APPLICABILITY OF MATHEMATICAL MODELLING FOR THE ESTIMATION OF SPECIFIC MIGRATION OF SUBSTANCES FROM PLASTICS

1- Introduction:

The European food contact legislation requires verification of compliance for migration of substances from plastics food contact materials with both overall and specific migration limits. To do so there are migration tests to be carried out using food or food simulants under well specified time and temperature conditions. As an alternative to experimental testing, estimation of specific migration is permitted using generally recognised models as a good manufacturing practice, quality assurance and compliance tool. More specifically, Annex V, chapter 2, § 2.2.3 of the European Regulation (EU) 10/2011 confirms that possibility. However, to demonstrate the non-compliance of a material or article, confirmation of the estimated migration value by experimental testing is obligatory.

A generally recognised model must also be based on scientific evidence, and this was achieved within the European project SMT-CT98-7513 under the 5th Framework Programme. The two major objectives of this project were:

a. To demonstrate that a correspondence between the specific migration limit (SML) and a permitted maximum initial concentration (MIC) of a substance in the finished product can be established.

b. To establish documentation that demonstrates the validity of underlying migration models for compliance purposes. Consequently, parameters used in the migration model were selected in a way that a “worst-case” estimate of migration rate was generated.


Notes:

- Migration modelling has the ability to estimate upper bound migration values, provided the boundary and simplifying assumptions are fulfilled.
- For other polymers and situations not listed in chapter 3 of this report, migration modelling can be used provided the procedures described in the Technical Guidance Document, in preparation, have been followed and that these are supported by the appropriate documentation to demonstrate that the diffusivity behaviour parameter, $A_p$ values are obtained or that the use of the model in that particular case leads necessarily to an overestimation.

This report is also based on the work and draft report of the subsequent European Joint Research Centre Task Force on migration modelling supervised by C. Simoneau and now E. Hoekstra with the specific contribution of O. Piringer, P. Mercea (Fabes GmbH) and R. Brandsch (MDCTech Ltd).
2- **Principle of migration modelling:**

The mass transport of a substance from the plastic material or article to food is governed by the 2nd law of Fick:

\[
\frac{\partial c}{\partial t} = D_p \frac{\partial^2 c}{\partial x^2}
\]

(*Equation 1*)

Where \(C\) is the concentration of migrant in the food contact material or article (P) at Time \(t\) at distance \(x\) from the origin of the x-axis and \(D_p\) is the diffusion coefficient in the food contact material or article.

The model relies on the following boundary conditions and assumptions reported below. The choice of these boundary conditions leads to overestimation.

In practice a monolayer homogenous plastic food contact material or article (P) can be regarded as a film or sheet of finite and constant thickness \(d_p\) being in contact with food of finite volume \(V_F\) and contact area \(A\). It is assumed that at the time of bringing in contact with \(F\) \((t = 0)\), the migrant is distributed homogeneously in \(P\). The possible mass transport resistance on \(F\) side is neglected; therefore the migrant is uniformly distributed in \(F\) at all times.

Under the above assumptions, the analytical solution of equation (1) is equation (2) (Cranck 1975):

\[
\frac{m_{F,t}}{A} = 0.1 c_{P,0} \rho_p d_p \left[ \frac{\alpha}{1 + \alpha} \right] \left[ 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1 + \alpha + \alpha^2 q_n^2} \exp \left( -D_p t q_n^2 d_p^2 \right) \right]
\]

(*Equation 2*)

With:

- \(M_{F,t}\): mass of migrant transferred from \(P\) into \(F\) after time \(t\), (mg)
- \(A\): area of \(P\) in contact with \(F\), (dm²).
- \(c_{P,0}\): initial concentration of migrant \(P\), (mg/kg)
- \(\rho_p\): density of \(P\), (g/cm³)
- \(\rho_F\): density of \(F\), (g/cm³)
- \(D_F\): diffusion coefficient in \(P\), (cm²/s)
- \(t\): migration time, (s)
- \(d_p\): thickness of \(P\), (cm)
- \(V_P\): volume of \(P\) (cm³)
- \(V_F\): volume of \(F\), (cm³)
- \(C_{P,\infty}\): equilibrium concentration of migrant in \(P\) (mg/kg)
- \(C_{F,\infty}\): equilibrium concentration of migrant in \(F\) (mg/kg)
- \(K_{P,F}\): partition coefficient of the migrant between \(P\) and \(F\)
- \(q_n\): the non-zero positive roots of the equation \(\tan q_n = -\alpha q_n\)

Where:

\[
\alpha = \frac{1}{K_{P,F}} \cdot \frac{V_F}{V_P} = \frac{c_{F,\infty} \rho_F V_F}{c_{P,\infty} \rho_P V_P}
\]
and

\[ K_{P,F} = \frac{c_{P,\infty} \rho_p}{c_{F,\infty} \rho_f} \]

Equation (2) can be rearranged to give equation (3) which can be used to estimate the maximum initial concentration of migrant (MIC) in the food contact material or article for not exceeding the specific migration limit.

\[
MIC = \frac{\text{SML} \cdot V_F \cdot \rho_F}{100} \left\{ \rho_p d_P \left[ \frac{\alpha}{1+\alpha} \right] \left[ 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp\left(-D_p t \frac{q_n^2}{d_P^2}\right) \right] \right\}^{-1}
\]

\[(\text{Equation 3})\]

Where: all parameters as for equation 2 apply, with
\[ \text{SML} \] specific migration limit (µg/g or mg/kg)
\[ \text{MIC} \] maximum initial concentration in P, (µg/g)

Note: whereas the analytical solutions of the Fick differential equation exist for a limited number of material and article geometry, numerical algorithms allows developing solutions for more complex shapes.

So, the key parameters necessary for migration modelling are the diffusion coefficient of the migrant in the plastic, \( D_p \) as well as the partition coefficient of the migrant between the plastic and the food or stimulant, \( K_{p,F} \). Both parameters play a crucial role in determining the level of migration in a real food packaging application. Due to a lack of knowledge of their exact values in any specific case, these values have been established in a more generalised and conservative way as described below

2-1 Diffusion coefficients:

Whereas theoretical estimation of diffusion coefficients in polymers are possible (P. Mercea 2000) but complex, a first approximation to estimate \( D_p \) is to correlate this coefficient with the relative molecular mass, \( M_r \), of the migrant with a polymer specific parameter \( A_P \) and the absolute temperature \( T \), based on empirical data. This approach has been used before (Piringer 1994, Hamdani et al. 1997, Limm and Hollifield 1996).

To pursue the goal of obtaining a simple formula for the estimation of \( D_p \), a refined equation for polyolefins and some other polymers has been developed (R. Brandsch et al. 2002). With this equation a polymer specific upper-bound diffusion coefficient, \( D_p^* \) of a migrant in the polymer matrix can be estimated and used instead of the actual diffusion coefficient \( D_p \). It must be emphasized that \( D_p \leq D_p^* \). Therefore, using such a \( D_p^* \) for migration estimations leads to “worst case” values. From phenomenological derivations and a statistical evaluation of experimental diffusion and migration data (Mercea and Piringer, 1998) \( D_p^* \) can be estimated by the following equation (4) (Piringer and Baner, 2000):

\[
D_p^* = 10^4 \exp\left[ A_P^* - 0.1351M_r^{2/3} + 0.003M_r - \frac{R \cdot 10454}{R \cdot T} \right]
\]
From equation (4) it can be recognised that there are key variables which determine the diffusion in a polymer. Two of them are not linked to the polymer and are the relative molecular mass of the migrant, \( M_r \), and the absolute temperature, \( T \), respectively.

The parameter \( A_p^* \) is linked to the polymer and describes the basic diffusion behaviour of the polymer matrix in relation to the migrants. In soft/flexible polymers, such as a low density polyethylene (LDPE), \( A_p^* \) values are reflecting a high diffusion behaviour (\( D_p^* \)) and hence high migration through the polymer, while stiff chain polymers such as polyesters have lower \( A_p^* \) values due to the lower diffusion behaviour and thus lower migration of the same migrant. Where \( A_p^* \) can vary with temperature, \( A_p'^* \) is a temperature independent term. \( A_p^* \) and \( A_p'^* \) are upper-bound values and have been derived statistically so that equation (4) generates upper-bound experimentally measured \( D_p^* \)'s. Using these \( D_p^* \)'s in equations (2) and (3), the migration will be overestimated and consequently worst case migration rates will be calculated within certain temperature ranges.

The parameter \( \tau \) together with the constant \( 10454 \) in equation (4) both contribute to the diffusion activation energy \( E_A = (10454 + \tau) R \), where \( R = 8,3145 \) (J/mol °K) is the gas constant. Upon analysing \( E_A \) data from literature for a large series of migrants in many polymer matrices, it was concluded that \( \tau = 0 \) for many polymers. Thus, setting \( \tau = 0 \) as a first approximation for LDPE gives \( E_A = 86,92 \) KJ/mol, which is in good agreement with the mean value of \( E_A = 87 \) (KJ/mol) found from literature data (P.Mercea 2000).

For other important groups of plastics relevant to food packaging, e.g high density polyethylene (HDPE) and polyethylene terephthalate (PET), a higher activation energy is generally observed. A good mean value for these matrices is \( E_A = 100 \) KJ/mol corresponding to \( \tau = 1577 \).

### 2-2 Partition coefficient

In absence of specific data, in order to model worst case scenarios, the partition coefficient of the migrant between polymer (P) and food (F) should be taken as \( K_{P,F} = 1 \) which means that the substance is very soluble in F; this option leads to the highest migration values, i.e complete transfer of the migrant from the food contact material to food at equilibrium. The question whether this equilibrium partitioning will be reached in a practical application depends on the polymer type and more specifically on the diffusion behaviour of the polymer under the practical contact conditions. For all other cases, that is for which the migrant is only sparingly soluble in F the partition coefficient should be set at \( K_{P,F} = 1000 \) (e.g for lipophilic substances when the polymeric material is in contact with
aqueous food or simulant). More realistic partitioning coefficients can be taken and relationships between $K_{P,F}$ and octanol/water partitioning coefficients used when experimentally available. (Ref: Correlation between partition coefficients polymer/food stimulant, $K_{P,F}$ and octanol/water Log $P(O/W)$. A new approach in support of migration modelling and compliance testing. Publication Deutsche Lebensmittel-Rundschau. Publisher Wiss. Verl.Gess Vol(ISS) Pg 106 (4) p203-208

3- Application of migration modelling to plastics:

From the work done within the frame of the SMT-CT98-7513 project and a subsequent Task Force co-ordinated by the Joint Research Centre and the most recent available data, the key modelling parameters have been established or refined and validated for a range of polymers and a large number of additives. These parameters are reported hereafter:

3-1 Polyolefins:

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T^\circ C$</th>
<th>Mr (g/mol)</th>
<th>$A_p'^*$</th>
<th>$\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>≤ 80</td>
<td>30 – 2000</td>
<td>11,5</td>
<td>0</td>
</tr>
<tr>
<td>LLDPE</td>
<td>≤ 100</td>
<td>30 – 2000</td>
<td>11,5</td>
<td>0</td>
</tr>
<tr>
<td>HDPE</td>
<td>≤ 90</td>
<td>30 – 2000</td>
<td>14,5</td>
<td>1577</td>
</tr>
<tr>
<td>PP (homopolymer)</td>
<td>≤ 120</td>
<td>30 – 2000</td>
<td>13,1</td>
<td>1577</td>
</tr>
<tr>
<td>PP (random)</td>
<td>≤ 120</td>
<td>30 – 2000</td>
<td>13,1</td>
<td>1577</td>
</tr>
<tr>
<td>Pp (rubber)</td>
<td>≤ 100</td>
<td>30 – 2000</td>
<td>11,5</td>
<td>0</td>
</tr>
</tbody>
</table>

Note:
- $C_{p0} < 1\%$
- $K_{P,F}$ 1 for high solubility of migrant in food and 1000 for low solubility of migrant in food.

3-2 Polystyrenes:

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T^\circ C$</th>
<th>Mr (g/mol)</th>
<th>$A_p'^*$</th>
<th>$\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>≤ 70</td>
<td>104 – 647</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>HIPS</td>
<td>≤ 70</td>
<td>104 – 430</td>
<td>1,0</td>
<td>0</td>
</tr>
<tr>
<td>SBS</td>
<td>≤ 70</td>
<td>84 – 689</td>
<td>10,5</td>
<td>0</td>
</tr>
<tr>
<td>PS/SBS blend</td>
<td>≤ 70</td>
<td>84 – 689</td>
<td>(see note below)</td>
<td>0</td>
</tr>
</tbody>
</table>

Note:
- blending PS with SBS results in a linear relationship of $A_p'^*$ value as a function of
- % SBS added to PS. The upper bound $A_p'^*$ value for a blend of PS with SBS can be described by the following relationship:
  $A_{p'}^* (PS) = -1 + 0,115\%SBS$
  (max 100% SBS gives $A_{p'}^* = 10,5$ and min 0% SBS (general purpose PS) gives $A_{p'}^* = -1$
- $C_{p0} < 1\%$
- $K_{PF} = 1$ for high solubility of migrant in food and 1000 for low solubility of migrant in food.

3-3 Polyesters:

<table>
<thead>
<tr>
<th>Polymer</th>
<th>T°C</th>
<th>Mr (g/mol)</th>
<th>$A_p^{**}$</th>
<th>τ</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET above Tg (70°C)</td>
<td>≤ 175</td>
<td>&gt; 32</td>
<td>6.4</td>
<td>1577</td>
</tr>
<tr>
<td>PET below Tg (70°C)</td>
<td>≤ Tg</td>
<td>&gt; 32</td>
<td>3.1</td>
<td>1577</td>
</tr>
<tr>
<td>PEN</td>
<td>≤ 175</td>
<td>&gt; 32</td>
<td>5.0</td>
<td>1577</td>
</tr>
</tbody>
</table>

Note:
- $C_{p0} < 1$
- $K_{PF} = 1$ for high solubility of migrant in food and 1000 for low solubility of migrant in food.

3-4 Polyamides:

<table>
<thead>
<tr>
<th>Polymer</th>
<th>T°C</th>
<th>Mr (g/mol)</th>
<th>$A_p^{**}$</th>
<th>τ</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA6</td>
<td>≤ 100</td>
<td>113</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PA6,6</td>
<td>≤ 100</td>
<td>32 - 587</td>
<td>2.0</td>
<td>0</td>
</tr>
<tr>
<td>PA12</td>
<td>≤ 100</td>
<td>197</td>
<td>2.6</td>
<td>0</td>
</tr>
</tbody>
</table>

Note:
- $C_{p0} < 1$
- $K_{PF} = 1$ for high solubility of migrant in food and 1000 for low solubility of migrant in food.

3-5 PVC:

3-5-1 Rigid PVC:

<table>
<thead>
<tr>
<th>Polymer</th>
<th>T°C</th>
<th>Mr (g/mol)</th>
<th>$A_p^{**}$</th>
<th>τ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid PVC</td>
<td>≤ 70</td>
<td>&gt; 225</td>
<td>-1</td>
<td>0</td>
</tr>
</tbody>
</table>

Note:
- $C_{p0} < 1$
- $K_{PF} = 1$ for high solubility of migrant in food and 1000 for low solubility of migrant in food.

3-5-2 Plasticised PVC:

For plasticised PVC only few data are available both for diffusion coefficients and migration data. Therefore, the model is not considered fully validated for plasticised PVC. However, the following parameter values and equation are provided for informative purposes only:
Since plasticisers are used at high concentration, the diffusion coefficient is expected to vary with the total concentration of plasticiser in PVC. For 30% (w/w) plasticised PVC based on data for 5 plasticisers ranging from Mw 370-419, an upper bound $A_p^{*}$ of 14.6 is considered reasonable. A linear relationship of $A_p^{*}$ value as a function of % plasticiser added to PVC exists. The upper bound $A_p^{*}$ value for plasticised PVC can be described by the following relationship:

$$A_p^{*} (\text{PVC}) = 1 + 0.52 \times (\% \ \text{plasticiser})$$

(max 30% plasticiser gives $A_p^{*} = 14.6$ and min 0% plasticiser (rigid PVC) gives $A_p^{*} = 1$)

3-6 Other polymers, migrants and other parameter range:

The model is not validated yet.

4- Migration modelling in practice:

For migration modelling as described above corresponding in-house computer programmes might be developed and applied. For convenience, there are computer programmes commercially or freely available on the market:

The model allows the following estimations:

- Based on knowledge of the existing initial concentration of a migrant of known molecular weight in a polymer its specific time and temperature dependent migration into a given food simulant or food can be calculated from Equation 2. This allows in particular to compare the estimated migration with the Specific Migration Limit (SML).

Note: as a general rule: in cases where the migration estimation scheme outlined above leads to results which are above the legal limits (SML), an experimental test of compliance is compulsory.

- Reversely, based on a given migration limit or SML value, the maximum initial concentration (MIC) of a migrant of known molecular weight in a polymer that can be used in a food contact can be estimated from Equation 3.

4-1 Compliance testing of substances with specific migration limits (SML):

One major objective of this document is to give guidance for compliance testing. Consequently, and as above mentioned, one major field of application concerns the control for compliance of substances listed in the Regulation (EU) No 10/2011 and its amendments with respect to their specific migration limit (SML). PM/REF-numbers, chemical names, molecular weight-, SML-values and highest concentrations, $C_{P,D}$ of some additives usually used in polyolefins and non-polyolefins can be found in Annex A.

It must be emphasised that before applying the model one always has to ensure that the model assumptions as listed in paragraph 2 are fulfilled for the compound(s) considered. At the present stage of knowledge, the migration model is only suitable for the polymers and under the conditions described in paragraph 3. In addition, the compounds that are theoretically eligible for modelling must meet the criteria listed below:
- All organic, non-gaseous substances with a well-defined molecular weight, soluble in the polymeric matrix, are eligible for migration modelling.

- All polymeric additives with a well-defined molecular weight distribution are eligible under reserve. Migration modelling is applicable provided the actual molecular weight distribution of the polymeric additive is available.

- All organic compounds known to deliberately bloom out from some polymeric materials, e.g. antistatic or antifogging agents incorporated in polyolefins, are not eligible for migration modelling.

- All organic mixtures with undefined molecular weight, typically derived from natural sources like fats and oils, rosins, waxes, starch, proteins, cellulose, cotton are not eligible for migration modelling. However, a specific substance with well-defined molecular weight below 2000 g/mol that is a component of a mixture can be addressed by migration modelling.

- All inorganic compounds, metals, metal oxides, metal salts, etc. are not eligible for modelling.

- Initial compound concentration $C_{p0}$ should be less than 1% and should not change the polymer properties unless the effect on parameters such as $D_{PS}$ and $K_{P,F}$ is known.

Even with these selection criteria, a considerable number of compounds are eligible for migration modelling. If the above criteria are met, then migration modelling can be applied for the substance, provided it is contained in one of the polymers specified in paragraph 3 and also the proper value for the partition coefficient, $K_{P,F}$ is used. If not known, the worst case applies.

Notes:

- As the margin of overestimation can vary with the type of polymer migrant, and contact conditions, it is generally higher in cases of lower diffusion (e.g. high molecular weights migrants, non-polyolefins) but might not always overestimate in all cases. Consequently, the model should be used in the range of temperatures and conditions that were experimentally tested. Therefore, it is recommended to check in more detailed boundaries and limitations of the model in the already mentioned JRC 59476 report.

- The problem of blooming must be considered case by case with respect to the polymer/migrant combination investigated. It is well known that antistatic and antifogging agents typically incorporated into polyolefins deliberately migrate at the surface of the polymeric materials. Alternatively, the same substance does not bloom out from a more polar polymeric material like polyester or polyamide. The user of the migration model is strongly advised to carefully consider the possibility of blooming, to avoid application of the migration model for special cases out of its scope. Blooming out of a given component from the plastic occurs if the difference in polarity between the component and the polymeric matrix is high, resulting in low solubility of the component in the polymer. Due to blooming, the component is migrating in short time at the polymer/air interface, resulting in high migration values for short contact times. When blooming occurs, modelling cannot be applied.
- the model cannot be used for migration predictions in test media with a high swelling power.

- A further point of discussion is the plasticising effect, when higher amounts of low molecular weight components are added to a polymeric material. Substances known to have a plasticising effect in given polymers. For these specific cases modelling is not applicable, unless a specific \( A_p \) value accounting for the plasticising effect has been determined by experiments.

4-2 Compliance control:

When the necessary inputs to the model are available, migration models can be used to optimise compliance control strategies.

Tables of PM/REF-numbers, chemical names, Mr-, SML-values and highest concentrations, \( C_{P,0} \) of some additives usually used in polyolefins and non-polyolefins can be found in Annex A.

It is the responsibility for every company involved in the production, conversion, import and retail sale of food contact materials (FCM) to demonstrate compliance with existing EU legislation. National authorities in turn are responsible to enforce that the legislation is followed. To fulfil their obligations both, companies (or the contracted control laboratories) and enforcement employ compliance testing of FCMs, e.g. by experimental chemical testing of migration, by organoleptic testing and/or testing specific migration limits (SML)) by migration models (MM).

The results obtained by modelling are however only as good as the data put into the model, and only valid if the assumptions of the model are fulfilled. To use MM successfully it is therefore essential to have a well-described FCM. This typically requires good traceability and information flow through the production chain, from raw material producers, to the food industry and to the “seller” of the finished FCM article.

It should also be emphasized, that MM can determine only the migration of known compounds with known initial concentrations. When testing compliance of a FCM, the first question to ask is which type of polymer is at hand – if in doubt an infrared spectroscopy (FTIR) can possibly be of some help. If the polymer is listed in tables of this guide, migration modelling can be applied. If not, the polymer specific constants (\( A_p \) and \( \tau \)) can be determined by a kinetic study e.g. as described in the procedure in the Technical Guidance Document (in preparation) and then the MM can be applied. Otherwise experimental migration-chemical testing needs to be performed.

Apart from the polymer identity, it is crucial to know:

- Which migrateable substances are present in the objects to test (e.g. additives, residual amounts of monomers).

- What are their initial concentrations, \( C_{P,0} \) (e.g. amount of additive as seen from recipe, or determined in an experimental test, see guidance in Feigenbaum et al. (2002)).

- What is the “worst-case” intended use (type of foodstuff, max. temperature and maximum. packaging time) in practical life, based on function of FCM and any
given advisory to the user. If the plastic material or article is intended to be used for one application only, then the specific contact time and temperature conditions for this application can be used.

**Note:** As a result of discussion and decision of the Plastics Implementing Measure (PIM) Technical Meeting a contact time of 10 days maximum still can be applied until more realistic $D_{ps}$ and $K_{pF}$ are determined, knowing that the model currently overestimate migration.

- What is the intended shape of the final article, specifically what surface area will contact what portion of food (i.e. the surface-to-volume ratio) ?

- Which of these substances can be used in practice in the polymer and fulfil the limitations of substances that can be modelled. As previously indicated blooming agents are not homogeneously distributed in the polymer and hence cannot be modelled) ?

The application of migration modelling is straightforward and extremely time saving. In particular if the model predicts migration below the SML and no further action needs to be taken. If the model predicts migration above the SML, experimental migration testing must be conducted. If migration still is above the SML, an additional useful option offered by the model to the producers is to use the MM to calculate the maximum allowed $C_{p0}$ (MIC) and then to reformulate the FCM; otherwise the necessary restrictions of use (e.g. food types, lower contact temperatures, times and/or surface-to-volume ratios) to keep migration below the SML could be put down in the declaration of compliance accompanying the food contact material.

As a first step in enforcement the authorities have to make an effort to retrieve the information from the production chain. If the information is available modelling can follow as described above. If the migrateable substances are known, but their $C_{p0}$ are unknown, then the usual maximum. concentrations ($C_{p0}$) of additives in various polymers listed in Table 1 (polyolefins) and Table 2 (non-polyolefins)) can be used. These tables were prepared by consulting the most important producers of plastic materials and the secondary literature referring additives for plastic materials (Zweifel, 2001). Nevertheless, as fully specified in reference (Milana and Piringer, 2002), these tables should be considered only as an example to offer a first guide in selecting specific additives if no other information is available about the composition of a sample to be tested. Alternatively a quick estimate of compliance can be made by assuming that 100% of the initial concentration migrates. This method might also be applied to known impurities, reaction and breakdown products.

4- **Practical examples:**

**Example 1:**

A film of LDPE with a thickness of 100 μm is used for sandwiches with fatty substances on the surface. This kind of food is stored at 4° C for maximum 7 days. It is known that the film contains Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (Irganox 1076) and Phosphorous acid, tris(2,4-di-tert-butylphenyl ester (Irgafos 168) as additives.

**What information can be obtained about the specific migration of the two additives by mathematical modelling?**
Modelling with a software requires providing the following information as input data:

- Information on the polymer

Polymer thickness: 0.01 cm  
Polymer density: 0.945 g/cm³  
Polymer type: LDPE (\(\text{AP}^- = 11.5, \tau = 0\))

Note: The density value 0.945 is the highest density for LDPE and gives a worst case for the amount of migrant per volume of polyolefin.

- Information on the migrant:

Migrant: Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate  
PM-Ref No: 68320  
SML: 6 mg/kg  
Molecular weight: 531  
\(C_{p0} : 3000 \text{ (mg/kg)}\)

Note: The initial concentration of 3000 mg/kg can be assumed as an upper limit for this additive in LDPE (see table 1 of Annex A).

- Information on the migration contact conditions:

Food simulant: oil (\(K_{PF} = 1\)) (good solubility in food simulant).  
Temperature: T1 (5° C).  
Time: t (10 days).  
Surface/volume ratio: 6 dm² / 1000 ml food.

Note: from the above data the software can calculate at T₁ the diffusion coefficient \(D₁\) in the polymer.

Calculation of migration under one side contact conditions should give the following result:
\(m_{F,t/A} = 1.68 \text{ mg/dm}²\)

Discussion of the result:

In conformity with Article 17 2 (b) of Regulation (EU) 10/2011, the specific migration shall be expressed in mg/kg applying a surface to volume ratio of 6 dm² per kg food expressed in mg/kg (when the actual surface/volume ratio is unknown).

For the above additive (Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate) the SML= 6 mg/kg. At this point the calculated migration, 10.08 mg/kg , exceeds the legal limit. However, the sandwiches with fatty substances on the surface belong to the category of food with the reference number 08.06 A in Regulation (EU) 10/2011 and the reduction factor X/5 is applicable. This means in the above example: \(10.08/5 = 2.02 < 6 \text{ mg/kg}\) and, consequently, it is in compliance with Regulation (EU) 10/2011.

For the second additive, phosphorous acid, tris(2,4-di-tert-butylphenyl) ester (PM/REF = 74240), with the molecular weight \(M_r = 647\) a smaller migration rate results compared to Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate with \(M_r = 531\). There is no migration limit allocated to phosphorous acid, tris(2,4-
di-tert-butylphenyl) ester and its level of migration is far below the Overall migration limit of 60 mg/kg. Therefore no further investigation is required.

**Example 2:**

An empty beaker made of PS is to be evaluated with respect to its compliance when intended for contact with milk products (yoghurt, and such products in association with fruit and fruit products) as categorised with the reference number 07.02 in the Directive 85/572/EEC. The product must be stored at 8°C. The beaker with a volume of 500 ml has a conic geometry and a wall thickness of ≤ 1 mm.

The requested test conditions in conformity with the Regulation (EU) 10/2011 are:

- 10 days at 20°C with simulant 50% ethanol.

**What information can be obtained about the specific migration of the two additives by mathematical modelling?**

Modelling with a software requires providing the following information as input data:

1. **Information on the polymer**
   - Polymer thickness: 0,1 cm
   - Polymer density: 1,1 g/cm³
   - Polymer type: PS ($\lambda^* = -1$, $\tau = 0$)

2. **Information on the migrant:**
   - Migrant: 2-(2-Hydroxy-5-methylphenyl)benzotriazole (PM-Ref No: 61440)
   - SML: 30 mg/kg
   - Molecular weight: 225
   - $C_{P0}$: 2500 (mg/kg)
   - SML: 30 mg/kg

3. **Information on the migration contact conditions:**
   - Food simulant: 50% Ethanol ($K_{PF} = 1$) (good solubility in food simulant is assumed)
   - Temperature: $T_1$ (20° C)
   - Time: $t$ (10 days)
   - Packaging geometry: conic trunk with $d = 6,8$ cm, $D = 8,8$ cm and $h = 10,5$ cm
   - Packaging volume: 500 ml

   Calculation of migration under one side contact conditions should give the following result:
   - $C_{PF,t} = 0,24$ mg/kg

**Discussion of the results**

The modelled migration is by far smaller than the SML value. Therefore no further investigation is required.
Example 3:

A steam sterilizable container made from PP polymer with a capacity of 500 ml and a cylindrical form, with a maximum wall thickness of 2 mm is used for liquid or paste with fatty substances on the surface, according to reference number 08.03 in the Directive 85/572/EEC. The additives used are Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (0.06 %) and Phosphorous acid, tris(2,4-di-tert-butylphenyl) ester (0.1 %). Compliance testing requires test conditions of 2h (t1) at 121°C (T1) followed by 10 days (t2) at 40°C (T2) using simulant D, olive oil.

Which information can be obtained by mathematical modelling?

- Information on the polymer
  
  Polymer thickness: 0.2 cm  
  Polymer density: 0.91 g/cm³  
  Polymer type: PP (Aν* = 13.1, τ = 1577)

- Information on the migrant:
  
  Migrant: Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate  
  PM-Ref No: 68320  
  SML: 6 mg/kg  
  Molecular weight: 531  
  Cp0 : 600 (mg/kg)  
  Phosphorous acid, tris(2,4-di-tert-butylphenyl) ester  
  PM-Ref No: 74240  
  No SML  
  Molecular weight: 647  
  Cp0,0 : 1000 (mg/kg)

3. Information on the migration contact conditions:

Food simulant: oil (KP/F = 1) (good solubility in food simulant is assumed)  
Temperature: T1 (121° C) followed by T2 (40°C)  
Time: t1 (2 hours) followed by T2 (10days)  
Packaging geometry: cylindric pack with D = 10 cm and h = 6.5 cm  
Packaging volume: 500 ml

Calculation of migration under one side contact conditions should give the following result:

Cp,t = 15.8 mg/kg for Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, and 17.0 mg/kg for Phosphorous acid, tris(2,4-di-tert-butylphenyl) ester

Discussion of the results

The calculated specific migration for Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate is likely to exceed the corresponding SML value. Therefore, a migration test is needed for final evaluation of compliance. The calculated specific migration value for Phosphorous acid, tris(2,4-di-tert-butylphenyl) ester is significantly smaller than the overall migration limit of 60 mg/kg. A migration test is not necessary in this case.
5- **Other information:**

The two following reports are under preparation at the European Joint Research Center:


*Note: the list of substances that is theoretically eligible for migration modelling will be published in this report which will also give a lot relevant references.*

- Technical guidance document to determine diffusion coefficients of migrants to update the Ap value of a food contact plastic for migration evaluation by mathematical modelling.

When published, these documents will be a useful additional source of information and recommendations on migration modelling.

**NOTE:** As current migration models overestimate migration; it has been shown that with contact times beyond 10 days, the Specific Migration Limits (SMLs) may be exceeded in numerous cases. Thus, in those cases, only the experimental specific migration test may confirm product compliance.

**Annex A:**

Table 1: PM/REF-numbers, chemical names, molecular weights (Mr), SML-values and highest concentrations, $C_{P,0}$ of some additives usually used in polyolefins.

| PM-REF | Chemical name                                      | Mr    | SML (mg/kg) | $C_{P,0}$%
|--------|----------------------------------------------------|-------|-------------|----------------
<p>| 38560  | 2,5-bis(5-tert-butyl-2-benzoazolyl)thiophene      | 431   | 0,6         |                |
| 38800  | N,N'-bis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl)-hydrazide | 553   | 15          | HDPE 0,2       |
| 38820  | Bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphate | 605   | 0,6         | PP 0,1; LDPE 0,06 |
| 38840  | Bis(2,4-dicumylphenyl)pentaerythritol diphosphate | 853   | 5           | LDPE 0,06      |
| 46640  | 2,6-Di-tert-butyl-p-cresol (BHT)                    | 220   | 3           | PP 0,2         |
| 48640  | 2,4-Dihydroxybenzophenone                          | 214   | 6           |                |
| 48720  | 4,4'-Dihydroxybenzophenone                         | 214   | 6           |                |
| 48880  | 2,2'-Dihydroxy-4-methoxy benzophenone              | 244   | 6           |                |
| 53670  | Ethyleneglycol-bis(3,3-bis(3-tert-butyl-4-hydroxyphenyl)butyrate) | 795   | 6           | PP 0,2; HDPE 0,1 |
| 54300  | 2,2'-Ethylidene-bis(4,6-di-tert-butylphenyl)-fluorophosphonite | 487   | 6           | PP 0,1; LDPE 0,06 |
| 60320  | 2-(2-Hydroxy-3,5-bis(1,1-dimethylbenzyl)phenyl)benzo-triazole | 448   | 1,5         |                |</p>
<table>
<thead>
<tr>
<th>Code</th>
<th>Chemical Name</th>
<th>Density</th>
<th>MFR</th>
<th>Formulation</th>
</tr>
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<td>60400</td>
<td>2-(2'-Hydroxy-3'-tert-butyl-5'-methyl-phenyl)-5-chlorobenzotriazole</td>
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<td>PP 0,4; HDPE 0,3</td>
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<tr>
<td>60480</td>
<td>2-(2'-Hydroxy-3,5'-di-tert-butylphenyl)-5-chlorobenzotriazole</td>
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<td>61600</td>
<td>2-Hydroxy-4-n-octylbenzophenone</td>
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<td>6</td>
<td>PP 0,5; HDPE 0,3; LDPE 0,5</td>
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<tr>
<td>68320</td>
<td>Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate</td>
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<td>6</td>
<td>PP 0,2; HDPE 0,1; LDPE 0,3</td>
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<td>Phosphorous acid, bis(2,4-di-tert-butyl-6-methylphenyl) ethyl ester</td>
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<td>80480</td>
<td>Poly(6-morpholino-1,3,5-triazine-2,4-diyl)-[(2,2,6,6-tetramethyl-4-piperidyl)imino]-hexamethylene-[(2,2,6,6-tetramethyl-4-piperidyl)-imino]</td>
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<tr>
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<td>PP 0,5; HDPE 0,2; LDPE 0,5</td>
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<td>81220</td>
<td>Poly-[6-[(N-(2,2,6,6-tetramethyl-4-piperidinyl)-nbutylamino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidinyl)imino]-1,6-hexanediyl][(2,2,6,6-tetramethyl-4-piperidinyl)imino]-alpha-[N,N,N',N'-tetrabutyl-N''-(2,2,6,6-tetramethyl-4-piperidinyl)-N'&quot;-[6-(2,2,6,6-tetramethyl-4-piperidinylamino)-hexyl]-[1,3,5-triazine-2,4,6-triamine]-omega-N,N,N',N&quot;-tetrabutyl-1,3,5-triazine-2,4-diamine]</td>
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<td>5</td>
<td>PP 0,2; HDPE 0,1; LDPE 0,1</td>
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<td>83595</td>
<td>Reaction product of di-tert-butyl phosphonite with biphenyl, obtained by condensation of 2,4 di-tertbutyolphenol with Friedel-Crafts reaction product ofphosphorus trichloride and biphenyl</td>
<td>991</td>
<td>18</td>
<td>PP 0,1; HDPE 0,05; LDPE 0,06</td>
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<tr>
<td>92880</td>
<td>Thiodiethanol-bis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate)</td>
<td>643</td>
<td>2,4</td>
<td></td>
</tr>
<tr>
<td>93120</td>
<td>Thiodipropionic acid, didotadecyl ester</td>
<td>515</td>
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<td>PP 0,1-0,5</td>
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<td>93280</td>
<td>Thiodipropionic acid, dioctadecyl ester</td>
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<td>2</td>
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<td>PM-REF</td>
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<td>Mr</td>
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<td>Cp0%</td>
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<tr>
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<td>2,4-Bis(octylthiomethyl)-6-methyl-phenol</td>
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<tr>
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<td>Reaction product of di-tert-butyl phosphonite with biphenyl, obtained by condensation of 2,4 di-tert-butylphenol with Friedel-Crafts reaction product of phosphorus trichloride and biphenyl</td>
<td>595</td>
<td>18</td>
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<td>83595</td>
<td>Triethyleneglycol-bis[3-(3-tert-butyl-4-hydroxy-5-methylphenyl) propionate]</td>
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<td>18</td>
<td>0,2</td>
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<td>0,2</td>
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<td>HIPS</td>
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<td>30</td>
<td>0,4</td>
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</table>

Table 2: PM/REF-numbers, names, Mr-, SML-values and highest concentrations, Cp0% of some additives usually used in some non-polyolefins
<table>
<thead>
<tr>
<th>Reference</th>
<th>Name</th>
<th>CAS</th>
<th>Cons</th>
<th>Min</th>
<th>Max</th>
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<tr>
<td>68320</td>
<td>Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate</td>
<td>531</td>
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<td>94400</td>
<td>Triethyleneglycol-bis[3-(3-tert-butyl-4-hydroxy-5-methylphenyl) propionate]</td>
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<td>0,2</td>
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<td>2-(2-Hydroxy-3,5-bis(1,1-dimethylbenzyl)phenyl)benzo-triazole</td>
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<td>0,2</td>
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<td>60480</td>
<td>2,2'-Methylenebis(4-methyl-6-tert-butylphenol)</td>
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<td>2,2'-Methylenebis(4-methyl-6-tert-butylphenol)</td>
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<td>83595</td>
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<td>92880</td>
<td>Thiodiethanol-bis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate)</td>
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<td>93120</td>
<td>Thiodipropionic acid, didodecyl ester</td>
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<td>3</td>
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</table>
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Mercea P. and Piringer O. Data bank to validate a mathematical model to estimate the migration of additives and monomers from polyolefines into foodstuffs and food simulants, EU-contract No. ETD/97/501370 (DG3) (1998).


O’Brien A. and Cooper I., Polymer additive migration to food- a direct comparison of experimental data and values calculated from migration models for polypropylene. Food Additives and Contaminants, 18, 343-355 (2001)


