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GLASS CONTAINER COATING

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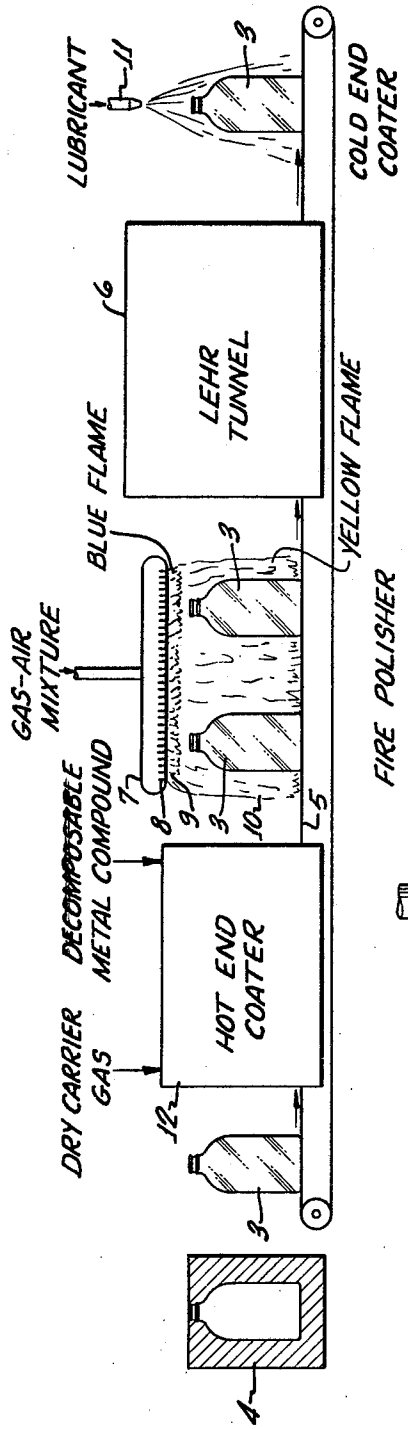


FIG. 1.

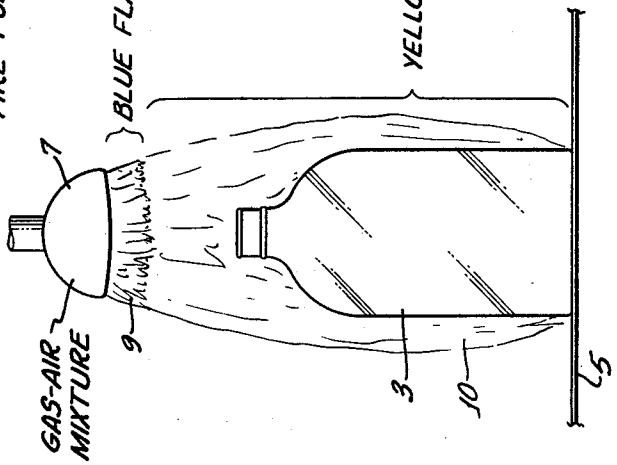


FIG. 2.

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GLASS CONTAINER COATING

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ABSTRACT OF THE DISCLOSURE

Impingement of the yellow cone of a hydrocarbon flame having not more than a 0.4 percent molar excess of oxygen on the surface of a glass container coated with the thermal decomposition product of a tin or titanium halide or ester avoids dull fault and streaking and reduces the electric potential of the surface by a factor of at least five minimizing the tendency of the containers to corrode metal caps.

BACKGROUND OF THE INVENTION

The glass container industry in the interest of saving manufacturing and shipping costs, has reduced the wall thickness of glass containers while compensating for strength loss by increasing the lubricity and chemical durability of the exterior surface of the containers. By thus increasing abrasion and scratch resistance, bursting by rubbing contact of the glass articles is substantially reduced and higher speed handling of the containers during filling, capping, labelling and packaging is possible.

A particularly effective manner of lubricity treatment is known as hot end coating in which newly formed hot containers are exposed to tin or titanium compounds which decompose and deposit a coating having characteristics of the corresponding oxides. In order to be commercially acceptable, the thickness of this coating must be controlled to avoid light interference effects contributing an iridescent appearance to the container. Furthermore, when moisture is trapped between the coated surface and a metal cap, a voltaic cell is formed having a voltage difference sufficient to corrode the cap, which is especially accelerated at pasteurization temperatures. Iron metal from the cap is electrolytically oxidized and deposits unsightly and commercially unacceptable rust stains on the lip of the container.

Furthermore, high quality production requires polishing the lip of the container. However, tin or titanium hot end coated containers when subjected to the usual fire polishing flames take on a dull, dirty appearance in the areas of flame impingement, the lip of the container showing dull gray fault and the sides displaying unsightly streaks.

Intending to correct the fire finishing and corrosion faults, applicants attempted during coating to mask the upper areas of the surface of the containers from the coating compound by placing screens or guards over these areas. This had very little effect on the results. Applicants then atempted, again without success, to protect these areas with a flow of air or a flame mask. All of these schemes proceeded on the basis of keeping the coating off the areas of the finish that are detrimentally affected by the flame.

It was completely unexpected that by the method of this invention the coating can be preserved in these areas without streaking or frosting during fire polishing, and that the capped container will show little tendency to rust. The inventive method is adapted to the normal sequence of hot end processing and does not require complex and difficult controls during the coating operation.

These and other advantages will become readily apparent as the description proceeds.

BRIEF DESCRIPTION OF INVENTION

In accordance with this invention, glassware of improved scratch resistance and chemical durability having the treated area free of streaking and frosting fault and having a substantially decreased tendency to corrode metal caps, are prepared by impinging on a portion of the coated ware the yellow cone of a luminous flame. Preferably, the flame is incompletely combusted, i.e. there is insufficient oxygen fed to the burner to oxidize all of the hydrocarbons in the burner gas and the flame is elongated in order to increase the cross section of the yellow cone. The larger fire area of a longer flame compensates for the lower temperature of the colder luminous flame.

DETAILED DESCRIPTION OF INVENTION

The invention will become better understood by reference to the following detailed description when considered in connection with the drawings in which:

FIG. 1 is a diagrammatic flow sheet of the hot end of a glass container forming machine; and,

FIG. 2 is an enlarged diagrammatic side view of the fire polisher illustrating the flame in contact with a coated container.

Referring now to the drawings, a bottle **3** is formed from a portion of soda-lime-silica glass in a mold **4** of a forming machine at about 2000° F. The bottles **3** are carried in single line on the conveyor **5** connecting the forming machine with the lehr **6**. The bottle **3** is conveyed to a hot end coater **12** and has cooled at this point to about 700° F. to 1100° F., preferably 800° F. to 1000° F. An atmosphere of dry carrier gas and fumes of decomposable metal compound is present in the hot end coater **12** and as the hot bottle passes through the chamber of the coater, the atmosphere impinges on the surface and the bottle exits coated with a decomposition product of the metal compound. Next in turn, the coated bottle passes under a fire polishing burner **7** to which is fed a mixture of hydrocarbon gas and air which is combusted into a downwardly directed flame spreading through screen **8** into a small blue portion **9** adjacent the screen and an exterior elongate yellow cone **10**. The yellow cone **10** of the flame plays down and envelops a substantial portion of the bottle, and raises the temperature of the lip surface to the flow point of the glass, about 1200° F., to effect a smooth fire polishing of the surface. The coated bottle then passes through the lehr tunnel **6** and is slowly annealed for about 30 minutes to two hours. In some instances when the bottle is fairly cool, it receives a coating by a spray of a lubricious material in cold end coater **11**.

The hot end coating follows procedures well known in the art. The decomposable compounds most widely recognized are the halides of tin or titanium and the lower esters of titanium. Tin or titanium tetrachloride and tetraisopropyl titanate are specific compounds utilized in hot end coating applications though others are available. Tin tetrachloride (stannic chloride) is favored since the higher vapor pressure permits easier application to the surface, the lubricity as produced is better, and there is less iridizing effect for the same thickness as compared to the titanium compounds.

Though the compounds can be transported to the hot glass article in a liquid form, for purposes of uniformity of the coating, the compounds are usually applied as a dispersion in vapor or as vaporous fumes. The concentration of the vapors in the treating gas mixture is not critical but with very high concentrations it is difficult to evenly coat the irregular surfaces of glass containers. The vapors of the compound are dispersed in an inert car-

rier gas such as nitrogen or air which preferably is anhydrous. Otherwise, the metal compounds can hydrate or hydrolize which fouls the coating equipment and affects the quality of the coating. For this same reason, the compounds themselves are utilized in anhydrous form. The air can be preheated to prevent fouling of the equipment by condensation, and the liquid coating compound can be vaporized into the heated carrier air.

Almost any form of enclosure that will provide impingement of the fume mixture on the hot glass surface will produce a coating. Recirculation of the vapor mixture is of considerable advantage in maintaining relatively uniform coatings on tall containers. The air-compound vapor mixture on contact with the hot surface of the newly formed ware decomposes and deposits a coating of controllable thickness providing the ware with both permanent lubricity and increased abrasion resistance.

The coating is extremely thin and very small amounts are applied to each bottle. Ten to fifteen pounds of stannic chloride or about 18 to 22 pounds of titanium ester per 24 hour day is all that is needed to coat 120 bottles per minute. The thickness of the coating should be controlled since when the coating exceeds one-quarter the wavelength of yellow-green light (530–560 millimicrons) light interference effects cause the coating to take on an apparent iridescent effect. Thickness of the coating also influences the tendency to electrolytically corrode iron caps. For these reasons, it is preferred to maintain the coating between about five and 100 millimicrons.

Thickness of the coating can also be correlated to electrical resistance. The coating which is substantially tin oxide behaves as a semi-conductor and as the thickness of the coating increases, the measured resistance decreases. Extensive laboratory testing of non-fire polished tin tetrachloride coated bottles has shown that minimum chemical utilization with adequate glass to glass contact abrasion resistance occurs with thin films having an electrical resistivity above about 190 megohms. Such coated containers have no visible haze to the eye on either hot or cold glass, although they will exhibit a slight difference in surface reflection when viewed beside an uncoated container.

The following example is offered by way of illustration of one procedure of preparing a fire treated container according to the invention.

EXAMPLE

Freshly formed eleven ounce beer bottles are passed single line on a conveyor connecting the forming machine with the lehr loader. The bottles at about 800–900° F. pass through a hot end coating chamber in which an atmosphere of dry heated air and stannic chloride vapors impinges on the exterior surfaces of the bottles and a film forming reaction occurs between the hot glass and the vaporous atmosphere. The stannic chloride is consumed on the basis of 0.009 pounds per 120 bottles. The coated ware emerging from the chamber is conveyed in the normal manner and near the entrance to and across the tunnel of the lehr the bottles are separated into columns and each bottle passes under and is enveloped by the luminous elongated yellow portion of a flame from a fire polishing burner for about one to three minutes. These burners are wide enough to accommodate the finish diameter of the container and long enough to provide adequate heating and fire polishing of the surface to cause rounding of any rough or sharp edges of the container finish. The fire polished bottles enter the lehr and are slowly cooled for about 45 minutes. After emerging from the lehr the bottles at about 300° F. receive a cold end coating of an aqueous emulsion of a low molecular weight oxidized polyethylene.

The above experiment repeated by varying the oxygen feed to the gas burner demonstrates the effect of the gas/air ratio of the flame on the finish marking of the

bottles. A Beckman Model E–2 Oxygen Analyzer is utilized to determine the percent oxygen by volume. The molar percent excess of oxygen in the combustible mixture of hydrocarbon gas and air is computed from 19.15 percent oxygen as the stoichiometric point at which all the hydrocarbons are oxidized, and the data is reported in the following table.

TABLE I

Percent oxygen (vol.)	Molar percent excess (+) or deficiency (−) of oxygen	Comments
18.40	−3.9	Initial conditions.
18.84	−1.6	No marks.
18.96	−1.0	Do.
19.10	−0.3	Do.
19.18	+0.2	Do.
19.26	+0.6	Marks.
19.30	+0.8	Do.
19.09	−0.3	No marks.
19.55	+2.0	Marks.

It is apparent that the burner cannot be operated with more than a slight excess of oxygen without effecting the bottle coating. Above about a 0.4 percent molar excess of oxygen cannot be tolerated and preferably the burner feed contains a deficiency of oxygen so that the flame is incompletely combusted to form a large yellow luminous glass contacting area.

The chemical nature of the coating as applied and the manner it is bound to the glass cannot readily be determined though the coating is believed to be a mixture of tin oxides, chlorides and oxychlorides. Examination of replicate flame polished uncoated samples compared to coated samples and to high molar oxygen excess flame polished coated samples under a 15,000 magnification electron microscope reveals that the uncoated samples have a rolling smooth surface with no other distinguishing feature. The coated bottle exhibits dispersed crystalline deposits while the unsatisfactory fire polished surface has a definite etched appearance between smooth areas. Apparently, pitting is occurring under the dispersed crystals. Since this pitting does not occur with the luminous flames of the invention, it is possible that either the cooler flame temperature, its more reducing nature or the higher water content of these flames avoids the pitting or etched nature of the surface finish.

In any case, the nature of the coating is definitely changed by exposure to a luminous flame, since containers fire polished according to the invention show a considerably different electrical potential indicating a change in the chemical or physical nature of the coating.

The voltaic cell causing cap corrosion is believed to be formed between the tin plated iron cap as the negative electrode potential and the bottle coating, tin oxide, as the positive electrode potential. Exposed iron on the cap is believed to be oxidized in the presence of entrapped water as the electrolyte to Fe^{+3}, while oxygen at the tin oxide electrode is forming OH^- ions. The product, $Fe(OH)_3$, adheres to the glass and dries to form Fe_2O_3 rust stains.

The change in character of the surface coating is demonstrated by the following tests. A voltage test procedure is established for determining the relative single electrode potential of the coated surfaces in reference to a sodium chloride electrolyte and a copper electrode. The threshold voltage for corrosion is established by a secondary autoclave test in which the pasteurization of the bottle is simulated.

The lip of a tin oxide coated bottle is covered with a filter paper wetted with a saturated solution of NaCl. The paper in turn is covered with a sheet of copper foil mounted on a base and a lead is connected to the coated surface of the bottle and a second lead to a point on the foil. The two leads are connected to a voltmeter and are moved around the lip and at room temperature various readings of voltage are recorded. The bottles are then capped with tin plated iron caps with water

entrapped between the finish and the cap and are steamed at 140° F. for one hour. The bottles are allowed to cool and dry and the caps are removed and the finish inspected for rust. The data is collected in the following table.

TABLE II

Experiment	Bottle coating (thickness)	Voltage (volts)	Appearance after steaming
1	Medium (N.F.P.)	0.2	Heavy rust.
2	do	0.3	Do.
3	Light (N.F.P.)	0.15	Do.
4	Light (F.P.)	0.02	Light rust.
5	do	0.03	Do.
6	do	0.01	No rust.

The bottles with a medium coating of tin oxide exhibit high voltage and deposit heavy rust stains. The voltage of non-fire polished (N.F.P.) lightly coated bottles in the test cell with sodium chloride and a copper electrode is as much as about eight times the voltage of the same cell with corresponding fire polished (F.P.) areas of the bottles. The light coated F.P. bottles average around 0.03 volt while the lightly coated N.F.P. bottles average around 0.15 volt, an average decrease in potential by a factor of 5. The autoclave test further established 0.01 volt as the threshold voltage value for rust formation. These tests demonstrate that thickness of the coating should be controlled and that since the fire polished bottles exhibit considerably lower electric potential, the nature of the finish has been modified by fire polishing in a luminous flame according to the invention.

Though the friction factor of titanium or tin halide or ester hot end coated bottles is drastically reduced, the lubricity of these bottles is further improved by a secondary cold end coating of a water soluble lubricious material. It is advantageous to combine these two coatings since enhanced lubricity is believed to be provided by a better bite of the cold end coating onto the hot end coating as compared to applying the cold end coating to the base glass surface. The hot end coating is also believed to orient the cold end coating as it dries. The cold end coating is typically applied as a spray of an aqueous dispersion of a low molecular weight water insoluble oxidized polyethylene. This coating can be applied to the annealed bottle cooled to 300° F. or a water insoluble polyoxyethylene stearate can be applied to the cooled, annealed, coated bottle at room temperature.

What is claimed is:

1. A process for producing a high lubricity and low electrical potential surface on a glass article comprising:

coating the surface of the article when at 700° F. to 1100° F. by exposure to vapors comprising thermally decomposable tin halides, tin esters, titanium esters or titanium halides; and,

enveloping the coated surface with the yellow cone of a flame which contacts said coated surface and contains not more than a 0.4 percent molar excess of oxygen whereby ething and marking of the surface contacted by said flame is prevented, said flame raising the temperature of said surface to a temperature which is sufficient to fire polish said surface.

2. A process according to claim **1**, in which the flame is impinged on the surface for a time sufficient to heat the surface to the temperature of flow of the glass to cause rounding of any roughness or sharpness in the surface finish.

3. A process according to claim **2**, in which the yellow cone of an incompletely combusted flame is impinged on the coated surface for about one to three minutes.

4. A process according to claim **1**, wherein during coating the hot surface of a newly formed glass bottle is exposed to an anhydrous mixture of stannic chloride and air and during flame impingement a portion of the coated surface is heated to about 1200° F. by a one to three minute impingement of the luminous yellow cone of an incompletely combusted flame.

5. A process according to claim **4**, in which the flame treated glass article is slowly annealed for 30 minutes to two hours and is further coated when substantially cool with a water insoluble lubricious material.

6. A process according to claim **5**, in which the lubricious material is an oxidized low molecular weight polyethylene or a polyoxyethylene stearate.

7. A process for producing a high lubricity and low electrical potential surface on a glass article comprising:

coating the surface with the decomposition product of a decomposable compound of tin or titanium; and

enveloping the coated surface with the yellow cone of a luminous flame until the electric potential across said surface, in reference to a sodium chloride electrolyte and a copper electrode, is reduced to substantially below 0.15 volt.

8. In a process of increasing the scratch resistance and chemical durability of the surface of a glass container by coating the surface with the thermal decomposition products comprising halides, tin esters, titanium halides or titanium esters, the further steps comprising:

forming a flame of a hydrocarbon gas and air containing not more than a 0.4 molar percent excess of oxygen, and

enveloping the coated surface with the yellow cone of a luminous flame until the electric potential across said surface, in reference to a sodium chloride electrolyte and a copper electrode, is reduced to substantially below 0.15 volt.

9. A process of producing a non-marked, scratch and abrasion resistant glass article, comprising:

forming a five to 100 millimicron coating of the thermal decomposition product of an anhydrous mixture of air and stannic chloride on the exterior surface of the glass article;

controlling the hydrocarbon gas-air feed to a flame burner so as not to exceed a 0.4 percent molar excess of oxygen;

forming a downwardly directed flame of said mixture;

reducing the average electrode potential across said surface, in reference to a sodium chloride electrolyte and a copper electrode, from about 0.15 volt to below 0.03 volt measured at room temperature, by passing for one to three minutes the coated article under said flame so as to envelop a substantial portion of the coated surface with the yellow cone of the flame whereby marking of the surface is avoided.

10. A non-marked, scratch resistant, abrasion resistant glass article having reduced tendency to corrode iron caps, produced by the process of claim **1**.

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