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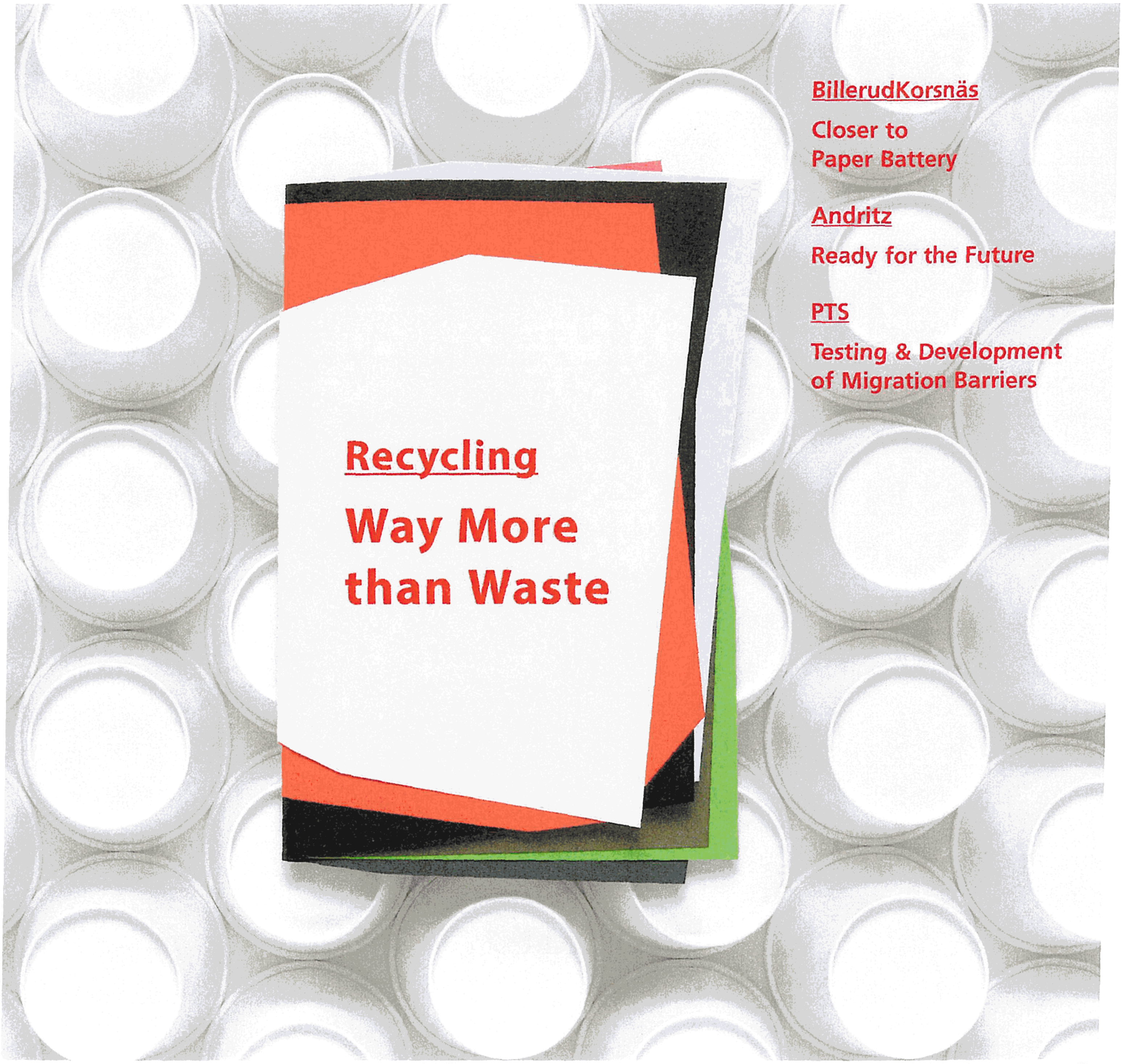

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Testing & Development
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Testing and Development of Migration Barriers

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The present publication includes at first the basic processes for the application of migration barriers and their general requirements. Subsequently testing and assessment of migration barriers are introduced. The influence of temperature, contact time and critical areas as cutting edges, inner flaps and creasing lines are discussed. In the second part, layer and formulation concepts for water-based barrier coatings are presented. Polymer coating agents are listed and effects by addition of pigments are illustrated. The publication is completed by a survey on potential cost scenarios and a short summary.

- Suitable for food contact (Recommendation XXXVI, FDA)
- Applicable with conventional coating units
- Barrier effect for vaporised hydrocarbons (mineral oil constituents)
- As few changes as possible in steam permeability
- No disruptive effects on the recyclability of paper and board
- No blocking
- No invisible set-off
- As few changes in the barrier properties as possible after creasing and folding operations
- The surface can be printed, glued and coated
- As few changes as possible in adhesive friction and slip values

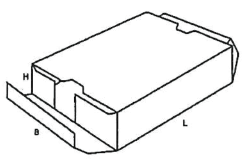


Fig. 1: Requirements profile based on folding boxboard

Developed and published by BASF AG

Gravimetrical determination of the amount of hexane, which evaporates through a (coated) paper sample (diameter 50 mm).

In the case of MOSH/MOAH a correlation with the results of the tenax method is possible.

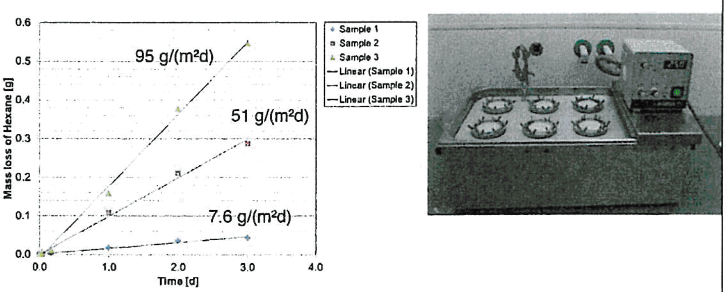


Fig. 2: Hexane Vapour Transmission Rate HVTR

Barrier functions can be applied to paper and board by three basic processes: Impregnation, coating and lamination. In the case of coating, it can be differentiated between the application of molten polymers by extrusion and water-based formulations. In practice, the applied process is determined by the sales quantity of the functionalized paper. Extrusion coating and lamination are chosen when rather small quantities are needed and are often used by paper converters and upgraders whereas water-based coatings are used by the paper manufacturer.

Before the development of a paper or board grade with an integrated migration barrier starts, the requirement profile should be determined in detail. As the case of a migration barrier on the reverse side of a carton board shows, the requirement profile could be rather complex including a lot of single points (Fig. 1).

Normally, a great number of coated samples must be tested and assessed during development work. To reduce the expenditure of time, pre-tests are extremely useful. A well-known and often used pre-test for pinholes in barrier coatings is based on dye solutions. In the case of migration barriers against mineral oil hydrocarbons (MOSH, MOAH), development time can be reduced by performing the HVTR-test (Fig. 2). The test method is based on the gravimetrical analysis of the amount of hexane evaporating through a paper sample and was introduced by BASF AG.

In the last years, extensive work was carried out to develop methods for the assessment of barrier coatings against migrating compounds. Up to now, the Tenax-migration method is most common (Fig. 3). The compounds migrating through the barrier layer are adsorbed to Tenax, afterwards extracted with an organic solvent and analyzed usually by chromatography (GC, LC). The use of migration cells made of stainless steel allows a space-saving storage in the oven for e. g. 10 days at 40 °C. The result is given as migrated substance in mg per dm^2 and needs recalculation for comparison with a limit in food (mg/kg) with the expected surface to volume ratio under real food contact conditions.

Tenax migration experiments can be carried out with contaminated paper and board samples respectively. But also a donor paper (filter paper) doped with surrogate substances can be used in order to get independent from appropriate contaminated paper substrates. In the migration cell the doped paper is placed beyond the barrier coated paper or board sample (Fig. 4).

Within research work, PTS identified surrogate substances for mineral oil hydrocarbons (MOSH: n-tridecane, 2,2,4,4,6,8,8-heptamethylnonane, heneicosane; MOAH: 1-phenyldodecane, biphenyl, 2,6-diethylnaphthalene), plasticizers (diisobutylphthalate, dibutylphthalate, diethylhexylphthalate) and photo initiators (benzophenone). The substances are commercially available and can be dissolved in n-hexane to give a surrogate solution (each substance with 1000 µg/l).

Different contact times and temperatures can be used in contact with Tenax (max. temperature is 175 °C). The values for temperature and time should be adequate for future contact conditions with food. As expected, the adsorbed amount of substances increased with rising contact time, but after very long contact times the amounts of substances in the donor paper are more and more exhausted and a leveling of the values occurs. Increasing temperature by decreasing contact time allows a ranking in the barrier effect of different coatings, but the accelerant effects are not equal in any case (Fig. 5).

In practice, creasing lines, inner flaps and cutting edges are critical zones for an additional mass transfer of migrating compounds. Up to now, there is no standard test method to determine the influence of cutting edges, inner flaps, creasing and folding lines. Practical considerations resulted again in using the tenax method but in a modified way. The modifications are mainly related to the samples (Fig. 6). The data gained from the measurements can be used for the estimation of the mass transfers of migrating compounds (e. g. mineral oil hydrocarbons) in packaging products like folding boxes (Fig. 7).

For the implementation of migration barrier coatings, a high number of water-based raw dispersions and aqueous polymer solution are available. They can be mixed up with further additives to optimize barrier effects and application properties. Besides migration barriers, additional barrier functions (against water vapor, oxygen, flavor compounds, fat and oil) can be added. In the case of food contact papers, compliance with the actual legislation has to be ensured. Inorganic pigments can be an important part of the whole barrier concept (cost optimization, precoatings, tortuosity effects). Besides the barrier properties, also converting and processing properties as well as recyclability are very important factors.

Homogenous films without any defects are necessary to reduce the amount of migrating compounds sig-

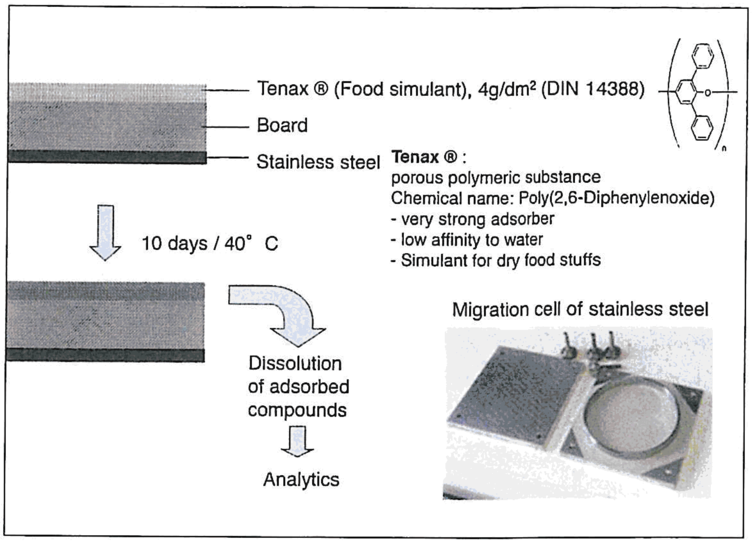
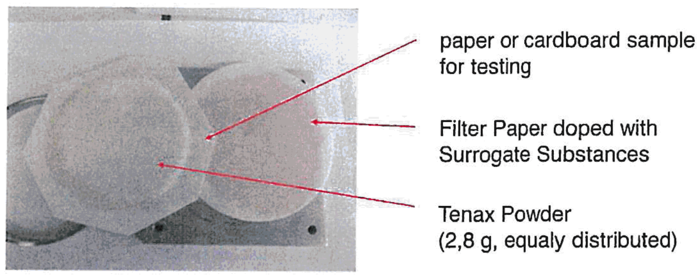


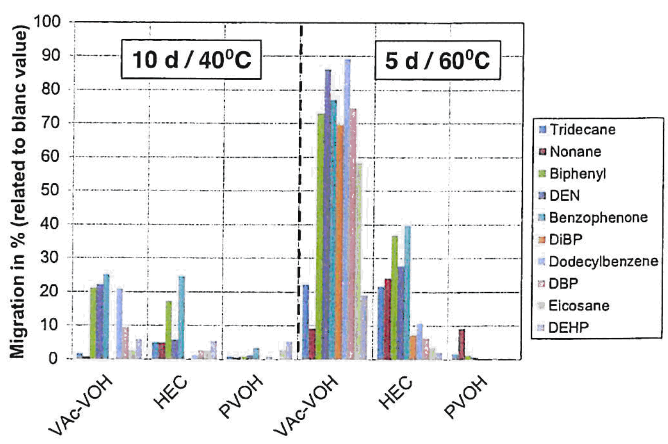
Fig. 3: Investigation of Migration using Tenax method

→ Independence from paper substrate



Size and dipole moment of important groups of compounds			
	Mineral oil HC	Phthalates	Benzophenone
Dipole moment [Debye]	0	2.6 - 3,0	2.9
Size [Angström]	7 - 20	7 - 10	6.5

Fig. 4: Working with Surrogate Substances

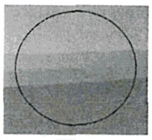


Substrate: Single sided machine calendered kraft paper (120 g/m²)
Coating: each with 15 g/m² of Vinylacetate-PVOH-Copolymer (Vac-PVOH), Hydroxyethylcellulose (HEC), Polyvinylalcohole, fully saponified (PVOH)

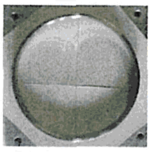
Fig. 5: Effect of temperature

Example: Whitelined chipboard WLC (GD2), 320 g/m², mineral oil barrier on the reverse side

Migration from an area of 0.71 dm² without creasing line / cutting edge:
45 µg MOH



Migration from an area of 0.71 dm² with **3 creasing lines**
9-9.5 cm length, 1 cm distance between, **28 cm** length in total:
130 µg MOH



Migration from an area of 0.71 dm² with **4 cutting edges**
of **18 cm** length in total :
132 µg MOH

Fig. 6: Migration testing on creasing lines and cutting edges

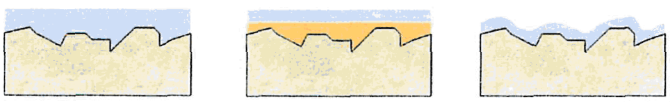
Position	Potentially migrating amount	Area or Length	Assessed amount	
			In the folding box[(1)]	In the food stuff[(2)]
Area	63 µg/dm²	15 dm²	945 µg	0.95 mg/kg
Cutting edges	6.8 µg/cm	116 cm	789 µg	0.79 mg/kg
Creasing lines	4.3 µg/cm	204 cm	877 µg	0.88 mg/kg
Sum				2.6 mg/kg
Liminting value[(3)]				**2.5 mg/kg**

[(1)] Dimension 20 cm x 5 cm x 26 cm (A x B x H, ECMA A1010)
[(2)] 1 kg Food stuff, e.g. noodles
[(3)] Sum of MOSH und MOAH

Fig. 7: Estimation of the amount of mineral oil hydrocarbons migrating from a folding box of common size

- For financial reasons, the quantity of barrier coating applied should be minimised if possible.
- Defect-free, uniform films with a grammage of 5-15 g/m² would frequently be adequate to produce the necessary barrier action.
- The surface to be coated is usually porous, rough and absorbent.

Scenarios illustrating a coating with a barrier effect for mineral oils:



Scenario A	Scenario B	Scenario C
Blade coating	Blade coating	Curtain coating
Single layer	Precoat + barrier	Single layer
20 g/m²	12 + 8 g/m²	12 g/m²

Fig. 8: Strategies for applying barrier coatings

nificantly. The surfaces for coating (e.g. reverse side of carton boards, testliners) are normally rather rough and have a high water uptake. To achieve a sufficient barrier against mineral oil hydrocarbons, several possibilities can be taken into account depending on the coating aggregates available. The options lead to strongly differing material and investment costs (Fig. 8).

A reduction of the coating weight of an expensive coating material, e. g. polyvinyl alcohol, can be achieved via a pre-coating. However in this case two coating aggregates are necessary. With a pre-coating made up with cheaper raw materials significant cost advantages can be obtained (Fig. 9).

During research work at PTS the barrier properties of different coating formulations against the already mentioned surrogate substances were determined via tenax method at 40 °C for 10 days (Fig. 10). Good barrier effects were achieved with polyvinyl alcohol, ethylen vinyl acetate-copolymers and cellulose derivatives (hydroxy ethyl cellulose and methyl hydroxyl propyl cellulose) although disadvantages in the practical application properties (especially low solids contents) are suspected.

Inorganic pigments can influence barrier properties in different ways (Fig. 11). The so called tortuosity effect leads to an increase in barrier properties at equal coating thickness when pigments are added. The effect should be more significant when the shape of the applied pigments is flaky. The theoretical predictions are based on strongly simplified assumptions so that an exact agreement in practical cases cannot be expected.

Within research work at PTS, the effect of flaky pigments in water-based coating formulations on migration barrier properties were studied. Equal amounts of pigments were mixed up with a biobased barrier polymer. These formulations were used in equal application weights on a paper substrate (Fig. 12; P1, P2: Kaolins; P3, P4: Talcs; P5 to P7: Bentonites; P8: Illite; P9: Mica; P10: PCC). The determination of the migration by the tenax method (60 °C/5 days) shows a reduction of mass transfer in all cases.

Based on an exclusively selected SEM picture a verification of the tortuosity effect and its theoretical magnitude was conducted (Fig. 13). For the preparation of the sample best possible free of artefacts an ion beam cross-section polisher was used. The SEM picture was analyzed by measuring the layer thickness and the length and thicknesses of all visually recognizable particles. The practice shows somewhat bigger but in the same order of magnitude lying layer reduction factors than in SEM picture analysis. The deviation between theory and practice can be explained by the rather crude theoretical model. The orientation of the pigments is in practice mainly parallel to the surface, but exceptions are visible

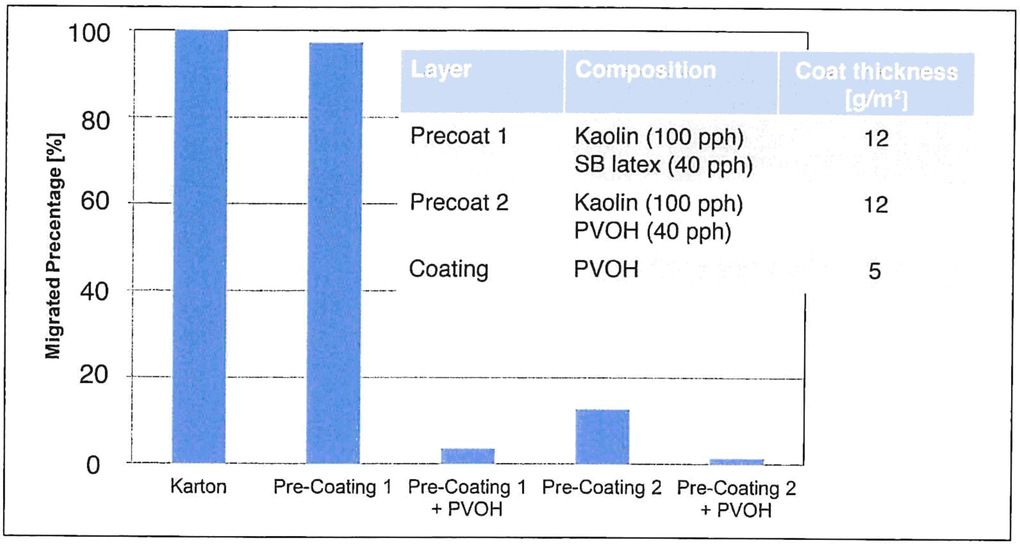


Fig. 9: Examples of the effects of precoats

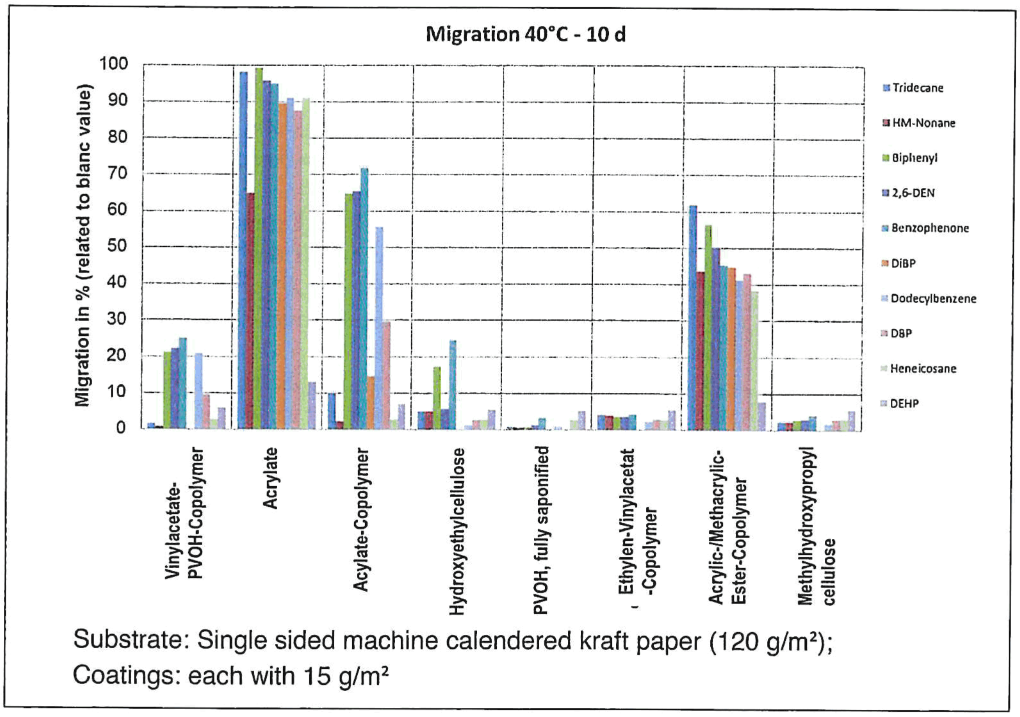


Fig. 10: Comparison of different migration barrier coatings

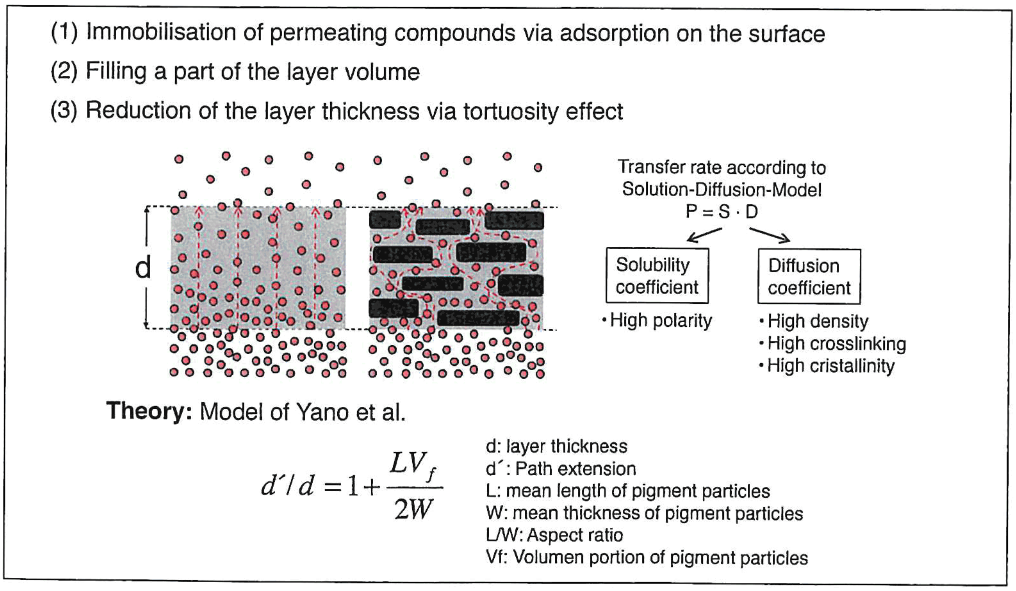
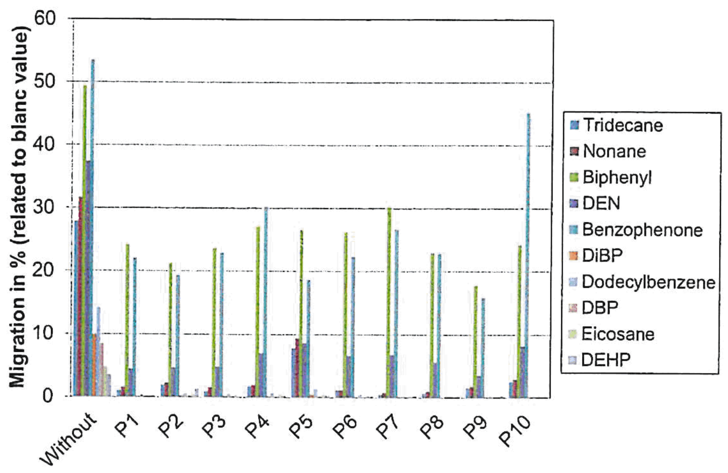
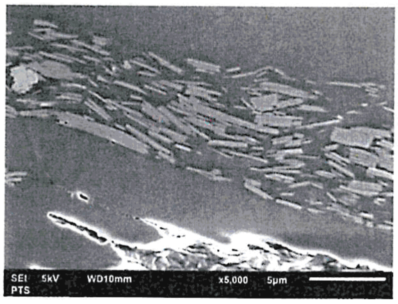


Fig. 11: Effects of pigments



Substrate: Single sided machine calendered kraft paper (120 g/m²)
Coatings: each with 15 g/m² of
Hydroxyethylcellulose (80 pph) + Pigment (P1-P10, each with 20 pph)

Fig. 12: Comparison of the effects of different flaky pigments



SEM picture of the cross section of a coated Sample at a magnification factor of 5000 (80% B10 / 20 % P2 (Kaolin), 15 g/m² on craft paper)

Evaluation of layer thickness, particle length and thickness:

Layer thickness (8 ± 1) µm.

Mean particle length 1,48 µm,
Mean particle thickness 0,26 µm.
Aspect Ratio 5,7.

Volumene portion of the pigment Vf 0,31.

d´/d = 1,9 (factor of about 2).

Experimental factors of 2-5!

Fig. 13: Theory and reality of the tortuosity effect

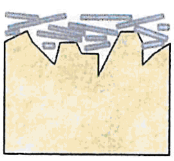
in the SEM picture. Additionally, an adsorption effect may also be present.

Based on the layer, reduction factor's potential cost savings were estimated for two different coating systems of high and middle price range (Fig. 14). The used quantity of pigments was fixed to 20 %, an amount secured by the experimental work. It is evident that with the addition of pigments significant cost savings can be achieved.

As summary for the practical development work the following points can be recorded:

- Besides an analysis of the target markets, the development of paper and board grades with a migration barrier requires an exact specification of all necessary properties at the beginning (definition of requirement profile).
- Based on that, a production concept can be developed, which includes the production processes and all needed raw materials as fundamental elements.
- In the case of aqueously applied migration barriers, the use of pre-coatings and pigments can be an important step to an improvement of the barrier functions in relation to costs.
- For the assessment of migration barriers, the tenax method is suitable, whereas the contact time and the contact temperature need adjusting to the demands (long and short time storage, relative and absolute comparison).
- The use of surrogate substances is a feasible tool to evaluate the barrier effect against single compounds and groups of compounds.
- With some restrictions, the Tenax method can be modified in such a manner that the influence of cutting edges, flaps, creasing and folding lines can be estimated.

Scenario A
Without Pigment
15 g/m²



Scenario B
With Pigment
15 g/m²

	Coating 1	Coating 2
Scenario A - without pigment		
Applied amount	15 g/m²	15 g/m²
Costs per kg [€]	8.00	4.00
Costs per m² at 15 g/m²	0.12	0.06
Scenario B - with pigment		
Costs per kg [€]	8.00	4.00
Costs of pigment per kg [€]	0.40	0.40
Rate barrier polymer / pigment	80 / 20	80 / 20
Reduced amount [%]	60	50
Reduced amount [g/m²]	9.00	7.5
Costs per m²	0.06	0.03
Cost reduction in %	**50**	**50**

Fig. 14: Cost scenarios

Acknowledgement

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