SUMMARY OF THE EUPIA MIGRATION STUDY

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1. Introduction

The large number of different surrogate components contained in the "model" printing ink and the associated analytical challenges make it difficult to draw fundamental conclusions from the original study[1]. Nevertheless, the study provides valuable information for our test practice. They emerge more clearly if one makes the attempt to fade out the questionable results due to analytical difficulties and relies on the verified data. That should be the aim of this summary.

2. Analytical challenges

The used model ink consisted of numerous and very different substances (Table 1).
The differences in molecular weight and polarity were deliberately chosen to cover a wide range of applications in different printing systems. However, the wide range of different substance properties had caused problems in terms of the reliability of the data obtained. For example, the high volatility due to low molecular weight caused difficulties in recovery (2-Methylpropane-1,3-diol, 2-ethylhexanol, C12). The large differences in polarity made it impossible to detect all of them with one analytical method, especially the very polar compounds (2-Methylpropane-1,3-diol). Some substances could also not be detected in the food due to interferences with food matrices (2-Methylpropane-1,3-diol, 2-Ethylhexanol, C-24, DiTMPTA, ESA, Irganox 1076). In addition, some substances were not further evaluated in kinetic migration tests due to inconsistent results that may be due to the analytes´ stability (ATBC, DiTMPTA, 2-methylpropan-1,3-diol, benzophenone and 2-phenoxyethyl acrylate) Taking all this into account, the list of substances to be evaluated is reduced to the following:

Table 1: Overview of representative surrogates for printing ink components

Surrogate	Molecular Weight (g/mol)	Log $P_{o/w}$
Irgacure 184 (CAS 947-19-3)	204.3	2.34
Di-tert-butylhydroxytoluene BHT (CAS 128-37-0)	220.4	5.32
Irganox 1076 (CAS 2082-79-3)	530.9	13.9
2,4,7,9-Tetramethyl-5-decin-4,7-diol (TMDDO) (CAS 126-863)	226.4	3.11
Hexadecane (C16) (CAS554-76-3)	226.6	9.26
Octadecane (C18) (CAS 593-45-3)	254.5	10.3
Eicosane (C20) (CAS 122-95-8)	282.5	11.4
Docosane (C22) (CAS 629-97-0)	310.6	12.4
Tetracosane (C24) (CAS 646-31-1)	338.7	13.5
The following surrogates are removed from the overall data set due to experimental inconsistences cited in the original report:		
Di(trimethylolpropane)tetraacrylate (DiTMPTA) (CAS 94108-97-1)	466.5	4.26
2-Phenoxyethyl acrylate (CAS 48145-04-6)	192.2	2.71
Acetyltributylcitrate ATBC (CAS 77-90-7)	402.5	6.92
2-Ethylhexanol (CAS 104-76-7)	130.2	2.82
Erucamide ESA (CAS 112-84-5)	337.6	8.87
Dodecane (CAS 112-40-3)	170.3	7.13
Benzophenone (CAS 119-61-9)	182.2	3.18
2-Methylpropane (CAS 2163-42-0)	90.1	0.24

[1] conducted at Fraunhofer IVV

3. Comparison of the simulant's performance

Focusing on the remaining substances, the following picture emerges depending on the test conditions. For a better overview, the homologous series of n-alkanes and the remaining analytes are considered separately.

3.1. Ethanolic simulants (OPP 50 µm)

3.1.1. n-Alkanes

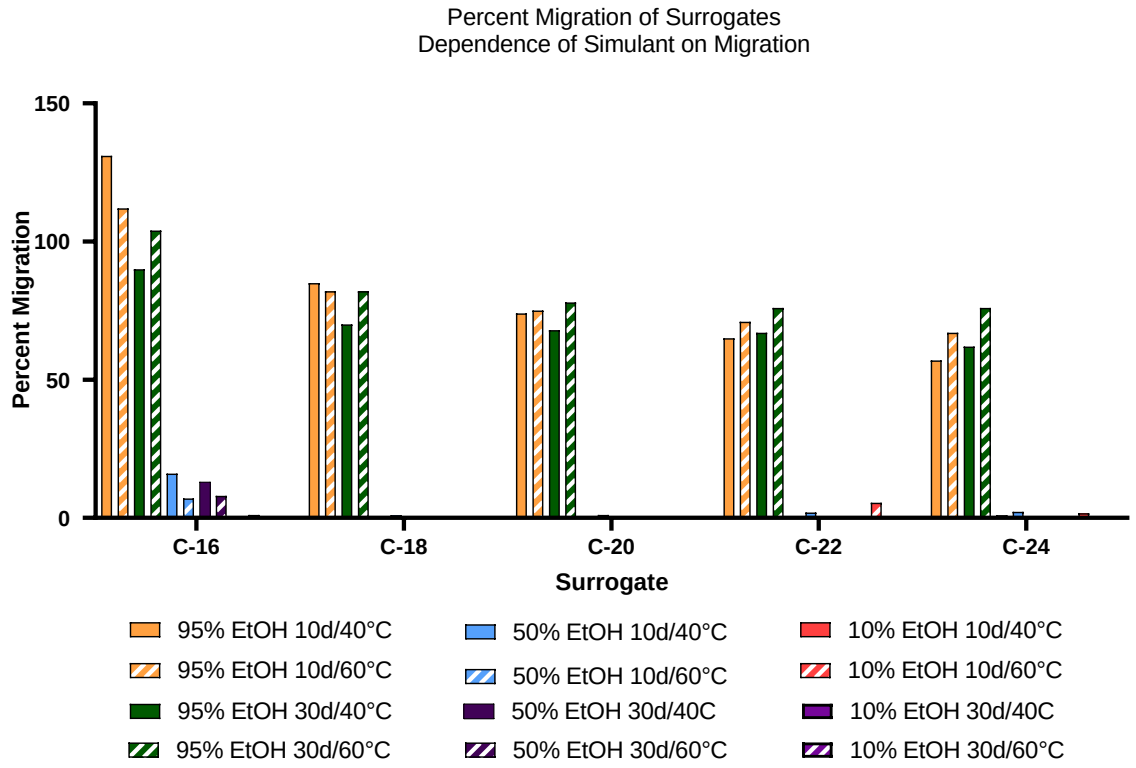

Figure 1: *10 days n-Alkane migration from printed PP film with ethanolic solutions at 40 and 60 °C – OPP*

With 95 % Ethanol the migration of the n-alkane series with carbon chain length 16 – 24 (226 – 339 g/mol) is at least 75 % or greater in all cases. It makes no difference whether 10 or 30 days, 40 or 60 °C is applied. This behavior is very unusual and underlines what was already seen in the kinetics experiments of the study, that with 95 % Ethanol extraction and no normal mass transport by diffusion takes place.

With 50 % Ethanol the migration is less than 10 %, with 10 % Ethanol, the migration is hardly measurable. This poor performance is explained by the poor solubility of the non-polar n-alkanes in these simulants.

3.1.2. Other surrogates

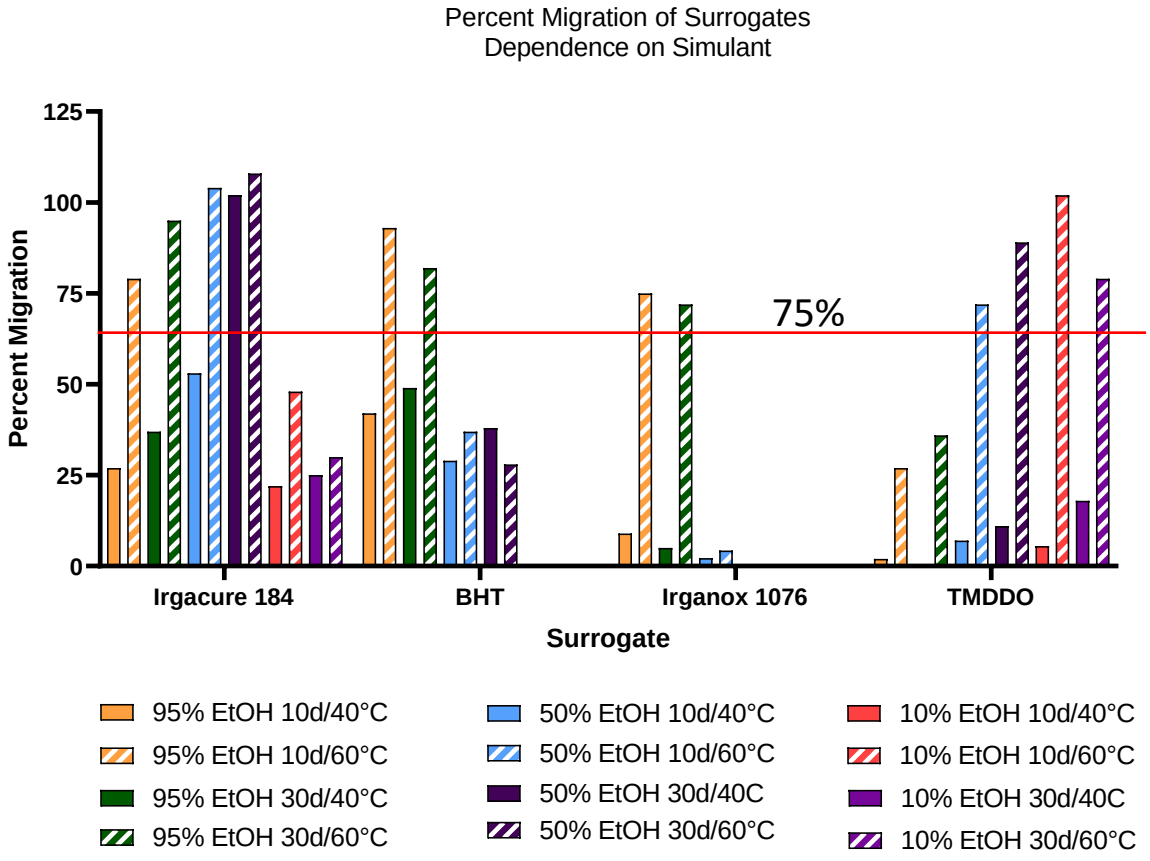

***Figure 2**: 10 days migration other surrogates from printed PP film with ethanolic solutions at 40 and 60 °C - OPP*

The picture for the other analytes is more differentiated. This is especially true for the quite polar analytes such as Irgacure 184 and TMDDO, but also for Irganox 1076 with its relatively high molecular weight.

Migration increases strongly for all ethanolic solutions when changing from 40 to 60 °C similarly when changing from 10 to 30 days. The increase is particularly marked for Irganox 1076 with 95 % Ethanol and even more for TMDDO with 10 % Ethanol. (Only exception is BHT with 50 % Ethanol at 60 °C / 30 days, probably due to stability reasons or measurement fluctuations.

Interestingly, migration is significantly higher with 50 % Ethanol than with 95 % Ethanol for the polar components such as Irgacure 184 (Log $P_{o/w}$ 2.34) and TMDDO (Log $P_{o/w}$ 3.11) The migration for TMDDO is even highest with 10 % Ethanol.

Again, this migration behavior of the components has to do with the solubility, a basic prerequisite for migration. The polar components are more soluble in 50 or even 10 % Ethanol than in 95 % and can thus be transported better. The same way in reverse with the non-polar Irganox (Log $P_{o/w}$ 13.9). It only dissolves to some extent in 95 % Ethanol, hardly at all in 50 and not at all in 10 % Ethanol.

3.2. Tenax® simulant

3.2.1. OPP 50 µm substrate

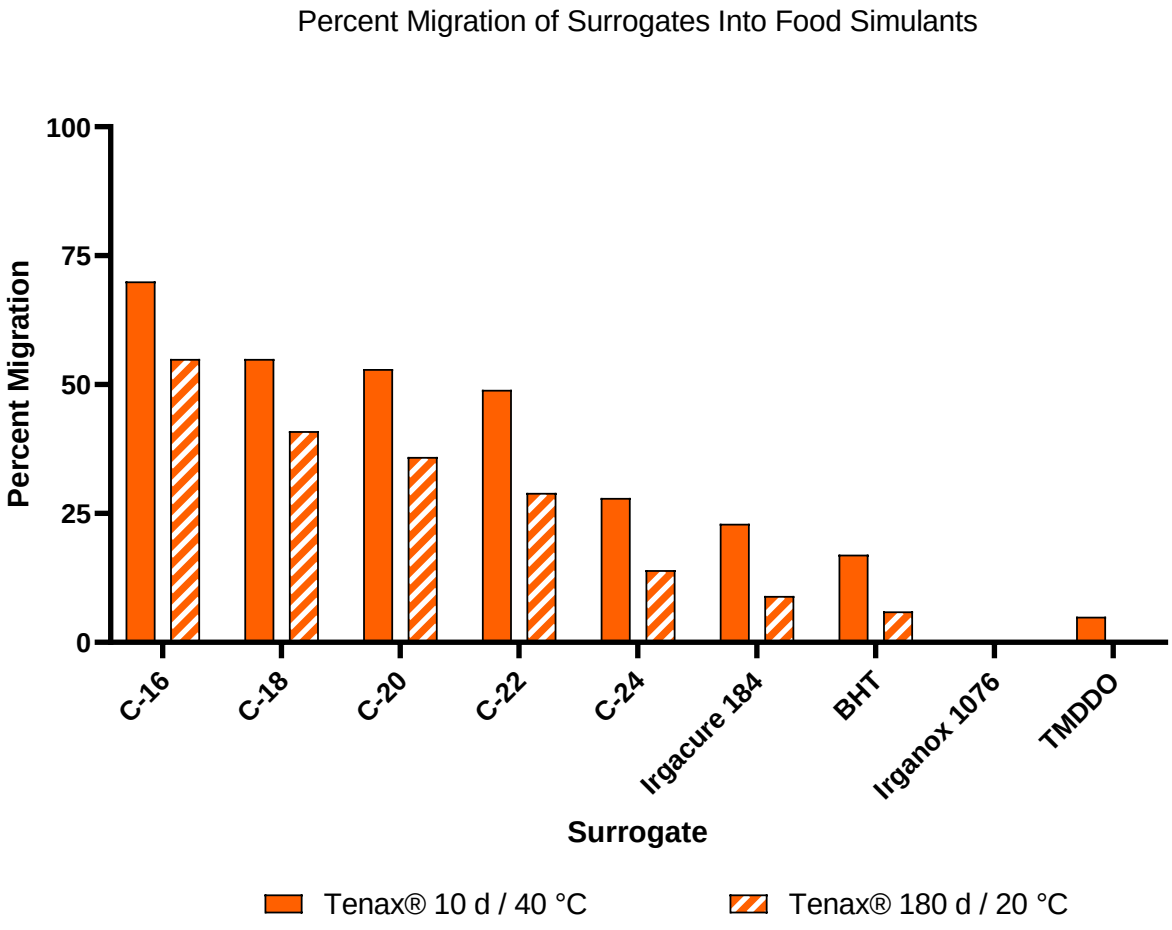

Figure 3: *Tenax® migration from printed PP film at 10 d / 40 °C and 180 d / 20 °C*

The 10-day migration at 40 °C exceeds the 180-day migration at 20 °C in all cases. This is somewhat surprising, since according to the Arrhenius equation, the accelerated migration conditions 10 days at 40 °C corresponds to only about 3 months storage time at room temperature.

As expected, the migration of the alkane homologues decreases with increasing carbon chain length or molecular weight. No migration could be measured for the relatively high molecular weight Irganox 1076 (531 g/mol).

3.2.2. Cardboard 240 g/m²

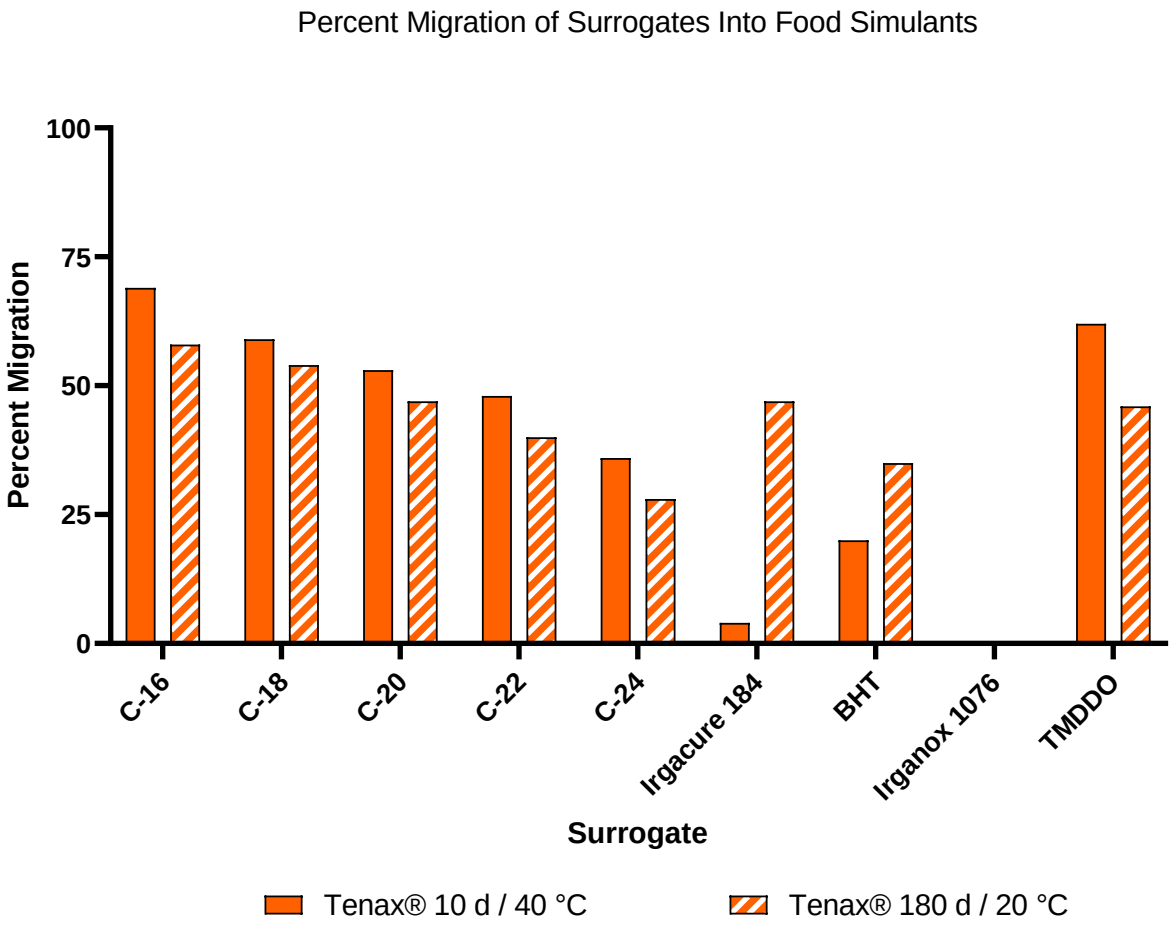

Figure 4: *Tenax® migration from printed cardboard at 10 d / 40 °C and 180 d / 20 °C*

The homologous alkane series on cardboard behaves similarly to OPP substrate, the Tenax® migration 10-day at 40 °C exceeds the 180-day migration at 20 °C, the same stands for TMDDO. Irgacure 184 and BHT behave surprisingly differently. The 10 days migrations at 40 °C are lower than the 180 days 20 °C migrations. The reason for this is unclear.

For TMDDO, the significantly higher migration on cardboard compared to OPP plastic substrate is also striking. “Heavy-weighted” Irganox 1076 shows no migration at all, as was already the case with cardboard.

4. Accelerated migration testing vs long-term foodstuffs storage

4.1. OPP substrate

4.1.1. n-Alkanes

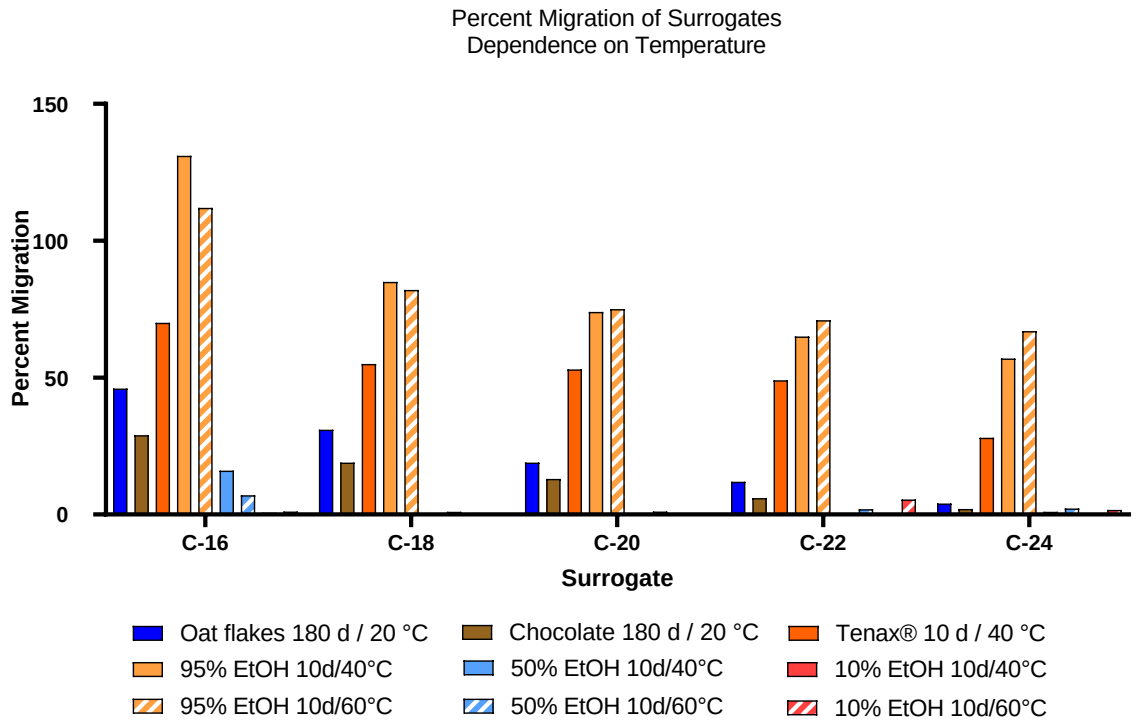

Figure 5: *Comparison of migration of n-Alkanes from a printed PP film onto Tenax®, ethanolic solutions, oat flakes and milk chocolate under defined test conditions*

Long-term food migration 180 days at 20 °C for oat flakes and chocolate is covered by 95 % Ethanol and Tenax®. The migration of the alkanes with 95 % Ethanol is strikingly strong. It is independent of the temperature around 70 – 100 % and thus cleary higher, 2 -10 times, than the migration into real food. The difference is especially extreme with Alkane C24. Practically no migration can be detected in the foodstuffs, but with 95 % Ethanol migration is still greater than 60 %.

Compared to 95 % Ethanol, Tenax® behaves more moderately. Depending on the alkane the migration is on the safe side, i.e. 1.5 to 4 times higher than the food migration and thus not as extremely overestimated as with 95 % Ethanol.

The fact that food migration with or from C24-Alkane onwards practically comes to a standstill is consistent with the investigations of mineral oil based hydrocarbons (MOSH/MOAH) done by Lorenzini et. al.[1].

As already stated in the comparison of simulants before, 50 and even more 10 % Ethanol is unsuitable to detect the migration of non-polar analytes such as alkanes into dry food.

4.1.2. Other surrogates

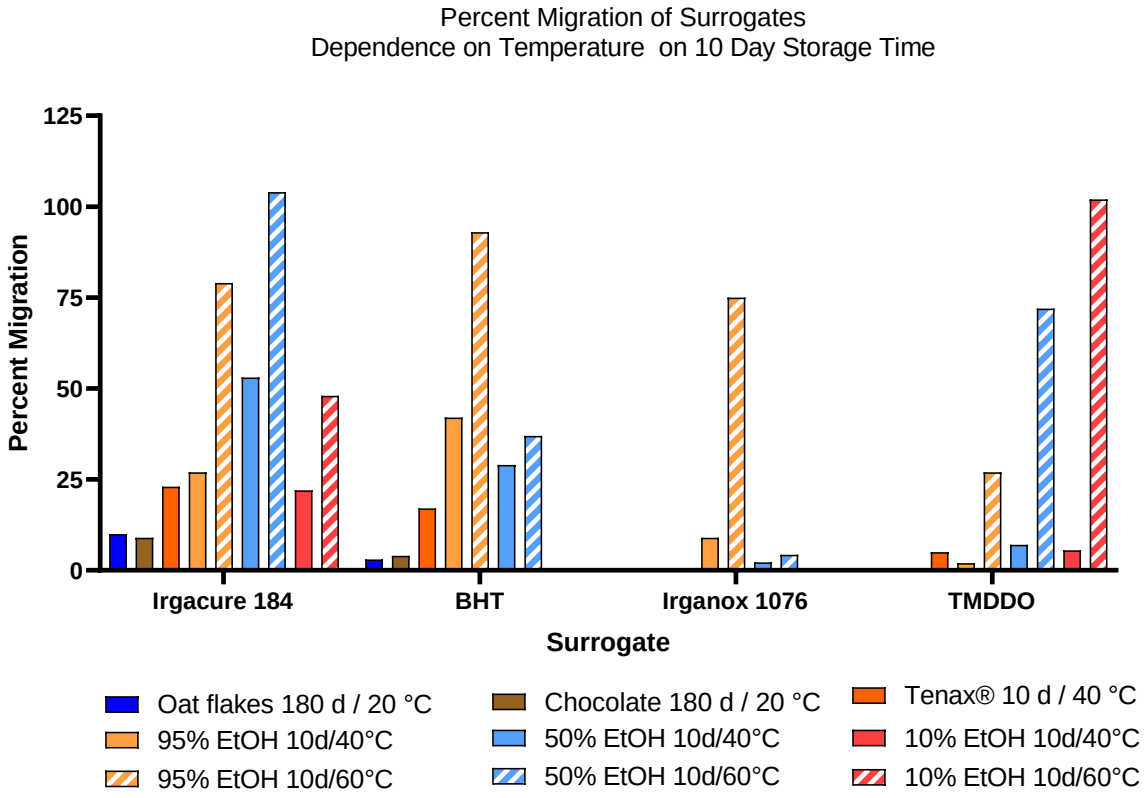

Figure 6: *Comparison of migration of other surrogates from a printed PP film onto Tenax®, ethanolic solutions, oat flakes and milk chocolate under defined test conditions*

The long-term food migration of these surrogate components is comparatively low. For Irgacure 184 and BHT it is about 10 % and lower. Irganox 1076 and TMDDO show no food migration after the 180 days at room temperature.

For the ethanolic simulants, the increase in migration when changing from 40 to 60 °C is extreme. The increase is particularly noticeable for Irganox and TMDDO. Migration is therefore much greater than food migration, 8 times or more!

Comparing the simulants and storage conditions, 95 % ethanol and even Tenax at 40 °C is more than sufficient to cover food migration of Irgacure 184 and BHT. It is 2-5 times higher for Tenax and 3 – 10 or more for Ethanol 95 %.

4.2. Cardboard (all surrogates)

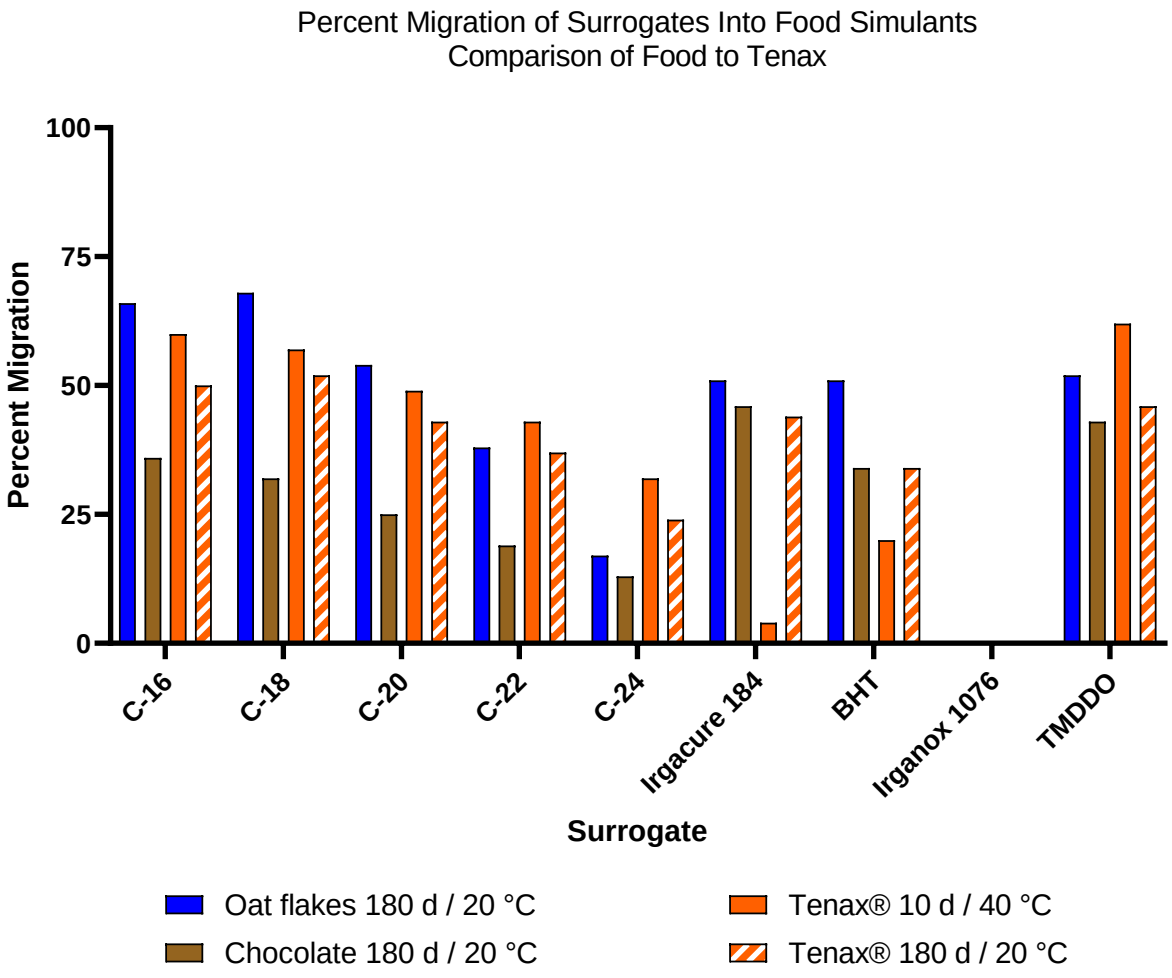

Figure 7: *Comparison of migration for all surrogates from printed cardboard onto Tenax®, oat flakes and chocolate under defined test conditions*

In the case of cardboard substrate, the clearer difference between the two foods is remarkable. Oat flake migration is higher in all cases. For the alkanes C16 – C22 it is about twice as high. The difference was not so pronounced for OPP substrate.

The Tenax® migration after 10 days at 40 °C just about covers the food migration and is thus too weak in the sense of moderate overestimation.

Unfortunately, other storage conditions for Tenax were not foreseen in the study.

5. Migration modelling

The experimental data were intensively analyzed and compared with modelled data using the migraSIM and AKTS software. Two scenarios were carried out, a moderate one and a worse case approach, which are available in two separate reports for interested parties. Overall, it can be said that migration modelling does not provide any additional insights that were not already evident when analyzing the experimental data.

6. Conclusion

A comparison of the simulants shows that 95 % ethanol is not the strongest simulant in all cases. The polarity of the surrogate components and their solubility in the respective simulant seem to be decisive. An example of this is the polar Irgacure 184 or the TMDDO. For the latter, the 10 % ethanol proved to be the strongest simulant. The opposite is true for the relatively non-polar n-alkanes. In 10 % ethanol none, but in 95 % ethanol 100 % migration can be detected.

At 60 °C, the migration usually increases significantly compared to 40 °C.

The decisive factor is the performance of the simulant compared to the actual food migration. The simulant is meant to overestimate food migration but not to an exaggerated degree. In the study, oatmeal and milk chocolate were chosen as the food. They were tested as dry and fatty foods.

Comparing the long-term food storage at room temperature with the performance of the simulants under accelerated storage conditions the current study demonstrate for printed BOPP substrate that:

- Accelerated migration tests at 60 °C in combination with ethanolic simulants 50 % and 95 %, strongly over-estimate migration in the real food for the analytes assessed in this study.

- Migration concentrations of >50% of the original amount in the ink layer were reported, indicating extraction may have taken place.

- In addition, migration into simulants incubated at 40°C is still significantly higher than migration in the real food, which still makes 40°C a valuable over-estimation for testing printed food contact materials.

- Tenax® turns out to be a surprisingly good simulant for PP substrate and for the tested food category (dry and fatty). Compared to 95 % Ethanol, Tenax® behaves more moderately. Depending on the surrogate component the migration is on the safe side, i.e. 1.5 to 5 times higher than the food migration and thus not as extremely overestimated as with 95 % Ethanol.

In the case of printed board, Tenax migraton 10 days at 40 °C just covers food migration, but not to the extent desired, e.g. 2-3 fold. Testing migration at 40 °C for incubation durations above 10 days, as suggested in the DIN SPEC 5010:2018-05 [2], could be a valid approach in this case. Further studies in this regard would be useful.

It should be noted that EU10/2011 contains the provision that the specified test conditions are not allowed to effect physical or other changes to the test specimen which do not occur in the worst foreseeable conditions of use. The large observed gap between the high migration with liquid food simulants at elevated temperatures compared to the migration with food suggests that such a change in the plastic substrate has taken place.

A follow-up study using additional methods to investigate if such a change may have occurred is highly recommended.

7. References

[1] Lorenzini R, Fiselier K, Biedermann M, Barbanera M, Braschi I, Grob K. 2010. Saturated and aromatic mineral oil hydrocarbons from paperboard food packaging: estimation of longterm migration from contents in the paperboard and data on boxes from the market. Food Addit Contam: Part A. 27:1765–1774.

[2] DIN SPEC 5010:2018-5. Testing of paper and board – Determination of the transfer of mineral oil hydrocarbons from food contact materials manufactured with portions of recycled pulp