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Low emission for the furniture industry

Today, houses have to be environmental friendly and safe for health. Therefore, manufacturers of furniture and building interiors demand adhesives that meet these requirements.

Christoph Funke, Ingo Horsthemke

In recent years, the awareness of consumers of ecologically sustainable and healthy living conditions has constantly grown. Architects now have to face critical questions from future home owners, which were no issue in the past. Due to the large variety of processed materials, ecological labels like Blue Angel, Green Building, EMICODE have become more present for the wider masses of people. This trend will become stronger in the future and furniture manufacturers therefore demand innovative adhesives which meet the new high standards.
The quality of the air inside rooms is now more important than it was, for instance, in the 1970s. Reports from that period about the negative effects of formaldehyde are still anchored in everyone's mind. Whether at home, at work or in public buildings – today, people spend much more time inside than they did in the past. Therefore, industry and research made significant efforts to reduce the emissions of formaldehyde from products. According to current numbers published by the German Federal Environmental Agency (Umweltbundesamt), the average person spends 80 to 90 % of time each day indoors /1/. The emission behaviour of building parts (emission of volatile organic substances (VOC: volatile organic compounds)) can have a major impact on the air quality in a room and, therefore, on the health and well being of people. From the present point of view, low-energy houses have minimised the air change rate and a reduced air flow due to the "airtight" insulation. This may lead to high concentrations of pollutants in the room air *(Figure 1)*.

Plasticisers indoors

Emissions of plasticisers into indoor air can have many different sources. In general, the biggest sources of emissions are building products, for instance floorings, but also furniture containing soft PVC (polyvinyl chloride) or adhesive and paints formulated with phthalate. /2/
Over the years, dispersions have become the established adhesive type for laminating wood-based materials which are processed for instance in the manufacture of doors and floorings. In general, thermoplastic foils (e.g. PVC), with or without primer application, and resinated thermoset decor papers (finish foils) are laminated using EVA copolymer dispersions. However, these adhesives had a major drawback due to the relatively high content of plasticisers. In addition, the plasticisers used were usually from the group of phthalate esters of which some are suspected of being mutagenic and toxic to reproduction.
In addition to the adhesive, the substrate also has to be checked for potential emissions. Floorings are generally made of PVC. Phthalate-based plasticisers are added to the PVC to modify the hard and brittle plastic and make it more flexible and smoother for processing and for a soft touch of the final product. Critical phthalate esters like DEHP (diethyl hexyl phthalate) which were used for this in the past have been replaced with alternative phthalates, like DINP (diisononyl phthalate) /3/. According to the latest EU directives, DINP does not need to be labelled as hazardous substance. However, as a precaution, the use in children toys is prohibited /4/.

Figure 1 > Emissions in modern buildings can have many different sources

Components/Raw materials	Mass fraction [%]
Basis dispersion	40 – 80
Filler	20 – 50
Softener	1 – 8
Soft resin	1 – 2
Dispersing agent	0.1 – 1.5
Defoamer	0.1 – 0.5
Biocide	0.1 – 0.5

Table 1 > This list shows the share of the individual raw material groups in the total emission from the formulation. It contains only the main groups of raw materials.

Due to the considerable amount of surface they cover in houses, floorings and doors have to be seen as potential sources of emissions. Manufacturers are aware of the importance of this issue and are currently qualifying plasticiser-free materials, like polyethylene terephthalate (PET), thermoplastic elastomers (e.g. TPU), polypropylene (PP) and other plastics. However, to ensure that the flooring product is completely free of plasticisers, not only the material in the top layer, i.e. the surface, has to be free of plasticisers, but also the laminating adhesive used in processing.

Emission-reduced adhesives (ER EVA dispersions) fulfil those requirements. They are practically free of plasticisers and facilitate a significant reduction of the total VOC emissions from compound materials.

Determination of emissions

Currently, there are a number of different European regulations and test methods in force regarding the determination of emissions, which deal mainly with emissions from wall paint. According to the European "Decopaint Directive" 2004/42/EG, VOC emitters are organic substances with a boiling point <250°C.

The VOC level is determined by measuring the VOC content of the fluid sample inside the container ("in-can") according to ISO 11890/2 through a gas chromatographic analysis (GC). The European Construction Product Regulation (CPR) No. 305/2011 led to the creation of concepts and regulations like the German AgBB (Committee for Health-Related Evaluation of Building Products) classification system or the French "Grenelle de l'environnement" (French Décret 2011-321). The latter evaluates the emissions from dried adhesive films, measured in a test chamber according to ISO 16000-9. The Décret also determines the limit values for emissions. Tests have shown that there is no correlation between the emissions measured in a test chamber and the plasticiser concentration of adhesives determined with the "in-can" method. Optimised adhesives based on internally plasticised dispersions which are free of plasticisers and coalescing agents are the top choice to meet the different European requirements for emissions indoors (**Figure 2**). After 28 days, the total amount of VOC and SVOC of these products is considerably lower than 1000 $\mu m/m^3$, and therefore in the lowest emission class. /5/

Dispersion adhesives and wall paint have to meet different requirements with regard to cohesion and adhesion. To join two substrates permanently and securely, the cohesion of a dispersion adhesive must be considerably higher than in a paint with a similar formulation which only has to stick to the wall. Therefore, the two types of dispersions – adhesive and paint – are formulated with different amounts of fillers. Adhesive manufacturers formulate each dispersion adhesive to fulfil the specific set of requirements for a certain application. The key properties which define the characteristics and the performance of an adhesive are:

- solids content,
- viscosity,
- pH value,
- resistance to low temperatures,
- minimum film forming temperature,
- open and closed assembly time,
- heat resistance and cold flow (creep behaviour).

An analysis of the emission measurement of standard dispersion adhesives in a chamber according to the AgBB system shows that several groups of raw materials have an increased amount of emission *(Table 1)*. Especially coalescing agents and plasticisers, soft resins, defoamers, dispersing agents, rest monomers and biocides show high emissions. A list shows

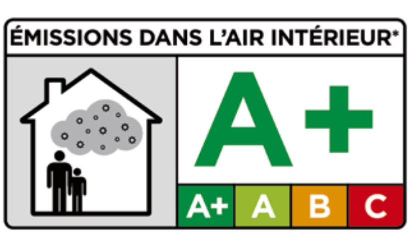

Figure 2 > A+ classification label

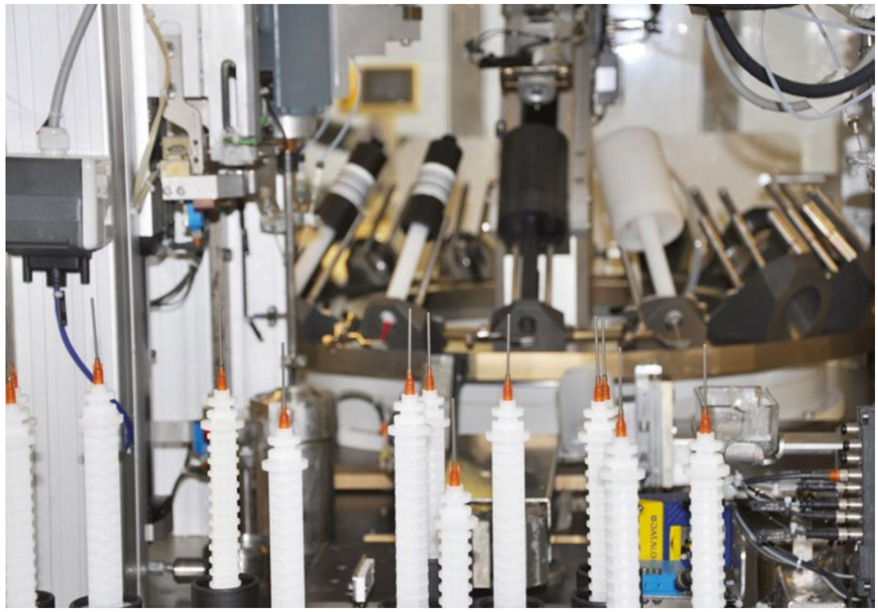

Figure 3 > Today, modern adhesive development is supported by software-assisted test planning (DoE). The photo shows the inside of the CLS (Compact Lab Station) lab robot from Bosch

the share of the individual raw material groups in the total emission from the formulation. For a better overview, the list contains only the main groups of raw materials. /6/

Plasticisers and coalescing agents are added to the formulation to decrease the minimum film forming temperature (MFFT). In dispersion adhesives, this also provides a softer adhesive film and improves the adhesion on difficult to bond surfaces. Products from the group of high boiling plasticisers are particularly suitable for lowering the MFFT (Info Box), a procedure which is also called external plasticisation. With those products, adhesive manufacturers have more leeway for the formulation of the adhesive and can adapt the amount of plasticisers to fulfil specific requirements. External plasticisation, however, always carries the risk that plasticiser which has not set chemically can migrate, diffuse and evaporate. This process depends on many factors, for instance on the size and structure of the molecules and on the volatility of the plasticisers used in the formulation. In the last few years, there has been a clear trend to use larger molecules with a lower volatility. As a response, regulations have been introduced to measure the SVOC and TVOC content, banning emissions of volatile compounds from adhesives. Therefore, the chemical alternative, the so-called internal plasticisation, is to be preferred. In this method, the glass transition temperature (Tg value) is lowered by chemically attaching the plasticising components to the polymer molecule. This provides a permanently soft plastic in which the plasticising component cannot diffuse.

Info Box
Film formation

Film formation in water-based dispersion adhesives is a complex process. During the evaporation in the aqueous phase of a dispersion adhesive, the dispersed particles move closer to each other. When a critical limit has been crossed, the particles will bond to each other when they come into contact. The remaining water continues to evaporate and the formerly spherical particles are deformed into a honeycomb structure (prism structure). The remaining polymer particles then form an even, homogeneous solid adhesive film through interdiffusion. The film forming process of dispersion adhesives depends on the following factors:
ambient temperature, minimum film forming temperature (MFFT) of the formulation, water absorption potential of the substrates, ambient humidity, evaporation speed.

Software-assisted test planning

Optimising the formulation of dispersion adhesives is very difficult due to the complex and diverse connections between raw materials and the manufacturing processes. Extensive test results are needed to determine how raw materials will affect a new product or how changing certain manufacturing parameters will impact the final result.

With statistical test planning (also called DoE = Design of Experiments), manufacturers can develop new products with the needed properties within a short period of time and with less testing, therefore reducing costs. The well-structured and result-oriented test planning is a very helpful and effective method to ensure reproducible results. /7/

In addition, it is possible to change the proportion of the components in the formulation to optimise the adhesive, and at the same time determine how it will affect the key characteristics of the product (viscosity, pH value, density, cohesion and

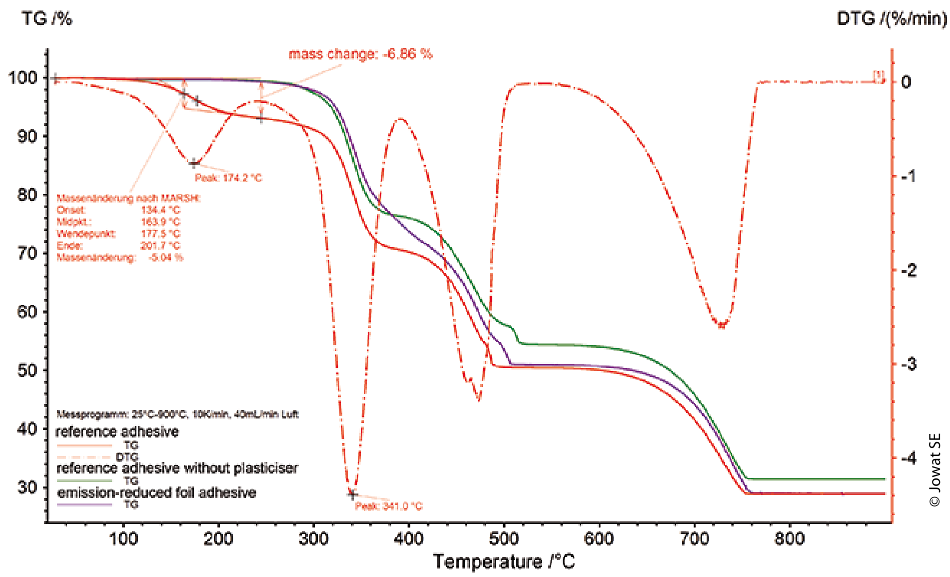

Figure 4 > Mass change of plasticisers through evaporation in thermogravimetric analysis of dispersion adhesives

adhesion) without further practical tests. The impact on the adhesion properties profile can be deduced directly. The 2D and 3D visualisation of the software is especially helpful for mixtures, where there is no linear correlation *(Figure 3)*. With modern analysis methods, VOC emitters can be identified easily.
The thermogravimetric analysis (TGA) can be used as a tool to support the evaluation of volatile substances or decomposition products due to alteration in individual components and in the adhesive formulation (**Figure 4**). It allows the manufacturer to identify volatile substances and their mass proportion fast, and to evaluate the emission potential of the formulation. The spectrum should be analysed according to AgBB and its reference substances, i.e. the temperature range up to 369 °C (boiling point C22 Alkan; Docosan). Although this does not replace a measurement in a test chamber, it helps identify and optimise products with low emissions.

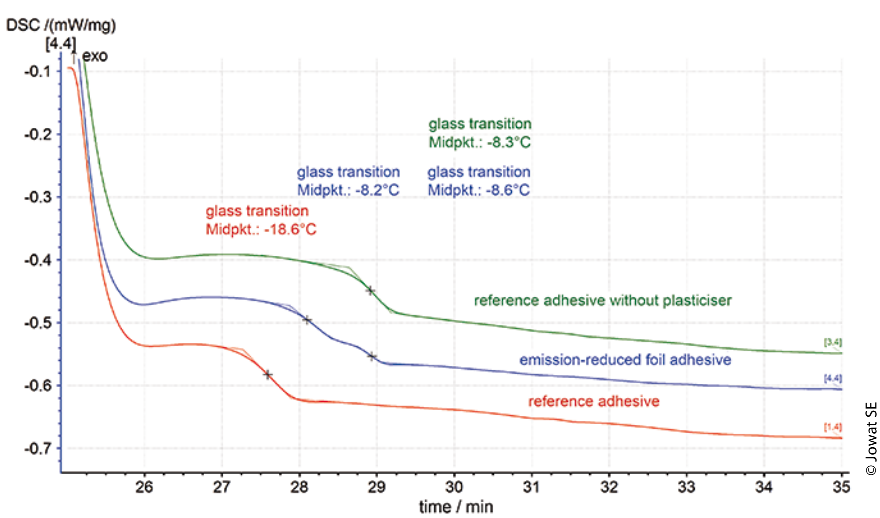

Figure 5 > 1. Heating phase of a dynamic differential calorimetry (DDK/DSC)

Depending on the ambient temperature, the mechanical properties of polymers can change significantly. This a significant aspect which has to be taken into consideration during the development of the adhesive and for the assessment of the cohesive properties later in the compound element. During the thermomechanical analysis, the heating of the adhesive leads to a moderate decrease of cohesion, which changes significantly when the glass transition point (Tg value) is reached. This phase transition is usually measured through the so-called dynamic differential calorimetry (DDK or DSC). /8/
This data helps to assess the adhesion properties profile of the adhesive. Reference formulations without plasticisers (green curve) form hard, at times brittle, films which are characterised by higher glass transition temperatures. Formulations containing plasticisers (red curve) form the opposite and show clearly lower Tg values *(Figure 5)*.
Compared to formulations with plasticisers, adhesives based on internally plasticised dispersions have a considerably higher heat resistance. As 2-components systems, they also provide a significantly higher adhesion. It has been confirmed that external plasticisers have an increased tendency to migrate at elevated tempera-

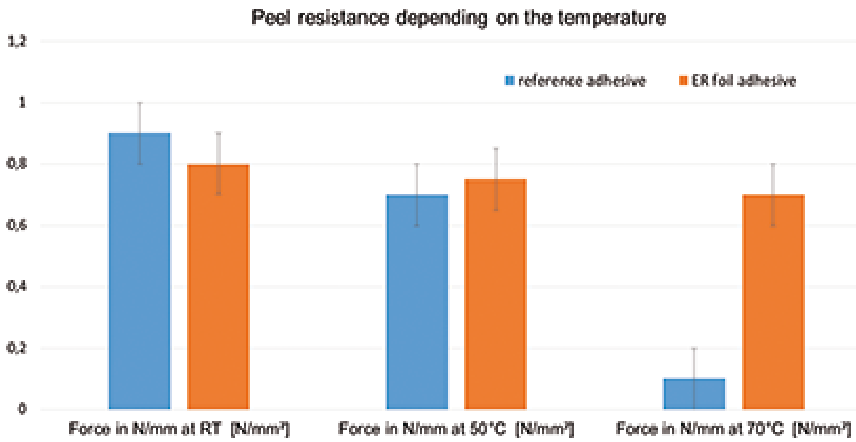

Figure 6 > Comparison between the peel resistances at different temperatures

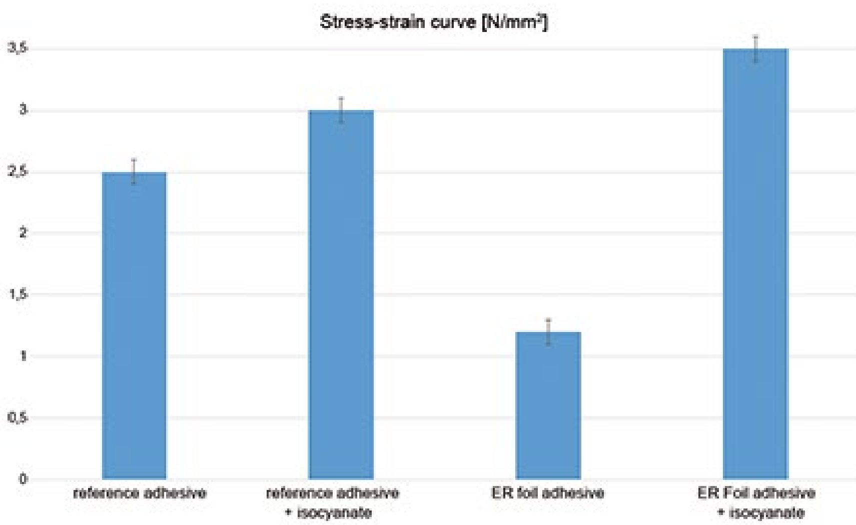

Figure 7 > Cohesion compared according to the stress-strain curve on dried dispersion films

tures, and the effects in the interface layer can have a negative impact on the adhesion. It also has been determined that the strength can be increased substantially by adding isocyanates, especially isocyanates from the group of aliphatic HDI prepolymers. Tests have proven that products containing isocyanates build up a considerably higher strength compared to standard adhesives. Therefore, these new products outshine standard systems in several different adhesion characteristics *(Figure 6, 7)*. Therefore, combining the standard requirement criteria with the given parameters for VOC reduction provides the test conditions to determine the optimal result for powerful dispersion adhesives with low emissions. By making optional adjustments in the formulation to the customers' processes or to potential requirements on the market provides low emission dispersion adhesives for one-component and two-component processing.
Emission-reduced dispersion adhesives provide superior results not only in the test chamber during the VOC emission test. Due to their high initial strength, these adhesives are also suitable for bonding relatively thick coating materials with high tension which are often used in the manufacture of floorings. During the joining process, the adhesive absorbs and compensates the tensions in the foil, therefore, ensuring failure-free bonding. In addition, the swelling of fibre based materials (lower tensions) is reduced significantly due to the high solids content of these adhesives. Low-emission adhesives facilitate more sustainable and viable products in the wood and furniture industry, with a higher environmental compatibility. With these adhesives, the industry is, therefore, well equipped to safeguard their future success.

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The Authors

Christoph Funke
(christoph.funke@jowat.de) is Head of the R&D Department for dispersion adhesives for wood and furniture industry at Jowat SE in Detmold.

Dipl-Ing. (BA) Ingo Horsthemke
(ingo.horsthemke@jowat.de) is a Product Manager for the Wood | Furniture | Construction division at the same enterprise.