Title: A METHOD OF PROCESSING PRODUCTS MADE OF SODIUM-CALCIUM-SILICON PACKAGING GLASS HAVING SURFACE MODIFIED WITH ALUMINIUM COMPOUNDS

Abstract: A method of processing products made of sodium-calcium-silicon glass consists in that, the temperature of products in the range of transformation temperature is maintained for 15 to 1800 seconds from the moment of spreading nanopowder on the product being on conveyor (3), and possibly additionally in first sections of the annealing lehr (7a, 7b) depending on the size of the product and speed of the conveyor (3). The nanopowder Al(OH)₃ is spread during formation in glass forming machine (1) by indirect spraying on shaping surfaces of the mould before their closing on the gob of molten glass, or it is spread directly on the products in the hot end coating hood placed on the conveyor, where the area of the hot end coating hood is closed by a thermal barrier on entrance and exit.
A METHOD OF PROCESSING PRODUCTS MADE OF SODIUM-CALCIUM-SILICON PACKAGING GLASS HAVING SURFACE MODIFIED WITH ALUMINIUM COMPOUNDS

TECHNICAL FIELD

The object of the present invention is a method of processing products made of sodium-calcium-silicon packaging glass having surface modified with aluminium compounds. The method refers to manufacturing of products formed with glass forming machine, in particular bottles and jars having surfaces modified with superficial ion exchange technology.

BACKGROUND ART

In case of majority of glass packaging products not only the hydrolytic resistance, and the optical quality is important, but also mechanical qualities of glass, exposed to burdens of utilization conditions, filling technologies, and multiple cycles of exploitation. It refers in particular to the superficial layer, whose state and properties determine significantly mechanical strength of the product. One of the
methods of glass surface modification consists in ion exchange carried out in order to obtain advantageous compressive stresses in surface layers. When ions having larger diameters are exchanged to ions of smaller radiuses, the chemical composition is changed, and additionally the coefficient of thermal expansion is lowered - resulting in obtaining advantageous stress pattern during annealing cooling of the product to ambient temperature. Known are methods of modification of sodium-calcium-silicon glass with utilization of aluminium compound, which after contact with hot surface of the glass having temperature in the range of transformation 450 to 700°C decomposes and creates oxide coating. At the same time metal oxide diffuses to superficial layers and structural bonds are formatted, advantageous for mechanical properties: smoothness, hardness, and impact resistance.

Particularly good results for packaging sodium-calcium-silicon glass were obtained by utilization of aluminium compound comminuted to nanoparticles. The method disclosed in patent specification No. PL202940 consists in spreading by spraying on the glass surface of aluminium compound nanopowder, favourably aluminium hydroxide
Al(OH)$_3$ having grains of size from 1 to 100 nm, and then in heat treatment of the product in the range of transformation temperatures 580 +/- 150°C, but not exceeding the deformation temperature. Nanopowder may be spread on hot surface of previously formed products or directly during formation. On the surface of the product a transient layer is formatted, creating glass structure strongly chemically bonded, in which aluminium is present in advantageous octahedral coordination.

Utilization of aluminium compounds for modification of glass products is also known from patent specification EP 1753702, where bringing the glass surface with metallic aluminium is carried out in temperatures 250 to 800°C, and where the aluminium is in the form of a shaping tool or part of a shaping tool. The method, because of low durability of aluminium form, is not useful for high volume and mass production of packaging products.

DISCLOSURE OF THE INVENTION

The method in accordance with the present invention solves the problem of industrial delimitation of technological process conditions of sodium-calcium-silicon glass packaging products production in glass
forming machine, in particular bottles, having surface modified by spraying of aluminium compound nanopowder in accordance with the invention disclosed by the patent specification No. PL202940 mentioned above. In the range of transformation temperatures 580 +/- 150°C, but under the deformation temperature, aluminium compound nanopowder, favourably Al(OH)₃, having granularity smaller than 120 nm, is sprayed on the surfaces of the product. The essence of the present invention consists in that the temperature of products in the range of transformation temperature is maintained for 15 to 1800 seconds from the moment of spreading nanopowder on the product being on conveyor, and possibly additionally in first sections of the annealing lehr, depending on the size of the product and speed of the conveyors. The result of glass modification depends on the moment, when the new chemical bonds forming microreaction is terminated, this determines the remodelling of the superficial layer structure - in specified temperature conditions of the process, and when the appropriate amount of nanopowder on the unit of product surface is spread.
The nanopowder Al(OH)$_3$ may be spread during formation in glass forming machine by indirect spraying on shaping surfaces of the mould before their closing on the gob of molten glass, or possibly directly on the products in the hot end coating hood placed on the conveyor, where the area of the hot end coating hood is closed by a thermal barrier on entrance and exit. The thermal barrier, which closes the area where nanopowder suspension flux is circulating, may be a barrier of flames or a gas injection barrier, where gas is heated to the glass transformation temperature.

It is advantageous, when the temperature of products in the range of transformation temperature on the conveyor between the glass forming machine and annealing lehr is maintained by protecting the conveyor with thermal shield, possibly equipped with reheating source of heat.

BEST MODE OF CARRYING OUT THE INVENTION

The following examples illustrate the invention without setting or delineating its limits. The examples show two technological processes of different glass packages manufacturing based on the production line diagram shown on the drawing.
The drawing illustrates production line comprising series-connected: glass forming machine 1, receiving machine pusher 2, belt conveyor 3 with possibly placed on it hot end coating hood 4, and tunnel thermal shield 5, loading machine 6, and multisection furnace annealing lehr 7.

Example 1

Glass packaging having capacity of 40 ml was formed in triple gob, ten section glass forming machine made by Emhart AIS Machine with utilization of set of forming parts by OMCO system. Bottles were formed from calcium-sodium amber glass gob, comprising about 47% of foreign cullet. Glass gob was formed in temperature about 1160°C in Narrow Neck Press and Blow process. Formed bottle were transferred by receiving machine pusher 2 from glass forming machine 1 to conveyor 3 with hot end coating hood 4 installed on it. It was empirically established, that at the moment of entering the chamber of the hot end coating hood 4 the products had the temperature about 590-610°C, what was in the range of desired transformation temperature of that glass.
Having regard to this, a thermal shield 5 was not used at the distance between the receiving machine pusher 2, and the hot end coating hood 4. Lack of thermal shield allowed for initial quality control of the bottles. Entrance and exit of hot end coating hood chamber 4 were protected by a thermal barrier formed by flames of gas burners, whose aim was to prevent nanopowder Al(OH)₃ sprayed in the chamber from getting outside. The nanopowder used had granularity lower than 80 nm. The nanopowder was dispensed into stream of air, whose circulation having eight-shaped trajectory was forced by a fan having diameter of 120 mm. The fan was situated in left front part above the entrance to the chamber. The nanopowder dispenser was located directly before the fan, what allowed for uniform distribution of the nanopowder in the inner area of the hot end coating hood chamber 4. The packagings with sprayed layer of nanopowder were transported further by conveyor 3 in the direction of annealing lehr 7. This section of conveyor 3 having length of about 8 m was protected by tunnel thermal shield 5 equipped with gas burners spaced in the distance 50 cm from each other. The gas burners maintained the temperature of transported bottles in the temperature
necessary for effective incorporation of nanopowder Al(OH)$_3$ into their external surface. When the conveyor 3 moved with speed of 0.5 m/sec, and the temperature of packagings measured at the entrance to the annealing lehr was about 500°C, the period of maintaining the products in the range of temperatures 500-600°C with nanopowder spread on them amounted to 15.8 seconds. The time period of 15.8 seconds was the average time period, taking into account forming bottles in ten section machine and queuing them before entering into annealing lehr 7.

The measurements of mechanical properties of bottles having surface modified with the method described above carried out after annealing showed increase of microhardness by 87% - what confirmed, that during 15.8 seconds Al(OH)$_3$ had rereacted effectively, incorporated in and modified structure of superficial surface of the bottle.

Example 2

Glass packagings having capacity of 1000 ml were manufactured in double gob, six section glass forming machine 1 in Blow-Blow technology. Because of necessity to keep the packaging in the range of
transformation temperature for the time period necessary for effective incorporation of nanopowder Al(OH)$_3$ into their surface, it was decided to spray the nanopowder at the step of forming in order to maintain the expected rate of production. Nanopowder having granularity of 80 nm was sprayed by nozzles installed in glass forming machine 1 and directed at the surface of blow mould, so after step of preforming in blank mould. Bottles were formed from transparent calcium-sodium glass gob in the temperature about 1200°C. The glass batch comprised about 33% of foreign cullet. Formed bottles were transported by belt conveyor 3 having length of 30 m to annealing lehr 7. As the speed of conveyor was low amounting to 0.02 m/sec, in order to avoid the cooling of bottles under the temperature of incorporation of nanopowder into glass surface structure, the section of the conveyor 3 between the glass forming machine 1, and the annealing lehr was covered with tunnel thermal shield 5 made of steel sheet. In addition the shield was equipped with gas burners spaced in the distance 0.5 m from each other that reheated the bottles. It was empirically confirmed, that installation of all those technical means allowed for maintaining the bottles temperature in the
distance between the glass forming machine 1, and the annealing lehr 7 in the range of 730-570°C.

The measurements of mechanical properties of annealed bottles showed that maximal increase of microhardness, up to 92%, had been obtained by prolonging the time of maintaining necessary temperatures to about 1550 seconds, what required that on the way between first 7a and second 7b section of annealing lehr 7 the temperatures were kept at the level of 560°C, and only then in next sections the temperatures were stepwise lowered to 60°C in last section 7n.
PATENT CLAIMS

1. A method of processing products made of sodium-calcium-silicon glass having surface modified with aluminium compounds, products formed by a glass forming machine, in particular bottles, consisting in application on the product's surface - in the range of transformation temperatures 580 +/- 150°C, but under the deformation temperature - of aluminium compound nanopowder, favourably Al(OH)$_3$, having granularity smaller than 120 run, and in carrying out the process of annealing by gradual reduction of temperature in annealing lehr to temperature lower than 200°C, characterised in that, the temperature of products in the range of transformation temperature is maintained for 15 to 1800 seconds from the moment of spreading nanopowder on the product being on conveyor (3), and possibly additionally in first sections of the annealing lehr (7a, 7b) depending on the size of the product and speed of the conveyor (3).

2. A method in accordance with claim 1, characterised in that, the nanopowder Al(OH)$_3$ is spread during formation in glass forming
machine (1) by indirect spraying on shaping surfaces of the mould before their closing on the gob of molten glass.

3. A method in accordance with claim 1, characterised in that, the nanopowder Al(OH)$_3$ is spread directly on the products in the hot end coating hood placed on the conveyor, where the area of the hot end coating hood is closed by a thermal barrier on entrance and exit.

4. A method in accordance with claim 1, characterised in that, the temperature of products in the range of transformation temperature on the conveyor (3) between the glass forming machine (1) and annealing lehr (7) is maintained by protecting the conveyor (3) with thermal shield (5), possibly equipped with reheating source of heat.
**INTERNATIONAL SEARCH REPORT**

**INTERNATIONAL APPLICATION**
International application No
PCT/PL2011/00Q108

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C03C17/00 C03C21/00
ADD.

**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)
C03C C03B

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)
EPO-Internal , WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<tr>
<td>X</td>
<td>PL 202 940 BI (WASYLAK JAN [PL] : DRAJEWICZ MARCIN [PL]) 31 August 2009 (2009-08-31) the whole document -----</td>
<td>1-4</td>
</tr>
<tr>
<td>Y</td>
<td>US 4 702 760 A (GARCIA DE LEON JOSE L [MX]) 27 October 1987 (1987-10-27) abstract figures 1,2 ------</td>
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</tr>
<tr>
<td>Y</td>
<td>US 4 290 793 A (BROCKWAY M CLIFFORD) 22 September 1981 (1981-09-22) abstract figures 1-4 ------</td>
<td>1-4</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

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<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
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<tr>
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<td>31-08-2009</td>
<td>NONE</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 4702760 A</td>
<td>27-10-1987</td>
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<tr>
<td>US 4290793 A</td>
<td>22-09-1981</td>
<td>NONE</td>
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