(12) UK Patent Application (19) GB (11) 2 139 647 A

(43) Application published 14 Nov 1984

(21) Application No 8404589

(22) Date of filing 22 Feb 1984

(30) Priority data
(31) 8305169 (32) 24 Feb 1983 (33) GB

(51) INT CL³
C23C 13/00 B65D 75/04 C23C 15/00

(52) Domestic classification
C7F 1V1 1V2 2A 2K 2Z11A2A 2Z11A2Y 2Z11AX 2Z11AY 2Z1 2Z3 2Z8 4H 4N 6A3 6A4 6A5 6D1A1 6F1 6F2
U1S 3028 3072 C7F

(56) Documents cited
GB A 2132229 GB 1489807

(58) Field of search
C7F

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(54) Bottled coated by ion-plating or magnetron sputtering

(57) The coating is typically transparent to visible light, but has a considerable degree of opaqueness to ultra-violet radiation, and is substantially impermeable to (atmospheric) gases and water vapour. The coating may be an oxide preferably indium oxide or nitride. The bottle is typically of plastics and is used for the storage of (typically carbonated) beverages.

In an alternative embodiment, rather than applying the coating to the bottle itself, the bottle is wrapped in a transparent plastics packaging material having an analogous coating.

GB 2 139 647 A

The drawing(s) originally filed was/were informal and the print here reproduced is taken from a later filed formal copy.

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FIG.1.

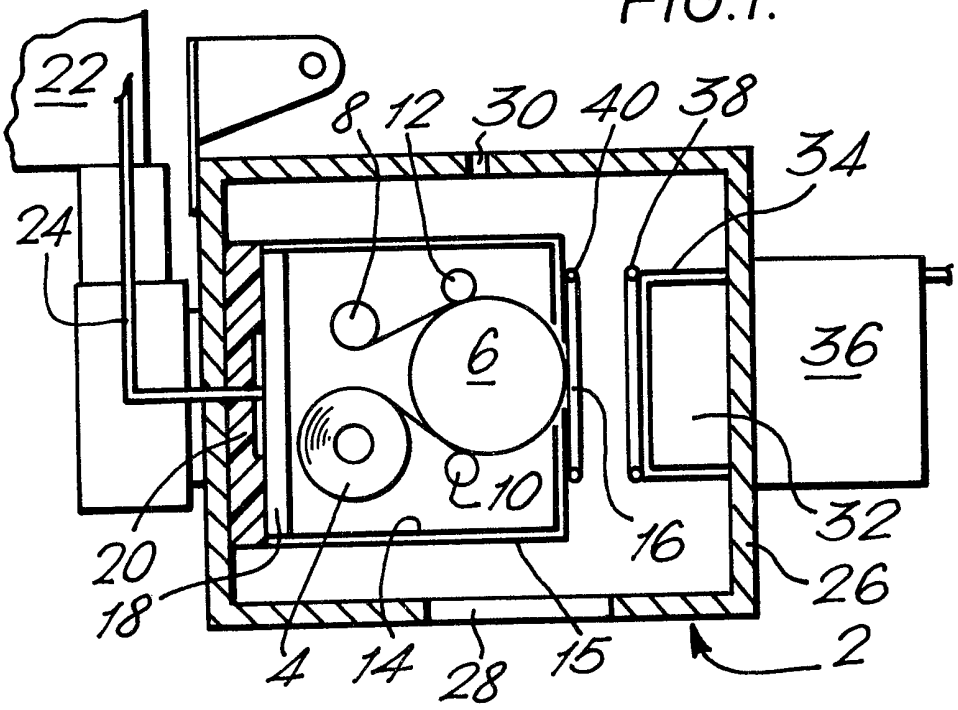
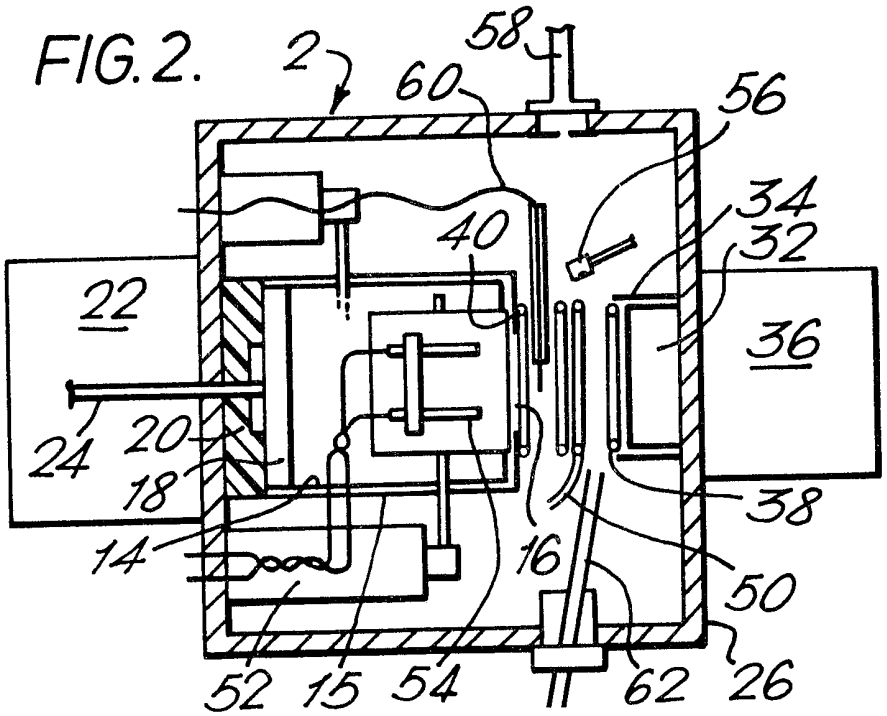


FIG.2.



SPECIFICATION

Containers

This invention relates to containers, particularly bottles for storing carbonated and other liquids which if desired may be potable.

Traditionally, carbonated beverages have been stored in flint white glass bottles. Forming the bottles of glass offers a number of advantages. Firstly, glass is a transparent, chemically inert substance. Thus, the purchaser of the bottle is able to see its contents and will known that there is no chemical reaction between the bottle and its contents that might adversely affect the quality of its contents. Second, closure technology has been developed to a point at which the bottles are for all practical purposes impermeable to gas. Indeed, using closures such as those of the metal roll on, crown and plastics types, carbonated beverages can be stored for period of the year or more without significant loss of carbonation. However, disadvantages are associated with the use of glass. First, glass is sharp and brittle. If it carries a local flaw, a thermal or mechanical shock applied to the flaw is known to cause the glass to shatter. The ballistic energy contained in the head space of a bottle of a carbonated beverage is then able to propel the resulting shattered glass fragments a considerable distance, thereby giving rise to significant risk of personal injury. The second disadvantage associated with the use of glass is that, in the soft drinks industry in particular, the very transparency of glass (which is in itselfaesthetically appealing) results in radiation, particularly in the UV range, being transmitted through the glass and causing photo-chemical degradation of substances dissolved in solution.

In recent years, a sizeable proportion of the market for glass bottles for containing carbonated beverages has given way to polyethylene terephthalate containers. Since this material is not brittle the hazard from explosive fragmentation associated with glass bottles is avoided. Nonetheless, there are disavantages associated with PET or other plastic bottles. First, although in comparison with other plastics PET is relatively impermeable to gas (and water vapour) its properties in this respect still fall far short of those of glass. Second, like glass, it transmits UV radiation.

Our co-pending application No. 8332792 entitled "Packaging" relates to a packaging material in which a plastics substrate bears a coating, said coating having been deposited on the substrate by an ion-plating method (typically a reactive ion-plating method) or a magnetron sputtering method. It is found that such a coating can improve the impermeability of the substrate to gas such as oxygen, and to water vapour, and can also be deposited such it is substantially opaque to ultra-violet radiation (or some wavelengths in the ultra-violet spectrum) while transmitting light in the visible spectrum. Another application of ion-plating is in the coating of lenses so as to render them opaque to ultra-violet radiation or at least some wavelengths in the ultra-violet spectrum. Such lenses can be used in spectacles or sunglasses and welder's goggles. We now believe that the ion-plating method may be used to deposit a thin layer or coating on a bottle, thereby making the bottle more suitable for the storage of for example carbonated beverages.

Accordingly, the present invention provides a bottle at least a part of whose external surface bears a coating, said coating having been deposited on the bottle by an ion-plating or magnetron spluttering method.

The coating may be of a chemical element deposited by a (non-reactive) ion-plating or magnetron sputtering method. The element may be a metal. Alternatively, it may be of an element such as silicon or germanium. It is also possible to deposit coatings of alloys. It is preferred however that the coating is deposited by a reactive ion-plating method and is a chemical compound, particularly an oxide (although for example a nitride coating may alternatively be used).

Although we do not wish to be limited by this theory, we believe that deposition of an oxide or nitride, in particular, by an ion-plating or magnetron sputtering method enables relatively large crystals to be formed in the coating, such crystals proving a barrier to the transmission of water vapour, oxygen or other gases.

We believe that coatings of oxides, in particular, and nitrides are preferable to coatings of the pure metal or alloy itself. Preferred coatings include indium oxide and tin oxide and mixed tin-indium oxide. The mixed tin-indium oxide may be formed by a reactive ion plating or magnetron sputtering method using a source of a chosen tin-indium alloy. The relative proportions of oxygen to metal atom or atoms in the coating may be chosen such that the oxide contains less than the stoichiometric quantity of oxygen, the stoichiometric quantity of oxygen, or, if this can be obtained, more than the stoichiometric quantity of oxygen. In general, it is preferred that the composition of the oxide is such that there is not a substantial deficit of oxygen. This, we believe, helps to keep to a minimum the number of sites in the crystal lattice of the coating through which oxygen can diffuse, although the invention should not be interpreted as being limited in any way by such theory.

The bottle is preferably of plastics material. (Although we do not exclude suitably coated glass bottles from the scope of this invention, it is to be appreciated that such bottles will still suffer from the drawback of being liable to undergo explosive fragmentation when subjected to mechanical or thermal shock). Typically, substantially all the external surface area of the bottle is coated, although, in general, it may not be necessary to coat the bottom of the bottle or its lip.

The bottle, be it of glass or plastics, may be colourless or flint white, or may be coloured e.g. amber or brown etc.

We believe that a bottle made of given plastics material and having a coating in accordance with the invention has a superior impermeability to atmospheric gases, carbon dioxide and water vapour than an uncoated bottle of the same plastics material. The plastics material of choice is typically transparent and may be polyethylene terephthalate, although other plastics materials, typically with inferior "barrier" properties to water vapour and carbon dioxide may be selected on the basis that such properties are improved by being coated in accordance with the invention. It is to be appreciated that the coating is typically formed as a thin layer such that (while it transmits visible light) it is substantially impermeable to ultra-violet radiation or at least the near visible part of the ultra-violet spectrum. This property thereby helps to improve the shelf life of beverages contained in bottles according to the invention where such beverages include one or more substances prone to decompose or be degraded on being subjected to ultra-violet radiation. Zinc oxide and indium oxide are particularly preferred coatings that can be deposited without substantially reducing the degree to which the substrate transmits visible light while at the same time substantially reducing the amount of UV (or of some wavelengths in the UV spectrum) that is transmitted. Typically, the coating may have a thickness in the order of a few hundreds of nanometres (say less than 500 nm). Preferably, at least if an oxide is the material of which the coating is formed, the thickness of the coating is less than 200 nm (and most preferably from 100 to 200 nm).

The invention includes within its scope a bottle according to the present invention holding a liquid, such as an (e.g. carbonated) beverage. The invention also includes within its scope methods of forming the bottles of the invention.

Ion-plating is the technique in which a DC potential or radio frequency bias is applied to or in front of the substrate (in this instance a bottle to be coated), and a glow discharge (or plasma) struck in an atmosphere of noble gas such as argon about the substrate such that the substrate is subject to continual noble gas ion bombardment. The source of the coating is desirably a planar magnetron spluttering source which itself is subject to a discharge.

It is possible however to use other kinds of sources particularly those that rely on bombardment of a target by charged or energetic particles (e.g. an electron beam). Evaporative sources are however not preferred. In reactive ion plating there is a partial pressure of a chemically active gas such as oxygen or nitrogen in the vicinity of the substrate such that there will be reaction between the metal sputtering source and the oxygen or nitrogen at the surface of the substrates; thus a metal oxide or nitride coating can be formed. With some source, for example, indium it is possible to deposit a coating by a magnetron sputtering method (preferably a planar magnetron sputtering method) without applying a DC or RF bias to or in front of the substrate. Although such a method can be referred to as an ion plating method, it is not so described herein. The term 'ion plating' is reversed herein for processes in which a DC or RF bias is applied to or in front of the substrate.

A reactive ion-plating process suitable for the manufacture of continuous ion-plated plastics sheet is described in the "The application of ion plating to the continous coating of flexible plastics sheet", Thin Solid Films, 80 (1981) pp.31 to 39, M.I. Ridge et al. The reader of this specification is particularly referred to the paper by ridge et al. It is to be appreciated that certain changes need to be made to the apparatus described by Ridge et al in order to coat bottles. However, it is still possible to use a planar magnetron sputtering source as described by a Ridge et al. In particular, it is necessary to substitute for the roll to roll feeder described by Ridge et al a suitable means for providing a rotary motion to the containers to enable them to be coated all round. It is for example possible to use a turntable with a plurality of planetary stations whereby the axial rotation of the table is able to move each station in turn past a planar magnetron or other sputtering source while the planetary motion of each station rotates each bottle through an angle of 360° as it passes the sputtering source to ensure that the containers are coated all round.

Alternatively, a so-called 'post cathode' may be employed at the centre of the turntable and be used to coat all the bottles on the table simultaneously. If necessary, the bottles may be reduced in temperature to below ambient temperature before being coated so as to dissipate the local heat created by the coating process and thereby to avoid causing the bottle to melt or otherwise damage them.

A planar magnetron supttering source for performing a reactive ion plating process is described in U.K. patent specification 1 489 807 and the reader's attention is also directed to this patent specification.

Instead of treating a plastics or other bottle according to the invention so as to reduce its transparency to UV radiation, the bottle may be wrapped (typically shrink wrapped) in a packaging material according to our aforesaid co-pending application, such packaging material being transparent to visible light but substantially opaque to ultra-violet radiation or at least a part of the ultra-violet spectrum. The chemical composition of the coating for such a wrapping may be the same as that described herein with reference to the coating for the container. The manufacture of such a coated wrapping is described by way of example with reference to the accompanying drawings in which:

Fig. 1 is a schematic drawing of a first ion plating apparatus for use in coating plastics films; and

Fig. 2 is a schematic drawing of a second ion plating apparatus for use in coating plastics films:

Fig. 1 and 2 of the accompanying drawings illustrate schematically the apparatus used to deposit coatings as described in the Examples below.

Referring to Fig. 1, an experimental ion plating apparatus 2 is shown. The apparatus 2 includes a set of rollers, including a roller 4 onto which plastics material is fed from the manufacturer's reel (not shown). During a coating operation, the plastics film is fed from the feed roller 4 around a main water-cooled roller 6 to a roller 8. The rollers 4, 6 and 8 each have full electronic motor control to ensure the correct tension of the plastics film during operation of the machine.

In addition, rubberised pinch rollers 10 and 12 co-operate with the roller 6 to prevent the plastics film from slipping on the surface of the roller 4. The rollers 4 and 8 act as tensioned unwind and rewind rollers respectively. Once loaded on the roller 4, the plastics material is cut and attached to the roller 8 on which it is rewound during subsequent coating operations.

The rollers 4, 6, 8, 10 and 12 are all located in an inner cage 14 which is in turn located within an outer cage 15. The cages 14 and 15 have contiguous openings 16 facing forwards to permit deposition of a coating on the plastics film as it passes along the opening in operation of the rollers. The opening 16 in the cage 15 is rectangular, being 60 mm by 80 mm.

The cage 14 is provided with water-cooled aluminium platten 18 in a rearward position and in electrically-conductive relationship with the cage 14. The platten 18 is insulated from earth by a polytetrafluoroethylene (PTFE) insulator 20. The drives (not shown) to rollers 4, 6 and 8 are also insulated. A radio frequency generator 22 is adapted to apply a radio frequency potential to the platten 18 through connectors 24. The generator 22 is an automatically controlled and tuned 2kw Plasma Therm HFS 2000D machine. The connectors 24 are water-cooled. The cage 15 connected to earth and in effect functions as a second electrode.

The rollers, the cage 14, which acts as an rf cage, the cage 15 which is earthed, and the platten 18 and insulator 20 are all located as a demountable assembly within an evacuable chamber 26, having a port 28 connectible to a vacuum (not shown) and a port 30 connectible to a Pirani gauge (not shown) or other vacuum measuring device.

A planar magnetron sputtering source 32 is provided within the chamber 26 opposite the opening 16 in the cage 15. The planar magnetron sputtering source 32 has associated therewith an earth shield 34, and water-cooled arc suppression means 36. The planar magnetron sputtering source has its own potential supply (not shown). A combination of motor generators and electronics supply was used to supply a DC potential to the sputtering source 32. An annular gas distributor 38 is located near to the planar magnetron sputtering source 32 and a similar distributor is about the opening 16 in the cage 15. The gas distributor 38 is connectible to a source (not shown) of argon under pressure and in operation distributes the argon generally radially inwards, and the gas distributor 40 is connectible to a source (not shown) of oxygen under pressure and adapted to distribute the oxygen radially inwards.

In operation, the chamber 26 is continuously evacuated, and typically an RF potential is applied to the platten 18 and the planar magnetron sputtering source 32 is activated. Plastics film is fed from the roller 4 to the roller 8 and passes along the opening 16 and argon and oxygen are passed into the chamber 26. The planar magnetron confines magnetically a toridal plasma of argon ions about the source to be sputtered. Atoms of the source material are thus emitted therefrom in the direction of the opening 16 in the cage 15. The rf potential creates a glow discharge about the plastics material to be coated, which glow discharge is confined to the region of the main roller 6. Typically a peak-to-peak rf suupply of 1000V may be employed. As the impinging atoms of the source material come into contact with oxygen on the surface of plastics film for the time being alongside the opening, an oxide coating is deposited. The thickness of the coating will depend on a number of parameters including the speed at which the plastics material is feed from the foller 4 to the roller 8. Typically, if the coating is electrically conducting, its resistance is monitored during its deposition and the rate at which oxygen is supplied controlled so as to give a constant resistance during deposition of a coating on a length of plastics film.

If desired, the apparatus shown in Fig. 1 may be operated purely as a planar magnetron

sputtering apparatus, in which instance no potential is applied to the electrode 18.

The apparatus shown in Fig. 2 is generally similar to that shown in Fig. 1 but includes an rf discharge coil 50 positioned intermediate the opening 16 and the planar magnetron sputtering source 32. This discharge coil 50 may be used as an alternative means of creating a bias in front of the substrate. The rf potential may be applied either to the electrode 18 or the coil 50 (but not to both) in the ion plating of a substrate. Applying the rf potential to the coil 50 rather than the electrode 18 enables the rollers 4, 6, 8, 10 and 12 to be earthed rather than being subject to an rf potential. For ease of illustration, the rollers 4, 6, 8, 10 and 12 are now shown in Fig. 2, but the main dirve unit 52 of the rollers is shown. Apart from the use of the coil 50, the operation of the apparatus shown in Fig. 2 is generally similar to that shown in Fig. 1.

Various means can be employed to control the deposition of coatings on the plastics film. Trailing contacts 54 may be employed to measure the electrical resistance of the coating. A quartz crystal monitor 56 can be used to measure the rate of deposition of the coating. A probe 58 leading to a mass spectrometer (not shown) can be used to measure the concentration of excited metal atoms emitted by the source. A probe 62 leading to a scanning spectrophotometer (not shown) may alternatively be used to monitor the concentration of metal atoms in the chamber 26. A Langmuir probe 60 may be used to measure the electrical characteristics of the glow discharge and hence to gain a measure of its chemical composition, and the induced dc bias in the coating may also be measured.

The apparatus shown in Fig. 1 was used to deposit the coatings in Examples 1 and 2 below, and the apparatus shown in Fig. 2 was used to deposit the coatings in Examples 3 to 10 below.

The invention is now illustrated by the following Examples. In each Example a length of Melinex (Registered Trade Mark) polyester (a polyethylene terephthalate (PET) 50,000 nm thick and 100 nm wide was coated to form a packaging material. The oxides save those of Example 1 and 2 were formed by a reactive ion plating method as described with reference to Fig. 1. The oxides of Examples 1 and 2 were prepared by a planar magnetron sputtering process *simpliciter*, i.e. no rf potential was applied to the electrode 18. Metal coatings were formed by a method similar to that described with reference to Fig. 1, save that no oxygen was supplied to the vacuum chamber 26, and hence a non-reactive ion plating was employed. In all instances, good adherence between the coating and the substrate was obtained without employing any intermediate layer there between.

EXAMPLE 1

An indium oxide coating was deposited. The rate at which oxygen was supplied was determined by the electrical resistance of the coating. The particular rate selected was that required to give an indium oxide coating having having a maximum electrical conductivity, the composition of the coating approximately to the formula In_2O_3.

EXAMPLE 2

An indium oxide coating was deposited. The rate at which oxygen was supplied was determined by the electrical resistance of the coating, and was chosen to give an oxide coating containing relatively more oxygen than the coating of Example 1.

EXAMPLE 3

A zinc oxide coating was deposited. The rate at which oxygen was supplied was determined by measuring the self-induced bias of the coating.

EXAMPLE 4

Another zinc coating was deposited. The rate at which oxygen was supplied was determined by measuring the self-induced potential bias of the coating.

EXAMPLE 5

A coating of aluminium metal was deposited.

EXAMPLE 6

A coating of aluminium oxide was deposited.

The partial pressure of oxygen and hence its rate of supply, was caused to oscillate such that the average intensity of the emission by aluminium of electromagnetic radiation of 396 nm wavelength was equal to half the sum of such emission at maximum intensity (corresponding to zero oxygen) and at minimum intensity (corresponding to the intensity at oxygen over-pressure).

EXAMPLE 7

A coating of zinc metal was deposited.

EXAMPLE 8

A further coating of zinc oxide was deposited. The oxygen partial pressure, and hence its rate of supply, was maintained at a value such that the intensity of the emission by zinc of eletromagnetic radiation of 636 nm was kept constant at half the sum of such emissions at maximum intensity (corresponding to zero oxygen partial pressure) and at minimum intensity (corresponding to the intensity at oxygen over-pressure).

EXAMPLE 9

A coating of tin oxide was deposited. The oxygen partial pressure and hence its rate of supply were determined by the resistance of the coating.

EXAMPLE 10

A coating of tin metal was deposited.

The conditions under which the coatings were deposited in Examples 1 to 10 are set out in Table 1 below. In each Example a partial pressure of argon of 3 millitor was employed, typically requiring a flow rate of argon of 100 to 120 cubic centimeters per minute.

The following physical properties were then measured in respect of the packaging material of each material.

A. Film thickness
B. Permeability to oxygen
C. Water vapour transmission rate (WVTR)
D. Transmission of light of 550 nm wavelength
E. Transmission of ultra-violet radiation of 360 nm wavelength.

Film thickness was measured using an ellipsometer (except where otherwise stated.

WVTR was measured according to British Standard BS 3177 at 25°C and 75% relative humidity using aluminium dishes almost filled with calcium chloride. The sample area was 50 cm^2. The coated side of the film was exposed to the high humidity.

Oxygen permeability was measured using the Mocon Paxtran *II* oxygen permeability tester at 23°C and a moist carrier gas of 1% hydrogen in nitrogen. The uncoated side of the film was exposed to air, the other side to the mixture of hydrogen and nitrogen. Where the material had a low permeability, pure oxygen was used in some examples instead of air, and the results obtained coverted to those that would have been obtained had air been used as the test gas.

It is to be appreciated that the packaging material may have a coating different in composition from those described in the Examples above. Essentially, the coating can comprise any metal, metal oxide or metal nitride or other compound which can be deposited by an ion plating method. Desirably, the coating is relatively inert, not being injuriously affected by the atmosphere, is formed of a relatively non-toxic substance, and is capable of being printed upon by an industrial printing process. Where it is desirable to have a transparent packaging material, coatings of materials known to have light absorptive properties (e.g. chromium) should preferably be avoided. The coating is preferably selected to be relatively hard and scratch resistant, and if for example one of the coatings described in the Examples as selected, there is generally no need to provide a further layer of protective material on top of it. If the coating is desired to be substantially transparent yet substantially opaque to UV radiation a material such as sinz oxide or indium oxide is desirably formed as the coating.

TABLE 1

EXAMPLE NUMBER	SPUTTERING VOLTAGE	SPUTTERING CURRENT	INDUCED BIAS VOLTAGE	PARTIAL PRESSURE	OXYGEN FLOW	ROLL SPEED
	V	A	V	of O_2	RATE/ $cm^3\ min^{-1}$	m min^{-1}
				MT (Millitorr)		
1	440	8	–	1.4	68.3	0.25
2	440	8	–	1.5	68	0.25
3	550	4	−100	2.4	66	0.25
4	550	4	−100	1.4	59	0.25
5	450	0.5	−75	–	–	0.1
6	410	1	−75	varying	varying	0.1
7	495	0.3	−75	–	–	0.25
8	390	0.5	−75	not measured	not measured	0.1
9	320	1	−75	1	24	0.1
10	580	1	−75	–	–	0.5

TABLE 2

EXAMPLE NUMBER	COMPOSITION OF COATING	COATING THICKNESS	WVTR	OXYGEN PERMEABILITY	%TRANSMISSION at 550 nm	%TRANSMISSION at 360 nm
		nm	gm m^{-2} day^{-1}	cm^3 m^{-2} day^{-1} atm^{-1}		
–	Uncoated Melinex PET (50,000 nm thick)	–	3.8	32.3	88%	83%
1	Indium Ozxide	145	0.2	less than 0.5	87%	34%
2	Indium Oxide	165	0.2	less than 0.5	79%	42%
3	Zinc Oxide	53	1.43	9.9	82%	46%
4	Zinc Oxide	140	0.36	2.2[a]	80%	18%
5	Aluminium	7–40[c]	0.52	3.2	33%	39%
6	Aluminium Oxide	84	0.81	4.1	73%	56%
7	Zinc	8–20[c]	3.4	20.0	24%	31%
8	Zinc Oxide	between 15 & 70[b]	2.1	14.1	86%	65%
9	Tin Oxide	63	+ 1.9	7.4	78%	61%
10	Tin	–	3.5	17.6	17%	22%

NOTES
(a) Oxygen used as test gas instead of air.
(b) Difficluties arose in measuring the coating thickness with any degree of precision owing to the refraction index of the coating.
(c) Coating thickness estimates based on bulk resistivity and optical constants.

CLAIMS

1. A bottle at least a part of whose external surfaces bears a coating said coating having been deposited by an ion-plating or magnetron spluttering method.

2. A bottle as claimed in claim 1, being of plastic material.

3. A bottle as claimed in claim 1 or claim 2, in which the plastics is polyethylene terephthalate.

4. A bottle as claimed in claim 1, being of glass.

5. A bottle as claimed in any one of claim 2 to 4, in which substantially all the external surface of the bottle bears said coating.

6. A bottle as claimed in any one of the preceding claims, in which the coating is substantially opaque to ultra-violet radiation or at least some wavelengths in the ultra-violet spectrum and substantially impermeable to atmospheric gases and water vapour.

7. A bottle wrapped in a packaging material bearing a coating, said coating having been deposited by an ion-plating or magnetron spluttering method and being transpared to visible light but substantially opaque to ultra-violet radiation or at least a part of the ultra-violet spectrum.

8. A bottle as claimed in any one of the preceding claims, the coating having been deposited by a reactive ion plating or planar magnetron spluttering method.

9. A bottle as claimed in any one of the preceding claims in which the coating comprises a chemical compound.

10. A bottle as claimed in claim 9, in which the chemical compound is an oxide.

11. A bottle as claimed in claim 10, in which the oxide is selected from one or more of zinc oxide and indium oxide.

12. A bottle as claimed in any one of the preceding claims, in which the coating has a thickness of up to 500 nm.

13. A bottle as claimed in any one of the preceding claims, in which the coating has a thickness of 200 nm or less.

14. A bottle as claimed in claim 13, in which the coating has a thickness in the range of 100 to 200 nm.

15. A container as claimed in any one of the preceding claims, in which a beverage is held.

Printed in the United Kingdom for Her Majesty's Stationery Office, Dd 8818935, 1984, 4235.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.