Abstract

The objective of this work is to coat tinplate with a hybrid film obtained from a sol-gel process constituted by the alkoxide precursor tetraethoxysilane (TEOS) and 3-trimethoxysilylpropyl methacrylate (TMSM), with the addition of cerium nitrate (0.01 M) and polyethylene glycol plasticizer (20 g L⁻¹) to the sol formulation. The films were obtained by dip-coating, applying one and two layers and curing them at different temperatures (60°C and 90°C) for 20 minutes, and adhering UV curing paint to each film respectively. The results showed that the double layered hybrid film obtained at 60°C had a higher layer of thickness and the best performance in the electrochemical assays, in other words, higher resistance to corrosion. Furthermore, in studies following the application of UV coating, the hybrid-film monolayer cured at 60°C which had an organic coating of cured UV applied to it, achieved a performance similar to that of the pretreated allyd greenhouse currently used in the metal packaging industry.

Keywords: Hybrid film; PEG; UV curing paint; Corrosion; Tinplate.

1 INTRODUCTION

Currently, tinplate, which is used in the packaging sector, is formed from a metal substrate comprised of a steel base that has undergone a surface treatment, to produce a fine FeSn₂ layer, a tin layer, and a layer of tin oxide [1,2].

The Tinplate is a laminated sheet of carbon steel, coated on both sides with tin by the electrodeposition process, producing a thin layer of FeSn₂, a layer of tin and tin oxide, because of the fusion process of Sn, after the electrodeposition [1-3]. The thickness of the metal sheets significantly influences the mechanical properties of the material. Over time, this thickness has been modified, to reduce the cost of the final product. The quality of the tinplate is related to the presence of tin oxides on the surface and the passivation layer. The tinplate usually has a full or partial tin oxide coating (SnOX), which may contain stannous oxide (SnO) or stannic oxide (SnO₂), including its hydrated forms. The presence of excessive amounts of these oxides can alter the appearance, weldability of the foil and the ability to receive organic coatings [1,3].

The tin, on the outside of the steel packaging, acts as a protective barrier, it suppressing the corrosion of the steel and resulting in the loss of the lower rates of tin, which does not become a problem because of the large area that has been tin coated and the small cathodic area (pore). On the other hand, when the tin does not act as a protective barrier, the ratio becomes large between the area that is cathodic versus that which is anodic, the iron in the steel exposed areas dissolves, and corrosion pitting can occur, promoting failures in the packaging [4].

The organic coating currently used in metal packaging are ultraviolet radiation-cures graphic inks. These coatings are applied internally and externally in a metallic container,
and their function is to insulate the surface of the container so that there is no interaction between the packaged product and the environment [5]. The UV curing process is an environmentally friendly process is what stands out as the main advantage of this technology [5]. However, there are disadvantages to the use of the radiation-curing ultraviolet process for example, the acrylic monomers normally have high levels of irritability, UV radiation can form ozone, and UV curing systems can cause poor healing in highly pigmented systems [6]. In addition, one of the main problems system is the fact that most of the cured coatings researched thus far have presented deficient mechanical [7].

This deficiency is mainly related to the poor adherence of the film and to the shrinkage of the film after curing [6]. Thus, it is necessary to coat the surface in a conventional manner through a thermal treatment system using solvents with high content of volatile organic compounds (VOCs), which pollute the atmospheric air due to their photochemical reactions with nitrogen oxides (NOx) that exist in the atmosphere [8]. With intention to replace the plating process, researchers have developed non-toxic pretreatments protect against corrosion, especially to obtain hybrid films through the sol-gel process. These hybrid films obtained through sol-gel method are typically homogeneous and exhibit good chemical and thermal stability. However, to increase he protective barrier, plasticizers such as polyethylene glycol, may be used to prepare such films [9]. In this context, the objective of the work is to increase the resistance to corrosion of packings of steel coated with tinplate, applying to the tin a hybrid film, obtained from sol formulation. The films were obtained through the dip-coating process, applying a monolayer and a doublelayer. It this study, we evaluated the influence of applying one and two layers to the films, cur them different temperatures (60°C and 90°C) for 20 minutes and the adhering the UV curing paint and applying it to each film, respectively.

2 EXPERIMENTAL

2.1 Metal Substrate and Surface Preparation

Tinplate samples with dimensions of 20 mm × 40 mm were obtained from an industrial sheet (Table 1), rinsed with acetone and dried. Then the plates were degreased through immersion in neutral detergent (pH = 7) at 70°C for ten minutes, washed with DI water, and dried.

The tinplate used in this study was manufactured by electrodeposition and after this it was performed the tin melt in a melting tower. The tinplate properties are shown in Table 2.

2.2 Development and Introduction of Hybrid Films and UV Ink

The silanes precursors used in this work, 3-(trimethoxysilyl)propyl methacrylate (TMSM) and tetraethoxysilane (TEOS), were obtained from Aldrich with 98% purity. Polyethylene Glycol 1500 (PEG) plasticizers were obtained from Selectophore®, Fluka and red metallographic (polyurethane acrylate) UV paints were obtained from Sellerink®.

The hydrolysis reactions were conducted with hybrid film silane precursors TMSM (C_{10}H_{20}O_{5}Si) and TEOS (C_{2}H_{5}SiO_{2}) with the addition of cerium nitrate in a concentration of 0.01 M. Ethanol and water, which were used as solvents. PEG was added in the formulation of the sol, at a concentration of 20 g.L⁻¹. In addition, a sample without plasticizer was studied. The hydrolysis time was 24 hours. The application of the hydrolyzed hybrid solutions was performed through a dip-coating process, with a removal rate of 10 cm/min⁻¹ and a permanence of five minutes in the solution. The films were obtained through a dip-coating process, applying one or two layers to obtain monolayered and doublelayered systems, and then they were cured at two different temperatures, 60°C and 90°C, for 20 minutes. The films with better performance were UV-cured (red colored). The quick peek equipment was used for the application of the organic coating, and for the cure, a UV curator was used at the industrial level. The cure parameters used were a 265 mJ.cm⁻² dose, a 395 mW.cm⁻² dose for intensity, and a belt speed of 18.5 m.min⁻¹.

Furthermore, the same UV coatings were applied to the same parameters mentioned using a melamine alkyd primer oven, which is the kind of oven currently used in the canning industry. The UV coating were then given a direct UV coating of tinplate without pretreatment. The thickness of the primer oven, which has an acceleration voltage of 20 kV using the signal-back-scattered electrons (BSE). The samples were observed from a top view and then a cross-sectional view to determine the layer thickness. Depositing a layer of gold

### Table 1. Specifications were provided by the supplier of the steel sheet before the tin electrodeposition was performed

<table>
<thead>
<tr>
<th>Element (%)</th>
<th>C_{max}</th>
<th>Mn_{max}</th>
<th>P_{max}</th>
<th>S_{max}</th>
<th>Si_{max}</th>
<th>Al_{max}</th>
<th>N_{max}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.06</td>
<td>0.2</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02-0.06</td>
<td>0.005</td>
</tr>
</tbody>
</table>

nanoparticles through a sputtering technique is necessary because the silane film is not a conductor. Energy dispersive X-ray spectroscopy was performed with Noran equipment, which is linked to the scanning electron microscope JEOL 5800.

The profilometry technique was used to measure the surface topography of the material. The profilometry 3D images and microrugosidade values of the samples were obtained with a PRO500 3D profilometer.

The thermogravimetric analysis (TGA) was performed with a 50-Shimadzu TGA instrument over a temperature range from 23°C to 700°C with a heating rate of 10°C.min⁻¹ under a nitrogen (N₂) flow rate of 50 mL.min⁻¹.

Table 2. Tinplate specifications

<table>
<thead>
<tr>
<th>Tinplate Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
</tr>
<tr>
<td>Thickness variation</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mechanical Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield strength</td>
</tr>
<tr>
<td>Resistance limit</td>
</tr>
<tr>
<td>Stretching</td>
</tr>
<tr>
<td>Hardness</td>
</tr>
<tr>
<td>R mean</td>
</tr>
<tr>
<td>Δr</td>
</tr>
<tr>
<td>Coating of tin</td>
</tr>
<tr>
<td>Oiling</td>
</tr>
</tbody>
</table>

Table 3. Description of the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP</td>
<td>Tinplate without hybrid film</td>
<td>TP&lt;sub&gt;UV&lt;/sub&gt;</td>
<td>Tinplate without hybrid film, but cured with an application of the organic UV coating.</td>
</tr>
<tr>
<td>TP-20-60M</td>
<td>Tinplate coated hybrid monolayer cured at 60 °C.</td>
<td>TP-20-60M&lt;sub&gt;UV&lt;/sub&gt;</td>
<td>Tinplate coated with hybrid film monolayer cured at 60 °C application organic coating UV coating.</td>
</tr>
<tr>
<td>TP-20-60D</td>
<td>Tinplate coated hybrid double layer cured at 60 °C.</td>
<td>TP-20-60D&lt;sub&gt;UV&lt;/sub&gt;</td>
<td>Tinplate coated with hybrid film double layer cured at 60 °C application organic UV cured.</td>
</tr>
<tr>
<td>TP-20-90M</td>
<td>Tinplate coated hybrid monolayer cured at 90 °C.</td>
<td>TP-20-90M&lt;sub&gt;UV&lt;/sub&gt;</td>
<td>Tinplate coated with hybrid film monolayer cured at 90 °C with an application UV coating.</td>
</tr>
<tr>
<td>TP-20-90D</td>
<td>Tinplate coated hybrid double layer cured at 90 °C.</td>
<td>TP-20-90D&lt;sub&gt;UV&lt;/sub&gt;</td>
<td>Tinplate coated with hybrid film double layer cured at 90 °C with an application organic UV coating.</td>
</tr>
<tr>
<td>TALP&lt;sub&gt;UV&lt;/sub&gt;</td>
<td>Tinplate coated with alkyd primer, thermally cured at 140 °C application of the organic UV coating.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. Flowchart of the preparation of the samples.
It was observed that the hybrid film TP-20-60M, showed no cracks. This result is associated with the lower curing temperature that does not promote the formation of cracks, however, there are some dark spots in the film, and these formed due to the retention of solvent that did not evaporate during the curing process. PEG has molecular weight and high viscosity, which limits evaporation of volatile organic compounds after application of the films during the curing process [12]. In the TP-20-90D system it was observed that increasing the curing temperature promoted the formation of microcracks, as compared to TP-20-60D system.

These results are in agreement with findings by various researchers [13] who reported a further increase in film thickness after adding more layers to promote an improved system of protection against corrosion. However, films exposed to high curing temperatures have microcracks due to the fragile state of their thicker layers, and there is then a subsequent decrease in corrosion resistance.

The layer thickness of the hybrid films was measured by cross section and examined by SEM (Figure 2). It is observed that the samples with the application of the double layer, or TP-20-90D and TP-20-60D samples, had higher layer thickness than the monolayer film, this observation was expected. The outcome is associated with the fact that the first layer adhered to the second layer well due to the presence of PEG plasticizer in the formulation of the sol, as the organic phase provides a better anchoring of the coating to be applied later [14]. From the results obtained by comparing the same number of applications, it was observed that the systems cured at 60°C showed greater layer thickness values than the systems cured at 90°C. This result is in agreement with the results of observations by other authors [15,16], who noticed that the rise in temperature of the curing process not only contributes to the good formation and performance of the silane film layer, but also decreases the film thickness. However, it is noted that the PD-20-60D sample showed a denser and more compact film thickness and perfectly adhere two layers of the TP-20-90D system that is associated with the fact that the excess heat from the silane cure process causes an increase in the reactions “cross-linking”, and thereby reduces its reactivity. This loss of reactivity is caused by the conversion of the silanol groups siloxanes. As a result the film becomes denser and the reaction and/or adhesion with subsequent layers becomes more difficult [17]. The TP-20-90M sample, despite having a weight value less than TP-20-60M, resulted in a more compact and uniform and potentially denser layer.

These results are consistent with the reports of a variety of researchers [16,18], who claim the higher layer of silane cure temperature improves the barrier properties due to cross-linking density, which gives rise to the formation of a porous layer and a less developed ability to protect itself from corrosion. When comparing the TP-20-90M and TP-20-90D samples, it was observed that the sample with monolayer deposition showed homogeneity without cracks in the film, indicating good adhesion between the film and the substrate. The sample double-layer is made thicker; in fact, of all the films studied, it had the densest film, the reaction between and/or adhesion of the layers more difficult. Thus, microcracks formed in the
Figure 2. SEM micrographs on the top surface obtained from the films (left column) and cross-sectional SEM micrographs to determine the layer thickness of the hybrid films (right column).

TP-20-60M

Tinplate
Resin
Hybrid Film
Thickness
0.98 ± 0.11 µm

TP-20-60D

Tinplate
Resin
Hybrid Film
Thickness
1.95 ± 0.10 µm

TP-20-90M

Tinplate
Resin
Hybrid Film
Thickness
0.73 ± 0.08 µm

TP-20-90D

Tinplate
Resin
Hybrid Film
Thickness
1.71 ± 0.12 µm

Retain solvent
Cracks
films. When comparing TP-20-60M and TP-20-60D samples, we can see that the sample with double layer deposition showed a more homogeneous film, density, compactness and thickness, and all of these features indicate a good adhesion between the film and the substrate. This result is associated with the fact that the first layer resulted in a better adhesion of the second layer due to the presence of the plasticizer formulation PEG in the sol, as the organic phase provides a better anchoring of the coating to be applied later. Therefore, considering the results analyzed and discussed, the TP-20-60D sample presented the best overall result. In relation to roughness values are summarized in Table 4, where Ra stands for arithmetic average, Rms represents average square roughness, and Rpp means maximum roughness or peak to peak. In relation to the samples with an application of a double layer, it was observed that the samples cured at 60°C showed a higher roughness than the ones cured at 90°C.

The results observed indicated that during the process of curing, the organic part that is unpolymerized can become volatile, creating tensile regions, that produce more irregular films [4]. It was observed that the tinplate showed low values of roughness. This result may be associated with the manner which tinplate is presented for uniform coverage due to the formation of tin oxide on the surface. The TP-20-90M sample showed the lowest value of surface roughness. However, the curing process at 90°C soon became sufficient to lead to increased reaction “cross-linking” and form more siloxane groups, which were responsible for the formation of a layer with a protective effect. This result indicated that there was the formation of a regular structure of the film formed with the formation of a crosslinked network of monomers with organic silicon atoms. This outcome formed a compact, homogeneous, and regular Si-O-Si film on the substrate. Moreover, the temperature of 90°C was adequate for the crosslinking of this film without causing cracks, as observed in the SEM (Figure 2). The sample with the application of the double layer cured at 60°C (TP-20-60D) showed the highest roughness relative to other hybrid films studied and in general relation to the substrate. This result is due to the formation of cracks and the peeling of the second film layer, as observed in the SEM (Figure 2).

Figure 3 shows the thermograms of the hybrid film cured at different temperatures. In both samples, we observed an initial stage of degradation up to 100°C, with a weight loss of about 5%, which we related to the degradation of the intrinsic water molecules.

A second stage of degradation hybrid film was observed between 100°C and 390°C, and it resulted in a mass loss of about 20%. This process is associated with the degradation of the silane groups, which are sensitive to high temperatures. The last stage of degradation hybrid film was observed between 400°C and 600°C, and it included a mass loss of about 20%, which we related to the degradation of the PEG present in the hybrid film. From 600°C, we observed the presence of approximately 55% residue (i.e., ash). These results revealed a thermal similarity of samples, demonstrating that the variation of the hybrid films cure temperature did not change the thermal stability.

As shown in another study by this group of researchers [6], good electrochemical performance of the samples with coating, which are displayed in the diagrams of Nyquist and Bode, proves the fact that the small increase in branch ethylene oxide (20 g.L⁻¹) is sufficient to reduce the condensation reaction rate of triorganosilanes groups. The condensation of the tetrafunctional alkoxide was also delayed in the presence of the monomer (PEG) due to the increased steric hindrance in the transition state; therefore, a more flexible film was obtained with improved substrate adhesion promoting an improvement in anticorrosive properties of the coating. Furthermore, the results of the impedance spectroscopy analysis showed that the TP-20-90M and TP-20-90D samples exhibited a marked reduction in total resistance values, and that this behavior may be associated with the presence of cracks and irregularities in the formation of these hybrid films, these cracks and irregularities allowed the electrolyte permeation and your contact with tin.

Another important technique used in the electrochemical study was the the mapping of anodic and cathodic activity that was obtained with the SVET (Figure 4).

The images and maps obtained, after one week of immersion, show that samples TP-20-60D and TP-20-90D presented better performance in relation to the other samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Roughness</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ra (µm)</td>
<td>Rms (µm)</td>
</tr>
<tr>
<td>TP-20-60M</td>
<td>0.5 ± 0.1</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>TP-20-90M</td>
<td>0.3 ± 0.1</td>
<td>0.4 ± 0.1</td>
</tr>
<tr>
<td>TP-20-60D</td>
<td>0.6 ± 0.1</td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td>TP-20-90D</td>
<td>0.5 ± 0.1</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>TR</td>
<td>0.4 ± 0.1</td>
<td>0.5 ± 0.1</td>
</tr>
</tbody>
</table>

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Figure 4. SVET current density maps and sample pictures acquired after 7 days and 21 days of immersion in 0.05 mol.L$^{-1}$ of NaCl. The scanned area was 5.2 $\times$ 4.7 mm$^2$. 
studied, in other words, they gave a better protection the tinplate. This was expected because the bilayer performs better than the monolayer. After three weeks of immersion all samples showed corrosion. While SVET presented instantaneous corrosion at the time of measurement, the optical pictures show that the corrosion accumulated during the 21 days of immersion. The localized nature of the process is patent in the optical pictures and highlighted in the SVET maps. An order of performance can be established as TP-20-60D > TP-20-90M > TP-20-60M ≈ TP-20-90D. While not shown, the bare substrate revealed the same pattern of corrosion with a faster rate; in fact, signs of corrosion appeared in the first hours of immersion, and in fewer than five days the aspect was like the worst systems under analysis.

3.2 Performance Evaluation of the Films with the Application of UV Paint

Figure 5 shows the appearance of the systems after the adhesion test. The evaluation of the samples was performed according to ASTM D3359 and is reported in

Table 5. This standard uses a rating scale (0B to 5B) in which 5B corresponds to an excellent adhesion (film intact) and the film at 0B represents no adhesion to the substrate (film removed).

As expected, UV paint applied directly to substrate did not have any grip (0B). The TP-20-90MUV, TP-20-90DUV, and TP-20-60DUV samples had a poor adherence (1B). The TP-20-90MUV, TP-20-90DUV, and TP-20-60DUV samples had a poor adherence (1B).

These results indicated that the temperature of 90°C and the double layer applied weakened the structure of the films, not favoring the adhesion of the film to the substrate. As mentioned previously, the excess heat in the silane cure

<table>
<thead>
<tr>
<th>Sample</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP-20-60MUV</td>
<td>3B</td>
</tr>
<tr>
<td>TP-20-90MUV</td>
<td>1B</td>
</tr>
<tr>
<td>TP-20-60DUV</td>
<td>1B</td>
</tr>
<tr>
<td>TP-20-90DUV</td>
<td>1B</td>
</tr>
<tr>
<td>TALPUV</td>
<td>3B</td>
</tr>
<tr>
<td>TRUV</td>
<td>0B</td>
</tr>
</tbody>
</table>

Figure 5. Adhesion test of UV paint applied on the hybrid films of the sample (a) TP-20-60MUV, (b) TP-20-60DUV, (c) TP-20-90MUV, (d) TP-20-90DUV, (e) TALPUV, (f) TRUV.
process causes an increase of the reactions “cross-linking”, which reduces its reactivity. This loss of reactivity is caused by the conversion of the silanol groups siloxanes [18] and, it results in the film becoming dense and the reaction with polymer becoming more difficult.

However, the TP-20-60M_{UV} pretreatment achieved the same degree of adhesion as the pretreatment currently used (TALP_{UV}) due to the fact that the temperature of 60°C was not sufficient for there to be a complete halftone increasing the reactivity of such pretreatment and making the reaction with the ink easier.

Figure 6 shows the samples to the pretreatment studied after the flexibility test with the tapered mandrel. For digital camera images, it was observed that only the sample without pretreatment showed detachment of the UV paint. However, by increasing the images and analyzing the under the optical microscope, we observed that only the TP-20-60M_{UV} pretreatments and TALP_{UV} performed well. In other words, there was an appearance of cracks or a detachment from the paint film that confirmed the good anchoring of these samples, as analyzed in the adhesion assay (Figure 5 and Table 4). However, the TP-20-90M_{UV} pretreatments, TP-20-60D_{UV}, and TP-20-90D_{UV} did not show good mechanical deformation with a UV coating and had the appearance of ruptures and cracks in them.

Figure 7 shows the images obtained for determining the contact angle by the sessile drop method, from which contact angle measurements were for UV systems were
Electrochemical and mechanical behavior of UV curing paint on hybrid films modified with polyethyleneglycol plasticizer applied on tinplate

With ink cured by UV, the TP-20-60M_{UV} sample results played mechanical characteristics similar to the pretreatment currently used (TALP_{UV}); this result was due to the fact that the temperature of 60°C was not sufficient for there to be a complete crosslinking. Furthermore, the polyethylene glycol had an affinity for the subsequent organic coating. Similarly, the TP-20-60M_{UV} sample showed the smallest value for the contact angle and its wettability factor was greater than other samples. Consequently, this system showed the best rates of UV ink adhesion and flexibility associated with the facts that the TP-20-60M sample did not make a complete cross-linking of the hydrophilic film but did enhance the reactivity of the system for subsequent application of the coating. Therefore, depending on the need or lack thereof to apply a particular product in real, industrial environment, one can decide which film is required based on the various specific characteristics.

Acknowledgements

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REFERENCES


Figure 7. Images obtained for the determination of the contact angle of UV coatings applied on the pretreatments by the sessile drop method.

analyzed. It was found that UV systems with smaller contact angle values, and therefore higher wettability, were pretreatments that showed good UV ink adhesion and flexibility. As mentioned, it confirms that the TP-20-60M_{UV} sample did not obtain a complete crosslinking making the film hydrophilic but increasing the reactivity of the system for subsequent application of the coating. The TALP_{UV} sample showed a hydrophilic behavior due to the fact that the esterification rate (introduction of alkyl groups in the melamine resins) is slower than the polymerization rate. However, it can be seen that the UV ink does not provide a hydrophobic barrier, because without a pretreatment system, it showed the lowest contact angle value. This is because the coating to be applied at a thickness of a lower layer (10 µm - 15 µm) is not a protective coating; rather, it is a surface film used for lithograph packaging (tinplate) accotding to aclient’s design.

4 CONCLUSIONS

Through comparing the hybrid films with the cure temperature variations and the numbers of application layers, we observed that the TP-20-60D sample demonstrated the best results, the film proved itself to be homogeneous, dense, compact and thick. This information verified that the film can be used as a corrosion barrier coating. In systems with ink cured by UV, the TP-20-60M_{UV} sample results played mechanical characteristics similar to the pretreatment currently used (TALP_{UV}); this result was due to the fact that the temperature of 60°C was not sufficient for there to be a complete crosslinking. Furthermore, the polyethylene glycol had an affinity for the subsequent organic coating.

Similarly, the TP-20-60M_{UV} sample showed the smallest value for the contact angle and its wettability factor was greater than other samples. Consequently, this system showed the best rates of UV ink adhesion and flexibility associated with the facts that the TP-20-60M sample did not make a complete cross-linking of the hydrophilic film but did enhance the reactivity of the system for subsequent application of the UV coating. Therefore, depending on the need or lack thereof to apply a particular product in real, industrial environment, one can decide which film is required based on the various specific characteristics.


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