Investigations of the formation of explosive mixtures in dryers for coatings

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Abstract

In the following we will discuss a specific problem of explosion protection in dryers for coatings. It is mainly encountered in chamber dryers as these pose specific problems as regards occupational safety and health.

During the drying process of most coatings, solvent vapours are released most of which can form explosive mixtures when a specific concentration, the lower explosion limit, is reached. The European Standard EN 1539:2000 requires explosion venting areas for most of these dryers without adequate explosion protection measures such as appropriate limitation of the solvent input being taken into account. Different aspects of the model underlying the calculations are evaluated, and it will be shown that this model is still reliable in most applications. The investigations consisted of three parts. At first there have been made investigations of the operating conditions in different enterprises aimed to get information about specific parameters, problems and failures. Laboratory experiments have been made to investigate in detail the major influencing parameters. Attempts to set up a simple but basic physical model for the experimental data have also been made. Evaporation and diffusion have been examined. The numerical models have been kept as simple as possible to be a potential tool for designers/manufacturers and users.
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1. Introduction

Most of the coatings used today still contain flammable solvents. The vapours of these solvents which are released during the drying process can form explosive mixtures. The safety requirements for dryers and ovens, in which flammable substances are released are described in the European Standard EN 1539:2000. In addition to explosion venting areas other preventive measures by avoiding explosive mixtures are described. These are based on an empirical model developed by Konschak et al. [1] and in the following are referred to as KLF model. It uses a simple mathematical function to describe the general time dependent development of the concentration of the solvent vapour. It is only scaled by the temperature and the ventilation characteristics (total volume of the dryer and air flow rate). These characteristic data can be used to calculate the maximum solvent load of the dryer for a certain maximum allowed concentra-

tion. Further properties of the drying goods (coated surface, heat capacity), the coating (solvents, relative solvent content) and handling (type of application, pre-drying) are not taken into account. Beside the original publication on the KLF-model by Konschak, Luchsinger and Freude [1] no further research work on this specific subject was published.

The general demand for explosion venting systems in EN 1539:2000 has posed a lot of problems for the manufacturers of this kind of dryers and ovens and also for the users. The design of explosion venting systems is difficult, as they mostly occupy a huge part of the dryer surface and are poor thermal insulators. The fundamentals for the design of explosion venting systems are primarily verified for dust explosions but not for turbulent gas/vapour explosions in low strength enclosures.

The operator not only has account for these economic and enviromental impacts but also has to ensure that nobody will be harmed in case the explosion venting system is activated. The general demand for explosion venting systems suggests a higher endangerment by explosions as in accordance with the facts.

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The experimental results reflect the experience gained with the KLF model over several decades. It originally started with an admissible concentration of c_{max} of 80% of the LEL as specified by the regulations of the German employers' liability insurance associations and decreased over the years down to 10% of the LEL for non-monitored dryers in the EN 1539:2000. Accidents with explosive events which cannot be traced back to faulty operation are not known to the German employers' liability insurance associations, a compulsory insurer for all trades.

A more detailed description of this work can be found at Stolpe and Förster [4].

2. The KLF model

The vapour concentration inside a dryer can be described by the following differential equation:

$$\underset{\text{concentration term}}{\mathrm{d}cV_0} = \underset{\text{source term}}{\mathrm{d}D} - \underset{\text{drain term}}{cL\mathrm{d}t} \tag{1}$$

V_0 is the total volume; c the solvent vapour concentration in V_0 at time t, $c = D/V_0$; D the volume of solvent vapour at time t; L the flow rate of fresh air.

This differential equation is solved by:

$$\frac{c}{c_{total}} = \frac{1}{\frac{t_0}{t_w} - 1}\left(\exp\left(-\frac{t}{t_0}\right) - \exp\left(-\frac{t}{t_w}\right)\right) \tag{2}$$

c_{total} is the volume fraction of the solvent vapour in V_0 after total evaporation of the solvent mass m; t_0 the time for complete evaporation of the solvent with a constant evaporation rate; t_w the time for a complete air change of V_0, $t_w = V_0/\dot{V}$.

t_0 is derived from the drying temperature and an empirical constant:

$$t_0 = \frac{\text{const.}}{T} \tag{3}$$

T is the temperature in °C; const. $9300\,\text{s}\,°\text{C}^{-1}$.

Fig. 1 gives a comparison of the time dependent solvent vapour concentration of the KLF model with experimental data.

The time of the maximum concentration can be derived from Eq. (2) as:

$$t_{max} = \left(\frac{t_0 \ln\left(\frac{t_0}{t_w}\right)}{\frac{t_0}{t_w} - 1}\right) \tag{4}$$

and the maximum of the concentration follows as:

$$\frac{c_{max}}{c_{total}} = \frac{1}{\frac{t_0}{t_w}}\exp\left(\frac{-\ln\left(\frac{t_0}{t_w}\right)}{\frac{t_0}{t_w} - 1}\right) \tag{5}$$

3. Operating conditions in enterprises

To get an overview of the operating conditions in paint shops we made some sampling measurements in different
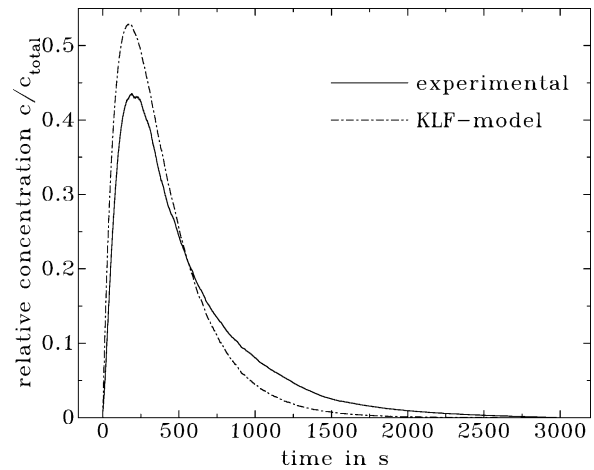

Fig. 1. Comparison of the time dependent solvent vapour concentration of the KLF model with experimental data.

enterprises. These samples ranged from small trade paint shops to a manufacturer of farming machinery.

To determine the concentration of solvent vapours, normally hydrocarbons, a flame ionization detector (FID) was used. For temperature measurement NiCr Ni thermocouples were employed. A multi-channel multimeter was used in combination with a PC for continuous data logging. An impeller anemometer served to determine exhaust flow rates by individual measurements.

The measurements were carried out in 11 different enterprises such as paint shops as well as from small trade, the automotive and electrical engineering industry and research and development and referred to the drying of different coatings on different drying goods. The dryers total vapour space volumes ranged from 2 to 143 m³. The drying goods ranged from small machine parts of only a few gram to a complete farm machine. The results can be summarized as follows. The measurements were performed under the conditions of everyday use: the dryers were not fully loaded, the rules of EN 1539:2000 were followed. Given these pre-conditions a 5% level of the lower explosion limit (LEL) never was exceeded.

These measurements constitute only a small sample and are not representative but it can nevertheless be concluded that a wide safety margin for the LEL is complied with when operating a chamber dryer in accordance with the rules EN 1539:2000. This result confirms the practical experience with the KLF model.

4. Laboratory experiments

Systematic measurements were conducted using a small laboratory size chamber dryer (vapour space volume 0.156 m³) and an industrial chamber dryer (vapour space volume 4.1 m³). The samples were coated with a common split-batch varnish or aluminium bronze. Table 1 compiles

Table 1
Characteristics of the varnishes used

	Varnish	Hardener	Reducer	Aluminium bronze
Flashpoint (°C)	25	>35	23	25
Ignition temperature (°C)	>200	>200	>200	240
LEL (g⁻³)	>35	>35	>35	0.6 vol.%
Boiling temperature (°C)	n.a.	n.a.	126–190	137–143
Vapour pressure (Pa)	n.a.	n.a.	500	900

some basic data of these varnishes which were applied by spraying or by brush.

In preliminary tests using the split-batch varnish it was observed, that during spraying approximately 20% of the solvent evaporates from the varnish aerosol. This kind of solvent loss is not observed for brush application.

The first influencing parameter we are going to discuss now is pre-drying. This is the only process besides spraying which leads to a remarkable loss of solvent. Experiments with the split-batch varnish showed constant solvent loss during the first phase (10 min) of pre-drying. In this case it amounts to $54 \, \text{g}^{-2} \, \text{h}^{-1}$ and is largely independent of the coating thickness (50 µm to ≈300 µm) and the kind of application (spraying or brush painting). The solvent loss from additional pre-drying decreases with increasing time (Fig. 2). From this it can be concluded that the first phase of pre-drying of varnishes based on solvents with high vapour pressure (≥2000 Pa at ambient temperature) can be estimated by simple preliminary tests. For the subsequent phases it is difficult to estimate the solvent loss. The solvent loss due to application and pre-drying is very small for aluminium bronze because it contains solvents with very low vapour pressures. In this case, pre-drying has no real relevance for practice.
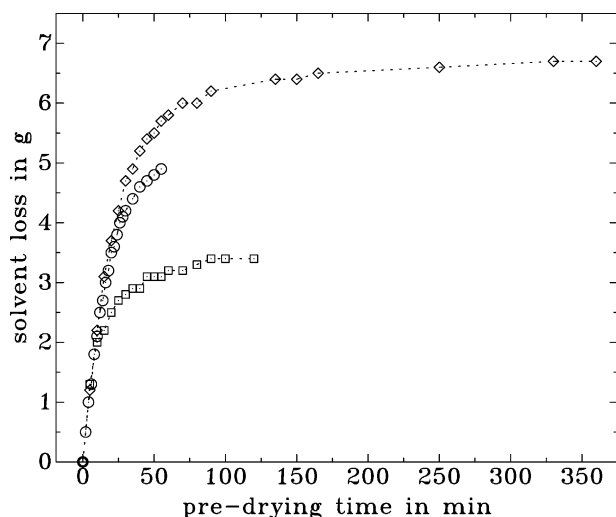

Fig. 2. Time dependence of the pre-drying solvent loss. (○) and (□) symbol are indicating spraying (solvent content of 33 and 35%) and (◇) indicates brush painting (solvent content of 49%).

4.1. Data analysis

Systematic solvent vapour concentration measurements were recorded as a function of drying time. The general data reduction was correcting for zero point, slope, response factor etc.. Then the maximum of the concentration and the time when it was reached were extracted. To become independent of the individual variation of the absolute solvent content, the measured concentration is normalized by the total concentration as described for the KLF model in Section 2. The time of the maximum concentration is often treated in a similar way, it is normalized by t_w. These normalizations allow significant comparison between model and experiment.

4.2. Determination of the mean response factor for FID's

The response factor of a gas monitoring system is characteristic of the combination of the sensor and the gas or vapour. For this research work FID's were used. The standard procedure to determine the response factor is to compare the instrument readings for a known test gas (in the majority of cases propane in air) with a well defined solvent vapour air mixture. This requires some sensitive devices: a dosing pump injecting the solvent into a definite air flow which will be heated in an evaporation line and homogenized in a heated mixing vessel. The escaping mixture is fed into the FID. To calculate the concentration of the mixture density and molar mass of the solvent used must be known.

An alternative method will be described in the following. The solvents for varnishes are always mixtures of several substances. For industrial applications a mean response factor of such composed solvents is often required. It is not necessary for the solvent to be tested to be available as a pure liquid, the varnish can be used directly.

The method is based on a comparison of the evaporated solvent mass during drying. The first mass value is determined by weighing a coated sheet metal before and after drying in a chamber dryer. The second mass value is determined from the concentration curve during drying, which can simply be done in the following steps:

(1) The recorded instruments readings (ppm e.g.) are converted into true decimal values.
(2) With the drying temprature and the exhaust flow rate the total volume of the solvent vapour is calculated.
(3) The total solvent mass is calculated with knowledge of the mean molar mass of the solvent. The mean molar mass can normally be found in the safety data sheet.
(4) The ratio of the two masses is the response factor.

The reading of the FID, the drying temperature and the exhaust air flow should be recorded over the whole drying time to obtain the most reliable results.

The measurement uncertainty for the concentration measurements in this project is 2.9% including the uncertainties of the instruments (FID and data logger) and the test gas.
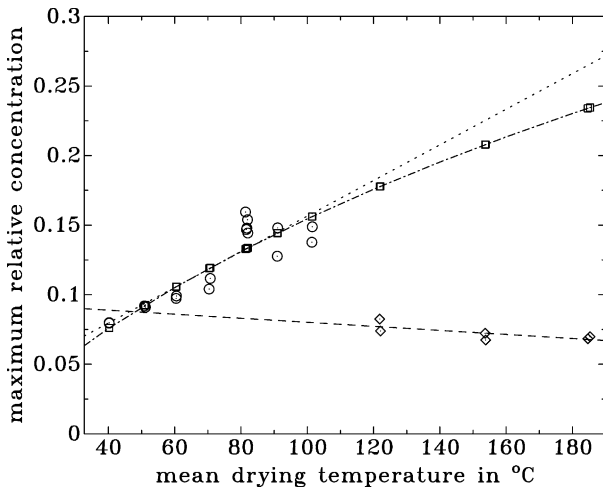
Fig. 3. Temperature dependence of the maximum relative concentration (($\bigcirc$) split-batch varnish, ($\diamondsuit$) aluminium bronze ($\square$) KLF model).

The concentration was measured as volume share. A more detailed description can be found at Stolpe and Förster [4].

4.3. Further experimental results

When increasing the drying temperature (air temperature in the dryer), the increase in the maximum relative solvent vapour concentration (c_{max}/c_{total}, see Eq. (5)) of the split-batch varnish is very characteristic (Fig. 3, ($\bigcirc$) symbol). The KLF model ($\square$ symbol) describes this very well. The aluminium bronze ($\diamondsuit$ symbol) which contains solvents with lower vapour pressures does not show significant variations within the observed temperature range (120–180 °C).

The influence of the air change on the solvent vapour concentration was examined using the split-batch varnish. It was examined for air change times from 80 to 290 s. As expected, the maximum of the concentration increases with
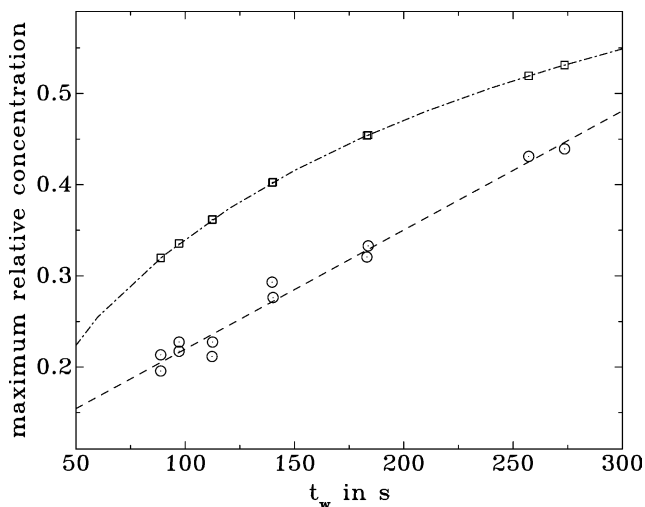

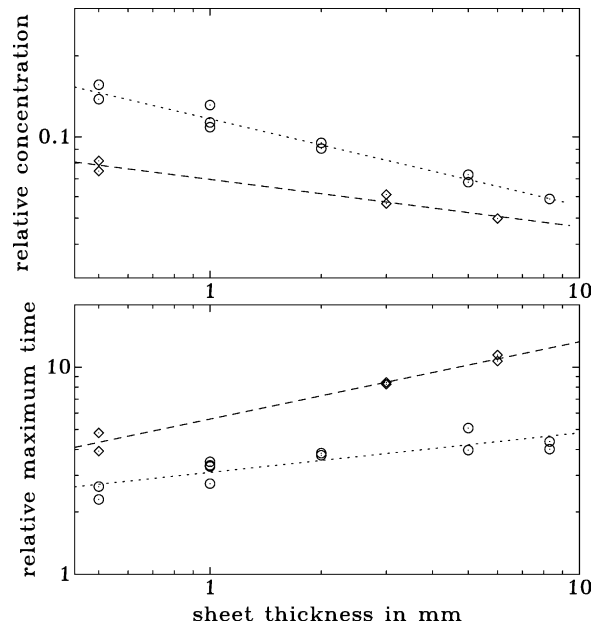Fig. 4. Influence of the air change time on the maximum of the solvent vapour concentration (($\bigcirc$) split-batch varnish, ($\square$) KLF model).

Fig. 5. Influence of the heat capacity (sheet thickness) of the drying goods (($\bigcirc$) split-batch varnish, ($\diamondsuit$) aluminium bronze).

increasing air change times (see Fig. 4). The maximum of the concentration (($\bigcirc$) symbol) satisfactorily agrees with the tendency of the KLF model (($\square$) symbol).

Certain parameters are not included in the KLF model. Some practically relevant parameters, solvent contents and coating thicknesses were also examined.

The maximum solvent vapour concentration in the chamber dryer showed to be approximately proportional to the initial solvent content of the varnish ($\geq 30\%$, split-batch varnish). This clearly emphasizes, that solvent content and solvent mass of the varnish used cannot be treated in the same way. They influence the drying process in different ways.

The heat capacity of the drying goods was examined under constant conditions by varying the thickness of painted aluminium sheets. As Fig. 5 illustrates, the maximum solvent vapour concentration decreases significantly with increasing heat capacity of the drying goods. The relative maximum time increases simultaneously.

A systematic variation of the coated area with a constant amount of varnish showed that there is no significant influence on the resulting solvent vapour concentration.

5. Modelling

The KLF model, in this case ((1)), suggests that the source term is obviously the best starting point to improve the modelling. The mass flow rate can be described as follows:

$$\left.\frac{dm}{dt}\right|_{source} = \frac{dc}{dt} V_0 + c(t)\dot{V} \tag{6}$$

This description of the mass flow rate allows its deduction from the experimental data. Fig. 6 shows two examples of these mass flow rates. The solid line indicates the mass flow
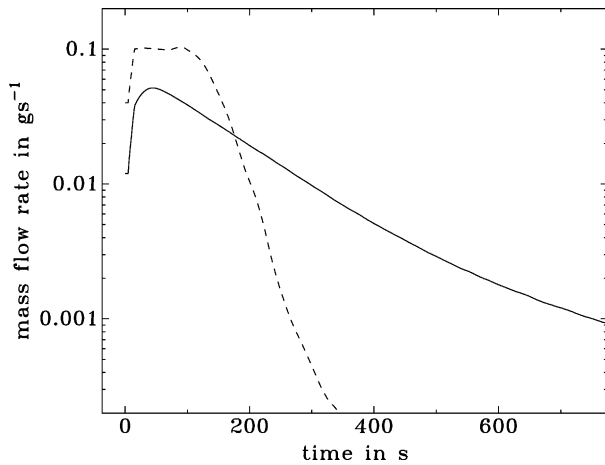
Fig. 6. Source functions of pure solvent (dashed) and varnish (solid)

Fig. 7. Comparison of the solvent vapor concentration of the evaporation model (dashed) and experimental data (solid).

rate of a drying varnish, the dashed line that of pure solvent. The curves indicate two different basic processes for these two experiments. The curve of the drying varnish is characterized by diffusion. The logarithmic plot shows a nearly linear curve over a long time. This is typical of diffusion. The pure solvent evaporates. This can be concluded from the nearly constant mass flow rate at the beginning and its abrupt decrease when most of the solvent has evaporated. On the basis of these observations, two basic attempts of modelling the formation of the solvent vapour air mixture were made.

5.1. Evaporation model

The evaporation model is based on the assumption of the similarity to the evaporation of spilled solvent. The source term for this description can be written as:

$$\left.\frac{dm}{dt}\right|_{\text{evaporation}} = k(v)\left[c_s(T_G) - c\right]F_L \tag{7}$$

v is the velocity of flow above the drying goods in m s^{-1}; $k(v)$ the evaporation rate coefficient in m h^{-1}; T_0 the operating temperature of the dryer in K; T_G the temperature of the drying goods in K; $c_s(T_G)$ the saturation concentration of the solvent vapour in g m^{-3}; F_L the total surface of the varnish in m^2.

The decrease in solvent concentration will be described as:

$$\left.\frac{dm}{dt}\right|_{\text{exhaust}} = cV \tag{8}$$

This approach allows some comparisons with measured data. The results can be summarized as follows:

(1) The values calculated for $c_{\max}/c_{\text{total}}$ are always higher than those measured, even in experiments with pure solvent (Fig. 7). It is obvious that this model gives higher concentration values and an earlier maximum than the experiments give for a decreasing solvent
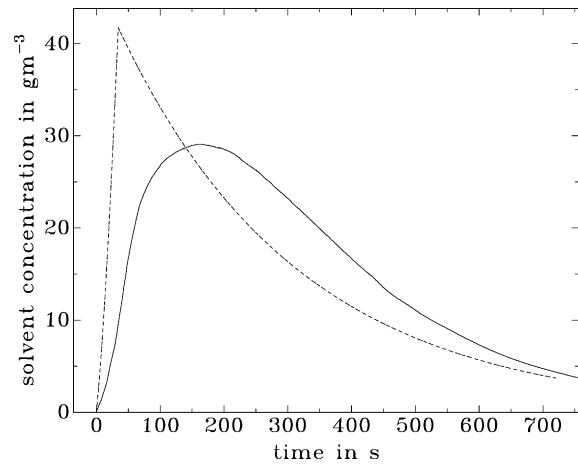
content. It can be assumed that these discrepancies result from the simplification of modelling the evaporation of a one-component solvent (Eq. (7)) which clearly is inappropriate to describe the evaporation of a multi-component solvent. Spot check calculations with a kind of multi-component solvent model lead to a definitely lower maximum concentration and an even lower temperature dependence.

(2) As to drying temperature, air change and heat capacity, this model correctly describes the dependencies found by the experiment. As to solvent content the experimentally found dependence of $c_{\max}/c_{\text{total}}$ underscores that drying of a real varnish cannot be simply modelled by evaporation.

5.2. Diffusion model

e basic structure of the KLF model is a simplified diffusion model. An approximation of a similar diffusion problem was given by Jost [2]. The concentration of a diffusing species in a solid layer is described by an exponential function in time:

$$\frac{dm}{dt} = \frac{M}{\tau}\exp\left(-\frac{t}{\tau}\right) \tag{9}$$

Jost [2] describes τ as:

$$\tau = \frac{8d^2}{\pi^2 D} \tag{10}$$

M is the total mass of the diffusing species; m the current mass of solvent in the solid; d the thickness of the solid; D the diffusion coefficient.

In this solution, τ is equivalent to t_0 in the KLF model. It should be noted that the physical interpretation of t_0 as a diffusion time constant is supported neither by the experiments nor by the calculation rules for the KLF model. Eq. (10) suggests a cubic dependence of the solvent vapour concentration on the layer thickness. It is also known that the diffusion coefficient strongly depends on the absolute
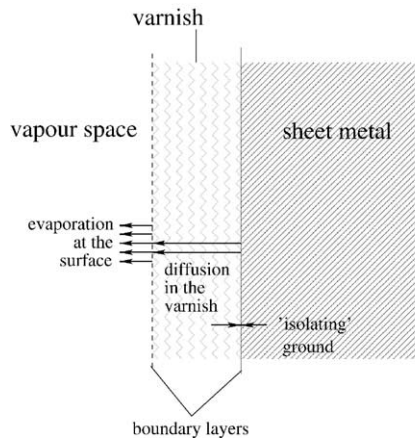
Fig. 8. Illustration of the diffusion scenario.

Fig. 9. Solvent mass in varnish layer from simulations (dotted, dashed) and experiment (solid).

temperature by an Arrhenius function. This is not found in the experiments. So Jost's relations are only valid as an approximation here. A simple one-dimensional numerical model was chosen to simulate the diffusion process. The following simplifications were assumed.

- Only one surface unity element and only the diffusion perpendicular to the surface are treated ↦ one-dimensional problem.
- Pre-drying is disregarded (no initial concentration gradients).
- A constant temperature is assumed for the whole drying time.
- The varnish does not shrink when drying.
- The diffusion coefficient is assumed to be independent in space and time.

Fig. 8 illustrates this scenario.

A finite difference method was chosen for this approach. The discretization in space and time is described by the following finite difference equation:

$$c_k(t + \mathrm{d}t) = c_k(t) + D(c_{k+1}(t) - 2c_k(t) + c_{k-1}(t)) \qquad (11)$$

c is the concentration; D the diffusion coefficient; t the time; k the index for location x.

For stable iteration, the following stability criterion has to be met:

$$\text{const.} = \frac{D\mathrm{d}t}{\mathrm{d}x^2} < \frac{1}{2} \qquad (12)$$

The descriptions of the boundary conditions are analogous to problems known from heat conduction (see Kakac, [3]):

(1) isolating boundary layer at the sheet metal:

$$\frac{\partial c}{\partial x} = 0 \mapsto c_{k-1} = c_k \qquad (13)$$

(2) surface, analogous to convective heat conduction:

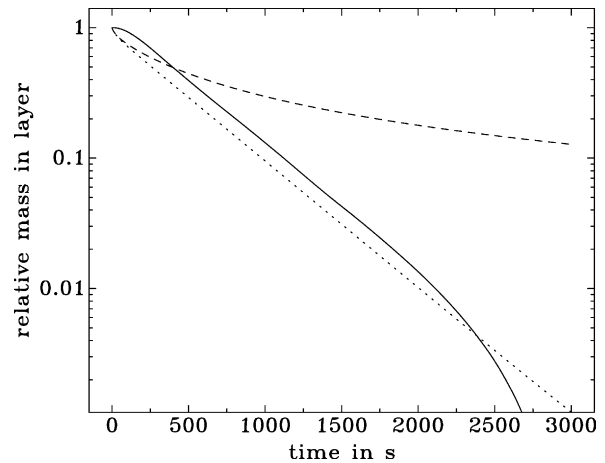$$\mapsto \Delta c_k = \frac{c_{k+1}}{1 + K_v \frac{\Delta x}{D} \Delta t} \qquad (14)$$

A basic introduction to solve numerical problems like those given can be found at Schmitter [5,6].

The only free parameter of this model is the diffusion coefficient. By variation of this coefficient it is possible to approximate the mass loss in an experiment (Fig. 9, dotted curve). The calculations were made with 10 spatial sampling points representing a 50 μm thick varnish layer.

The main interest is to be focussed on the first 200 s. During this time the maximum of the solvent vapour concentration was reached in almost all experiments. It is therefore a basic demand that the model should be able to reliably describe the experiment especially during the first 500 s.

Two attempts were made to improve the calculations:

(1) During drying, the varnish gets harder and the diffusion coefficient decreases. The diffusion coefficient was linked with the remaining solvent mass in the varnish layer like:

$$D_{t+1} = D_t c_{\text{total},t} \qquad (15)$$

$c_{\text{total},t}$ is the remaining solvent concentration at time t. The result was an even more pronounced deviation from the experiment (Fig. 9, dashed curve).

(2) In this attempt the diffusion coefficient was linked with the solvent concentration in the surface element.

$$D_{t+1} = D_t c_{k,t} N \qquad (16)$$

$c_{k,t}$ is the concentration in the surface element at time t and N the number of elements/sampling points.

This variation did not produce an improvement either.

From these examples, some further tests and comparisons with the experiments we concluded:

- The diffusion coefficient does not depend on the temperature in the same way as an Arrhenius function.
- The models do not describe the observed dependencies concerning surface and thickness of the varnish layer in a correct way.

- Especially in the important starting range, the description by the model fails.
- These simulations and especially even more sophisticated approaches are up to now not suitable and anyway too complicated to become an accepted tool for design and operation of a dryer.

6. Conclusions

Several sets of experiments relating to different physical parameters (pre-drying, drying temperature, air change, solvent content, heat capacity etc.) were made and compared with the KLF model. The maximum concentration and the point in time when it was reached were always predicted by the KLF-model in a manner reliable from the point of view of safety engineering.

Our experiments showed that dryers operated under normal operating conditions can have a solvent load accounting for up to 35% of the LEL without any concentration monitoring and there is still a safety margin of a factor of 3.

It was attempted to find a simple and physical description for the source function of the drying process to improve the KLF model. It became obvious that an improvement suitable for practice is not readily at hand. Staying with KLF model the constant in t_0 (Eq. (3)) depends on the kind of drying process. It is optimized for surface coatings, but it can also be determined for mould varnish and impregnated resin varnish drying instead of using some simple scaling factors as done in EN1539:2000. For non-transient applications it will be appropriate to determine this constant more precisely.

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