Production Equipment for Plasma Enhanced CVD Permeation Barrier Coating of PET Beverage Bottles

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ABSTRACT

There are different methods for improving the barrier performance of PET bottles used in industry today. Among those, Plasma Enhanced CVD is still less common today but offers a very favorable combination of high oxygen and CO_2 permeation barrier performance and good cost efficiency for large volumes. It is easy to coat the bottle inside by this method. This has the advantage that migration of oxygen or constituents of the plastic wall material into or flavors out from the beverage can be suppressed as well.

An increasing number of production PECVD coating machines are offered from different vendors, all based on single bottle plasma processing cavities. These can be arranged in large arrays or up to 100 being (un)loaded and processed at a time. Alternatively, some 20 or more reactors are mounted on a carousel that is continuously loaded and unloaded. The typical throughput of these production plants presently is in the range of 10,000 bottles per hour.

The coatings currently on the market are either based on amorphous carbon (made from acetylene) or silicon dioxide ("SiOx", from silicon organic precursors and oxygen). Both types of coating proved to be very good barriers with the main difference in the optical appearance. Very thin (several tens of nm) but highly efficient diffusion barriers against oxygen, carbon dioxide, water vapor and other materials can be deposited within seconds. Extensive tests have shown that the barrier performance can be very stable against severe mechanical deformation of the bottles.

The paper reviews the current machinery solutions on the market with reference to the coating properties.

INTRODUCTION

Bottles made from PET (polyethylene terephthalate) have found very good acceptance in the market specifically for carbonated soft drinks and mineral water. In competition with glass, metal, or cardboard, the plastic material offers an attractive combination of desired properties: Packages are lightweight, unbreakable, optically very transparent, and—most important to the designers and stylists—easy to be shaped and colored. However, the barrier properties against diffusion of oxygen, carbon dioxide, and other molecules are usually not sufficient for packaging of sensitive beverages such as beer, juices, tea, or mineral water.

As can be seen from Table 1, it is not only permeation *through* the bottle walls that damages the product inside. The amount of oxygen *dissolved in the plastic material* can be sufficient to badly effect the quality of beer. Furthermore, acetaldehyde and other decomposition products from PET processing can migrate from the bottle wall into the beverage causing an off-taste of mineral water. These problems can be met with the respective oxygen and acetaldehyde scavengers, however at additional cost. On the other hand, flavors may migrate out from the beverage into the plastic, thus "scalping" the desired taste. Therefore, it is clearly preferable to have the barrier inside the bottle wall.

Table 1: Diffusion problems with plastic containers.

Substance	**Diffusion from**	**to**	**Effect**
O_2	Outside Wall or	Inside	Decomposition of flavors, vitamin C, color
CO_2	Inside	Outside	Loss of foam build-up and pearl effect
H_2O	Inside	Outside	Recessive filling level
	Outside	Inside	Moisture uptake
Flavors	Inside	Outside	"Flavor Scalping"
	Inside	Wall	"Flavor Scalping", transfer into wall material
	Wall	Inside	Flavor transfer into beverage
Plastic constituents	Wall	Inside	Off-taste

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HISTORY

The diffusion barrier properties of PECVD (if carbon based, also called "plasma polymer") coatings are well known for a long time. However, the road to commercial products was long, and only a few of the milestones will be mentioned here.

In 1986, the Institute for Plastics Processing at Aachen, Germany, patented the use of microwave (MW) plasma polymerization for container barrier coating in general, including a basic concept for the coating device [1]. Polyplasma suggested the deposition of permeation barriers by MW plasma deposition on the basis of different chemistries, including amorphous carbon and silicon oxide ("SiOx") [2]. The barrier properties of Plasma-CVD SiOx coatings as deposited on plastic web in roll coating machines have been investigated at Airco's. It turned out that the so-called "Quartz-like Film" ("QLF") compared very well with silicon dioxide films as deposited by E-beam evaporation or sputtering [3]. A very interesting feature was the superior stretching behavior of the QLF. The coated PET samples could be stretched up to 5% before cracks and breakdown of the barrier properties occurred [4]. Optimum thickness for good SiOx-barriers on PET films was found to be only some tens of nm [5]. An early attempt was made by Airco to commercialize this for containers in a joint venture and a QLF machine for batch coating bottles and jars was patented [6]. Further efforts to commercialize PECVD barriers were focusing on blood sampling tubes [7], car fuel tanks [8], and again, plastic bottles [9,10,11].

In 1994, the Kirin brewery together with Samco International patented an RF-powered PECVD device for inside coating of bottles with "diamond-like", amorphous carbon [12]. A first production machine based on that work was built by Nissei. Schott developed a rapid SiOx inside coating process for plastic bottles and issued numerous patents, including the deposition of multilayer barrier coating on containers [13] and SiOx or TiOx as an outside barrier for plastic bottles after filling and sealing in 1998 [14]. At about the same time, Tetra Pak [15], Sidel [16], and finally in 2002, SIG/-Schott [17] filed patents on their current production equipment, as will be further detailed below. Recently, rapid SiOx barrier coating processes have also been developed by Dow Chemical [18] and Tetra Pak, reaching a deposition time of 3.0 s only [19]. Another machine for a carbon coating was introduced by Kirin and Mitsubishi Heavy Industries in late 2003 [20]. Most recently, Nano Scale Surface Systems is pursuing a new approach for a SiOx bottle coating machine on pilot scale to be fully commercial in 2005 [21].

PLASMA-ENHANCED CVD BARRIER COATING OF BEVERAGE BOTTLES TODAY

Processes

Among the different barrier coating methods for containers, the PECVD processes offer the best inside coating capability under industrial conditions. The precursor gas is fed into the bottles together with an RF voltage or microwaves. The plasma is generated selectively inside the bottles at a pressure around 1 Pa. The pressure outside the containers is chosen high or low enough to suppress plasma ignition. Outside coating is also possible (but less favorably) by inverting the pressure drop (approximately 1 order of magnitude) between the inside and outside during the plasma. If tuned properly, the plasma is self-aligned close to the wall of the bottles. The PECVD processes in commercial use for containers today are generally non-directional (in contrast to common PVD processes such as evaporation or sputtering) without any shadow effects. As a result, conformal and homogeneous coatings all over the container inside are comparably easy to achieve. Coating the inside is not only preferable from a packaging point of view. It also solves the common problems with build-up of unwanted coating inside the coating chamber such as on the reactor wall, and any windows, because the container basically is the plasma reactor wall. Therefore, the Plasma-CVD processes can be run very stably even in large scale production.

Amorphous (or "diamond-like") carbon barrier coatings can be deposited from hydrocarbons, most simply from acetylene, that reacts easily in the plasma. For SiOx coatings, a silicon-organic compound such as hexa-methyldisiloxane (HMDSO) is reacted with oxygen.

Current production coating machines are coating the bottles individually in small vacuum chambers as described above. The main difficulty is to load and unload a multitude of these chambers with plastic bottles at high speed for reasonable throughput. The bottles, usually made from PET, are lightweight (typically 25 to 50 g), have an unfavorably high center of gravity and, depending on the blowing process, sometimes deviations in their dimensions. Presently, there are two fundamentally different ways of bottle transport and (un)loading.

The Tetra Pak "BC-2" plant (Figure 1) is loading, SiOx-coating, and unloading batches of 100 bottles (up to 1l in volume) at a time. For this, a horizontal array of 10 by 10 bottles is loaded into some shuttle by a simple robot system. The shuttle then transfers the bottles into a vertical carrier that moves them between the two halves of the vacuum chamber (with 100 individual coating chambers). The vacuum chamber is then closed and the pumping/plasma/venting cycle started. This approach does not require very short deposition times. It also is very conservative vacuum-wise in that there are no mechanical movements inside the vacuum apart from the vacuum valves. All the bottle handling is done outside at the ambient atmosphere.

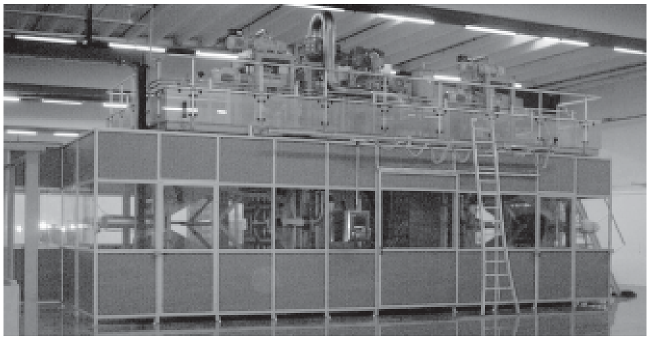

Figure 1a: PECVD bottle coating machine (BC-2 by Tetra Pak) consisting of two batch coating modules for 100 bottles each. The bottle (un)loading system for the carriers is still to be placed on the opposite side.

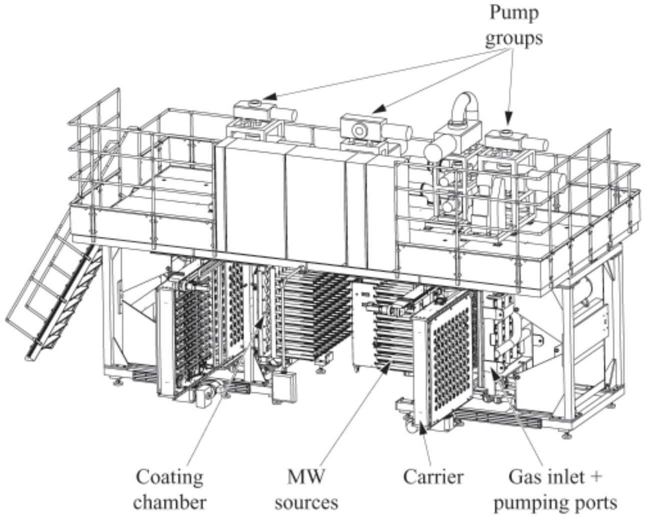

Figure 1b: Sketch of the above machine from the (un)loading side showing the two coating modules with the left vacuum chamber opened and the carrier being moved out.

In contrast, the "ACTIS-20" coating machine by Sidel (Figures 2 and 3) is based on the moving platform of a rotary stretch blow moulding machine (SBM). Instead of the mould tools, 20 single bottle MW-plasma reactors (now for bottles up to 1l) are mounted on a carousel that is continuously rotating. During the motion of 7 s along the circumference, the plasma reactors are loaded, closed and evacuated, gas is admitted, the plasma coating (with a carbon layer) performed, the reactors are vented and finally unloaded. For this concept, the deposition time is crucial, being 3 s for the regular "ACTIS" and < 2 s for the "ACTIS light" process. Since the reactors are always in motion, the continuous media supply is a challenge, specifically for the vacuum. The latter problem is solved elegantly by one large, rotary disc valve steering the roughing and the process vacuum lines for all plasma reactors. The obvious advantage of this revolutionary PECVD machine is the proven, continuous, simple, and compact loading mechanism. However, the vacuum system is less trivial.

Figure 2a: Process chambers of the ACTIS-20 bottle coating machine during (un)loading (courtesy of Sidel).

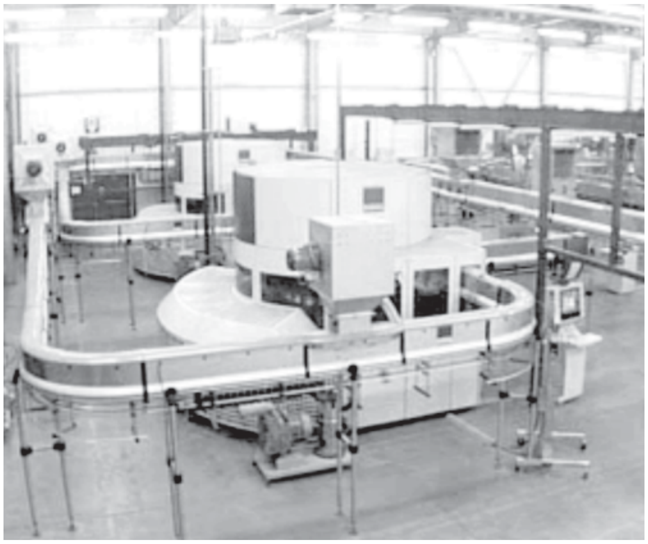

Figure 2b: Two rotary PECVD bottle coating machines integrated into a production line (courtesy of Sidel) [22].

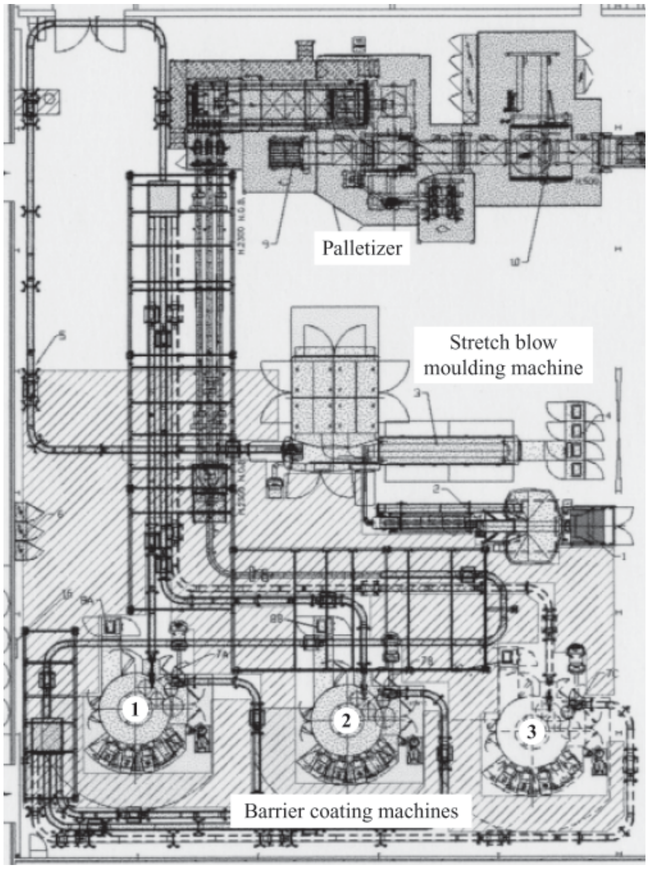

Figure 3: Layout of a current production line for beer bottles with three ACTIS coaters [22] (courtesy of Sidel).

The more recently developed "Plasmax 12D" coater by SIG and Schott (Figure 4) is also based on a commercial rotary SBM platform. It is fitted with 12 double cavities (saving parts and complexity) for SiOx coating of bottles up to 1l volume. The microwave plasma is pulsed for a better controlling of the deposition process ("Plasma Impulse Chemical Vapor Deposition, PICVD"). During coating, the bottles are kept in neck-down position to minimize contamination with particles. The process is pumped by one dedicated pump for each double cavity, all mounted on the same carousel whereas a separate pumping module is used for pumping down from atmosphere.

Figure 4: PCVD bottle coater with 12 double stations based on a SBM (courtesy of SIG).

The typical throughput of these current production plants is in the range of 10,000 bottles per hour (bph), depending on the size and shape of the bottles and the required thickness of the coating. Because of the single bottle reactor concepts, the process can be monitored for individual bottles in situ by any direct or indirect method for quality control.

Recent Developments

Kirin, together with Mitsubishi Heavy Industries and Mitsubishi Shoji Plastics Corporation, announced that they have developed a new rotary coating system to be delivered in spring 2004. Unique sliding seal discs are used for applying the vacuum, the plasma is generated by RF [20]. Small sized bottles (0.3 to 0.5l) as well as large ones (1 up to 3l in volume) can be coated with Diamond-Like Carbon (DLC) having small thickness (10 to 30 nm) and light color but good barrier properties. The expected output is 18,000 bph for 0.3 to 0.5l bottles and 12,000 bph for 0.5 to 1.5l bottles.

Nano Scale Systems is pursuing a new machine approach for SiOx bottle coating using an RF plasma. They are working on a pilot line towards a fully commercial machine targeting at > 20,000 bph in 2005 [21].

Sidel has announced an even larger ACTIS coating machine for 30,000 to 40,000 bph to be introduced in 2005 [22].

The coatings currently on the market are either based on amorphous carbon with a thickness from 80 to 160 nm or hydrocarbon doped silicon dioxide that typically has a lower thickness of around 40 nm. Figure 5 shows a two layer SiOx coating by Schott consisting of a base coat with higher hydrocarbon content and a rather inorganic Silicon dioxide barrier layer on top. This double layer approach is very similar to the one by Tetra Pak and Dow. It turned out that the base coat has a positive effect on the barrier performance and the robustness of the coating. However, a two-step process is more demanding on a rapid, rotary system. That leaves only less than 4 s for the plasmas and the switch over time in between.

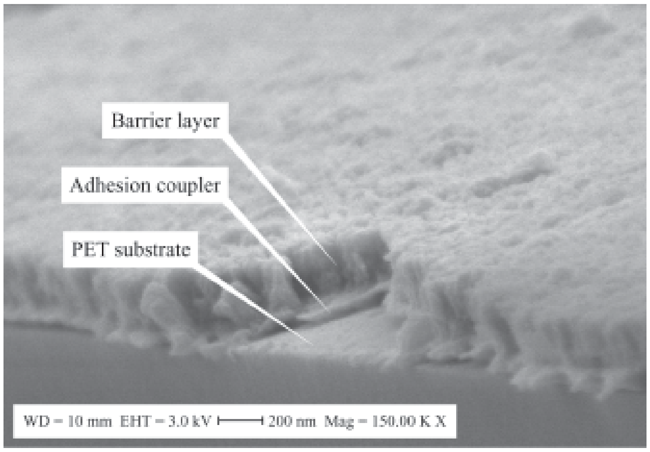

Figure 5: Scanning electron micrograph of a SiOx double layer lab test coating having much larger thickness than normal for obtaining a better picture (courtesy of Schott).

Both types of coatings, amorphous carbon and SiOx, proved to be very good barriers against oxygen, carbon dioxide, and other molecules. Extensive tests by Tetra Pak have shown that the barrier performance of their SiOx-coated ("Glaskin™") 0.5l-bottles against oxygen is improved by some barrier improvement factor (BIF) of 10 to 30 (with absolute transmission rates down to 0.0015 cm^3O_2/day package) compared to the respective non-coated ones. CO_2 permeation (out from a dry bottle having 4 bars of CO_2 inside) was found to be reduced to one fifteenth by the coating as determined by FTIR. The water vapor transmission was decreased by some factor of 2.5 to 4. The diffusion from acetaldehyde out from the PET wall material into the liquid was found to be decreased to one third, the transfer of esters to one fifth or less.

Specific tests proved that the coating is mechanically very stable. Neither a drop test of the filled bottle from 1.5 m nor mechanical deformation of 20% along the diameter caused significant increase of the oxygen permeation. Permeation also stays low when the coatings are stressed by creep of the plastic at inside pressures up to 6 bars, depending on the bottle design and blowing quality.

Overall, quite similar coating performance data have been reported by Schott/SIG for their SiOx coatings and Sidel and Kirin for their carbon coatings. Before comparing all these data too quickly, it has to be pointed out that the barrier improvement by a coating is strongly dependent on the material, design and moulding quality of the respective bottles. In other words, the often and for simplicity used barrier improvement factor (BIF) is only a measure for the quality improvement of a given bottle by a given coating procedure. It cannot simply be used to compare the quality of different types of coatings. Neither, this figure (defined as the permeation of specific molecules without/permeation with the coating) gives an indication on an absolute quality of the package. The quality of the package is strongly depending on the design (wall thickness, type of closure) and moulding quality as well and should rather be defined by the shelf life of a given product stored inside that package.

A major shelf life test was done with beer in Glaskin™-coated PET bottles (0.5 l, barrier cap with oxygen scavenger, filled in a commercial line). A taste test panel of beer experts from the Technical University of Munich at Weihenstephan came to the conclusion that beer kept in Glaskin™–coated bottles for nine months is at least equivalent in taste to the same beer stored the same time in conventional glass bottles.

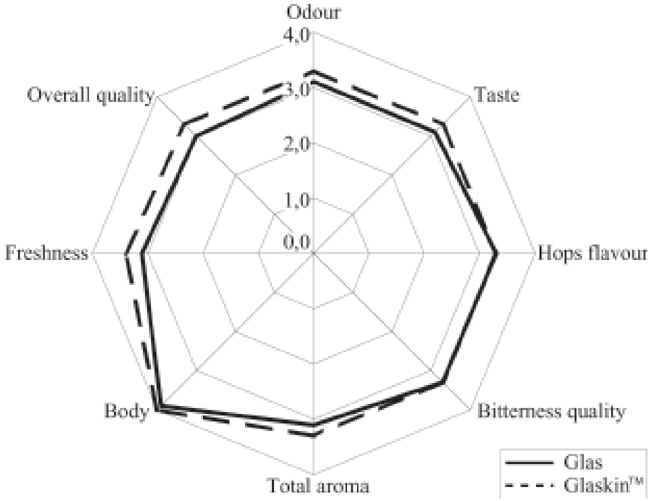

Figure 6: Result of a quality comparison of beer stored for nine months in Glaskin™-coated bottles versus glass bottles by a taste test panel of beer experts at the Technical University of Munich. The quality rating scales with the figures.

Apart from the chemical composition, the main difference between carbon and SiOx coatings is in the optical appearance. SiOx coatings are typically completely colorless, whereas carbon coatings have a yellowish to brownish tint, depending on the thickness.

Cost of the Coatings

The figures (for example: 12 to 15 € [23] or 9.2 US$ [20] per 1000 coated bottles) as given by different machine vendors cannot be compared directly because of different methods of calculation. However, the fact that one production line recently has been started up for delivering beer to Aldi, one of the major European discounters [22], indicates nicely that PECVD coating has become a cost-competitive method for barriers.

Figure 7: Selection of Glaskin™-coated juice and beer bottles produced in a central plant for the markets in Switzerland, Austria, Germany, and Sweden.

The recycling capability of plastic bottles has become a big issue due to their increasingly widespread use. Because of the versatility and high value of the plastic material, PET bottles can be recycled economically to fibers for textiles and carpets, films, or bottles again. However, these applications are crucially depending on quality and cost of the recycled material. Contamination of the PET within the cycle can effect these very badly. Specifically, the injection moulding of the preforms for the bottles is very sensitive to any contamination of the PET. This would result in poor optical and mechanical properties of the bottles blown from them. So, any coating should effect the processing properties of the PET, its transparency and color to the lowest possible degree.

Here, vacuum deposited coatings have an advantage to multilayer or lacquered bottles because they are very thin and do not negatively effect the mechanical properties of the PET when mixed into it. SiOx coatings do not change the appearance of colorless PET at all.

Tests with Glaskin™-coated bottles have shown that coated production scrap (not filled and thus, uncleaned) could be reground and added to virgin PET for injection moulding of preforms up to a percentage of at least 30% without any detrimental effects. The material from coated and filled bottles can be reused again after suitable grinding, washing and annealing (for recombination of ruptured chains) to 100% for even the highest requirements including high performance fibers and new PET bottles. No discoloration of the recycled material due to the SiOx coating was detected. The processing parameters of such recycling material were changed only in limits such that the economics are still fine.

CONCLUSION

PECVD bottle coating has proven its readiness for large volume production and is now established in the PET bottle market. The products filled into Plasma-CVD coated bottles to date are beer, juice, green tea, and carbonated soft drinks (CSD). Some examples from the European market are shown in Figure 7.

In comparison to other methods for barrier improvement, such as multilayer moulding or oxygen and acetaldehyde scavenging additives, the technical performance of this inside coating method generally is wider and often better. In addition, the recycling capability is very good. However, any coating requires a dedicated, additional machine for the bottle producer while for producing multilayer or scavenger bottles just a different type of preforms for the stretch blow moulding machine is required. Clearly these are more expensive than conventional monolayer preforms. However, these additional costs are variable while the investment into an additional machine causes fixed cost that will pay off in the long run. For this reason, it is not to be expected that Plasma-CVD will immediately take a large share of the market, although it has the potential to be a most cost-effective method. Rather, it will make its way from the high performance end of the market and grow from there as the cost saving potential becomes more obvious with larger volumes.

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