New methodology for
determining the chemical composition of individual layers in sandwiches of plastics

Description of the problem
The demand for smart debit and ID card reliability is increasing despite longer lifespans and more frequent usage, and the card body, as the carrier for the functional electronic unit, plays a crucial role in this, since it must remain intact over the entire lifespan. This is especially true in the area of security documents, not least because of the need to guard against counterfeiting.

Given their thin design, the feasible lifespan of a plastic card is very much dependent on the plastic films that are used. The stringent demands that are placed on identification documents to ensure that they cannot be forged and the lifespan they are required to achieve mean that precisely specified and approved materials must be used. However, deviations from the specifications repeatedly occur during manufacture with cheaper materials being used (e.g. polyvinyl chloride instead of polycarbonate). Normally, it is only individual layers of the sandwich that deviate in this way.

The use of cheaper materials that have not been approved by the customer can, however, result in undesired changes in the properties of the overall product. These may, for example, manifest themselves in the form of poorer bonding strength or reduced resistance to external stresses of a mechanical or chemical nature. Consequently, the customer has a justifiable interest in ensuring that the specifications have been adhered to and this includes identifying the materials of the individual layers in a multi-layer card.

In order to make this possible, Fogra has developed a method that can determine the chemical composition of the inner films in a sandwich.

General approach
Deviations in the chemical composition of a sandwich from the specifications often only relate to individual film layers and this therefore means that chemical composition of every individual film layer of a sandwich needs to be checked.

During manufacture, the individual layers are laminated to each other at high temperature since it is important that it is impossible to separate the finished multi-layer sandwich into its original individual components, not least in order to prevent counterfeiting. Consequently, without further preparation, the methods that have been used up until now such as Attenuated Total Reflectance Infrared spectroscopy (ATR-IR) have only been able to investigate the outer layers. Since a commercial ATR unit requires an area of...
about 2 mm x 2 mm in order to take is measurements, such units are unable to measure the individual layers in cross section, since the lateral resolution is clearly too low.

The new approach uses milling to uncover larger areas of the various layers of the sandwich so that the individual layers can be analysed.

The following scheme visualises the procedure to analyse the different layers within a card body:

- Cross section characterization
  - (Card structure)
- Uncovering the layers
- Verification of the milling depth
- Identification of the layers

In order to be able to analyse the chemical composition of the individual layers, the first step is to determine the layer structure and the thickness of each film layer. This information is obtained by studying the cross section of a card. Fogra has the facilities to produce high-quality cross sections in a two-stage process so that layer thicknesses can be determined more precisely. Preliminary preparation consists of conventional mechanical preparation using a microtome with a firmly clamped blade to produce thin strips. Irregularities in the blade together with the presence of components that have differing mechanical properties (e.g. antenna wires, pigments) mean that such a process usually results in the formation of grooves that can make it difficult or impossible to determine the layer boundaries. That is why Fogra has added a second stage to the preparation of the specimens in which a contact-free Leica TIC 3X ion beam milling system is used to “polish” the specimens and produce extremely smooth surfaces regardless of the material composition of the cards.

The individual layers in card cross sections prepared in this way can then be identified by means of scanning electron microscopy and their thicknesses determined. The advantage of the scanning electron microscope (SEM) over the light microscope is that it is possible to differentiate between superimposed films of the same kind more effectively.

Accurate measurement of the individual layers is vital for the subsequent milling stage. The depth of the individual milling steps depends on both the layer thicknesses and the position of the film layer in the sandwich. Fig. 2 shows the cross section of a seven-layered card. The analytical method being presented here is...
suitable for the layer thicknesses shown in red whereas those shown in white are too thin.

The layers that are to be investigated are revealed by means of a milling head that removes a strip of about 2 cm starting from the edge of the card. In order to precisely position the milling head at the vertical level of the uncovered surface within the multi-layer sandwich it is necessary to know its precise position before the start of material removal. This is determined by means of a reference level. Using this position as a starting point, the milling depth can then be adjusted to an accuracy of c. 20 µm.

The next step is to check the uncovered areas to determine the extent to which they lie within the layers in question. A light or scanning electron microscope is used here to determine the distance between the uncovered layer and the card surface (see Figure 3).
Identification

The Energy Dispersive X-ray Spectroscopy (EDX) detection system that the Fogra scanning electron microscope features is only able to differentiate polyvinyl chloride (PVC) from the other standard materials, using the presence of chlorine to do so. However, this detection method is unable to differentiate between any of the other polymer compounds and so the only question this detection method is able to answer adequately is whether or not polyvinyl chloride has been used.

However, it is possible to use Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR) on the uncovered layers to record the spectra of each individual layer and then by cross-referencing the spectra with a database that Fogra has expanded it is possible to characterize the chemical nature of the layer material.

Depending upon wavelength, the depth that the measurement beam penetrates into the substrate varies from c. 0.5 µm to 3.5 µm. This allows individual layers to be selectively measured. Since the measurement area of the ATR unit is c. 2 mm x 2 mm, this technique cannot be used directly on the cross section of a card sandwich. By uncovering the individual layers from above or below it is possible to create areas that are large enough for measurement. Milling is a practical method for removing material to the right depth that offers sufficient accuracy for individually uncovering each identified film layer.

Limitations of the method

The new process described above does, however, have some limitations:

- Only layers that can be differentiated by means of a scanning electron microscope can be analysed (possible problems with coextruded layers)
- Currently, very thin layers (< 50 µm) cannot be prepared with sufficient accuracy, which also means that they cannot be identified (e.g. laser receptive layer...)
- Various modifications of the same type of polymer — for example, differences in the plasticizer content, the orientation (through stretching) or in the crystallinity of the polymer — cannot be differentiated.

Figure 4: left: measurement spots shown at the cross section of a card body; right: exemplary IR spectra.