Adhesion of Aluminium Foil to Coatings – Stick With it

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ABSTRACT

Aluminium foil is widely regarded as the most effective barrier material in flexible packaging, giving almost perfect protection against light and suppressing any transport of matter. Foil is usually converted to flexible packaging laminates by traditional converting processes, such as lacquering or 2-component-adhesive lamination, but more and more extrusion coating and extrusion lamination are being used.

Almost all aluminium is put through an annealing process, to produce an appropriate surface, which is as good and homogeneous as possible with regard to unwinding properties (at high speed), wettability, adhesion and chemical resistance.

The effects on adhesion performance as a result of replacement of traditional sealants and adhesives by extrusion coatings are described for selected types of packages and packaged goods. Aspects relating to the foil’s surface and coatings’ barrier will be discussed.

1. INTRODUCTION

Looking at flexible packaging, there is a distinct trend towards the use of extrusion coating and extrusion lamination for converting aluminium foil. A number of substantial benefits can be gained from manufacturing without solvents, achieving high line-speed, saving space for drying channels, saving on investment for solvent recovery equipment or saving storage space for crosslinking adhesives and cutting lead times.

Requirements on packaging machinability, especially seal performance are usually mastered, but major effects such as the interactions between package and the filled good are often forgotten.

The main reason for using aluminium foil in flexible packaging lies in the need to completely suppress migration or permeation through the package and shield the packaged good from the environment in the most suitable way.

In borderline cases involving delicate packaged goods or thermal package treatment, it is very important to guarantee functional migration resistance of the coatings and maintain adhesion and package integrity.

The aim of this presentation is to explain the adhesion performance of aluminium foil and illustrate the demands placed on the adhesion of lacquer, adhesive-bonded film and extrusion coating by particular packaged goods and package treatment.
2. MANUFACTURING ALUMINIUM FOIL

Aluminium foil is usually produced by rolling down strip in a number of subsequent cold-rolling steps, which reduce the material thickness by almost a half in each step.

**Figure 1: Cold rolling of foil**

For a final foil thickness of below 60 µm, two layers of foil are wound together before the last rolling step. Rolling oil is sprayed between the two layers as a release agent and the “twin foil” is rolled down to the desired final thickness. After the final rolling step, the foils are separated in a “de-doubling“ machine, slit and wound in the form of a coil to the customer’s desired width and length. Most of the foil in this so-called “hard“ state is subsequently annealed as a coil, where the grain structure is recrystallized and the rolling oil is removed.

**Figure 2: Precipitations and grain structure in non-annealed and annealed foil**
2.1 FORMATION AND COMPOSITION OF ALUMINIUM FOIL’S SURFACE

Besides recrystallising the grain structure of the foil and removing the rolling oil as far as possible, the main tasks of annealing are to produce a surface which is not only even, homogeneous and resistant but also displays good wettability and adhesion properties. Good unwinding properties must also be maintained, meaning that any uncontrolled oxide growth on the surface, which could lead to the foil sticking together during unwinding, has to be avoided.

To aid understanding of the processes involved, a two-layer-model of the oxide - consisting of a top layer and a barrier-type bottom layer – on the foil’s surface is used [1].
After rolling, a continuous amorphous oxide layer is formed immediately due to the reaction between oxygen and humidity in the environment and newly produced metal surface. This is a so-called “room-temperature” oxide [2].

During annealing typically at temperatures of around 300°C, this oxide, which forms the barrier, grows thicker due to the increased diffusion of oxygen through the oxide and reactivity with the metal in the oven atmosphere. The type of oxide in the top layer also changes during annealing; this change is accompanied by a loss of water and leads to a more compact oxide of generally higher resistance. This oxide growth takes place at the interface between oxide and metal. The resulting barrier layer provides the corrosion resistance of the metal while the top layer ensures adhesion to coatings.

The best layer integrity without any defects is seen in pure aluminium foil. Theoretically, therefore pure aluminium also has the best resistance to chemical attack. Since there is a need for mechanical strength in converting and packaging applications, however, alloys with a specified grain structure and distribution as well as precipitations of a particular type and size are required. Regarding the number and size of precipitations, some are embedded in the surface while bigger ones can disturb the uniformity of the oxide and even break through the oxide layer. Because precipitations like AlFeSi or Al3Fe are more noble than the surrounding metal matrix in the presence of an electrolyte, the aluminium itself can act as a sacrificial anode to be locally electrochemically converted to oxide. Usually this can only occur at elevated temperatures and in the presence of humidity, electrolyte and oxygen.

![Electrochemical reaction diagram](image)

**Figure 5: Oxide growth electrochemically driven at a precipitation**

In meeting border-line demands, it has to be considered that foil with a higher content of Fe or Si, might be more susceptible to corrosion than pure aluminium.
During annealing, there is a marked difference in the atmosphere from the outside to the inside of the coil, with more oxygen (and humidity) present at the edges; this continuously decreases towards the middle. This profile results in the growth of a thicker oxide layer along the edges with only slight growth occurring in the middle of the web width.

During annealing, the initial amount of rolling oil – about 10mg/m² - is not completely removed from the coil; a residual amount of around 1 mg/m², determinable as carbon, remains. Investigations show that there is slightly more hydrocarbon in the centre than in the edges. Wettability is therefore lower in the middle and higher in the edges.
Since the first pre-requisite for good adhesion of coatings is good wetting, foil is classified according its wettability. Class A means that a continuous layer of water can be spread on the surface over the complete width and does not drip-off. Class B means that wetting occurs in any zone of the coil with 90% water/10% alcohol, class C with 80% water/20% alcohol etc. Since there is a certain wettability profile with lower wettability in the middle than in the edges, the surface tension of the liquid might exceed the foil’s surface tension significantly and the wetting threshold becomes visible as the so-called “non-wettable width” (NWW).

**Figure 8: “Non-wettable width“ of a foil**

The wettability class indicates the position of lowest wettability in a coil. Highest wettability is required if aqueous lacquer systems or glues are applied, but adhesives (solvent-based and solvent-free), solvent-based lacquers or extrusion coatings also spread well on foil of lower wettability levels.

<table>
<thead>
<tr>
<th>Categories of foil wettability [mN/m]</th>
<th>A: Water</th>
<th>B: Water/Ethyl alcohol 90% : 10%</th>
<th>C: Water/Ethyl alcohol 80% : 20%</th>
<th>D: Water/Ethyl alcohol 70% : 30%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Water</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>B: Water/Ethyl alcohol 90% : 10%</td>
<td>72.0 mN/m</td>
<td>47.0 mN/m</td>
<td>38.5 mN/m</td>
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</tr>
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</tr>
</tbody>
</table>

**Figure 9: AFCO-classification of foil wettability**
A compromise has to be found between the highest wettability level and the best unwinding properties: higher unwinding speeds without the risk of web break can be achieved for wettability classes B or C.
Annealing coils “as dry as possible” to achieve class A-wettability can be accompanied by the interlinking of the oxide growing on adjacent coiled foil surfaces, especially closed to the edges. Such interlinkings lead to sticking of the foil and can cause web breaks during unwinding. Consequently, “C“-annealed thin foil ensures the best unwinding performance at high speed and exhibits excellent adhesion to PE extrusion coatings.

3. CASES CHALLENGING ADHESION

To achieve good adhesion of a coating on foil, good spreading of the coating is an essential prerequisite, to be fulfilled. Good wetting and spreading of the matter to be coated on the aluminium foil is fulfilled, if the coating’s surface tension is similar to or falls below the foil’s surface tension. When lacquers are applied, the degree of spreading is almost 100% complete; when using dried adhesives or melts, even of low surface tension, spreading is impaired by their high viscosity. Consequently, wetting on the web has to be forced by the pressure in the laminator’s nip. When adhesive layers are as thin as the roughness of the metal or have to cover printing inks or melts grow stiff during spreading, complete overbridging of the materials can not be ensured. Secondly, a sufficiently high number and concentration of interfacial bonds and forces determines the adhesion level.
Due to the chemical solubility of the oxide layer, which is stable inside the range of pH 4 to pH 8.5, there are numerous acid containing packaged goods, which can attack the aluminium, if the coatings do not prevent the foil from the acids.

![Figure 10: Permeants and Conditions Potentially Affecting Aluminium - Plastic Adhesion](image-url)
3.1 LACQUERED AND EXTRUSION-COATED DAIRY LIDDING

Dairy lidding for fill & seal machines is largely dominated by heat-sealable aluminium foil. Vinyl-based heat seal lacquers not only ensure robust performance but also give excellent barrier properties. Polyethylene-based extrusion coatings, which are used increasingly, display very different behaviour with regard to adhesion to the foil.

Progressional oxide growth on the foil during storage can lead to adhesion failure between the metal surface and the coating. Such oxide growth is due to the foil's reaction with oxygen and/or humidity present in the headspace of packages. With regard to dairy products, the 1%-content of lactic acid in a yoghurt, for example, can attack the metal if the lacquer carries pinholes. An extrusion coating should have no pinholes at all. Nevertheless, extrusion coatings sometimes appear to be “sensitive” to loss of adhesion.

To evaluate the availability of oxygen and humidity at the interface lacquer/Al, permeation rates through the lacquer or coating have been acquired.

<table>
<thead>
<tr>
<th></th>
<th>5 µm</th>
<th>20 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>WVTR</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>OTR</td>
<td>380</td>
<td>7000</td>
</tr>
</tbody>
</table>

Figure 11: Oxygen and water vapour permeation of a heat seal lacquer and a coex-coating

A typical lacquer coating on the lid of a yoghurt cup exhibits a water vapour permeation rate higher than the polyolefin, which is 4 times thicker. In sharp contrast, the polyolefin coating allows 20 times more oxygen to pass than the vinyl system. Since yoghurt pots are made of polypropylene or polystyrene, oxygen is always available in the headspace. Regarding the loss of adhesion, the oxygen permeation plays a more important role in polyolefin coatings than in vinyl lacquers.
3.2 ADHESIVE LAMINATES AND RETORTING

Retortable standup pouches PET/Al/PA/PP are usually laminated with 2-component polyester-polyurethane adhesives. During the retorting of the filled pouches, water vapour can pass through the plastic layers, but this normally has a positive impact on adhesion: the silanol groups of silane-functionalised adhesives, formed by hydrolysis react with the hydroxylated oxide surface progressively. Here the hydroxylation step of the oxide is substantial, because exclusively in this state the oxide reacts with the silanol groups and adhesion is improved [3].

![Figure 12: Interaction between silanol and alumina during retorting](image)

During retorting, however, bubbles may form between the aluminium and the adhesive, and these are often accompanied by strong oxide growth.

![Figure 13: Bubble formation of a pouch laminate during retorting](image)
During retorting, the water vapour and oxygen permeability through the plastics can increase by some decimal digits. If there are “dry spots“ with no adhesion on the aluminium, because the adhesive has been applied on the printing ink, oxide growth can start in this area neighbouring precipitations. Depending on the availability of electrolyte and oxygen, the bubble can expand and is usually accompanied and favoured by the formation of hydrogen.

**Figure 14: Bubble formation during retorting**

In retortable pouches, “dry spots“ with no adhesion can occur before retorting and oxide spots, with precipitations enclosed, can be found after retorting.

**Figure 15: Oxide growth around precipitations**
3.3 SEALANT – PACKAGED GOOD INTERACTIONS

During hot-filling, pasteurising or retorting, oxygen and water vapour can pass through coatings with ease, relative to normal environmental temperature. Very little data on other permeants migrating from packaged goods into and through internal coatings at elevated temperatures is available. Some permeation data on “similar” substances through LDPE, HDPE and polypropylene is shown in figure [4].

![Figure 16: Permeation coefficient trends for elevated temperatures.](image)

Certain components from packaged goods, especially fat and fatty acids, can permeate polyolefin coatings at high temperature due to elevated mobility inside the plastic and their chemical similarity to and solubility in the polyolefins. Long chain fatty acids do not react with aluminium at ambient temperature, but they do above 100°C, forming aluminium soaps or carboxylates. The presence of these Al-soaps at metal-coating interfaces [5,6] in the case of adhesion failure has been proved. Bonding between extrusion coated acid copolymers and aluminium partly also occurs by soap-formation. So soap formation with a high-molecular plastic promotes adhesion and with low molecular compounds leads to adhesion failure.
Since industrially filled goods are not homogeneous, paste-like simulants were used in tests, the packages retorted and the coatings and interfaces examined. Triglycerides have been found to migrate into the coating, accompanied by attendant substances like phospholipids (natural emulsifiers) and, depending on their degree of viridity, smaller amounts of free fatty acids. Fat uptake was detected by ATR-infrared, recording a layer depth of about 3 µm.

**Figure 17: Bonding between acid copolymers and aluminium**

**Figure 18: Fat uptake of a coating during retorting**
This fat uptake can even lead to layer destruction, causing fat-filled voids, flaws and cavities in a coating after retorting in the presence of fat, shown by extraction with a solvent for fat.

Figure 19: Deterioration of a coating due to fat uptake

In retorting tests with simulants containing fatty acids, delaminations occured, similar to the defects found in everyday packages.

Figure 20: Delamination phenomena with simulant pastes
At such delaminating interfaces in the plastic, additional aluminium soaps were also observed, indicating the reaction of fatty acid with the oxide.

![Graph showing species at the adhering interface in a plastic after retorting](image)

**Figure 21:** Species at the adhering interface in a plastic after retorting

The same species occur on the aluminium surface, but these can be rubbed-off and washed-off, except most of the strongly adhering soaps.

![Graph showing proof of soap adhesion on Al](image)

**Figure 22:** Proof of soap adhesion on Al
The following diagram explains this type of failure, which results from the progressive replacement of bonds between plastic and oxide with fatty acid soap bonds, leading to a weak interface. The plastics concerned have thus failed as a functional barrier to protect the adhering interface.

Figure 23: Adhesion failure by bond replacement and saponification

Comparing the internal faces of coatings, significant differences can be seen in the amount of migrating compounds, the coating allows through. Such differences aid the selection of the most suitable tie resin to maintain good bonding.

Figure 24: Barrier selectivity for bonding resins
4. CONCLUSIONS

Aluminium foil surface is well-prepared for efficient wetting, bonding and adhesion durability. Coatings or adhesives provide the most important pre-requisite for durability, if they spread the foil surface completely. Since the surface of aluminium acts as a barrier in a laminate, migrating compounds can enrich or react there and lead to adhesion failure by infiltration or replacement reactions. The same reactions which make bonding, also occur during bond replacement between migrated compounds and the foil surface. The effect of short-time package treatment by pasteurising or retorting on adhesion can be more extreme than seen in even long-term storage. Plastic coatings are not as dense as expected for migrating compounds at elevated process temperatures and in order to maintain adhesion the right choice for the functional barrier must be taken. Regarding particular package treatment and packaged goods, there is no blanket solution but one has to stick with it.

5. REFERENCES


6. ACKNOWLEDGEMENTS

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Structure

- Manufacturing Aluminium Foil
- Formation and Composition of Aluminium Foil Surface
- Cases challenging adhesion
  - lacquered and extrusion-coated dairy lidding
  - adhesive laminates and retorting
  - sealant - packaged good interaction
- Conclusions
Cold Rolling of Aluminium Foil

- Cold rolling
- Doubling
- Cold rolling
- Separating and Slitting
- Annealing
- Foil

Precipitations and Grain Structure in Non-Annealed and Annealed Foil

- Foil after finishing
- Foil after annealing (soft annealing)
- Grains
- Precipitations
- Precipitations, also close to the surface
Coil during annealing

Coil of Aluminium Foil

Oxide growth during annealing and precipitations embedded in the surface

Oxide layers formed in a humid environment at room temperature

After annealing

P = Precipitation (like AlFeSi, Al$_3$Fe)
T = Top layer
B = Barrier layer

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Contact Corrosion Analogon in the Presence of Electrolyte

Reactions depend on the availability of oxygen and water, pH and temperature.

Oxide Thickness by IR-Absorption

![Graph showing oxide thickness by IR-Absorption](image-url)
Non-Wettable Width of a Foil Web

Surface Tension and Wettability Categories for Aluminium Foil (AFCO)

<table>
<thead>
<tr>
<th>Category</th>
<th>Solution Composition</th>
<th>Wettability</th>
<th>Surface Tension [mN/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Water</td>
<td>100%</td>
<td>72.0</td>
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<td>Water/Ethyl alcohol 90% : 10%</td>
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<tr>
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<td>Water/Ethyl alcohol 70% : 30%</td>
<td>33.0</td>
<td></td>
</tr>
</tbody>
</table>
**Oxide Thickness and Wettability Profile**

![Graph showing oxide thickness and water contact angle variations](image)

- Oxide thickness [nm]
- Water contact angle [°]
- Distance from left edge [cm]

- Oxide thickness, annealed
- Oxide thickness, non-annealed
- "Non-wettable" width

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**Foil Annealing Requirements**

- Recrystallising grain structure
- Removing rolling oil
- Maintaining good unwinding properties
- Providing homogeneous wettability
- Providing strong adhesion
Permeants and Conditions Potentially Affecting Aluminium - Plastic Adhesion

- Oxygen
- Water
- Acetic acid
- Citric acid
- Lactic acid
- Vitamin C
- Preservatives
- Fat
- Emulsifiers
- Salt
- Hot filling
- Pasteurising
- Retorting
- Storage time
- Light

Permeation Measurements of Dairy Lid Coatings

<table>
<thead>
<tr>
<th>Coating Type</th>
<th>WVTR [g/d·m²] @ 20°C/ 100% r.h.</th>
<th>OTR [ml/d·m²·bar] @ 23°C/75% r.F.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lacquer (5 µm)</td>
<td>30</td>
<td>380</td>
</tr>
<tr>
<td>Coex-coating (20 µm)</td>
<td>5</td>
<td>7000</td>
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</table>

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Interaction Between Silanol and Alumina During Retorting

Bubble Formation in a Retortable Stand-Up Pouch

Adhesive remaining on PET
Bubble Formation During Retorting

"Dry Spots" With No Adhesion and Oxide Layer Spots Grown in a Bubble
Temperature Dependence of Permeation Through Plastics

Bond Formation of Acid Copolymers on Aluminium Foil
Fat Absorbed in a Sealant Coating After Retorting (IR)

During retorting in contact with:
- Only water
- Low fat content
- High fat content

During retorting:
- No fat
- Low fat content
- High fat content

Penetration depth for IR-ATR: 3 µm

Plastification of Coatings During Retorting

STEM images:
- SEM (no fat)*
- SEM (high fat)*

(* specimen extracted)
Delaminations During Retorting

Glossy aluminium surface
Coating film

Film from the smooth-walled container, forming a pouch

Packaged good: Simulant paste with fat and fatty acid

Species at a Delaminated Aluminium-Plastic Interface after Retorting

Retorting in contact with
- Water
- Low fat content
- High fat content

Tie resin's C=O bonds
Triglyceride
Fatty acid
Al-soaps

Penetration depth for IR-ATR

Extrusion

Wave number [cm$^{-1}$]

1900 1800 1700 1600

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Abrasion Proofness and Bonding of Soap Species to the Aluminium Surface

![Graph showing IR-ATR on the metal before and after rubbing/washing the surface.](image)

Aluminium soaps adhere well to the metal surface!

Adhesion Failure as a Result of Saponification

![Diagram showing adhesion failure due to saponification.](image)
Conclusions

✧ The surface of aluminium foil is well-prepared for adhesion, chemical resistance and acts as a barrier

✧ Complete spreading of coatings on foil is essential for durability

✧ Adhesion to foil can be affected by extreme migration during thermal treatment

✧ Under these conditions plastics are not as dense as expected and allow such migration

✧ Particular foil applications need a “smart“ functional barrier in the coating