Preform, method for producing a preform and a container

A preform has a body (3) comprising layer means (6, 8; 29, 30) and barrier means (7; 7'; 31) adjacent to said layer means (6, 8; 29, 30), said barrier means (7; 7'; 31) being substantially impermeable to visible light, said layer means (6, 8; 29, 30) and said barrier means (7; 7'; 31) being made of polyethylene terephthalate; a method for obtaining a preform (1; 1') comprises providing a body (3) of said preform (1; 1') provided with layer means (6, 8; 29, 30) and barrier means (7; 7'; 31) adjacent to said layer means (6, 8; 29, 30), said barrier means (7; 7'; 31) being substantially impermeable to visible light, said providing comprising forming said layer means (6, 8; 29, 30) and said barrier means (7; 7'; 31) by co-injection; a container delimited by wall means (5, 13) comprising layer means (14, 15; 29, 30) and barrier means (16; 16'; 31) adjacent to said layer means, said barrier means being substantially impermeable to visible light, wherein said layer means (14, 15; 29, 30) and said barrier means (16; 16'; 31) is made of polyethylene terephthalate.
Description

[0001] The invention relates to a preform, starting with which it is possible to obtain a container, for example a bottle by "blow moulding" techniques such as stretch-blow-moulding. The invention furthermore relates to a method for producing such a preform. Lastly, the invention relates to a container, for example a bottle obtained by shaping the preform.

[0002] In the packaging of food products, such as milk, it is advisable to use containers having properties of barriers to visible light in such a way as to prevent or slow down the processes of degradation of the food products that are activated in the presence of light.

[0003] In order to overcome these drawbacks, IT 139643 discloses a container suitable for containing milk and consisting of three layers of high-density polyethylene (HDPE). These layers comprise a first external layer containing titanium dioxide, a second intermediate layer containing carbon black and a third internal layer that may contain titanium dioxide. The first external layer enables the light rays to be stopped that have a wavelength equal to or greater than 800 nanometres, whereas the second intermediate layer enables the light rays to be stopped that have a wavelength that is less than 800 nanometres, between which visible light is comprised. The third internal layer prevents the milk contained in the container from coming into contact with the carbon black contained in the second intermediate layer.

[0004] The containers according to IT 139643 are obtained by a process of coextrusion in which the polymers, initially in the form of granules or powder, intended to form the three layers disclosed above, are heated to the softening temperature and are subsequently extruded through the respective extrusion outlets such as to obtain the container, for example the bottle, according to the desired geometry.

[0005] The companies that package and market food products inside containers of the type disclosed in IT 139643 must be equipped in such a way as to carry out by themselves the process of coextrusion and subsequently fill the containers obtained by the process with the desired food product. In order to do so, the companies must be equipped with relatively big extrusion machines provided with a polymer supply zone, a softening zone comprising respective extrusion screws and finally an outlet zone in which the extrusion outlets are located. It is furthermore necessary to provide storage areas of the raw materials, namely polymers in the form of granules or powder, normally arranged outside the production facilities and provided with silos of great capacity.

[0006] The coextrusion process is relatively difficult to control inasmuch as a large number of process parameters has to be monitored and it is necessary to ensure that their value remains within preset ranges.

[0007] Lastly, the HDPE containers disclosed in IT 139643 have relatively high permeability to the oxygen contained in the air, which means that when the contain-
as better seen from the enlarged detail in Figure 1, an
stretch-to handle it during the forming process. At the end of the collar or ring 10 that enables the preform to be grasped the threaded end 2 and the body 3 there is interposed a site the threaded end 2 by a concave wall 18. Between a substantially cylindrical shape closed at its end oppo-
tainer 11. The body 3 comprises a tubular wall 9 having ed end 2 suitable for forming a threaded neck of the con-
[0023] The preform 1 comprises a body 3 and a thread-
ed end 2 and the collar 10 remain substantially undeformed whereas the body 3 is shaped in such a way as to form a wall 13 of the container 11.
[0024] The body 3 is made of three layers comprising, as better seen from the enlarged detail in Figure 1, an
internal layer 6, an external layer 8 and a barrier layer 7 interposed between the internal layer 6 and the external layer 8. Both the internal layer 6 and the external layer 8 and the barrier layer 7 are made of polyethylene terephthalate (PET).
[0025] In particular, the barrier layer 7 contains pig-
ments that make it substantially impermeable to visible light so as to protect the contents of the container 11 from light rays, thereby extending its shelf life. For example, the barrier layer 7 can be made of PET coloured black, comprising a transparent (Clear) polymer mixed with a black polymer (Master Batch) or mixed with a black pig-
ment in liquid paste. Both the transparent polymer and the black polymer intended to form the barrier layer 7 can be totally or partially obtained from virgin or recycled PET (PC-PET, post-consumer plastics, and/or processing off-
cuts of PET).
[0026] The black colour can be obtained by using car-
bon black. In order to have good light barrier properties it is also possible to use, in addition to carbon black, or as an alternative to it, other materials such as iron pow-
ders, aluminium powder, black iron oxides, organic and inorganic grey and/or amber and/or brown and/or green and/or blue dyes with absorption of the visible light be-
tween 350nm and 600nm.
[0027] A possible composition of the barrier layer 7 comprises clear polymer and black pigment, the latter being present in percentages varying between 2% and 8% in weight of clear polymer. In this composition, the pure carbon black represents about 25% of the black colouring master batch.
[0028] The internal layer 6 is made of PET suitable for contact with food products whereas the external layer 8 is chosen in such a way as to be aesthetically pleasing to the user. In particular, the internal layer 6 and the ex-
ternal layer 8 can both be formed of white-coloured PET in such a way as to suggest an impression of hygiene and cleanliness.
[0029] The white dye contained in the external layer 8 and in the internal layer 6 has a good capacity of reflection of the visible light and of the radiation with wavelengths longer than 800nm.
[0030] Furthermore, the combination of the colouring additives with the PET polymer enables the reflecting of the light rays to be improved.
[0031] The white-coloured PET comprises a transpar-
ent (clear) polymer mixed with a white polymer (master batch) or mixed with a white dye in liquid paste. Both the transparent polymer and the white polymer are obtained from virgin material, i.e. which is not recycled to ensure maximum safety when the container is in contact with the food product. The white colour can be obtained by using titanium dioxide and/or zinc oxide and/or calcium carbonate and/or magnesium carbonate and/or barium sulphate. To the white colour slightly yellow or cream-coloured shades can be added with the addition of a suit-
able colouring mixture. In a possible composition, the white dye is present in a percentage varying between 2%

Figure 1 shows a schematic section of a preform with three layers;
Figure 2 shows a schematic section of a container with three layers obtained by stretch-blow-moulding from the preform shown in Figure 1;
Figure 3 shows a schematic section of a preform with three layers according to an alternative version;
Figure 4 shows a schematic section of a container with three layers obtained by stretch-blow-moulding from the preform shown in Figure 3;
Figure 5 shows an enlarged detail of a wall of a con-
tainer with five layers.

[0020] With reference to Figure 1, there is shown a preform 1 that is usable to obtain a container 11 by stretch-blow-moulding, for example a bottle, of the type shown in Figure 2.
[0021] The preform 1 is particularly suitable for forming a container 11 intended to receive a food product, for example fresh pasteurised milk, extended shelf life ESL pasteurised milk, long-life UHT milk, cream, fermented milks, milk-based liquid products and fermented milk-
based products with the addition of other ingredients, fruit juices or the like, drinks containing fruit juices and milk and/or yoghurt.
[0022] Filling of the bottles/containers obtained from the preforms of the present invention occurs with liquid food products at a temperature of between 0°C to 50°C.
[0023] The preform 1 comprises a body 3 and a thread-
ed end 2 suitable for forming a threaded neck of the con-
tainer 11. The body 3 comprises a tubular wall 9 having a substantially cylindrical shape closed at its end oppo-
site the threaded end 2 by a concave wall 18. Between the threaded end 2 and the body 3 there is interposed a collar or ring 10 that enables the preform to be grasped to handle it during the forming process. At the end of the stretch-blow-moulding process of the container 11, the threaded end 2 and the collar 10 remain substantially undeformed whereas the body 3 is shaped in such a way as to form a wall 13 of the container 11.
[0024] The body 3 is made of three layers comprising, as better seen from the enlarged detail in Figure 1, an
and 10% in weight of the clear polymer and the pure titanium dioxide forms about 65% of the white colouring master batch.

The thickness of the body 3 is comprised between 2.5 and 5 mm and preferably varies between 3.0 and 3.2 mm.

The preform 1 is manufactured by a process of co-injection of the type disclosed in US 5582851, WO 99/22926, WO 99/59795, WO 01/34378 or WO 2004/067254. Reference is made to the above patent documents, the contents of which are included here, for a detailed description of the process of co-injection and of the apparatuses in which the process can be actuated.

In these apparatuses, the clear polymer is first mixed with the white polymer or the white dye in the quantities indicated previously so as to obtain a white-coloured PET that will constitute the internal layer 6 and the external layer 8. In similar ways, the clear polymer and the black dye or the black polymer are dosed in the requested quantities and are mixed so as to obtain a black-coloured PET that will constitute the barrier layer 7. The white-coloured PET and the black-coloured PET coming from respective supply conduits flow into a single injection conduit ending in a mould that reproduces the shape of the preform 1. The injection conduit, which may be selectively opened or shut by a shutting needle, is arranged near the concave wall 18. At the point in which the plastics enter the mould, a protuberance 19 remains on the concave wall 18. For reasons connected with the supply sequence of the white-coloured PET and of the black-coloured PET, and with their viscosity, the white-coloured PET is arranged in the mould in such a way as to form both the internal layer 6 and the external layer 8. These two layers thus have the same composition. The black-coloured PET forms the barrier layer 7 instead.

The known processes of co-injection of preforms fall into two categories, namely parallel-flow processes and step processes. In the first case, the flows of plastics intended to form the different layers of the preform advance simultaneously inside the mould in which the preform is obtained. In the step process, on the other hand, the plastics intended to form the different layers of the preform are injected one after another.

In an embodiment obtained by the parallel-flow process, the internal layer 6 could be formed of a quantity of plastics in a range around 20% in weight of the preform 1. The quantity of material used to form the barrier layer 7 may vary between 4% and 14% in weight of the preform 1. As a result, the material of the external layer 8 varies between 66% and 76% in weight of the preform 1. This means that the thickness of the internal layer 6 could be constant whereas the thickness of the barrier layer 7 and of the external layer 8 may vary according to the percentage in weight of plastics from which they are formed in relation to the weight of the preform 1.

In the version shown in Figure 1, the barrier layer 7 starts immediately below the collar 10 and extends along the entire body 3, it is namely present both in the tubular wall 9 and in the concave wall 18. On the other hand, the threaded end 2 has a single-layer structure. A preform of this type can be obtained by the process of parallel-flow co-injection.

Figure 2 shows a container 11 obtained from the preform 1 by a known process of stretch-blow-moulding. Inside the container 11 a cavity 4 is identifiable that is suitable for receiving contents, for example a food product, and is delimited by a side wall 13 and by a bottom wall 5. The container 11 furthermore comprises a threaded neck 12 on which a cap can be screwed that is not shown to close the container 11.

The side wall 13 and the bottom wall 5 comprise a first layer 14 facing the cavity 4, a second layer 15 facing the outside of the container 11 and an intermediate layer 16 interposed between the first layer 14 and the second layer 15. The first layer 14 is obtained by shaping the internal layer 6 of the preform 1, whereas the intermediate layer 16 and the second layer 15 are respectively obtained from the barrier layer 7 and from the external layer 8. Accordingly, the first layer 14 is made of white PET, the intermediate layer 16 is made of black PET and the second layer 15 is made of white PET. In particular, the intermediate layer 16 acts as a barrier to light enabling the contents of the container 11 to be protected from light rays.

With reference to the bottle-shaped container 11 with a body diameter of about 85 mm, 38 mm mouth diameter and about 250 mm height, the thickness of the first layer 14 can be comprised between 20 and 100 micrometers, the thickness of the second layer 15 between 100 and 200 micrometers and that of the intermediate layer 16 between 20 and 100 micrometers. In an alternative embodiment, shown in Figure 3, there is provided a preform 1’ that differs from the preform 1 shown in Figure 1 because it is provided with a barrier layer 7’ that affects only a part of the body 3. In particular, the barrier layer 7’ extends along the tubular wall 9, but not in the concave wall 18, which therefore has a single-layered structure. The barrier layer 7’ extends upwardly to the concave wall 18, which therefore has a single-layered structure. The barrier layer 7’ extends upwardly to the collar 10, as already disclosed with reference to Figure 1.

The barrier layer 7’, shaped as shown in Figure 3, can be obtained by the process of step co-injection. If this process is used, preforms are produced in which the internal layer 6 and the external layer 8 substantially have the same thickness. The barrier layer 7’ can be formed of a quantity of plastics that varies between 20% and 30% in weight of the preform 1’, whereas the internal layer 6 and the external layer 8 are each formed of a quantity of plastics variable between 40% and 35% in weight of the preform 1’.

By subjecting the preform 1’ to a process of stretch-blow-moulding, a container 11’ of the type shown in Figure 4 is obtained, provided with an intermediate layer 16’ that extends along the side wall 13, without however being present in the bottom wall 5. Even if the intermediate layer 16’ does not extend into the bottom wall 5, correct conservation of the food product arranged in-
side the container 11' is not compromised. The bottom wall 5 is in fact intended to be rested on a surface, for example of a shelf, and is not therefore hit by the light. A similar situation also occurs in the threaded neck 12, in which a cap normally engages that prevents the passage of light.

[0043] In a preform according to a version that is not shown, the barrier layer does not stop near the collar, but also extends through the threaded end.

[0044] In another embodiment, shown in Figure 5, the body of the preform and the walls of the container obtained therefrom can be provided with five layers comprising a first peripheral layer 29, a second peripheral layer 30 and barrier means 31 interposed between the first peripheral layer 30 and the second peripheral layer 29. The barrier means 31 comprises a first barrier layer 32 adjacent to the first peripheral layer 29 and a second barrier layer 33 adjacent to the second peripheral layer 30. Between the first barrier layer 32 and the second barrier layer 33 a central layer 34 is interposed.

[0045] The preform comprising the aforementioned five layers can be manufactured by means of co-injection, in particular of the parallel-flow type. In this case the first peripheral layer 29, the second peripheral layer 30 and the central layer 34 are made with a first common material, whereas the first barrier layer 32 and the second barrier layer 33 are formed of a second common material. In particular, the first barrier layer 32 and the second barrier layer 33 are substantially impermeable to light in such a way as to protect the food product contained inside the container. For this purpose, the first barrier layer 32 and the second barrier layer 33 can be made of black-coloured PET, having a composition similar to that previously disclosed with reference to the barrier layer 7 of the preform 1 shown in Figure 1. The first peripheral layer 29, the second peripheral layer 30 and the central layer 34 can on the other hand be made of a material suitable for contact with food products, for example the white-coloured PET in the compositions previously disclosed in Figure 1.

[0046] The plastics are distributed in the five layers that constitute the preform in this way: the central layer 34 comprises 20% in weight of the plastics constituting the preform, whereas the black-coloured PET forming the first barrier layer 32 and the second barrier layer 33 is present in a quantity varying between 4% and 5% in weight of the preform. As a result, the white-coloured PET that forms the first peripheral layer 29 and the second peripheral layer 30 varies between 75% and 76% in weight of the preform.

[0047] In an embodiment that is not shown, the preform and the container obtained from it may have a two-layer structure comprising a barrier layer in black-coloured PET and a layer in white-coloured PET arranged outside or inside the barrier layer.

[0048] The PET has good barrier properties to oxygen; nevertheless, it is possible to improve these properties, if for example a food product that easily deteriorates in the presence of even very small quantities of oxygen has to be packaged, by introducing a polymer with great impermeability to oxygen such as polyamide MXD6 in the PET of the intermediate layer. Furthermore, in the present invention it is possible to introduce into the intermediate-light barrier layer substances absorbing oxygen in such a way as to further improve the impermeability of the PET to oxygen and to thus confer particular protection on the food products that would otherwise be easily oxidizable. In this case substances are used such as reduced iron, Amosorb etc.

[0049] The invention was tested by manufacturing different preforms by triple-layer co-injection, each layer comprising a barrier layer in black-coloured PET with different percentages of black-coloured polymer varying from 2% to 6%; corresponding to percentages of pure carbon black varying from 0.5% to 1.5%. The barrier layer is interposed between an external layer and an internal layer in white-coloured PET obtained by adding varying quantities of white polymer to the transparent polymer.

[0050] The invention was furthermore tested by manufacturing triple-layer preforms with different additions of white polymer in such a way as to have in the internal and external layer percentages of transparent polymer from 4% to 8%; corresponding to percentages of pure Titanium dioxide from 2.6% to 5.2%.

[0051] The external layer consists of 70% in weight of the material making up the preform, whereas the barrier layer and the internal layer are respectively formed of 10% and of 20% of the total material.

[0052] Triple-layer preforms with different combinations of white and black colours have been made in accordance with the percentages quoted above.

[0053] The preforms disclosed above were subjected to a stretch-blow-moulding process using cavity moulds such as to obtain bottles of different shapes, each comprising a first layer arranged in the inside of the bottle and having a thickness of about 40 micrometers, a second layer arranged in the outside of the bottle and having a thickness of about 179 micrometers and an intermediate layer of about 38 micrometers. In order to check the high degree of protection of the barrier layer introduced with the present invention, filling of the bottles with a food product very sensitive also to oxygen such as milk was used. The bottles were aseptically filled at 28/30°C with UHT milk sterilised in a continuous flow with a direct treatment by steam injection or by steam infusion at temperatures comprised between 145°C and 150°C for periods from 1 to 4 seconds. The bottles containing UHT milk obtained in the different experimental conditions with triple-layer preforms of different composition of the colouring substances and with milk corresponding to different treatment conditions were subjected to long-life conservation tests. Some bottles were then exposed to natural light with a day-night cycle, at a temperature of about 20°C for three months whereas other bottles were exposed to artificial light in a continuous manner on display benches of commercial type at a temperature of about
20 °C for 6 weeks, corresponding to a period of three months with alternating light/dark cycle.

[0054] During the conservation tests and also at the end of the respective exposure periods the different milk properties were monitored by sensor panels and by chemical analyses; it was established that the milk was always of excellent quality both in the case of bottles exposed to artificial light and in the case of the bottles exposed to natural light.

[0055] This constitutes a significant improvement on the single-layer PET bottles, i.e. devoid of the intermediate layer substantially impermeable to light, in which the milk cannot be conserved for periods longer than 7 days.

Claims

1. Preform having a body (3) comprising layer means (6, 8; 29, 30) and barrier means (7; 7'; 31) adjacent to said layer means (6, 8; 29, 30), said barrier means (7; 7'; 31) being substantially impermeable to visible light, said layer means (6, 8; 29, 30) and said barrier means (7; 7'; 31) being made of polyethylene terephthalate.

2. Preform according to claim 1, wherein said barrier means (7; 7'; 31) is of a dark colour.

3. Preform according to claim 2, wherein said barrier means (7; 7'; 31) is black in colour.

4. Preform according to any preceding claim, wherein said barrier means (7; 7'; 31) are made of a material comprising a dye selected from a group consisting of: carbon black, grey dye, amber dye, brown dye.

5. Preform according to claim 4, wherein said barrier means (7; 7'; 31) comprises a quantity variable between 2% and 8% in weight of said dye.

6. Preform according to claim 4 or 5, wherein said dye comprises approximately 25% in weight of carbon black.

7. Preform according to any preceding claim, wherein said barrier means (7; 3'; 31) comprises recycled PET.

8. Preform according to any one of claims 1 to 6, wherein said barrier means (7; 3'; 31) comprises virgin PET.

9. Preform according to any preceding claim, wherein said layer means (6, 8; 29, 30) is made of a material suitable for coming into contact with food products.

10. Preform according to any preceding claim, wherein said layer means (6, 8; 29, 30) is of a light colour.

11. Preform according to claim 10, wherein said layer means (6, 8; 29, 30) is white in colour.

12. Preform according to any preceding claim, wherein said layer means (6, 8; 29, 30) contains a colouring substance selected from a group consisting of: titanium dioxide, zinc oxide, calcium carbonate.

13. Preform according to claim 12, wherein said layer means (6, 8; 29, 30) comprises a quantity variable between 2% and 10% in weight of said colouring substance.

14. Preform according to claim 12 or 13, wherein said colouring substance comprises about 65% in weight of titanium dioxide.

15. Preform according to any preceding claim, wherein said layer means (6, 8; 29, 30) comprises virgin PET.

16. Preform according to any preceding claim, wherein said layer means (6, 8; 29, 30) comprises an external layer (8; 30) and an internal layer (6; 29), said barrier means (7; 7'; 31) being interposed between said external layer (8; 30) and said internal layer (6; 29).

17. Preform according to claim 16, wherein said external layer (8; 30) and said internal layer (6; 29) have the same composition.

18. Preform according to claim 16 or 17, wherein said internal layer (6) is formed of a quantity of material equal to about 20% in weight of said preform (1), said barrier means (7) is formed of a quantity of material varying between 4% and 14% in weight of said preform (1) and said external layer (8) is formed of a quantity of material varying between 66% and 76% in weight of said preform (1).

19. Preform according to claim 16 or 17, wherein said internal layer (6; 29) and said external layer (8; 30) have a substantially equal thickness.

20. Preform according to claim 16, or 17, or 19, wherein said internal layer (6) is made of a quantity of material varying between 35% and 40% in weight of said preform (1'), said barrier means (7) is made of a quantity of material varying between 20% and 30% in weight of said preform (1') and said external layer (8) is made of a quantity of material varying between 35% and 40% in weight of said preform (1').

21. Preform according to any one of claims 16 to 20, wherein said barrier means (7; 7'; 31) comprises a single layer (7; 7') having a surface in contact with said external layer (8) and a further surface in contact
with said internal layer (6).

22. Preform according to any one of claims 1 to 20, wherein said barrier means (7; 7'; 31) comprises a first barrier layer (32) and a second barrier layer (33) between which there is interposed a central layer (34).

23. Preform according to claim 22, as appended to any one of claims 16 to 20, wherein said barrier means (7; 7'; 31) comprises a first barrier layer (32) and a second barrier layer (33) between which there is interposed a central layer (34).

24. Preform according to any preceding claim, wherein said body (3) comprises a side tubular wall (9), said barrier means (7) extending along said side tubular wall (9).

25. Preform according to any preceding claim, wherein said body (3) comprises an end wall (18), said barrier means (7) extending along said end wall (18).

26. Preform according to any preceding claim, and furthermore comprising a threaded end (2), said barrier means extending into said threaded end (2).

27. Method for obtaining a preform (1; 1'), comprising providing a body (3) of said preform (1; 1') provided with layer means (6, 8; 29, 30) and barrier means (7; 7'; 31) adjacent to said layer means (6, 8; 29, 30), said barrier means (7; 7'; 31) being substantially impermeable to visible light, said providing comprising forming said layer means (6, 8; 29, 30) and said barrier means (7; 7'; 31) by means of co-injection.

28. Method according to claim 27, wherein said layer means (6, 8; 29, 30) and said barrier means (7; 7'; 31) is made of polyethylene terephthalate.

29. Method according to claim 27 or 28, wherein said co-injection occurs by simultaneously injecting a first material forming said layer means (6, 8; 29, 30) and a second material forming said barrier means (7; 31).

30. Method according to claim 27 or 28, wherein said co-injection occurs by injecting in sequence a material forming said layer means (6, 8; 29, 30) and a further material forming said barrier means (7).

31. Method according to any one of claims 27 to 30, wherein said layer means (6, 8; 29, 30) comprises an external layer (8; 30) and an internal layer (6; 29), said barrier means (7; 7'; 31) being interposed between said external layer (8; 30) and said internal layer (6; 29).

32. Method according to claim 31, wherein said external layer (8; 30) and said internal layer (6; 29) are obtained by injecting into a mould material coming from a single supply channel.

33. Container delimited by wall means (5, 13) comprising layer means (14, 15; 29, 30) and barrier means (16; 16'; 31) adjacent to said layer means (14, 15; 29, 30), said barrier means (16; 16'; 31) being substantially impermeable to visible light, characterised in that said layer means (14, 15; 29, 30) and said barrier means (16; 16'; 31) are made of polyethylene terephthalate.

34. Container according to claim 33, wherein said barrier means (16; 16'; 31) is of a dark colour.

35. Container according to claim 34, wherein said barrier means (16; 16'; 31) is black in colour.

36. Container according to any one of claims 33 to 35, wherein said barrier means (16; 16'; 31) contains a dye selected from a group consisting of: carbon black, grey dye, amber dye, brown dye.

37. Container according to claim 36, wherein said barrier means (16; 16'; 31) comprises a quantity variable between 2% and 8% in weight of said dye.

38. Container according to claim 36 or 37, wherein said dye comprises approximately 25% in weight of carbon black.

39. Container according to any one of claims 33 to 38, wherein said barrier means (16; 16'; 31) comprises recycled PET.

40. Container according to any one of claims 33 to 38, wherein said barrier means (16; 16'; 31) comprises virgin PET.

41. Container according to any one of claims 33 to 40, wherein said layer means (14, 15; 29, 30) is made of a material suitable for coming into contact with food products.

42. Container according to any one of claims 33 to 41, wherein said layer means (14, 15; 29, 30) is of a light colour.

43. Container according to claim 42, wherein said layer means (14, 15; 29, 30) is white in colour.

44. Container according to any one of claims 33 to 43,
wherein said layer means (14, 15; 29, 30) is made of a material comprising a colouring substance selected from a group consisting of: titanium dioxide, zinc oxide, calcium carbonate.

45. Container according to claim 44, wherein said layer means (14, 15; 29, 30) comprises a quantity variable between 2% and 10% in weight of said colouring substance.

46. Container according to claim 44 or 45, wherein said colouring substance comprises about 65% in weight of titanium dioxide.

47. Container according to any one of claims 33 to 46, wherein said layer means (14, 15; 29, 30) comprises virgin PET.

48. Container according to any one of claims 33 to 47, wherein said layer means (14, 15; 29, 30) comprises a first layer (14; 29) facing the inside of said container (11; 11') and a second layer (15; 30) facing the outside of said container, said barrier means (16; 16'; 31) being interposed between said first layer (14; 29) and said second layer (15; 30).

49. Container according to claim 48, wherein said first layer (14; 29) and said second layer (15; 30) have the same composition.

50. Container according to claim 48 or 49, wherein said first layer (14) is made of a quantity of material equal to about 20% in weight of said container (11), said barrier means (16) is made of a quantity of material varying between 4% and 14% in weight of said container (11) and said second layer (15) is made of a quantity of material varying between 66% and 76% in weight of said container (11).

51. Container according to claim 48 or 49, wherein said first layer (14; 29) and said second layer (15; 30) have a substantially equal thickness.

52. Container according to claim 48 or 49 or 51, wherein said first layer (14) is made of a quantity of material varying between 35% and 40% in weight of said container (11'), said barrier means (16') is made of a quantity of material varying between 20% and 30% in weight of said container (11') and said second layer (15) is made of a quantity of material varying between 35% and 40% in weight of said container (11').

53. Container according to any one of claims 48 to 52, wherein said barrier means comprises a single layer (16; 16') having a surface in contact with said second layer (15) and a further surface in contact with said first layer (14).

54. Container according to any one of claims 33 to 52, wherein said barrier means (16; 16'; 31) comprises a first barrier layer (32) and a second barrier layer (33) between which there is interposed a central layer (34).

55. Container according to claim 54, as appended to any one of claims 48 to 52, wherein said central layer (34) is made of a quantity of material equal to about 20% in weight of said container, the whole of said first barrier layer (32) and of said second barrier layer (33) is made of a quantity of material varying between 4% and 5% in weight of said container and the whole of said first layer (29) and of said second layer (30) is made of a quantity of material varying between 75% and 76% in weight of said container.

56. Container according to any one of claims 33 to 55, wherein said wall means (5, 13) comprises a side wall (13), said barrier means (16; 16') extending along said side wall (13).

57. Container according to any one of claims 33 to 56, wherein said wall means (5, 13) comprises a bottom wall (13), said barrier means (16) extending along said bottom wall (13).

58. Container according to any one of claims 33 to 57, and furthermore comprising a threaded neck (12), said barrier means extending in said threaded neck (12).

59. Container according to any one of claims 33 to 58, and having the shape of a bottle.
## DOCUMENTS CONSIDERED TO BE RELEVANT

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- The present search report has been drawn up for all claims.
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**TECHNICAL FIELDS SEARCHED (IPC)**

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**CATEGORY OF CITED DOCUMENTS**

- T: theory or principle underlying the invention
- E: earlier patent document, but published on, or after the filing date
- D: document cited in the application
- L: document cited for other reasons
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- Y: particularly relevant if combined with another document of the same category
- O: non-written disclosure
- P: intermediate document
- S: member of the same patent family, corresponding document
CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):
  11-26, 33-59

- No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

- All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

- As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

- Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

- None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:
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