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(21) International Application Number: PCT/EP94/00119 (22) International Filing Date: 14 January 1994 (14.01.94) (30) Priority Data: 93300293.3 18 January 1993 (18.01.93) GB (71) Applicant (for AU BB CA GB IE LK MN MW NZ SD only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB). (71) Applicant (for all designated States except AU BB CA GB IE LK MN MW NZ SD): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL). (72) Inventors: GOTHAM, Simon, Martyn; 89 Putnoe Lane, Bedford MK41 9AZ (GB). HAYWOOD, Paul, Anthony; 9 Foxglove Close, Peverel Manor, Rushden, Northampton NN10 0TS (GB). (74) Agent: ROSCOE, Brian, Corrie; Unilever plc, Patent Division, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB).		(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: IMPROVEMENTS IN OR RELATING TO CARBONATION (57) Abstract Disclosed is a method of carbonating a sterilised product in a container, comprising adding to the container an appropriate amount of a sterile substance capable of generating carbon dioxide gas and sealing the container.		

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5 Title: Improvements in or relating to Carbonation

10 Field of the Invention

This invention relates to a method of carbonating products and to carbonated products produced by the method. The invention finds particular application in
15 connection with liquid products, such as drinks, including water, soft drinks and alcoholic drinks.

20 Background of the Invention

Current methods of carbonating products, such as drinks, involve treatment with gaseous carbon dioxide under
25 pressure and then placing the resulting carbonated product in suitable containers.

However such techniques cannot readily be used if the product is to be packaged under aseptic conditions (e.g. if the product contains no preservatives).

To date, no convenient solution to the problem of
35 aseptically filling containers with a carbonated product has been disclosed.

40 Summary of the Invention

In a first aspect, the invention provides a method of carbonating a sterilised product in a container, comprising adding to the container an appropriate amount
45 of a sterile substance capable of generating carbon dioxide gas and sealing the container.

It is recognised by those skilled in the art that sterility (the complete absence of any viable micro-organisms) is difficult to achieve and difficult to measure and, furthermore, not strictly necessary. As long as the viable count of micro-organisms is reduced to below a certain number the product will not be spoilt or become dangerously contaminated within its shelf-life. Thus the term "sterile" as used herein is intended to mean "effectively sterile", which is understood by those skilled in the art to refer to conditions where the number and type of viable micro-organisms is not significant. For example, conventional pasteurisation of milk does not sterilise the milk (i.e. reduce the viable micro-organism count to zero) but renders the product safe and greatly reduces the rate of spoilage. As a guide, the upper accepted limit for microbial contamination of soft drinks is typically around 1 yeast or mould colony forming unit per 25 m/s of product and around 100 bacterial spores per ml.

The product to be carbonated is typically in liquid form. Thus the method of the invention finds particular application in the production of carbonated drinks.

Generally the product to be carbonated will be sterilised by "flash pasteurisation" (e.g. at 75°C for 30 seconds). Alternatively, depending on the nature of the product, it might be possible to filter sterilise the product. It is preferred that the sterile substance capable of generating carbon dioxide (CO₂) does not impart any undesired flavour or other characteristic to the product.

The most preferred substance capable of generating carbon dioxide gas is solid carbon dioxide.

However, other substances will be apparent to those skilled in the art. For example, the product to be

carbonated might contain a reagent (reagent I). Thus the substance capable of generating CO₂ gas might be an appropriate amount of another reagent (reagent II) which when reacted with reagent I gives rise to carbon dioxide gas. For example reagent I might be an acid and reagent II might be a carbonate (or vice versa). Citric acid and ammonium carbonate are considered particularly suitable substances.

Clearly, after the addition of the substance capable of generating gaseous carbon dioxide, it is necessary to seal the container so as to be substantially air-tight. This prevents the carbon dioxide coming out of solution and preserves the sterility of the product once the container is removed from aseptic conditions.

It will be appreciated by those skilled in the art that the rate of formation of gaseous CO₂ might be very rapid - if say, solid CO₂, was used as the substance capable of generating gaseous CO₂. When solid CO₂ is added to the product it begins to sublime. However, the rate of sublimation is much greater than the rate of dissolution of the gas into the product. This can lead to very high pressures of CO₂ within the container which could compromise the integrity of the container.

It is therefore a highly preferred feature of the invention that the product is partially carbonated prior to the addition of the substance capable of generating CO₂ gas, such that the carbonation is achieved in two steps. The initial partial carbonation may conveniently be performed after sterilisation using simple conventional methods (e.g. using gaseous carbon dioxide at slightly elevated pressure). Typically the product will be initially carbonated to around its saturation level, but could be carbonated to anywhere between 66-100% saturation. This initial carbonation therefore reduces

the amount of gaseous carbon dioxide required subsequently to bring the product to the desired final carbonation level.

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Thus in a preferred embodiment the invention provides a method of carbonating a product, comprising sterilising the product, performing an initial carbonation of the product under sterile conditions, aseptically filling a container with the product, adding to the container an appropriate amount of a sterile substance capable of generating carbon dioxide gas so as to perform a second carbonation, and sealing the container.

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When CO₂ is forced into a liquid some CO₂ will dissolve, until the liquid is saturated with CO₂. After that point - extra CO₂ may be forced into the liquid under pressure. This extra CO₂ does not dissolve but becomes "entrapped" between the molecules of the liquid.

The amount of "entrapped" CO₂ in carbonated products may be more, less, or about the same as the amount of CO₂ actually dissolved in the product, depending on the degree of carbonation.

The amount of dissolved and entrapped CO₂ in a product may be determined by methods well known to those skilled in the art. Conveniently this may be done by disturbing the product (e.g. shaking it) to force the entrapped CO₂ out. The volume of the entrapped CO₂ forced out may then be measured from which a simple calculation yields the amount of dissolved CO₂. Suppose, for example, that 2 litres of CO₂ was collected from 1 litre of product, then the product could be said to have been carbonated to "2 volumes".

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The degree of "overpressure" necessary to achieve the desired degree of carbonation will vary according to the temperature of the liquid in which the CO₂ is dissolved (the solubility of gaseous carbon dioxide in liquids being increased at lower temperatures). Generally an overpressure of 1-4 bar of carbon dioxide will be sufficient to achieve carbonation of 1 volume of carbon dioxide at temperatures ranging from about 1°C-10°C.

It is preferred that once the product has been at least partially carbonated it should be held at the same or a lower temperature than the temperature at which the carbonation occurred. This is because, if the temperature is increased, CO₂ gas will tend to come out of the product.

The amount of carbon dioxide required to bring the product to its final level of carbonation will of course depend on the conditions under which the final carbonation takes place and the degree of saturation achieved during the initial carbonation.

Typically about 1.5 volumes of CO₂ will be dissolved in the initial carbonation and about a further 1 volume of CO₂ will be added in the final carbonation in the container. Generally, therefore, the degree of carbonation of the final product in the container will be in the range of 1.5-5.0 volumes of CO₂. The amount of the substance capable of generating gaseous CO₂ added to each container can therefore be adjusted to give the desired level of final carbonation.

Currently, carbonated products such as drinks are

frequently sold in bottles comprising polyethylene terephthalate (PET), which may be used once and then discarded, ("single trip" bottles) or may be refillable/reusable bottles, which are commonly known as "PRBs" (PET returnable bottles). Although very light and reasonably strong, this material may become deformed if exposed to considerable internal pressures of CO₂. This is one of the reasons for the preferred initial carbonation step, as it reduces the pressure of CO₂ required for the carbonation inside the container.

The use of PET results in another problem when solid CO₂ is used as the substance capable of generating gaseous CO₂. When solid CO₂ is added to the product it tends to sink to the bottom of the bottle and becomes surrounded by frozen product. The region in direct contact with this carbon dioxide/ice is subjected to very low temperatures, which can cause stress cracking of materials such as PET.

It is therefore a preferred feature of the present invention particularly when using containers of PET that, following addition of a substance capable of generating carbon dioxide and sealing, the container is inverted.

Preferably the container should be inverted 2-10 times. As well as preventing any part of the bottle being exposed to low temperatures for too long, this inversion has the advantage of aiding dissolution of the gaseous carbon dioxide.

Apparatus for inverting containers is already widely used in the relevant industry. It can be readily modified if necessary, to invert containers a number of times.

The precise conditions preferred may vary as different PET bottles produced by different manufacturers have different characteristics. As a result, the optimum and/or maximum values of certain criteria (e.g. degree of carbonation) may be varied in a manner predictable to those skilled in the art.

In another aspect the invention provides a container comprising a sterile carbonated product, produced by the method defined above.

The invention is further described in the following illustrative example.

Example

A batch of mineral water was flash pasteurised and subsequently maintained under sterile conditions. The water was chilled to 2°C and carbonated using gaseous carbon dioxide at an overpressure of 2 bar to 1.6 volumes of CO₂. The initially carbonated water was then used to fill 1.5 litre single trip PET bottles and 1.5 litre refillable PRBs supplied by Wellstar (similarly suitable bottles are obtainable from several other manufacturers), the temperature being maintained at 2°C throughout the process and subsequent final carbonation. Next, approximately 2.7 grams of solid CO₂ was added to each container and the bottles stoppered as quickly as possible. 2.7 grams of solid CO₂ equates to 0.9 volumes. Thus, upon dissolution of the solid CO₂, the final product was carbonated to approximately 2.5 volumes. Inversion of the bottles helped prevent stress cracking of the bottles due to low temperatures.

Claims

- 5
1. A method of carbonating a sterilised product in a container, comprising adding to the container an appropriate amount of a sterile substance capable of generating carbon dioxide gas and sealing the container.
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2. A method of carbonating a product, comprising sterilising the product, performing an initial carbonation of the product under sterile conditions, aseptically filling a container with the product, adding to the container an appropriate amount of a sterile substance capable of generating carbon dioxide gas so as to perform a second carbonation, and sealing the container.
- 15
3. A method according to claim 2, wherein the product is initially partially carbonated to 66-100% saturation.
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4. A method according to claim 2 or 3, wherein the amount of the sterile substance capable of generating carbon dioxide gas added to the product is sufficient to generate about 1 volume of carbon dioxide.
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5. A method according to any one of the preceding claims, where in the sterile substance capable of generating carbon dioxide gas is solid carbon dioxide.
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6. A method according to any one of the preceding claims, wherein the container comprises polyethylene terephthalate.
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7. A method according to any one of the preceding claims, wherein the container is inverted following the addition of a substance capable of generating carbon dioxide gas.

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8. A method according to any one of the preceding claims, wherein the final product is carbonated in the range of 1.5-5.0 volumes of CO₂.

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9. A method according to any one of the preceding claims, wherein one or more of the steps is performed at a temperature in the range of 1-10 °C.

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10. A container comprising a sterile carbonated product produced by the method of any one of claims 1-9.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 94/00119

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 A23L2/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 A23L B01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,1 336 720 (H.BAULIG) 13 April 1920 see claims; figures 4,8 see page 1, line 48 - line 49 see page 1, line 60 - line 61 see page 1, line 73 - line 94 see page 2, line 51 - line 56	1,4,7-10
Y	see page 2, line 119 - line 125 see page 3, line 78 - line 110 ---	1,2
Y	DE,A,28 46 800 (BERTUZZI) 3 May 1979 see page 8, paragraph 2; claims --- -/--	1,2

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

10 June 1994

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 9240, Derwent Publications Ltd., London, GB; Class D13, AN 92-327612 & JP,A,4 234 967 (SAHI BREWERIES) 24 August 1992 see abstract ---	1,5
X	J.G.WOODROOF ET AL. 'Beverages:carbonated and noncarbonated.Revised edition' 1981 , AVI , WESTPORT,CONNECTICUT pages 148,208-212,217 see page 148 : "Cold sterilization of acid beverages" see page 208,first paragraph-page 209,sixth paragraph see page 217 : "Cooling the ingredients",table 6.2 see page 212:"The carbonation process" ---	1-3,8-10
X	EP,A,0 144 450 (AOKI) 19 June 1985 see the whole document ---	1,6
A	US,A,4 620 962 (H.D.BRODBECK) 4 November 1986 see column 1, line 10 - line 13 see column 2, line 40 - line 41; claim 1 -----	1,10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-1336720		NONE	
DE-A-2846800	03-05-79	NONE	
EP-A-0144450	19-06-85	NONE	
US-A-4620962	04-11-86	NONE	