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(54) Title: SYNTHETIC STOPPERS FOR BOTTLES

(57) Abstract: Synthetic stoppers for bottles to be used in the food industry, based on an elastomer known as SEEPS and optionally comprising, in addition to this elastomer, one or more blowing agents, one or more fillers, polyethylene and EVA. The stoppers according to the present invention are adapted, among other applications, for use in glass bottles and particularly for bottles containing wines and liqueurs.



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SYNTHETIC STOPPERS FOR BOTTLES

Technical Field

The present invention relates to a stopper for bottles for food use. In particular, the stopper for bottles is based on a particular block copolymer known as SEEPS.

Background Art

Stoppers for different containers, based on elastomers are already known. The properties of such stoppers vary depending on the elastomers that are used and on the remaining substances used to provide such stoppers. In particular, stoppers for bottles made using block copolymers are disclosed in WO 94/25513 by Supreme Corq, which discloses the use of the polymers SEPS, SEBS, SBS and SIS and of mixtures thereof together with a blowing agent in order to produce stoppers for wine bottles.

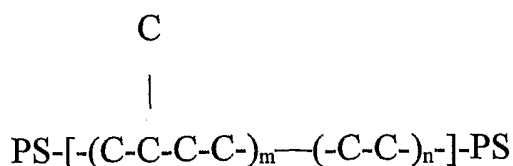
The aim of the present invention is therefore to provide a synthetic stopper for bottles for food use which has particular and improved features of chemical and mechanical resistance required for the use of such stoppers.

Disclosure of the Invention

Surprisingly, it has now been found that it is possible to provide a stopper which has said particular and improved characteristics of chemical and mechanical resistance required for the use of said stoppers by using a polymeric mixture which is based not on known polymers but on a polymer known as SEEPS (styrene-ethylene-ethylene/propylene-styrene), which contains approximately 30% styrene.

The structure of the SEEPS elastomer is as follows:

25



30 where PS stands for polystyrene and m and n are whole numbers greater

than zero and m can be different from n or equal to it.

It has been found that the block composition of the SEEPS copolymer offers good resistance to traction stresses as well as good chemical-physical behavior at high temperatures. The presence of the ethylene-
5 ethylene/propylene block favors the preservation of the mechanical properties even at low temperatures.

The Shore A hardness values of the SEEPS copolymer according to the present invention can vary from 5 to 95.

The SEEPS copolymer has excellent wettability and good resistance
10 to acids, alcohols and alkali; moreover, its SO_x gas retention, verified by combustion according to the JIS K-7217 standard, has been advantageously found to be nil.

The polymers produced by Kuraray Co. under the name SEPTON® can be used as SEEPS hydrogenated copolymers to be used in the present
15 invention. Two different types thereof, one with a medium molecular weight and one with a high molecular weight, are preferably used.

According to the invention, the polymeric mixture is constituted by the SEEPS copolymer, which can receive the addition of 5 to 30% on the total weight of the mixture of paraffin oil in order to improve its fluidity
20 characteristics.

The polymeric mixture according to the invention receives the addition of additives such as blowing agents, fillers, polyethylene and EVA (ethylene vinyl acetate).

It is possible to use as blowing agents two different products, i.e., the
25 blowing agent EXPANCEL®, which is of the physical type, and the blowing agent HYDROCEROL®, which is of the chemical type.

The EXPANCEL® blowing agent is constituted by microspheres of a copolymer with acrylonitrile-methacrylonitrile, which contain an expanding gas (isopentane) which, when heated, increases in pressure and swells,
30 increasing the volume of the cells. Usually, the temperature at which the

action of the blowing agent occurs ranges from 80 to 190°C. The expanded microspheres have the main characteristic of increasing the resiliency of the final product. In particular, the EXPANCEL® microspheres are white and have a density of approximately 1.2 g/cc. The initial diameter of the microspheres is approximately 28-38 µm and their volume under the action of the gas can increase by even more than 40 times. The percentage of EXPANCEL® ranges preferably from 1 to 5% of the final weight of the mixture.

The second product used in combination with EXPANCEL® is HYDROCEROL®, a chemical compound which contains calcium oxide, which under the action of heat (heating temperature of approximately 140-160 °C) breaks down, releasing CO₂, and therefore the particles of this gas allow to increase the flexibility and elasticity of the product. The percentage of HYDROCEROL® ranges preferably from 1 to 10% of the final weight of the mixture.

EXPANCEL® is produced by the EXPANCEL company, with headquarters in Sundsvall (Sweden), while HYDROCEROL® is a product of Clariant Masterbach GmbH & Co. OHG, with headquarters in Ahrensburg (Germany).

It is possible to use as filler calcium carbonate in a preferred percentage ranging from 5 to 25% calculated on the total weight of the mixture. Due to its fine particle size, calcium carbonate facilitates nucleating action and cell formation; moreover, if it is present in suitable proportions, it increases the cooling rate of the mixture.

As regards polyethylene, linear low-density polyethylene (LLDPE) is preferably used. Low-density polyethylene is very easy to mold, has good chemical resistance, and is highly impact-resistant at low temperatures. Moreover, its structure facilitates resistance to prolonged exposure to high-medium temperatures such as those that occur during wine pasteurization. The percentage of LLDPE that is present in the mixture ranges preferably

from 5 to 15%.

As regards EVA (ethylene vinyl acetate), the percentages of VA (vinyl acetate) range preferably from 9 to 18% and the values of MFI (ASTM D 1238) range preferably from 2 to 12 gr/10 min (weight 2.16 kg).

5 "MFI" stands for Melt Flow Index, a parameter which indicates the viscosity of the polymer in the melted state; in particular, the higher the MFI, the higher the fluidity of the substance, where the MFI is used as control parameter. The addition of EVA allows to increase the flexibility and impact resistance at low temperatures of the mixture. It is added in percentages
10 ranging preferably from 30 to 70% on the total weight of the mixture.

The two preferred blowing agents according to the present invention act inside the mixture differently due to the different mechanical characteristics and dimensions of the cells that they form. EXPANCEL® (a blowing agent of the physical type) forms rigid cells, which when
15 compressed undergo deformation and tend to recover rapidly their original shape due to the action of the gas that they contain. The HYDROCEROL® blowing agent (a blowing agent of the chemical type) instead forms hollows inside the matrix of the polymeric mix, caused by the gas released due to the heat, which penetrate between the microspheres of EXPANCEL®. These
20 hollows allow to reduce the density of the mixture and increase the deformation capacity.

This combination allows to achieve the best results in terms of flexibility, elastic recovery and post-process dimensional stability, allowing the stoppers inserted in the bottle to withstand pressures higher than 3 atm,
25 i.e., pressures typical of sparkling wines.

Therefore, the stoppers according to the invention are particularly suitable for use in the food industry in order to close glass bottles which contain wines and liqueurs.

The stoppers according to the invention can be prepared industrially
30 according to the technologies that are typical of the field.

The disclosures in Italian Patent Application No. MI2005A000129 from which this application claims priority are incorporated herein by reference.

CLAIMS

1. A synthetic stopper for use in bottles for food applications, characterized in that said stopper is based on the elastomeric block copolymer SEEPS (styrene-ethylene-ethylene/propylene-styrene) containing
5 approximately 30% styrene.
2. The synthetic stopper according to claim 1, characterized in that the SEEPS copolymer is a mixture of SEPTON® with medium and high molecular weight.
3. The synthetic stopper according to claim 1 or 2, characterized in
10 that the stopper further comprises paraffin oil.
4. The synthetic stopper according to claim 3, characterized in that the paraffin oil is present in an amount ranging from 5 to 30% on the total weight of the mixture.
5. The synthetic stopper according to claim 3, characterized in that the
15 stopper further comprises one or more blowing agents.
6. The synthetic stopper according to claim 5, characterized in that the blowing agent is a mixture of EXPANCEL® and HYDROCEROL®.
7. The synthetic stopper according to claim 6, wherein EXPANCEL® is present in a percentage preferably ranging from 1% to 5% and
20 HYDROCEROL® is present in a percentage ranging from 1% to 10% by weight, calculated on the final weight of the mixture.
8. The synthetic stopper according to claim 3, characterized in that the stopper further comprises a filler.
9. The synthetic stopper according to claim 8, characterized in that the
25 filler is calcium carbonate.
10. The synthetic stopper according to claim 9, characterized in that the calcium carbonate is present in a percentage ranging from 5% to 25% by weight, calculated on the final weight of the mixture.
11. The synthetic stopper according to claim 3, characterized in that
30 the stopper further comprises polyethylene.

12. The synthetic stopper according to claim 11, characterized in that the polyethylene is of the linear low-density type (LLDPE).

13. The synthetic stopper according to claim 12, characterized in that the polyethylene is present in a percentage ranging from 5% to 15% by weight, calculated on the final weight of the mixture.

14. The synthetic stopper according to claim 3, characterized in that the stopper further comprises ethylene vinyl acetate.

15. The synthetic stopper according to claim 14, characterized in that the percentages of vinyl acetate range from 9% to 18%.

16. The synthetic stopper according to claim 15, characterized in that the ethylene vinyl acetate is present in a percentage ranging from 30% to 70% by weight calculated on the final weight of the mixture.

17. The stopper according to one or more of the preceding claims for use in glass bottles.

18. The stopper according to one or more of the preceding claims, for use in bottles containing wines and liqueurs.