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(54) Low permeability device for closure of barrels

(57) A device for closing wooden casks suitable for preserving wine, such as barriques, kegs and barrels of different capacities, comprising a stopper made of plastic material chosen among the thermoplastic elastomers, such as copolymers in blocks of the styrene type [such as] "styrene-ethylene-butene-styrene" (SEBS), having a mean permeability to oxygen lower than 4,000 $cm^3/mm/m^2/day/atm$ calculated according to the method described in standard ASTM-D1434.

EP 1 541 482 A1

Description

[0001] The present invention refers to a closing device or stopper for barrels, particularly for wooden barrels, such as barriques or other containers with different capacities.

[0002] Barriques, wooden casks able to contain wine during partial or total fermentation, and/or subsequent refining, are closed with a frustoconical-shaped stopper, which is forcibly inserted into the wine input hole, so as to create a very tight seal against gas and liquids.

[0003] The material most frequently used today for production of stoppers for barriques is high-purity silicone rubber that complies with the international standards which govern use thereof in contact with foodstuffs, in this instance alcoholic beverages.

[0004] As a general rule barriques, once filled with wine, perform the functions described below:

- release by the wood from which the barrique is made of aromatic components, which modify the organoleptic characteristics of the wine increasing its complexity and pleasantness;
- micro oxygenation related to the porosity of the woods from which the barrique is made, which favours the evolution of the wine and ageing thereof.

[0005] These desirable functions are associated with a drawback related to absorption of a certain percentage of wine by the wood and to the continuous, albeit limited, evaporation of wine through the wood. The more the environment in which the barriques are stocked is characterised by a low level of relative humidity, the more pronounced the latter phenomenon will be.

[0006] The resulting decrease in the initial level of filling generates a pressure difference between the inside and the outside of the barrique. This pressure difference draws in air and thus oxygen, which permeates mainly through the closing device.

[0007] It is obvious that the amount of permeated oxygen is a function of the pressure difference between the inside and the outside of the barrique and of the specific degree of permeability of the materials of which said stopper is made.

[0008] The transfer of oxygen to the inside of the barrel is harmful in that it can lead to the growth of strains of aerobic bacteria in the wine: among these the most harmful are acetic bacteria. In the presence of oxygen and of favourable thermal and ecological conditions, there is an easy development in the wine of acetic bacteria whose metabolism provides for attacking and for degrading ethyl alcohol with the formation of acetic acid, as well as for attacking other substances with the formation of various secondary products.

[0009] The possible formation of such microorganisms therefore leads to a decrease in the quality of the wine and to the implementation of actions aimed at eliminating such microorganisms through antibacterial substances.

[0010] From studies carried out it has been noted that the concentration of these microorganisms, when present, is highest in wine that is in contact with the stopper and in the area adjacent to the stopper of the barrique, since this is the area with the greatest passage of oxygen.

[0011] The object of the present invention is to reduce part of the drawbacks of the prior art, proposing a closing device which provides lower gas permeability than that of current closures and therefore minimises the transfer of oxygen, thus reducing the possibility of growth of the above-mentioned microorganisms.

[0012] Another object of the present invention is to provide a closing device for barrels that is practical, versatile and cheap thanks to the use of thermoplastic elastomers which simplify the production process by eliminating the need to use the reticulating agents currently used in the production of silicone rubber stoppers and which allow recovery of the core through regranulation.

[0013] These objects are achieved according to the invention with the device described in appended independent claim 1.

[0014] The advantages of a closing device for barrels according to the invention are obvious. In fact the use of thermoplastic elastomers, namely copolymers in blocks of the styrene type such as styrene- (ethylene-butene)-styrene (SEBS), reduces the permeability of the stopper, thus reducing the transfer of oxygen from the external environment to the inside of the barrique and thereby limiting the growth of aerobic bacteria.

[0015] In particular, the materials used are characterised by hardnesses ranging between 20 and 70 ShA, calculated according to IS0868 standards, with a compression set below 40% with a test piece maintained at 23 °C for 72 hours according to IS0815 standards. Among these materials, purely by way of example, it is possible to cite the Shell Kraton G2706, G2705, G2701 and G1650 family or the Kraiburg Thermolast K range or the Polyone Polyone - Softer Bergaflex83F line.

[0016] These materials can be used pure, and therefore at 100%, or mixed with other elastomers, for example with olefinic elastomers. It is further possible to reduce the density of the end product by proceeding with a slight expansion of the stopper through the addition, during its production by injection moulding, of expanding agents such as azodicarbonamide or sodium bicarbonate, in order to reduce the density of the stopper by about 10% to improve the adaptability of the closing device to the bung-hole in the barrel.

[0017] Purely by way of example, the mean permeability to oxygen of a silicone rubber used for the application in question is about 20,000 $cm^3/mm/m^2/day/atm$, measured according to the ASTM-D1434 method, whereas the permeability of a SEBS elastomer with equivalent mechanical characteristics, measured according to the ASTM-D1434 method, is lower than 4,000 $cm^3/mm/m^2/day/atm$ (preferably about 3,500 $cm^3/mm/$

m^2/day/atm). SEBS therefore allows permeability to be reduced about five times with respect to silicone rubber, from which it can be deduced that the amount of permeated oxygen is five times less with an SEBS stopper than with a silicone rubber stopper with the same geometric shape. Again by way of example, it should be noted that permeability to other gases also decreases. For example, permeability to carbon dioxide (CO_2) is of about 200,000 $cm^3/mm/m^2$/day/atm for the silicone rubber and lower than 3,000 $cm^3/mm/m^2$/day/atm. (preferably about 2,500 $cm^3/mm/m^2$/day/atm) for SEBS, entirely to the advantage of the wine contained inside the barrel.

[0018] The following test was carried out at the Department of Microbiological and Food Science and Technology of the University of Agricultural Science of Milan.

[0019] A series of glass tubes with an opening [whose diameter is] equal to that of a barrique (45 mm) was closed with stoppers in SEBS-type elastomeric material and with traditional silicone rubber stoppers.

[0020] The tubes were fluxed with inert gas (nitrogen) by means of a side opening and subsequently said side opening was sealed with very high gas barrier material. At set intervals, the amounts of oxygen that had migrated from the outside environment to the inside of the tube through the closure were calculated by non-invasive methods.

[0021] The tests were conducted on a statistically significant number of samples and the results showed that the permeability of the silicone rubber stoppers was, on average, 7 to 10 times higher than that of the stoppers according to the invention.

[0022] The duration of the test was 12 months; during said time the rates of transfer of oxygen remained constantly within the ratios mentioned above.

[0023] The above confirms the advantageous results obtained with the closing device according to the invention.

Claims

1. A device for closing barrels comprising a closing stopper made of plastic material, **characterised in that** said plastic material is chosen among the thermoplastic elastomers.

2. A device according to claim 1, wherein said plastic material belongs to the family of copolymers in blocks of the styrene type and in particular styrene - (ethylene-butene) - styrene.

3. A device according to claim 1 or 2, **characterised in that** said plastic material has a mean permeability to oxygen lower than 4,000 $cm^3/mm/m^2$/day/atm calculated according to the method described in standard ASTM-D1434.

4. A device according to claims 1 or 2, wherein said plastic material has a mean permeability to carbon dioxide (CO_2) lower than 3,000 $cm^3/mm/m^2$/day/atm calculated according to the method described in standard ASTM-D1434.

5. A device according to any one of the preceding claims, wherein said plastic material is used in a mixture with olefinic type elastomers.

6. A device according to any one of the preceding claims, wherein the hardness of said plastic material is between 20 and 70 ShA.

7. A device according to any one of the preceding claims, wherein said plastic material has a compression set lower than 40% calculated at 23°C for 72 hours according to IS0815 standards.

8. A device according to any one of the preceding claims, wherein said plastic material is of the expanded type, with a density 10% lower than that of said material unexpanded.

9. A device according to any one of the preceding claims, wherein the application of said plastic material does not require reticulating agents.

10. A device according to any one of the preceding claims, wherein said stopper is frustoconical in shape.

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EUROPEAN SEARCH REPORT

Application Number
EP 03 42 5788

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 4 826 029 A (SKOGLIE LARRY) 2 May 1989 (1989-05-02) * column 6, line 55 - column 7, line 37 * ---	1,10	B65D39/00
X	DE 20 12 630 A (FA. C. A. NEUBECKER) 30 September 1971 (1971-09-30) * page 2, paragraph 2; figures * ---	1,10	
X	US 2002/090475 A1 (LAUER EDUARDO ET AL) 11 July 2002 (2002-07-11) * page 3, paragraph 45 - paragraph 47 * ---	1,2,5	
X Y	EP 1 182 223 A (SUPREME CORQ) 27 February 2002 (2002-02-27) * column 3, line 46 - column 5, line 6; figures * ---	1,2,5,6 3,4	
X	WO 00/26103 A (PLIMMER PETER N ;SUPREME CORQ INC (US); ZECH JEROME M JR (US)) 11 May 2000 (2000-05-11) * page 5, line 16 - page 6, line 16; figures * ---	1,2,5	TECHNICAL FIELDS SEARCHED (Int.Cl.7) B65D
Y	WO 03/074379 A (BACCHUS WINE CLOSURES LTD ;TAYLOR DAVID GRAHAM (GB)) 12 September 2003 (2003-09-12) * page 5, paragraph 2 * -----	3,4	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	8 April 2004	Derrien, Y

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 03 42 5788

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08-04-2004

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4826029 A	02-05-1989	NONE	
DE 2012630 A	30-09-1971	DE 2012630 A1	30-09-1971
US 2002090475 A1	11-07-2002	US 6355320 B1	12-03-2002
		AU 6520999 A	08-05-2000
		WO 0023259 A1	27-04-2000
EP 1182223 A	27-02-2002	US 5496862 A	05-03-1996
		EP 1182223 A1	27-02-2002
		AT 216411 T	15-05-2002
		AU 2387099 A	10-06-1999
		AU 691497 B2	21-05-1998
		AU 6783894 A	21-11-1994
		BG 63016 B1	31-01-2001
		BG 100118 A	31-07-1996
		BR 9406394 A	13-02-1996
		CA 2161673 A1	10-11-1994
		CN 1124968 A ,B	19-06-1996
		CZ 9502880 A3	14-02-1996
		DE 69430424 D1	23-05-2002
		DE 69430424 T2	05-12-2002
		EP 0698054 A1	28-02-1996
		ES 2176246 T3	01-12-2002
		FI 955287 A	03-01-1996
		HU 73270 A2	29-07-1996
		JP 3420238 B2	23-06-2003
		JP 9500074 T	07-01-1997
		NO 954417 A	03-01-1996
		NZ 266368 A	26-11-1996
		PL 311642 A1	04-03-1996
		PT 698054 T	30-09-2002
		RO 115528 B1	30-03-2000
		RU 2127699 C1	20-03-1999
		SK 136995 A3	04-12-1996
		WO 9425513 A1	10-11-1994
		US 5480915 A	02-01-1996
		US 6127437 A	03-10-2000
		US 5692629 A	02-12-1997
		US 5710184 A	20-01-1998
		US 5855287 A	05-01-1999
WO 0026103 A	11-05-2000	AU 1340400 A	22-05-2000
		WO 0026103 A1	11-05-2000
		ZA 9906914 A	17-05-2000

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 03 42 5788

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

08-04-2004

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 03074379 A	12-09-2003	WO 03074379 A2	12-09-2003

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82