How tin oxide coatings affect closure rusting

Gary L Smay considers the effect of tin oxide coatings on the severity of closure rusting.

Potentially, a low level of tin oxide hot end coating will be deposited onto the finish of glass containers in normal commercial production due to the environment surrounding recently formed bottles and to the device used to deposit these coatings. These coatings can interact with iron-bearing closures via electro-chemical reactions to cause oxidation of the closure. For bottles with minimal amounts of tin oxide on the finish, insignificant amounts of closure rusting will be produced. However, as the thickness of tin oxide increases, the severity of closure rusting also increases eventually to objectionable levels. Thus, it is important to limit the amount of coating deposited onto the finish of containers in order to avoid potential problems with closure rusting in the trade.

The glass packaging industry has generally established that 17 CTU is the maximum thickness of tin oxide that can be tolerated on the finish of containers without creating objectionable levels of closure rusting. Data is presented in this paper to confirm this threshold value.

BACKGROUND

Rusting is a problem that can occur under certain conditions with iron-bearing crown or twist crown closures after being applied to the finish of glass containers. Closure rusting can occur by three mechanisms: Normal atmospheric oxidation; corrosion in the presence of a liquid; or by electro-chemical reactions with tin oxide coating on the glass surface. Of these three mechanisms, the electro-chemical reactions are the most problematic. Since the extent of rusting is more pronounced and occurs more quickly compared to simple oxidation reactions in air, which are relatively minor, or by corrosion reactions with water. The focus of this study was on the more severe electro-chemical reactions.

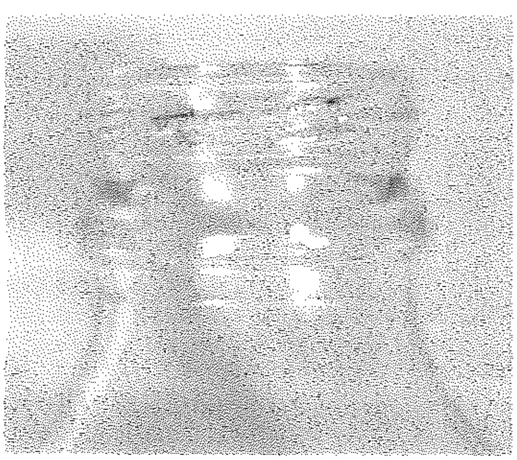


Figure 1: Example of the effects of closure rusting.

Electro-chemical reactions between tin oxide coatings and elemental iron in closures occur according to the following half-cell chemical reactions (with a liquid providing the electron pathway between the two surfaces):

Fe^{0} (closure) ==> Fe^{+2} + 2 electrons
Sn^{+4} (hot end coating) + 2 electrons ==> Sn^{+2}

In these reactions, elemental iron in the closure is oxidised, while tin (+4) in the coating is reduced. The oxidation of iron is manifested visually as rust, which can be observed on the interior surface of the closure and as a corresponding deposit on the finish of the bottles, as shown by the example in figure 1.

One method of avoiding closure rusting by the electro-chemical process is to assure that all liquid is removed from the region between the closure and the finish surface during the filling process. If the electron pathway is eliminated, the electro-chemical reactions will not occur, even in the presence of significant thicknesses of tin oxide. This is nearly impossible to do and some liquid, either in the form of the product or rinse water, will inevitably be trapped beneath the closure and the glass surface. Thus, since the presence of water cannot be totally avoided, it becomes necessary to consider how tin oxide coatings may affect closure rusting.

Tin oxide hot end coatings are deposited mainly from the pyrohydrolytic reaction of stannic chloride or monobutyl tin trichloride (MBTC) vapours with hot glass surfaces. These coatings are applied at the hot end of glass container plants, immediately after the freshly formed containers have been placed onto the flight conveyor and during their passage to the annealing lehr. Prior unreported studies at American Glass Research have indicated that these coatings consist almost entirely of stannic oxide (Sn^{+4}). Furthermore, the chemistry of the resultant deposited tin oxide coating is independent of the two predominant source materials. No anionic or hydrocarbon remnants of these materials have been found in the deposited tin oxide coatings. This is due to the relatively high glass temperatures encountered when the coating is deposited, completely decomposing the source materials.

Most commercial hot end coating application devices have some means of assuring that this coating is deposited onto the sidewall regions of bottles, while limiting the amount of coating deposited onto the finish regions. However, due to the nature of producing bottles at rates of up to 750 bottles/min and due to air currents in the environment surrounding the bottles and application hood, potentially some tin oxide can be deposited onto the finish of containers. Thus, since neither liquids trapped beneath the closure nor tin oxide coatings deposited onto the container finish can be totally avoided, some level of electro-chemical reactions will possibly occur and these situations must be considered.

The purpose of the current study was to determine the relationship between tin oxide coating thicknesses and the severity of closure rusting when subjected to conditions promoting electro-chemical reactions. The study was undertaken in the laboratory, under controlled experimental conditions, so as to avoid any confounding influence of extraneous variables on the results.

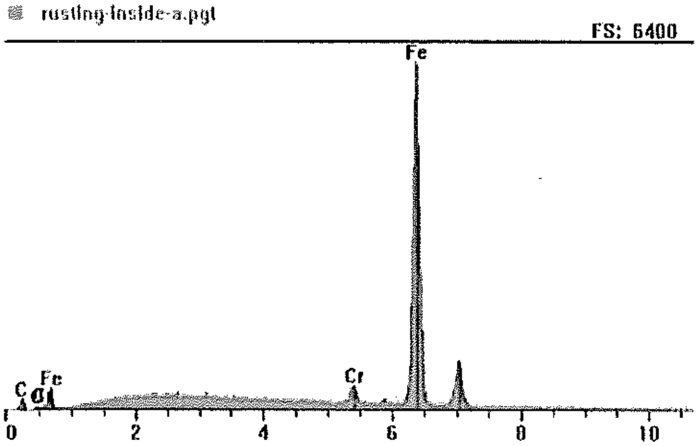


Figure 2: EDX analysis of closure metal.

Coating range (CTU)	Mean coating thickness (CTU)	Mean rust severity	Number of samples
0	0	2.4	24
1 - 5	3.1	2.3	22
6 - 10	7.8	3.9	11
11 - 15	13.4	4.5	13
16 - 20	18.0	5.3	18
21 - 25	22.4	4.9	7
> 25	25.5	6.0	1

Table 1: Rusting tests using lacquer-coated closures on finishes with various thicknesses of tin oxide.

EXPERIMENTAL PROCEDURE

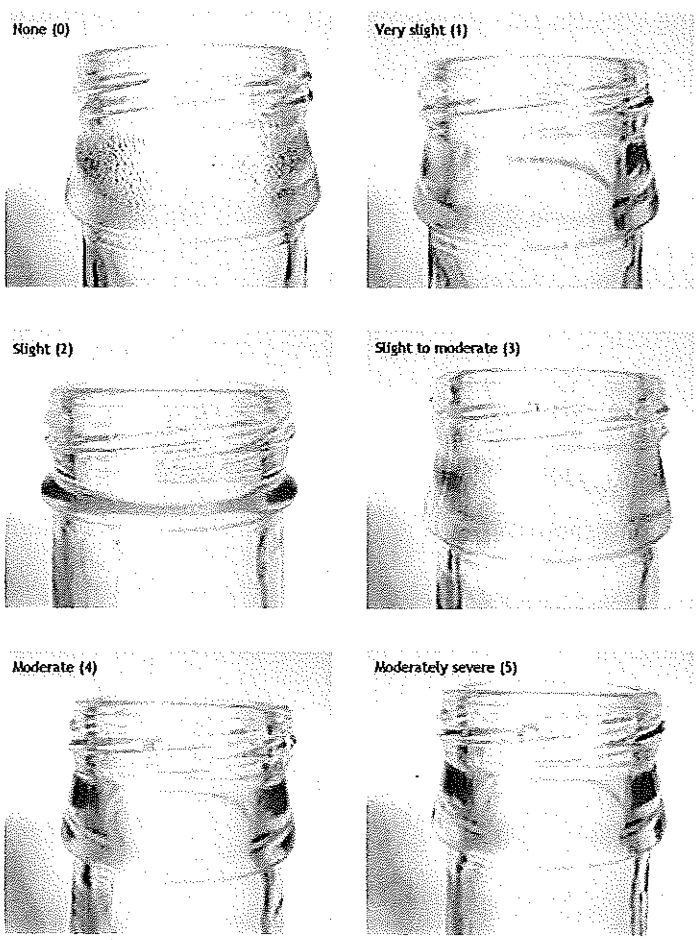
Bottle samples: Twelve ounce capacity, non-refillable, flint beverage bottles (with a twist-crown finish) were used as the substrate in these studies. Flint glass containers were chosen intentionally, since rust deposited onto the finish would be more visible than with the use of amber containers. Thus, the relationship between tin oxide coating thicknesses and closure rusting could be determined more accurately.

These glass samples were obtained from a container production plant in which the tin oxide hot end coating was deposited from a commercial system using MBTC. During selection of the samples, the MBTC application hood was intentionally miss-adjusted to allow the deposition of tin oxide onto the container finishes. The MBTC flow rates and adjustments of the application hood were varied to achieve coating thicknesses in the ranges of 0-10 CTU, 10-20 CTU and 20-30 CTU. A final group of samples were selected with the coating hood turned off and with barriers placed in the hood to inhibit fugitive vapours from contacting the glass surfaces. This was undertaken to produce a group of uncoated samples that were used as a baseline in the rusting tests. The sample bottles were all selected at the end of the lehr after normal, commercial annealing and prior to the application of any cold end coating.

To assure that no hot end coating was present on the baseline, uncoated group, the finishes of these samples were subsequently treated with hydrofluoric acid in the laboratory, prior to use in the experiments. This acid chemically removed any trace of tin oxide that might have been inadvertently deposited during the preparation of these samples in the glass plant.

Closure samples: The typical, commercially available crown closures used in this study were composed of a metal alloy, consisting mostly of iron, with a smaller amount of chromium, as shown by an energy dispersive X-ray spectrum in figure 2. Metal on the interior of the closure was coated with a normal, thin layer of a lacquer material. All of the closures were applied to the test containers by a hand-operated device. Capping forces were adjusted to achieve a crimp level of 1.130, a value that is typical of twist-crown closures.

Test environment: As discussed previously, a liquid (either product or rinse water) is a necessary component in the electro-chemical process to allow electrons to flow from the closure to the hot end coating. To ensure that liquid was present between the closure and the glass finish in these laboratory studies, the capped bottles were inverted and the neck and finish regions were immersed in ordinary tap water for a few minutes. Any air bubbles >



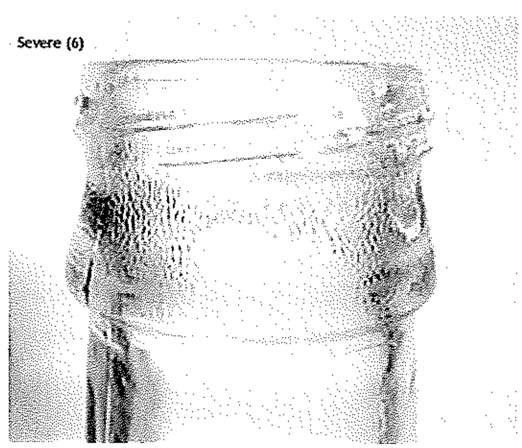


Figure 3: Examples of rust classifications.

trapped at the interface between the closure and finish surface were removed with a needle. These samples were then removed and placed upright in a closed chamber to inhibit water evaporation. Once the containers were placed upright, some of the tap water flowed from beneath the closure as a result of gravity. The remainder of the water was held between the closure and container finish due to surface tension effects. This experimental procedure was used to mimic the conditions typically encountered in the trade when liquids are not totally eliminated from beneath the closure skirt prior to storage.

In actual practice, rusting would occur only in those regions of a closure where the lacquer material had been disrupted during the capping process, thereby exposing the underlying iron-bearing metal, allowing it to be oxidised (atmospheric oxidation, liquid corrosion or electrochemical reaction). However, electrochemical rusting will occur only in those isolated areas where a liquid coincides with the region where the lacquer material was disrupted. Thus, closure rusting becomes somewhat of a probability issue, related to exposure of the iron metal combined with those locations where liquid was present. Such random events are typical of commercial practice and the current study was designed to simulate those situations.

Rust assessment: After 24 hours of storage, the samples were withdrawn from the chamber and the closures were immediately removed. The samples were allowed to air dry and the extent of rust on the finish of the container was subjectively determined by visual observation. The extent of the closure rusting was classified as: None, very slight, slight, slight to moderate, moderate, moderately severe and severe. Representative examples of these rust classifications are shown in figure 3.

These subjective classifications were assigned numerical values of 0, 1, 2, 3, 4, 5 and 6, respectively. These numerical values were used to characterise analytically the amount of rust on each sample, so that comparisons between rust severities and coating thicknesses could be performed.

Hot end coating thicknesses: Tin oxide coating thicknesses were measured with an AGR Finish Coating Measurement System (FCMS), at four evenly spaced circumferential locations on the E-wall of the test bottles. This device measures the intensity of light reflected from the glass surface and converts the signal into a coating thickness unit (CTU) that is calibrated to the amount of tin oxide present on the glass surface.

Typically, tin oxide is the only compound present and the light reflectance is solely due to this coating. However, in the present situation, some iron oxide may also be on the glass surface, making it necessary to remove it from the finish of the bottles to avoid any spurious light reflection that would interfere with the accurate determination of tin oxide coating thicknesses. This was done by immersing the finish regions of the bottles in concentrated hydrochloric acid (HCl).

Since iron oxide is soluble in HCl, while tin oxide is not, this process was effective in removing any rust that might be present on the finish surface, without affecting the amount of tin oxide that was present. The resulting measured four coating thicknesses thus obtained from each sample were averaged to obtain an overall assessment of the amount of tin oxide that was present on the finish of each sample bottle.

Number of samples and data comparison: Twenty four samples were selected from each of the four targeted coating groups, as described previously. Thus, a total of 96 bottles were used in these studies. The average coating thickness obtained from each bottle was calculated and recorded as noted above. The results were then grouped according to their average coating thicknesses into the following ranges: 0 CTU, 1-5 CTU, 6-10 CTU, 11-15 CTU, 16-20 CTU, 21-25 CTU and greater than 25 CTU. For all bottles within each of these seven groups, mean coating thicknesses were calculated and compared to the mean numerical value associated with the rust severity.

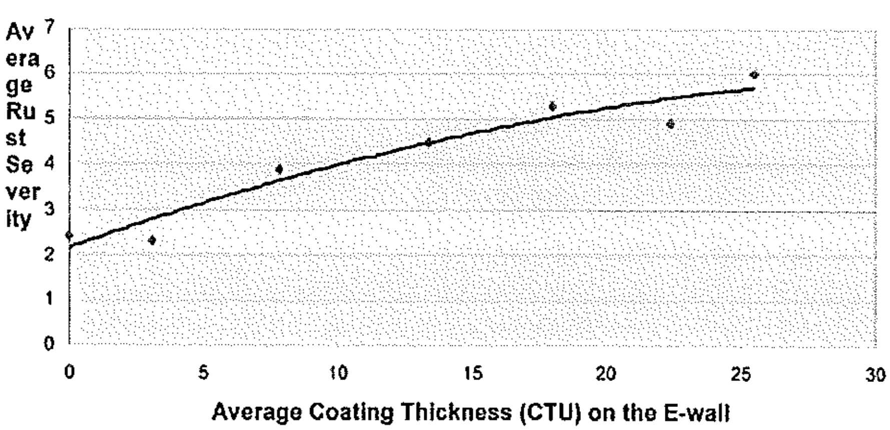


Figure 4: Closure rusting as a function of tin oxide thickness

RESULTS

Data correlation between closure rusting and tin oxide coating thicknesses are summarised in Table I and plotted in figure 4. As shown in this figure, some level of closure rusting occurred, even in the absence of tin oxide coatings (uncoated, baseline samples – 0 CTU). This relatively minor level of rusting is attributed to the corrosion mechanism between ions in the tap water and iron in the closure. If the corrosion mechanism was the predominant cause of closure rusting, this same minor level of rusting would be observed independent of tin oxide coating thicknesses. However, as shown by the data, closure rusting increased to more severe levels as the thickness of tin oxide increased. Thus, it was concluded that the electro-chemical reactions predominated over the corrosion mechanism as the thickness of tin oxide increased.

Based on this result, it is important to establish limits on the maximum thickness of tin oxide that can be tolerated on the finish of a container, without creating visually objectionable levels of closure rusting. Throughout the international container industry, the general guideline for the maximum tin oxide coating thickness that can be tolerated on the finish of containers, without any adverse effects on closure rusting, is 17 CTU, when measured with an FCMS. As shown in figure 4, greater thicknesses of tin oxide cause more severe closure rusting while lower thicknesses cause less severe rusting. Thus, caution must be exercised in the deposition of tin oxide to assure that only minimal amounts are deposited onto the finish of containers.

Routine testing using an FCMS should be implemented to ensure that coating thicknesses on the finish of the containers are limited to a maximum value of 17 CTU. Otherwise, there is an increased risk of having excessive and subjectively objectionable levels of closure rusting, depending on whether the conditions for electro-chemical reactions are present.

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