypropylene (PP), polyethylene (PE) and other related copolymers, polyester (PES), polyethylene terephthalate (PET), polypivalidene chloride (PVDC), polyvinylidene fluoride (PVdF), Saranex, type barriers (PVdC multi-layered films), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVdF), ethylene tetrafluoroethylene (ETFE), ethylene chloro-trifluoroethylene (ECTFE), fluorinated ethylene propylene (FEP), Perfluroalkoxy vinyl ether (PFA), and other suitable fluoropolymers. The present invention is unique in many different aspects includ-
ing strength, barrier properties and flavor inertness. The high strength allows the multi-layered barrier to maintain its performance after being compressed and forcefully inserted into the opening of the wine bottle. The high strength provides barrier integrity and also allows for a more robust manufacturing process and provides one of the strongest, thinnest moisture barriers available.

[0013] FIG. 1 shows a stopper 1 comprising a body 3 having a top end 5 and a bottom end 7 with at least one side portion 9 located between the top end 5 and the bottom end 7. At least one end of the body 3 is covered with a polymer portion 10 comprising a fluoropolymer. In a preferred embodiment, the polymer portion 10 is adhered to the at least one end and a side portion 9 of the body 3. The polymer portion 10 may be adhered in part or whole to the surface of the at least one end, or alternatively, only the perimeter of the polymer portion 10 may be adhered to the body 3. In some desired applications, the polymeric portion covers between 2 and 10 mm up the side of the cork body 3. In a preferred embodiment, the polymer portion 10 is not adhered at interface between the body 3 and the end of the cork. It is preferred that at least 25 percent of the polymer portion 10 is adhered to the body 3 surface. In one aspect, the present invention is able to provide a transparent polymer portion 10 which is highly undetectable when adhered to a natural cork, thus preserving the aesthetic value of natural corks.

[0014] The polymer portion 10 comprises at least two parts, namely (a) a water and ethanol barrier 40 such as a PTFE film and (b) an aroma barrier 18 such as an ethylene vinyl alcohol copolymer film, subsequently referred to as EVOH, nylons, polyvinylidene chloride (PVDC), polypropylene and fluorohydrogenated materials, such as tetrafluoroethylene (TFE); ethylene tetrafluoroethylene (ETFE), ethylene chloro-trifluoroethylene (ECTFE), polychlorotrifluoroethylene (PCTFE); and other suitable materials. The polymer portion 10 may exist as a multi-layered film which is bonded together with a tie layer 20. The tie layer 20 may be any suitable material which joins the polymer portion 10 to the aroma barrier 18. Examples include fluoropolymer layers, adhesives, thermoplastics, and the like. The polymer portion 10 is disposed over at least one end of the stopper 1 and adapted to conform to and seal an opening in a bottle neck. The body 3 of the stopper 1 is comprised of natural cork in a preferred embodiment, but other types of materials may be used, including agglomerated cork, polyoleins, or other synthetic materials. The most common stoppers are cylindrical in form, but other shapes are contemplated and may be employed by the present invention.

[0015] FIG. 2 shows a cross section of the polymer portion 10. The polymer portion 10 is depicted as a multi-layer barrier film which protects the contents of a container from flavor and/or taste influences. The present invention is particularly useful for natural wine corks, especially for preventing 2,4,6-trichloroanisole (TCA) taint from natural cork, and flavor scapling common with natural and synthetic closures. Previous attempts to prevent TCA contamination by shutting off one mechanism of permeation, either diffusion or solubility, have been largely unsuccessful. It has been found that the mechanism of TCA contamination of wine is the combination of permeation and solubility. Fluoropolymer based water and ethanol barriers and aroma barriers individually do not prevent TCA contamination, but the combination of the two barriers appears to be much more effective. A multi-layer polymer portion 10 adhered to a closure can prevent permeation and extraction of taint caused by TCA and other wine contaminants. For instance, an aroma barrier 18 prevents the diffusion of TCA and tainting compounds from the cork across the water and ethanol barrier into the wine. As an example, a PTFE based water and ethanol barrier is able to prevent the solubilization of EVOH by water and ethanol, thus preventing the extraction of TCA from the cork into the contents of the wine via water and ethanol.

[0016] Surprisingly, the present invention keeps the product flavors pristine in that flavors are neither added nor removed from the product by the stopper 1. Polymers that do not absorb flavors are typically highly crystalline. Many highly protective aroma barriers are crystalline but typically hydrolyze in wine over time and thus reduce their barrier properties, lose their inherent strength, or absorb flavors. The present invention provides a polymer portion which is strong, flexible, and crystalline but does not absorb flavors. There are also no flavors added to the contents of the stoppered container, nor are there extractables present. As shown in the examples, compared to several other standard food packaging films, fluoropolymer based water and ethanol barriers such as polytetrafluoroethylene did not exhibit a recognizable flavor difference when tested in wine.

[0017] As shown in FIG. 2, the multi-layer barrier film 15 is comprised of at least two layers, an outer water and ethanol barrier 40, preferably fluoropolymer based, and an aroma barrier 18 layer. As shown in FIGS. 3A-3E different configurations of the polymer portion 10 may be assembled which are in accordance with the present invention. For instance, a three-layer multi-barrier film may be formed by adding an adhesive 22 layer to the fluoropolymer layer and aroma barrier 18 layers. In a preferred embodiment, the multi-layer barrier film is comprised of at least four layers, an outermost fluoropolymer layer, a tie layer, an aroma barrier 18 layer, and an adhesive 22 layer to bond the film to the stopper or cork body 3. The entire polymer portion 10 is crystalline to provide barrier and flavor inertness properties. The multi-layer barrier film may be present covering the surface of the cork, or alternatively may infiltrate the interfaces of the cork to provide a filled surface.

[0018] The fluoropolymer based water and ethanol barrier layer is the outermost layer on the film and is hydrophobic, food safe, non-flavor absorbing, and provides water and ethanol barrier properties. The low water and ethanol permeability of the fluoropolymer layer provides low relative humidity at the aroma barrier 18 layer, maintaining the permeation performance of aroma barriers, such as EVOH. The water and ethanol barrier properties of the fluoropolymer layer also prevent wine (approximately 13 percent ETOH, >80 percent H2O) from permeating into the cork, solubilizing TCA and extracting the TCA back across and into the wine. Suitable examples of a fluoropolymer based barrier layer include PTFE, PCTFE, ETFE, ECTFE, FEP, PFA, PVdF. The fluoropolymer barrier layer helps provide the polymer portion 10 with strength and also provides protection from the industrial bottling process to the layers beneath and prevents the take-up of flavors from wine. In certain embodiments, the fluoropolymer layer may be coated on to the ends of a stopper body. One example of this would be PTFE coated on the ends of a cork or other stopper.
A tie layer 20 is in contact with the fluoropolymer layer. Suitable tie layers include, but are not limited to, fluorinated ethylene propylene copolymers, perfluoroalkoxy copolymers, ethylene tetrafluoroethylene, polyethylene, polyurethanes, silicones, EVA, polyvinylidene chloride, polyvinylidenefluoride, poly(chlorotrifluoroethylene), ECTFE, and combinations thereof. A tie layer 20 provides a heat bondable surface to adhere the water and ethanol barrier to the aroma barrier 18. The fluoropolymer based tie layer 20 must also be food safe, have no extractable compounds, and be non-absorbing of flavors and aromas. It is a further option to remove the fluoropolymer based tie layer 20 and bond the aroma barrier 18 directly to the outer water and ethanol barrier layer when using a fluoropolymer based water and ethanol barrier suitable for direct bonding.

The aroma barrier 18 layer is located between the water and ethanol barrier layer and the stopper 1. The aroma barrier 18 prevents flavor changes from occurring as well as maintaining the scents desirable in quality wines. PCTFE and EVOH both provide very good aroma and flavor barrier properties. PCTFE is used in pharmaceutical packaging applications. EVOH is used in food packaging applications such as paste toothpaste tubes and ketchup bottles. It performs best when protected and kept in a low relative humidity environment. It has been found that matching the aroma barrier 18 with a strong, flexible fluoropolymer based moisture and ethanol barrier maintains a low relative humidity at the EVOH layer and provides barrier integrity. The EVOH provides permeation resistance against TCA, preventing TCA from diffusing from the cork matrix into the wine.

An adhesive 22 layer may be used to adhere the aroma barrier 18 layer to the body 3, such as natural or synthetic cork. In a preferred embodiment, the aroma barrier 18 layer is also in contact with the tie layer 20 which ties it to the water and ethanol barrier layer. The adhesive 22 layer is preferably an EVOH film with ethylene content sufficient to achieve an adequate bond (measured by peel strength) between the EVOH and the natural cork surface. Preferably, the adhesive 22 layer has a lower melting temperature than the melting temperatures of the aroma barrier layer. In one preferred embodiment, the adhesive 22 layer is an extruded commercial EVOH film that is heat laminated to a second EVOH film which provides aroma barrier properties. Other suitable adhesive 22 layers such as polyethylene, polyurethane, or ethyl vinyl acetate need to be food safe, hydrolysis resistant, and provide adequate bond strength. A layer is considered to be a continuous or discontinuous planar portion comprising essentially one material or combination of materials. The material may be homogeneous or non-homogenous in nature. Additionally, the adhesive 22 may attach the barrier to the body 3 in a continuous or discontinuous manner.

The present invention provides overall barrier properties such as water and ethanol barrier desirable for wine storage. PTFE based water and ethanol barriers are very good barriers for polar compounds making it a good moisture barrier and also a good ethanol barrier. Many commercial barrier films are good moisture barriers, but in the presence of thirteen percent ethanol (typical wine concentration) some good moisture barriers lose effectiveness. Moisture barriers such as nylon, polyvinylidene chloride, and polyethylene have a loss in moisture barrier performance of roughly 10-100 times their original properties in the presence of ethanol. The water permeation properties of fluoropolymer films, such as PTFE, are not significantly changed by the addition of 13 percent ethanol into solution. This is important because TCA is readily soluble in ethanol and the fluoropolymer based water and ethanol barrier prevent the permeation of ethanol into the cork, preventing TCA from being extracted from the cork into the wine. Further, the combination of a hydrophobic fluoropolymer based water and ethanol barrier with the EVOH based aroma barrier maintains a low humidity at the EVOH surface, allowing the EVOH to provide aroma barrier properties.

FIGS. 3A-3C show various cross sectional views of the polymer portion 10 of the present invention. In FIG. 3A, the water and ethanol barrier layer 40 is bonded to an aroma barrier 18 layer without the use of a tie layer 20. The aroma barrier 18 is then joined to the stopper 1 surface via an adhesive 22. FIG. 3B shows a tie layer 20 present connecting the water and ethanol barrier layer and the aroma barrier 18 layer. The aroma barrier 18 is then joined to the stopper 1 surface via an adhesive 22.

FIG. 3C shows an asymmetric fluoropolymer barrier film wherein the inner side of the fluoropolymer barrier film comprises a more porous structure into which the aroma barrier 18 layer is at least partially penetrated.

FIG. 3D shows a polymer portion joined to the surface of the stopper body 3, without a tie layer. In FIG. 3E, the polymer portion 10 of a water and ethanol barrier layer 40 and aroma barrier 18 are joined via a tie layer 20 and then contacted to the stopper 1 without the need for adhesive.

A wine protection factor associated with flavor and product is described at Example 4. A good quality wine is considered to be greater than forty.

In one aspect, the present invention provides a stopper 1 with a cork body 3 having a flavor scalp factor of less than 2.0 and a daily water permeation factor of less than 6.0 g/m² per mm thickness. In another aspect, the present invention provides a stopper 1 comprising a cork body 3 having a flavor scalp factor of less than 2.0 and a TCA permeation factor of less than 4.0 percent. In yet another aspect of the present invention, a stopper 1 is provided comprising a cork body 3 having a daily water permeation factor of less than 6.0 g/m² per mm thickness and a TCA permeation factor of less than 4.0 percent.

A wine protection factor may be computed by considering flavor scaling effects, TCA permeation, and water permeation. As shown in FIG. 3, the wine protection factor may be computed as:

\[
100 \times \frac{[\text{Scalp Factor} + \text{TCA Permeation Factor} + \text{Water Permeation Factor}]}{100}
\]

In this manner the total protection output of a barrier may be compared to other barriers. It has been found that an ideal wine protection factor for wine is greater than forty.

Traditionally, the six main chemical compounds associated with flavor scaling in wines are Ethyl Hexanoate (eH), Ethyl Octanoate (eO), Ethyl Decanoate (eD), Rose Oxide (RO), Damascenone (D), and Beta Ionone (BI). TDN and naphthalene are additionally widely regarded as measurable flavor factors. However, it is unclear if removal of
these two compounds enhances or diminishes the quality of wine. Therefore, for the purpose of the present invention, they have not been included as measured scalp factors. It has been found to be desirable that the multi-layer barrier film portion of the stopper 1 has a scaling percentage for eH of less than 0.9. The multi-layer barrier film portion of the stopper 1 has a scaling percentage for eO of less than 0.9. The multi-layer barrier film portion of the stopper 1 has a scaling percentage for eO of less than 3.0. The multi-layer barrier film portion of the stopper 1 has a scaling percentage for D of less than 0.9. The multi-layer barrier film portion of the stopper 1 has a scaling percentage for Bi of less than 2.0.

[0031] The most common taint compound found in natural corks is known as 2,4,6-trichloroanisole (TCA). It is preferred that the amount of TCA that is allowed to leach into the wine is less than 5 nanograms per liter of wine.

[0032] In one embodiment of the present invention, the stopper comprises a cork body having at least one end suited to close a container opening; and a multi-layered polymer portion 10 comprising PTFE or PCTFE or SARANEX™ disposed on said at least one end, wherein the stopper is adapted to conform to and seal said container opening. A tie layer may be present if desired.

[0033] Similarly, in another embodiment of the present invention, the stopper comprises a cork body having at least one end suited to close a container opening; and a multi-layered polymer portion comprising PTFE and ethylene vinyl alcohol disposed on said at least one end wherein the stopper is adapted to conform to and seal said container opening.

[0034] In these embodiments, it is advantageous that the wine protection factor is greater than 20, and even more advantageous that the wine protection factor is greater than forty. The multi-layer barrier film portion of the stopper 1, not including the adhesive 22, is able to be constructed to a thickness of less than 0.035 mm.

[0035] While particular embodiments of the present invention have been illustrated and described herein, the present invention should not be limited to such illustrations and descriptions. It should be apparent that changes and modifications may be incorporated and embodied as part of the present invention within the scope of the following claims.

EXAMPLES

Example 1
Cork Taint Testing

[0036] Evaluation of the ability to prevent TCA contamination was conducted at ETS labs in St. Helena, Calif. ETS is a privately owned wine analytical laboratory, located in Napa valley (ETS Laboratories, 899 Adams St., Suite A, St. Helena, Calif. 94574) and has a unique expertise in TCA analysis. ETS has developed a TCA QC method called releasable TCA (rTCA) for the Cork Quality Council and has established the test as a global TCA QC tool using gas chromatograph-mass spectroscopy (GCMS). Traditional TCA test methods were destructive, but the releasable TCA test is not. The rTCA test is based on the effect that a cork releases the same amount of TCA when soaked in wine to reach a repeatable equilibrium concentration. This releasable TCA amount reaches equilibrium in the first 24 hours and is repeatable 100 times or more. In the trial, 400 natural corks were each spiked with 100 ng of TCA. The corks were grouped into 20 bulks (groups) of 20 corks and each bulk was tested for releasable TCA via GCMS. ETS found rTCA numbers in the range of 5 to 30 nanograms TCA/L, which is typical for naturally contaminated corks. After the bulk test was performed, each individual cork in a bulk was wrapped with a barrier material. Each bulk of 20 corks was wrapped with the same barrier.

<table>
<thead>
<tr>
<th>TABLE 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>MATERIAL</td>
</tr>
<tr>
<td>PTFE + EVOH</td>
</tr>
<tr>
<td>PCTFE + EVOH</td>
</tr>
<tr>
<td>FEP + EVOH</td>
</tr>
<tr>
<td>Saranex23</td>
</tr>
<tr>
<td>Nylon + EVOH</td>
</tr>
<tr>
<td>EVOH</td>
</tr>
</tbody>
</table>

TABLE 1

Material. The 20 individually wrapped corks of the same material were then recombined into a bulk and soaked to determine the Releasable TCA (rTCA) with the barrier present. The results of the cork taint analysis (TCA) of selected material used in the test are shown below in table 1.

[0037] Multiple barrier materials were used, including PTFE, FEP, Nylon6, EVOH, Saranex 23, PCTFE, and combinations thereof. Materials were obtained from Goodfellow Corp. (Goodfellow Corp., 237 Lancaster Ave., Suite 252, Devon, Pa. 19333) and EVALCA (EVALCA, INC., 2625 Bay Area Blvd., Suite 300, Houston, Tex. 77058). The materials were soaked in a control wine for 12 weeks at room temperature and the releasable TCA was then measured to determine the ratio of TCA detected initially without a barrier to the TCA detected with a barrier. The TCA permeation factor is defined as the ratio of the amount of TCA measured in the wine after soaking with the barrier present to the amount of TCA measured in the wine without the barrier.

Example 2

Moisture Vapor Permeation Testing

[0038] To judge the performance of the water/ethanol barrier, we tested multiple combinations of barrier films at MOCON Labs (MOCON INC., 7500 Boone Ave. North, Minneapolis, Minn. 55428) that specializes in permeation testing. Experiments were conducted to determine the moisture barrier performance of various food packaging barrier materials in the presence of ethanol. Scientific literature provides water vapor permeation values for each of the barrier materials. To prove our concept that barrier performance is not compromised when placed in contact with wine, each material was challenged with a permanent of 13 percent Ethanol in H2O. The permeation tests were performed at 25° C. and had 100 percent nitrogen gas, dry at ambient pressure as the carrier gas.

[0039] The results from MOCON are reported as water vapor transmission rate and can readily be normalized to thickness to compare different thickness materials. In general, the results show a clear agreement with theoretical values for water vapor transmission rate. The following results below in table 2 illustrate the data from the MOCON testing.
TABLE 2 Water Vapor Transmission Rates normalized for sample thickness

<table>
<thead>
<tr>
<th>Material</th>
<th>Overall Thickness (mm)</th>
<th>Average WVTR (g/m²·day)</th>
<th>WVTR Thickness (g-mm/m²·day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE + PolyChloroTriFluorEthylene (PCTFE)</td>
<td>0.032</td>
<td>0.0765</td>
<td>0.0024</td>
</tr>
<tr>
<td>PTFE + EVOH</td>
<td>0.035</td>
<td>0.1625</td>
<td>0.0057</td>
</tr>
<tr>
<td>Unconsolidated PTFE + EVOH</td>
<td>0.088</td>
<td>0.0780</td>
<td>0.0089</td>
</tr>
<tr>
<td>PTFE + PolyVinylidene Chloride (PVdC)</td>
<td>0.032</td>
<td>0.2415</td>
<td>0.0077</td>
</tr>
<tr>
<td>Polypropylene (PP) + EVOH</td>
<td>0.022</td>
<td>0.6575</td>
<td>0.0145</td>
</tr>
<tr>
<td>PerfluoroAlkoxy VinylEther (PFA) + EVOH</td>
<td>0.062</td>
<td>0.3275</td>
<td>0.0204</td>
</tr>
<tr>
<td>Polyethylene (PE) + EVOH</td>
<td>0.037</td>
<td>0.6065</td>
<td>0.0227</td>
</tr>
<tr>
<td>Fluorinated Ethylene Propylene (FEF) + EVOH</td>
<td>0.062</td>
<td>0.3720</td>
<td>0.0232</td>
</tr>
<tr>
<td>LDPE/PVdC/EVA (Saranex 23)</td>
<td>0.051</td>
<td>0.4760</td>
<td>0.0242</td>
</tr>
<tr>
<td>Polyamide (Nylon 66) + PVdC</td>
<td>0.037</td>
<td>0.8955</td>
<td>0.0331</td>
</tr>
<tr>
<td>EthyleneTriFluoroEthylene (ETFE) + EVOH</td>
<td>0.062</td>
<td>1.191</td>
<td>0.0343</td>
</tr>
<tr>
<td>Polyethylene Terephthalate (PET) + EVOH</td>
<td>0.025</td>
<td>3.0815</td>
<td>0.0770</td>
</tr>
<tr>
<td>Polyamide (Nylon 66) + EVOH</td>
<td>0.062</td>
<td>3.6395</td>
<td>0.2271</td>
</tr>
<tr>
<td>Ethylene Vinyl Alcohol (EVOH-XL)</td>
<td>0.012</td>
<td>27.08</td>
<td>0.3250</td>
</tr>
</tbody>
</table>

[00040] As observed from the above results, the materials that perform the best are the PCTFE and PTFE based materials. The key point in this data is that some of the aroma barrier materials that performed well when combined with PTFE, such as PCTFE, PVdC, and EVOH, are very dimensionally unstable and not likely strong enough to survive an industrial bottling process on their own. By combining these dimensionally unstable materials with the PTFE based water and ethanol barrier, the integrity and performance of the aroma barriers is greatly improved.

[00041] Because of the importance of having a barrier to the polar solvents found in wine that would extract TCA from cork, such as water and ethanol, the water vapor transmission rate, normalized to thickness is defined as our Water Permeation Factor. We have created the Water Permeation Factor to help build the Wine Protection Factor as the material placed on the stopper must be able to withstand water/ethanol without degradation and prevent permeation of water/ethanol to the cork. The H₂O Permeation Factors for selected performers from the above list of MOCON samples is shown below in table 3.

TABLE 3

<table>
<thead>
<tr>
<th>WATER PERMEATION FACTORS FOR VARIOUS BARRIER FILMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O VAPOR FLUX (g/m²·day)</td>
</tr>
<tr>
<td>PTFE + EVOH</td>
</tr>
<tr>
<td>Unconsolidated PTFE + EVOH</td>
</tr>
<tr>
<td>PCTFE + EVOH</td>
</tr>
<tr>
<td>FEP + EVOH</td>
</tr>
<tr>
<td>Saranex23</td>
</tr>
<tr>
<td>Nylon + EVOH</td>
</tr>
<tr>
<td>EVOH</td>
</tr>
</tbody>
</table>

Example 3

Flavor Compound Scoping Testing

[00042] Provisor is an independent testing lab located in Australia (Provisor Pty. Ltd., ABN 41 101 149 482, Hartley Grove, Urbrase SA 5064) that specializes in grape and wine research, and provides analytical testing for chemical compounds in wine, such as taint and scalp. We provided samples to Provisor to determine the amount of flavor and aroma compounds removed (scalloped) from the wine. Scalp analysis is assessed through gas chromatography-mass spectrometry measurements of flavor compounds remaining relative to an untreated control. The ability of the materials to not scalp flavors from wine was evaluated using 8 standard flavor compounds. The compounds were ethyl hexanoate, ethyl octanoate, ethyl decanoate, rose oxide, naphthalene, TDI (1,1,6-trimethyl-1,2-dihydronaphthalene), dimethylone, beta-ionone. To evaluate each material sample, a wine solution was dosed with a measured amount of the flavor compound and then the material was soaked in the solution at a contact ratio of 1:50. A contact ratio of 1:5 shows the same closure surface area as that found in a standard bottle of wine, a contact ratio of 1:50 provides 50 times the closure area as compared to a standard bottle.

[00043] The percent of compound scalped is calculated by applying the following formula:

\[
\text{Percent Scalloped} = \left( \frac{\text{Concentration in wine after contact with material} - \text{Concentration in wine with no added material}}{\text{Concentration in wine with no added material}} \right) \times 100
\]

where both wine solutions have been dosed with the chemicals of interest.

[00044] To facilitate differentiation between the materials tested, the raw values have been included in table 4. Table 4 below shows, for each material tested, the percent compound scalped for each individual compound. The scalp factor is defined as the cumulative amount of scalped compound. The overall trend for the known materials is as expected with the cork samples showing scalping of all compounds and significantly less scalping for SARANEX™ (screw-cap liner). For the other materials, even though many of the values are <10 percent scalped, a cumulative picture facilitates differentiation between materials.
TABLE 4

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>ETHYL HEXANOATE</th>
<th>ETHYL OCTANOATE</th>
<th>ETHYL DECANOATE</th>
<th>ROSE OXIDE 162</th>
<th>DAMASCENONE</th>
<th>BETA JONONE</th>
<th>SCALP FACTOR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE + EVOH</td>
<td>0.0</td>
<td>0.0</td>
<td>1.0</td>
<td>7.0</td>
<td>0.0</td>
<td>1.0</td>
<td>9.0</td>
</tr>
<tr>
<td>PCTFE + EVOH</td>
<td>2.0</td>
<td>8.0</td>
<td>16.0</td>
<td>0.0</td>
<td>1.0</td>
<td>2.0</td>
<td>29.0</td>
</tr>
<tr>
<td>FEP + EVOH</td>
<td>11.0</td>
<td>4.0</td>
<td>4.0</td>
<td>7.0</td>
<td>0.0</td>
<td>1.0</td>
<td>27.0</td>
</tr>
<tr>
<td>Saranex23</td>
<td>1.0</td>
<td>0.0</td>
<td>18.0</td>
<td>6.0</td>
<td>3.0</td>
<td>9.0</td>
<td>37.0</td>
</tr>
<tr>
<td>Nylon6 + EVOH</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>3.0</td>
</tr>
<tr>
<td>EVOH</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Natural Cork</td>
<td>8.0</td>
<td>15.0</td>
<td>36.0</td>
<td>5.0</td>
<td>13.0</td>
<td>19.0</td>
<td>96.0</td>
</tr>
<tr>
<td>Agglomerate Cork</td>
<td>10.0</td>
<td>21.0</td>
<td>49.0</td>
<td>5.0</td>
<td>16.0</td>
<td>27.0</td>
<td>128.0</td>
</tr>
</tbody>
</table>

Example 4

Wine Protection Factor

[0045] When evaluating the performance of a closure suitable for applications where wine or other beverages with alcohol are present, a measure that takes into account the multiple performance facets is desirable. In addition to creating a quality seal with the container, the closure must minimize the amount of flavor compounds added or removed from the wine. The Wine Protection Factor is provided as a means to describe and compare various closures in the three performance aspects needed for a wine closure.

The Wine Protection Factor is computed by the following equation:

\[
\text{Wine Protection Factor} = \frac{100}{[\text{Scalp Factor} + \text{TCA Permeation Factor} + \text{Water Permeation Factor}]}
\]

The Wine Protection Factor takes into account the critical performance features of a wine closure and quantifies the three aspects central to the contamination mechanism of wine: flavor scalping, TCA permeation, and TCA extraction. In this manner the total protection output of a barrier may be calculated as shown below for selected materials:

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>WINE PROTECTION FACTOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE + EVOH</td>
<td>45.7</td>
</tr>
<tr>
<td>PCTFE + EVOH</td>
<td>19.5</td>
</tr>
<tr>
<td>FEP + EVOH</td>
<td>14.5</td>
</tr>
<tr>
<td>Saranex23</td>
<td>11.6</td>
</tr>
<tr>
<td>Nylon6 + EVOH</td>
<td>4.3</td>
</tr>
<tr>
<td>EVOH</td>
<td>0.7</td>
</tr>
</tbody>
</table>

The Wine Protection Factor provides a comparison by which to determine the best materials to create closures for wine.

The invention claimed is:
1. A stopper comprising:
   a) a body having at least one end suited to close a container opening; and
   b) a polymer portion comprising at least one fluoropolymer disposed on said at least one end, wherein the stopper is adapted to conform to and seal said container opening.
2. The stopper of claim 1, wherein the polymer portion further comprises at least one aroma barrier layer.
3. The stopper of claim 1, wherein the fluoropolymer is a water and ethanol barrier.
4. The stopper of claim 3 wherein the polymer portion is a multi-layer barrier film further comprising a fluoropolymer tie layer bonding the water and ethanol barrier layer to an aroma barrier layer.
5. The stopper of claim 2 further comprising an adhesive layer joining the aroma barrier layer to the stopper body.
6. The stopper of claim 1 wherein the body is comprised of cork.
7. The stopper of claim 3 wherein the water and ethylene barrier layer comprises a polytetrafluoroethylene.
8. The stopper of claim 1 wherein the aroma barrier is an ethylene vinyl alcohol copolymer film.
9. The stopper of claim 1 wherein the aroma barrier is a polyvinylidene chloride.
10. The stopper of claim 1 wherein the aroma barrier is a polypropylene.
11. The stopper of claim 7 wherein the aroma barrier is bonded to the PTFE.
12. The stopper of claim 1 wherein the polymer portion is adhered to the at least one end and a portion of the body.
13. The stopper of claim 12 wherein the polymer portion is adhered to the entire face of at least one end.
14. The stopper of claim 13 wherein the perimeter of the polymer portion is adhered to the body.
15. The stopper of claim 14 wherein the polymer portion is only adhered to a side of the body.
16. A stopper comprising a cork body having a flavor scalp factor of less than 2.0 and a daily water permeation factor of less than 6.0 g/m² per mm thickness.
17. A stopper comprising a cork body having a flavor scalp factor of less than 2.0 and a TCA permeation factor of less than 4.0 percent.
18. A stopper comprising a cork body having a daily water permeation factor of less than 6.0 g/m² per mm thickness and a TCA permeation factor of less than 4.0 percent.
19. A stopper comprising a cork body having a Wine Protection Factor of greater than 5.
20. A stopper comprising a cork body having a Wine Protection Factor of greater than 20.
21. A stopper comprising a cork body having a Wine Protection Factor of greater than forty.
22. The stopper of claim 2, wherein the aroma barrier layer comprises ethylene vinyl alcohol.
23. The stopper of claim 1, wherein the Wine Protection Factor is greater than 5.
24. The stopper of claim 1, wherein the Wine Protection Factor is greater than 15.
25. The stopper of claim 1, wherein the Wine Protection Factor is greater than 20.
26. The stopper of claim 1, wherein the Wine Protection Factor is greater than 40.
27. The stopper of claim 1, wherein the polymeric portion is transparent.
28. The stopper of claim 1, wherein the polymeric portion is less than 0.035 mm in thickness.
29. The stopper of claim 1, wherein the polymeric portion has a scalping percentage for eH of less than 0.9.
30. The stopper of claim 1, wherein the polymeric portion has a scalping percentage for eO of less than 0.9.
31. The stopper of claim 1, wherein the polymeric portion has a scalping percentage for eD of less than 3.0.
32. The stopper of claim 1, wherein the polymeric portion has a scalping percentage for BI of less than 2.0.
33. The stopper of claim 1, wherein the polymeric portion covers a distance of greater than 2 mm on the cylindrical body.
34. The stopper of claim 1, wherein the polymeric portion has a thickness of less than 60 microns across the entire polymer portion.
35. The stopper of claim 1, wherein the polymer portion has a Wine Protection Factor greater than 20 and a thickness of less than 60 microns across the entire polymer portion.
36. The stopper of claim 1, wherein the polymer portion extends past the sealing end over the cylindrical body side for a distance of greater than 1 mm.
37. The stopper of claim 1, wherein the polymer portion comprises polychlorotrifluoroethylene.
38. The stopper of claim 2, wherein the aroma barrier layer comprises polychlorotrifluoroethylene.
39. A stopper comprising:
   a) a cork body having at least one end suited to close a container opening; and
   b) a multi-layered polymer portion comprising at least one polytetrafluoroethylene layer and at least one ethylene vinyl alcohol based layer covering said at least one end, wherein the stopper is adapted to conform to and seal said container opening.
40. A stopper comprising:
   a) a cork body having at least one end suited to close a container opening; and
   b) a polymer portion comprising polychlorotrifluoroethylene disposed on said at least one end, wherein the stopper is adapted to conform to and seal said container opening.
41. A stopper comprising:
   a) a cork body having at least one end suited to close a container opening; and
   b) a multi-layered polymer portion comprising PTFE and ethylene vinyl alcohol disposed on said at least one end, wherein the stopper is adapted to conform to and seal said container opening.

* * * * *