Title: COMPOSITE STOPPER MADE OF SYNTHETIC MATERIALS

Abstract: A composite stopper (1) made of synthetic materials, particularly for bottles and similar containers, comprises a substantially cylindrical central body (2) made of thermoplastic material and defining a longitudinal axis (L), with a side surface (3) and two substantially flat end faces (4, 4'), and at least two elastic rings (5, 6) located in corresponding annular seats (7, 7') on the side surface (3). The two elastic rings (5, 6) are made of plastic materials which are different from each other and from the base material of the central body (2). The base materials of the elastic rings (5, 6) are non-toxic, in particular at least one of them being made of nitrile rubber having a formulation able to ensure optimum gas impermeability, and at least the other one being made of silicone rubber having a formulation able to ensure complete compatibility for alimentary use and a high resistance to ageing.
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.
COMPOSITE STOPPER MADE OF SYNTHETIC MATERIALS

Technical field

The present invention is applicable in general in the field of stoppers for bottles and similar containers and relates in particular to a composite stopper made of synthetic materials according to the preamble of Claim 1.

Background art

In the wine-making industry, the most widely known stoppers for bottles are traditional stoppers made of cork.

Although for the user cork stoppers are synonymous with quality, the industry is starting to use stoppers made of plastic material. Research has led to a new generation of stoppers, made of various types of thermoplastic materials, such as polypropylene. Some synthetic stoppers comprise thermoplastic polyolefins, thermoplastic rubbers and wax-based additives. Stoppers made of thermoplastic materials have a number of objective advantages.

The increase in demand for cork and the limited resources available make cork stoppers increasingly expensive. On the other hand, the base materials for synthetic stoppers are practically inexhaustible. In addition to this, the methods for manufacturing them may be automated easily, making the unit cost of a synthetic stopper highly competitive.

Cork stoppers may have internal cavities and suffer from flaking owing to their structural form and also, in some cases, poor drying. Synthetic stoppers, however, are made of thermoplastic material and have a coherent mass owing to the raw materials which have a constant density and compression during the moulding step. These differences in characteristics result, only in the case of cork stoppers, to oxidation and lack of uniform vinification between bottles in the same batch.
Cork has an elastic hysteresis curve with a long recovery time, meaning it is slow to recover its original volume following the compression undergone during bottling. On the other hand, the plastic materials generally used in this sector have a much faster hysteresis curve. This means that bottles with cork stoppers may loose some of the liquid inside immediately after bottling and must be kept at an angle and in a damp environment in order to assist the absorption of moisture by the stopper and its consequent expansion. Bottles with synthetic stoppers, however, may be handled immediately after bottling and may be stored in a vertical position, saving space and volume, and do not require a damp environment.

The structure and shape of cork stoppers depend on numerous factors, including the region of origin, the thickness and density of the bark, the ageing after harvesting and the degree of processing and finishing. Stoppers which are nominally identical, but which in practice differ notably from each other, create problems during the automatic bottling step and are unpredictable as regards sealing of the bottled product over time. Stoppers made of plastic material are generally manufactured by means of injection moulding with dimensional tolerances smaller than those of cork and using a highly repeatable process. This ensures more reliable results as regards automatic handling of the stoppers and constant sealing of the bottled wine over time.

Cork is an organic material and, as such, may in many cases be attacked by mould. The smell of mould contaminates the contents of the bottle with an incidence which varies between 0.5% and 10%. The plastic materials used to make stoppers, however, are inert and free from contamination.

In practice, it has been observed that well-known synthetic stoppers, such as that described in US patent No. 5,496,862, despite having numerous advantages compared to cork stoppers, have a lower sealing action in the long term. Cork has the advantage that, in the presence of external moisture and a damp surrounding environment, it expands until it adheres completely to the inner walls of the bottle. Ordinary stoppers made of thermoplastic material only absorb moisture in
negligible quantities and can only rely on their intrinsic resilience to adhere to the inner walls of the bottle. Gaps are therefore created between the stopper and the glass wall and, via them, oxygen is able to filter from the surrounding atmosphere into the bottle.

US patent No. 5,904,965 describes a synthetic-material stopper which is formed by a rigid inner portion and a covering layer having a greater density and may be engaged in the neck of the bottle by means of friction. This solution, in addition to being expensive, does not completely eliminate the formation of gaps between the stopper and the glass, and therefore oxidation of the bottle’s contents.

US patent No. 6,179,138, European patent No. 0,629,559 and French patent No. 2,731,677 describe stoppers which have on their external surfaces annular elements able to interact with the inner wall of the bottle and prevent oxygen from entering the bottle.

A limitation of these solutions consists in the fact that the annular elements are all made from the same material and sometimes from the same material used for the central portion of the stopper.

In order to guarantee the sealing action, the material used for said annular elements must therefore embrace various properties, such as high elasticity, low gas permeability, high compatibility for alimentary use and a cost which is not excessively high. It is difficult to achieve a good compromise between these properties without affecting the sealing action of the stopper.

**Disclosure of the invention**

A primary object of the present invention is that of eliminating the abovementioned drawbacks by providing a stopper made of plastic material, which stopper is effective and has a relatively low unit cost.
A particular object is that of providing a stopper which has optimum features as regards sealing action, prevention of loss of the liquid contents and instantaneous elastic recovery after bottling.

A further object of the invention is that of providing a stopper which allows the bottles to be laid down or handled immediately after bottling and be stored in a vertical position, saving space and volume.

A further particular object is that of providing a stopper which does not require a damp environment in order to guarantee the sealing action preventing the passage of air and gas.

A further object of the invention is that of providing a stopper whose dimensions, surface characteristics and compactness are repeatable and suitable for automatic handling.

These objects, together with others which appear more clearly hereinafter, are achieved, according to Claim 1, by a composite stopper made of synthetic materials, in particular for bottles and similar containers, comprising a substantially cylindrical central body made of thermoplastic material and defining a longitudinal axis, with a side surface and two substantially flat end faces, and at least two elastic rings located in corresponding annular seats on said side surface, characterized in that the elastic rings are made of elastomeric materials which are different from each other and from the base material of the central body.

Conveniently, the base materials of the elastic rings are non-toxic and, in particular, at least one of them is made of nitrile rubber and the other of silicone rubber.

Owing to this particular configuration, it is possible to reconcile in a single composite stopper different characteristics, such as a high sealing action against
air and gas, total compatibility for alimentary use, optimum tolerances in terms of
dimensions and form, and structural compactness.

Preferably, the minimum diameter of the annular seats is slightly greater than the
inner diameter of the elastic rings at rest. In this way, the elastic rings are retained
in the corresponding annular seats without adhesives and only by virtue of their
elastic properties.

Thanks to these features, it is possible to provide a composite stopper which is
devoid of any type of adhesive and, therefore, has a high compatibility for
alimentary use and is easy to assemble.

Moreover, with said configuration, it is possible to obtain a stopper which, owing to
its own elasticity, adapts its shape rapidly to the neck of the bottle and ensures
that there are no losses immediately after bottling.

**Brief description of the drawings**

Further features and advantages of the invention will be more clearly understood
from the detailed description of a number of preferred but not exclusive embodi-
ments of the stopper according to the invention, illustrated by way of a non-
limiting example with the aid of the accompanying figures, in which:

Fig. 1 shows a side view, in partial cross section, of the stopper according
to the invention as a whole;

Fig. 2 shows a cross-sectional side view of a component of the stopper
according to the invention;

Fig. 3 shows a side view of another component of the stopper according to
the invention.

**Detailed description of a preferred embodiment**
With particular reference to the abovementioned figures, a stopper is shown according to the invention, denoted in its entirety by reference number 1 and suitable in particular for bottles and similar containers.

The stopper 1 comprises a substantially cylindrical central body 2 made of thermoplastic material defining a longitudinal axis L. This central body 2 has a side surface 3 and two substantially flat end faces 4, 4' which are mutually parallel and perpendicular to the axis L. At least two elastic rings 5, 6 are housed in corresponding annular seats 7, 7' on the side surface 3. Said elastic rings 5, 6 are both made of non-toxic material.

The central body 2 and the two elastic rings 5, 6 are made of three different plastic materials. In particular, the central body 2 is made of thermoplastic material, preferably polypropylene, while a nitrile rubber is used for the elastic ring 5 and a silicone rubber for the ring 6.

The nitrile rubber used is a butadiene/acrylonitrile copolymer and is such that it ensures optimum air and gas impermeability. Further formulations are possible in order to increase in particular the gas impermeability of the nitrile rubber. The silicone rubber used is a polysiloxane polymer and has a formulation able to guarantee complete compatibility for alimentary use, a very high resistance to ageing, physiological and biological non-toxicity, and almost total resistance to micro-organisms, such as bacteria and fungi.

The elastic rings 5, 6 have a roughly toroidal form with an internal diameter DI which, at rest, is smaller than the minimum diameter DM of the annular seats 7, 7'. During assembly of the stopper, the elastic rings 5, 6 are stretched and then inserted into the seats 7, 7', where they remain elastically under tension owing to the fact that the internal diameter DI of the elastic rings 5, 6 increases until it is the same as the minimum diameter DM of the annular seats 7, 7'. The elastic rings 5, 6 are retained in their seats 7, 7' only by virtue of their elastic properties and the use of any adhesive is not envisaged.
The elastic ring 5 made of nitrile rubber and the elastic ring 6 made of silicone rubber form a first pair 8 of elastic rings arranged longitudinally staggered at a predetermined distance. Preferably, the pair 8 of elastic rings 5, 6 is located close to one of the two flat faces 4, 4' of the central body 2.

In addition to the first pair 8, the stopper 1 comprises a further elastic ring 9 made of nitrile rubber and a further elastic ring 10 made of silicone rubber. These further elastic rings 9, 10 are arranged longitudinally staggered at a predetermined distance in two further annular seats 11, 11' on the side surface 3 so as to form a second pair 12 of elastic rings 9, 10. The second pair 12 is positioned on the side surface 3 so as to form a mirror image of the pair 8 of elastic rings with respect to a central plane P of said central body 2, said central plane being parallel to said flat faces 4, 4'. This means that the two pairs 8, 12 of elastic rings are close to either longitudinal end of the central body 2. This mirror-image arrangement of the two pairs 8, 12 and the total interchangeability between the rings 5, 9 and the rings 6, 10 mean that the stopper 1 may be inserted into the neck of the container or bottle irrespective of which end faces inwards.

The elastic rings 6, 10 made of silicone rubber of both the pairs 8, 12 are located closer to the flat faces 4, 4' than the elastic rings 5, 9 made of nitrile rubber.

From an operational point of view, the stopper 1 is inserted by means of pressure into the neck of the container or bottle so that all the elastic rings 5, 6, 9, 10 are compressed against the inner surface of the neck of the bottle. The elastic rings 5, 6, 9, 10, despite being under tension in the respective annular seats 7, 7', 11, 11', retain a certain residual elasticity, which allows them to deform elastically on coming into contact with the inner wall of the neck of the bottle. This means that the elastic rings 5, 6, 9, 10 adhere completely to the bottle neck along their entire circumference.

At this point, it is possible to understand why the elastic rings 6, 10 made of
silicone rubber, as opposed to the elastic rings 5, 9 made of nitrile rubber, have 
been positioned at the ends. In this way, when the stopper 1 is inserted, the liquid 
contained may only come into contact with one of the two elastic rings 6, 10 made 
of silicone rubber, which is distinguished by the complete absence of toxicity and 
the high degree of compatibility for alimentary and even sanitary use. Therefore, 
the ideal positioning of the elastic rings 6, 10 is in the areas of the stopper which 
may interact most easily with the contents of the bottle on one side and with the 
external environment on the other side, namely the portions close to the 
longitudinal ends of the stopper 1. The elastic rings 5, 9 made of nitrile rubber, 
however, are distinguished by their optimum air and gas impermeability and may 
therefore perform their tasks in an optimum manner when positioned further inside 
longitudinally.

From what has been described above, it is clear that the stopper according to the 
invention achieves the predetermined objects and, in particular, guarantees a high 
performance in terms of sealing action and preventing losses of the liquid inside 
the bottle. Moreover, the stopper has a low unit cost because it may be 
manufactured easily and handled automatically, and its manufacturing process 
results in low dimensional tolerances, a reduced number of rejects and low degree 
of non-conformity.

The stopper according to the invention may be subject to numerous modifications 
and variations, all of which fall within the inventive idea expressed in the 
accompanying claims. All the details may be replaced by other technically 
equivalent elements and the materials may by different according to the 
requirements, without departing from the scope of the invention.

Although the stopper is described with particular reference to the accompanying 
drawings, the reference numbers employed in the description and the claims are 
used to facilitate understanding of the invention and do not constitute any limitation 
on the protective scope claimed.
CLAIMS

1. Composite stopper (1) made of synthetic materials, particularly for bottles and similar containers, comprising a substantially cylindrical central body (2) made of thermoplastic material and defining a longitudinal axis (L), with a side surface (3) and two substantially flat end faces (4, 4'), and at least two elastic rings (5, 6) located in corresponding annular seats (7, 7') on said side surface (3), characterized in that said at least two elastic rings (5, 6) are made of plastic materials which are different from each other and from the base material of said central body (2).

2. Stopper according to Claim 1, characterized in that the base materials of said at least two elastic rings (5, 6) are non-toxic.

3. Stopper according to Claim 2, characterized in that at least one of said elastic rings (5, 6) is made of nitrile rubber having a formulation able to ensure optimum gas impermeability.

4. Stopper according to Claim 3, characterized in that at least the other of said elastic rings (5, 6) is made of silicone rubber having a formulation able to ensure complete compatibility for alimentary use and a high resistance to ageing.

5. Stopper according to Claim 1, characterized in that the minimum diameter (DM) of said annular seats (7, 7') is slightly greater than the inner diameter (DI) of said elastic rings (5, 6) at rest.

6. Stopper according to Claim 5, characterized in that said elastic rings (5, 6) are retained in said annular seats (7, 7') without adhesives by their own elastic properties.

7. Stopper according to Claim 4, characterized in that said at least two elastic rings (5, 6) comprise at least one first pair (8) of rings which are
longitudinally staggered and located at a predetermined distance, one ring (5) of said pair (8) being made of nitrile rubber and the other (6) being made of silicone rubber.

8. Stopper according to Claim 7, characterized in that said first pair (8) of elastic rings (5, 6) is located close to one of said end faces (4, 4').

9. Stopper according to Claim 8, characterized in that said at least two rings comprise at least one second pair (12) of rings (9, 10) which are longitudinally staggered and located at a distance similar to that of the first pair (8), one ring (9) of said second pair (12) being made of nitrile rubber and the other (10) being made of silicone rubber.

10. Stopper according to Claim 9, characterized in that said predetermined distance between the rings (5, 6, 9, 10) of said first and second pair (8, 12) is relatively small with respect to the total length of said central body (2).

11. Stopper according to Claim 10, characterized in that said first and second pair (8, 12) of rings (5, 6, 9, 10) are arranged in substantially symmetrical positions with respect to a central plane (P) of said central body (2), said central plane being substantially perpendicular to said longitudinal axis (L).

12. Stopper according to Claim 11, characterized in that the elastic rings (6, 10) made of silicone rubber of said first and said second pair (8, 12) are closer to said end faces (4, 4') than the elastic rings (5, 9) made of nitrile rubber of the same pairs (8, 12).

13. Stopper according to Claim 1, characterized in that the material of said central body (2) is polypropylene.