Extrusion-Lamination of Flexible High Barrier Laminates
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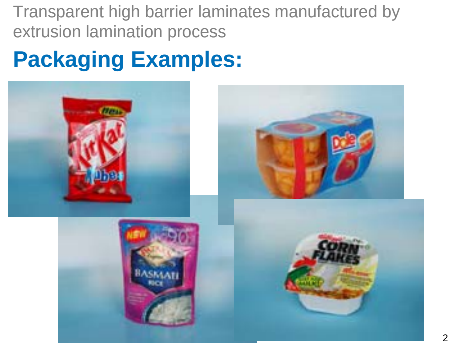
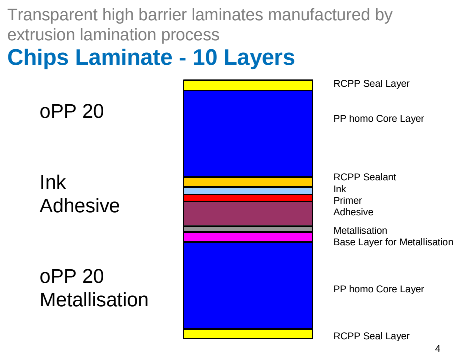
Introduction

Most important function of packaging materials is to protect food and pharmaceutical products from spoilage and decay.

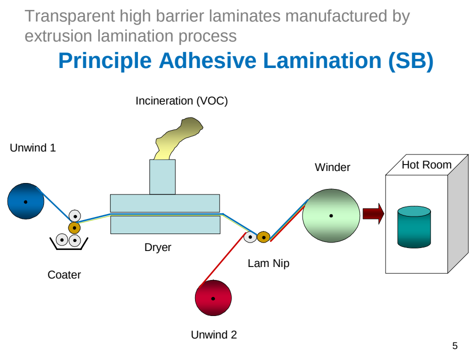
For this purpose, in flexible packaging, different materials are combined such that they exhibit the required barrier properties, in the first place, against the migration of oxygen and/moisture (Slide 2).



To the consumer in general, the intricate construction of such packaging materials is hardly noticeable. Who would actually suspect that the material of a simple chips pouch consists of a 10-layer construction (Slides 3+4).



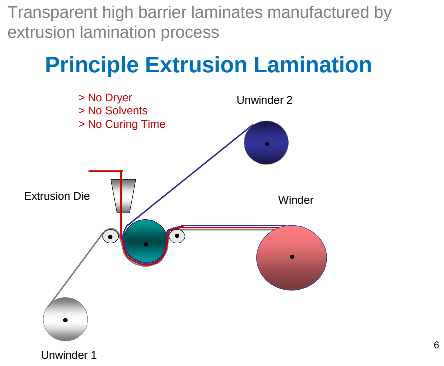
The combination of these various web materials can be affected by a number of different techniques. The big share is done by adhesive lamination. This process involves the use of solvent based as well as solvent free adhesives (Slide 5).



Both systems have the chemical basis in common, which depends predominantly on the use of aromatic isocyanates. This PUR technology has been in use for many years and this is also reflected by the fact that it leads to outstanding bond strengths in laminates. Yet, this technology also contains significant drawbacks. For instant, such adhesive systems, in most cases, must be cured between 3 and 10 days at elevated temperatures, also the solvent based adhesives develop considerable amounts of VOCs and there is the risk of the forming of aromatic isocyanates. Thus, there is sufficient cause for the development of low risk and ecologically unobjectionable alternatives to the conventional adhesive systems.

One alternative to these conventional systems is extrusion laminating (Slide 6). In these case, instead of adhesives applied by roll coating, polymer melts are (co)-extruded in-between the substrates.

This technology has already successfully entered a number of sectors. For instance a big share of potato chip packaging is being made by this process. And remarkably, laminating speeds of over 500 m/min can be reached.

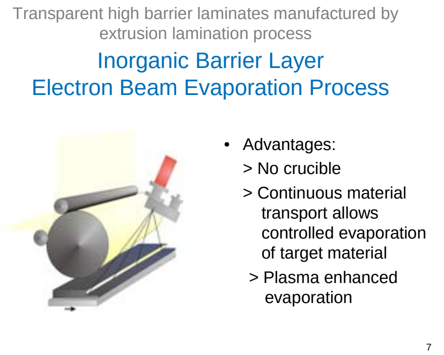


However, as far as the application of this technology in the production of transparent high barrier materials is concerned, this has not yet progressed beyond the early stages. The main cause in the past was the lack in the availability of suitable substrates. But now, with the development and the commercial availability of transparent barrier substrates, especially tailored to the extrusion process, the basis for the ongoing development of this technology is here.

To address the technical problems of the new technology and to promote new ecological sound production processes three years ago a shared industry project, sponsored by the German government was started. The findings of this project are partly the base of this presentation.

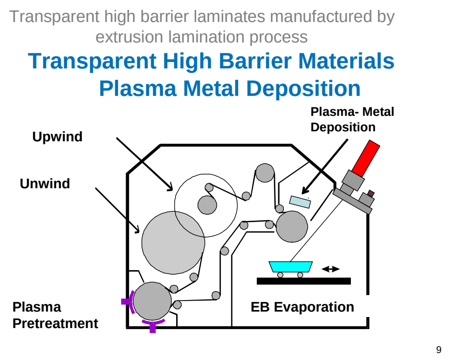
Technology

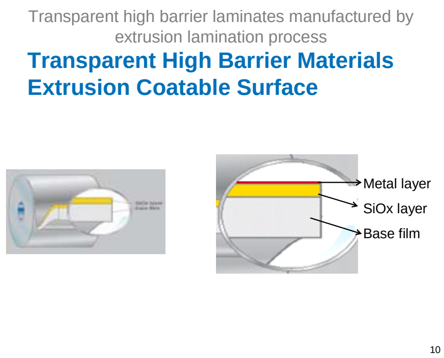
Barrier Materials & Performance
Modern transparent high barrier materials, which are suitable for coating or laminating consist of high-vacuum coated oriented films. Base materials are mainly oPET, oPA or oPP. The coatings used are SiOx or AlOx (Slides 7+8).



These barrier coatings hardly contain any functional groups that allow to bond today's common tie layers as EAA, Surlyn or maleic-anhydride modified polymers, to the SiOx coating.

To overcome this problem you can use primers which are applied to the SiOx layer. However, as a fact, extrusion coating equipment in many cases has no primer stations with the necessary dryer systems. Due to this Alcan Packaging has developed a new, patented technology to prepare the SiOx layer for accepting current extrudable bonding agents. Hereby, after the SiOx





coating process, still in the vacuum environment, an additional metallic layer with a gage of a few atomic layers is applied to the SiOx coat (Slide 9+10). This layer cannot be perceived visually, but does, due to its metallic character, form a good base for practically all polymer bonding agents, even for oxidized LDPE (Slide 11) as well as for inks.

Transparent high barrier laminates manufactured by extrusion lamination process

Transparent High Barrier Materials
Adhesion of Different Extrusion Coating Resins

Basic Substarte	µm	Tie Layer	µm	PE EXBE	µm	Extr. Temp.	Bond N/15mm 90°, 50mm/min.
PET -SiOx-pnb	12	Pure LDPE	20	LDPE	20	310	not separable
PET -SiOx-pnb	12	Low acid EAA 1%	20	LDPE	20	280	not separable
PET -SiOx-pnb	12	High acid EAA 8%	20	LDPE	20	280	not separable
PET -SiOx-pnb	12	High acid EMAA 9.2	20	LDPE	20	300	not separable
PET -SiOx-pnb	12	Ionomer	20	LDPE	20	260	not separable
PET -SiOx-pnb	12	LLD-MAH	20	LDPE	20	310	4.9
PET -SiOx-pnb	12	PP-MAH	20	LDPE	20	280	0.1
PET -SiOx-pnb (high level)	12	PP-MAH	20	LDPE	20	280	3.6

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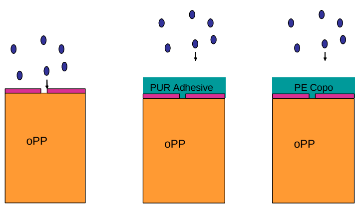
Depending on the base materials coated with SiOx the oxygen and water vapour barrier is different. SiOx coated PET will give you a excellent oxygen barrier compared to a SiOx coated oPP. Reason for that is the different barrier level you start with. As PET has much lower oxygen diffusion you also will end up with a better barrier compared to oPP.

The usual theory relating to the diffusion of gases through inorganic barrier layers teaches that the gas molecules migrate through defects in the approximately 40 to 80nm thin coating (Slide 12). The layers bordering to the SiOx barrier layer therefore have a decisive effect on the diffusion. Since olefin based bonding agent's exhibit practically no oxygen barrier, this contrary to the PUR based adhesives, poorer oxygen barrier properties result in extrusion lamination compared to adhesive lamination (Slide 13).

Transparent high barrier laminates manufactured by extrusion lamination process

Diffusion Trough Inorganic Barrier Layers



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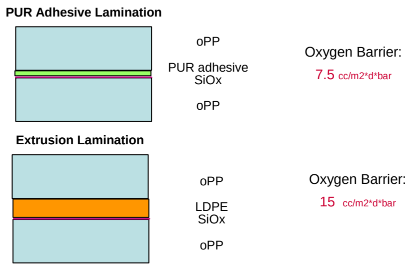
Transparent high barrier laminates manufactured by extrusion lamination process

Barriers of Adhesive vs. Extrusion Laminated Inorganic Barrier Structures



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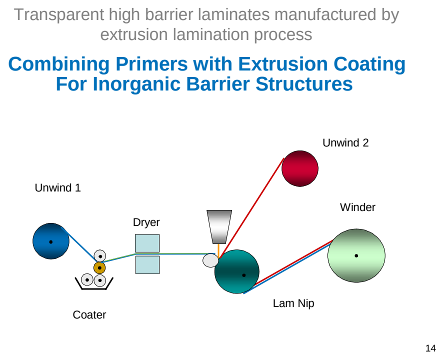
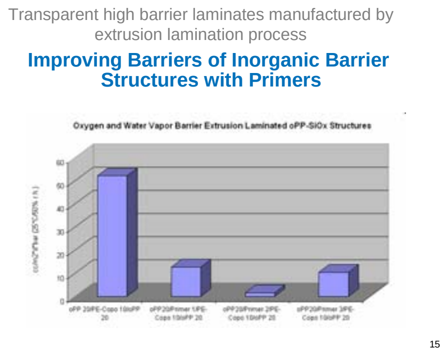
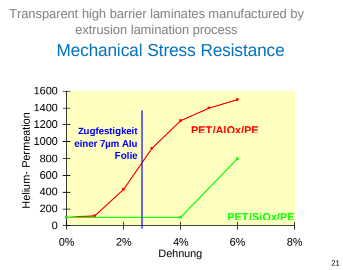
This leads us back to the extrusion lamination process where we use a primer (Slide 14). As shown before the layer bordering to the SiOx layer has the most important influence on the barrier properties of the final laminate. If you smartly choose a primer with good barrier properties you also can improve the barrier performance of the final laminate (Slide 15).





Lamination technology
There is a difference in the strain exerted on the materials used when processed by extrusion lamination versus adhesive lamination.
Critical is in this connection the associated thermal strain put on the unprotected SiOx coating at the point of lamination, which can depending on the bonding agent used, go up to 300°C. The presently used barrier films as e.g. PET-SiOx can, however, tolerate 4% extension (Slide 21). In processing these films it is important that the thermal and tensional strain exerted is as low as possible. Apt web guidance and suitable web tension are therefore a prerequisite that the barrier properties remain intact.



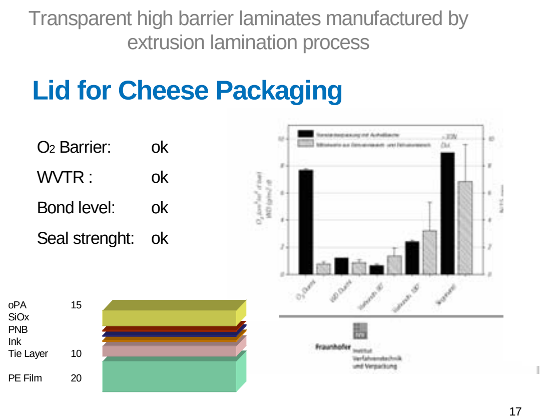
Use of printing inks
One of the challenges in changing the converting process to extrusion lamination is the adhesion to printing inks. The major part of the printed laminates on the market is reverse printed i.e. the printing ink is in-between substrate and the laminating agent.
The current printing inks and adhesive systems have been mutually optimized in the process of many years of development and application. Therefore they show corresponding good bonding properties, since the inks and the adhesive system penetrate each other mutually. Contrary to this, the mutual penetration is absent in extrusion lamination, because the polymeric materials due to higher viscosity and the lack of functional groups cannot react with the printing ink. So a careful selection and appropriate testing of the ink systems applied is essential.

Sealing characteristics
Extrusion laminated materials can show, when compared to adhesion laminated ones, a different sealing characteristic. Especially in the case of extrusion laminations between oriented films as oPET or oPA there is a tendency to shrinking in the sealing seam. To prove the appearance and performance of a laminate the material has to be tested on the packaging line. Only then the final appearance will be revealed.

Product Examples (from the industrial project)

Lid for cheese slice packaging – oPA-SiOx/HV/PE coating (Slide 17)

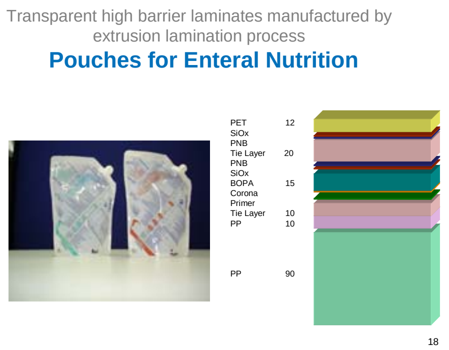
The aim was the replacement of the barrier structures made with PUR adhesives and metalized oPA or EVOH using the adhesion laminating process by oPA-SiOx structures made by co-extrusion coating, which is complicated by the fact that a partial reverse print is needed. Therefore the bonding agent must develop its action towards the metal coated SiOx surface as well as to the printing inks and the PE side. After optimizing of the printing inks, the bonding agent and the production process all the requirements as gas barrier, interlaminate bond strength and sealing seam strength were met and the first extrusion laminated sliced cheese package could be successfully produced at the packer.

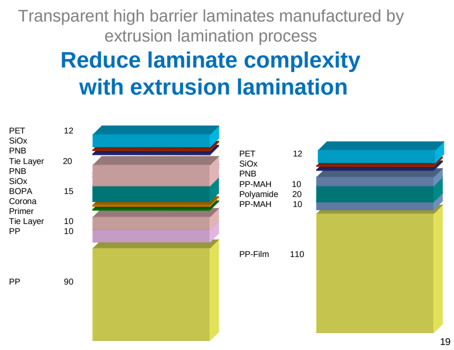


Pouch for enteral nutrition – PET-SiOx/HV/oPA/HV/PP-film *(Slide 18)*

The production of retortable, extrusion laminated flexible materials is for sure a challenging task. And this not only because of the thermal stresses, but also because of the required heat stability for these products mainly polypropylene sealing layers and as bonding agent PP grafted with maleic anhydride is used. For bond development this not only calls for sufficient heat, but in addition enough time for curing to reach the required bond strength. This time, however, is usually not at disposal during the extrusion laminating process. The dwell time in the nip gap amounts to 3 to 10 milliseconds, depending on the laminating speed, and this is in most cases insufficient for the development of the required bond on the metal coated SiOx layer. During the retorting process, which usually takes place at 120 to 130°C and that can last up to 2 hours including the heating up and cooling down phase, in most cases, an additional bond strength improvement takes place. In addition, extrusion primers to improve the interlaminate bond strength can be applied.

All in all, however, it becomes obvious that under optimized conditions also transparent, retortable high barrier structures can be produced by the extrusion lamination process (Slide 20). You even can reduce the complexity of such a laminate by replacing the oPA layer with a 3-layer co- extrusion lamination using a Polyamide core layer (Slide 19) The application of the reverse printed ink still is the biggest handicap. Therefore, in the case of retortable structures, it is better to switch to surface printing, with the addition of an overlacquer to start.





Transparent high barrier laminates manufactured by extrusion lamination process

Results: Laminate for Enteral Nutrition

Manufacturing ways:
> with tie layer: PP-MAH or LLDPE-MAH
> with pnb or retortable primer

> Manufacturing	→ reduced complexity
> Barrier	→ ok
> Bond level	→ ok (improves during retorting)
> Seal behaviour	→ different to adhesive laminates
> Pouch performance	→ to be verified

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Summary and outlook

The work presented shows new possibilities to replace adhesive technology by extrusion lamination to manufacture transparent high barrier laminates, therefore addressing the need for sustainable and clean converting processes.
To be sure, further improvements are called for, especially in the area of bonding the printing inks to the polymeric materials used. To what extent this new technology will succeed in the market will depends to a large extent on the cost level tat can be reached. Important is here that also soft factors, as no need for curing, resulting in shorter delivery times, are taken into consideration. The best argument for the new technology is, however, a real cost advantage.

Thanks
Base for the work presented was the industry project sponsored by the German ministry for research.
Therefore my best thanks for their excellent cooperation goes to all BMBF project partners:

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