CODEN STJSAO
ZX470/1470

ISSN 0562-1887
UDK 66.047.7-035.67:543.613

Theoretical and Experimental Study for the Drying Process of Glass Colour According to Mass Transfer Laws

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Original scientific paper

A drying process is commonly used in industry. Textile, glass, ceramic, dye and food could be accepted as leading sectors where the drying process take parts. During the drying process the aim is to remove water or solvents from the structure of material which is needed to be dried. For most cases, drying occurs between production steps and the effectiveness of the drying is quite important for the coming steps of relevant production processes. Not only are the properties of material which are needed to be dried, but also the method of drying is important regarding both effectiveness of drying and energy cost. Today in industry, besides the importance of first investment cost of systems the running costs of the systems, have a highly increasing importance. It is well-known that the energy cost is a considerable part of running costs. In this study, concerning the above mentioned reasons, we aim to create a mathematical way to optimise the drying process concerning “effectiveness of drying” and “energy cost”. Basically the drying process is a “mass transfer” phenomenon. In this study, by means of mathematical statements of mass transfer phenomenon, the drying speed of a liquid with well-known physical properties has been calculated in a theoretical way and the calculations have been tested by experimental ways. The results obtained from both mathematical and experimental ways have been evaluated. A new method is reached by means of a combination of theoretical calculation and experimental studies to determine the partial pressure of liquids whose physical properties are not well-known. At the end, experimental studies have been done to understand the drying properties of glass colours and results have been evaluated.

Teorijska i eksperimentalna studija procesa sušenja staklene boje koristeći zakon održanja mase

Izvornoznanstveni članak

Proces sušenja staklene boje najčešće se koriste u industijskim područjima tekstila, stakla, keramike, boja kao i u području sušenja hrane. Procesom sušenja se odstranjuje vlaga iz strukture sušenog materijala. Ne samo da svojstva sušenog materijala nego i sama metoda sušenja ima veliki utjecaj kako na efikasnost tako i na cijenu koštanja. Danas u industriji pored velike važnosti investicijskih troškova, također i pogonski troškovi sušenja su od velikog značaja. Dobro je poznato da je u tim pogonskim troškovima bitan trošak na uloženu energiju u sam proces sušenja. Ovim radom se želi kreirati matematički put iznalaženja optimalnog procesa sušenja u pogledu njegove efikasnosti i cijene koštanja. U osnovi je proces sušenja proces prijenosa (transporta) mase. Ovim radom se pomoću matematičkog modela prikazuje teorijski način fenomena transporta mase, zajedno s dobro poznatim fizikalnim svojstvima, brzinom sušenja. Odstranjivanja same kapljevine i rezultati tog teorijskog modela se kompariraju s eksperimentalnim vrijednostima. Rezultati dobiveni teorijskim i eksperimentalnim načinom su evaulirani. Razvijena je nova metoda pomoću koje se teorijski računom i eksperimentalnim rezultatima određuje percijalni tlak kapljevine čija fizikalna svojstva nisu dobro poznata. Na kraju su učinjene eksperimentalne studije, da bi se pomoću njih razumjela fizikalna svojstva staklenih boja i rezultati su evaluirani.

Keywords
Drying Glass Enamels
Modelling of Drying

Ključne riječi
Modeliranje sušenja
Sušenje staklenog emajla

Received (primljeno): 2010-04-01
Accepted (prihvaćeno): 2010-08-31

1. Introduction

Ceramic enamels and silver pastes which have both visual and functional objectives have been used on automotive glasses for many years. Ceramic enamels and silver pastes need to be dried or cured after a silk screen printing process to gain resistance against handling operations. Both ceramic enamels and silver pastes reach final resistance by firing process at tempering or laminating furnaces where the glass is shaped. [2]

Symbols/Oznake

C	- molar concentration, kmol/mol^3 molarna koncentracija
C_A	- molar concentration of A, kmol/mol^3 - molarna kocentracija komponente A
C_B	- molar concentration of B, kmol/mol^3 - molarna kocentracija komponente B
D_{AB}	- Mass diffusivity for binary gas mixture, m^2/s - masena difuzivnost binarne plinske smjese
h	- height from water surface to top of tube, m - visina od površine vode do vrha cijevi
$\dot{J}_A$	- mass flux of A, kg/(s·m^2) - gustoća masenog toka komponente A
$\bar{J}_A$	- molar flux of A, kmol/(s·m^2) - gustoća molarnog toka komponente A
$\dot{m}_{water}$	- mass flux of water vapour kg/(s·m^2) - gustoća masenog toka toka vodene pare
M_{water}	- molar mass of water, kg/kmol - molarna masa vode
$\dot{n}_{water}$	- molar flux of water vapour, kmol/(s·m^2) - gustoća molarnog toka toka vodene pare
P	- pressure, kPa - tlak
P_{water}	- partial vapour pressure of water vapour , kPa - parcijalni tlak vodene pare
$\bar{R}$	- universal gas constant, 8.314 kJ/(kmol·K) - univerzalna plinska konstanta
R_{water}	- gas constant for water vapour, kJ/(kg·K) - plinska konstanta vodene pare
T	- temperaure, K - termodinamička temperatura
x_A	- mole concentration rate of A in a mixture, $\neq P_A/P$ - molarna koncentracija komponente A u smjesi
x_{water}	- mole concentration rate of water vapour in a mixture, $\neq P_{water}/P$ - molarna koncentracija vodene pare u smjesi
$x_{water,\infty}$	- mole concentration rate of water vapour at top of tube, $\neq \varphi_\infty \cdot P_{water}/P$ - molarna koncentracija vodene pare na vrhu cijevi
$x_{water,0}$	- mole concentration rate of water vapour at water surface, $\neq \varphi_0 \cdot P_{water}/P$ - molarna koncentracija vodene pare na vodenoj površini
ρ	- density, kg/m^3 - gustoća
ρ_A	- density of A, kg/m^3 - gustoća komponente A
ρ_B	- density of B, kg/m^3 - gustoća komponente B
φ_0	- relative humidity at water surface, % - relativna vlažnost na vodenoj površini
φ_∞	- relative humidity at top of tube , % - relativna vlažnost na vrhu cijevi

Screen printing enamels typically consist of an inorganic part which is a black stained frit powder and an organic vehicle called medium. Organic media are available for IR- drying and for UV curable pastes [4].

The major component of IR-media is solvent e.g. pine-oil and some organic resins. After screen printing the solvent is removed by a drying process, taking several days at room temperature or a few minutes with infrared dryers. The resin is kept in the printed layer to provide acceptable green strength. It is burned off during firing of the enamel [5].

UV-pastes are formulated from acrylic compounds capable of curing in a few seconds under UV radiation. Prints do not need any drying at elevated temperatures. No evaporation of solvents occurs. Despite this UV-pastes are more complex in chemistry and need more care in storage. [8]

The aim of a drying or curing process can be listed as follows [6]:

- Firing of wet enamel at high temperature causes fast evaporation of solvents which creates pin holes at print surface, drying process prevents the pin holes.
- Wet enamel could be damaged easily after screen printing; drying or curing gives enamel resistance against handling operations.
- For double printed glasses like heated rear windows, after first printing the enamel must be dried or cured so the second screen printing could be done.

A good quality print could be reached by proper drying or curing process. Since the usage of IR drying enamels are more common compared with UV curable enamels, this paper deals with the drying process of IR drying enamels.

1.1. Functions and Contents of Ceramic Enamels

Today, the installation of automotive glasses to the car body is done by polyurethane glue. Polyurethane glue could not withstand UV radiation. Therefore the polyurethane needed to be shielded from UV radiation in the average daylight as, otherwise, its properties will rapidly diminish and glass will simply fall out of the car after time [3].

The main task of ceramic enamels is protecting the polyurethane glue from UV radiation of the sun. In addition to its main task ceramic enamels are used to improve the visual quality of the automotive glasses [3].

The contents of both IR drying and UV curable enamels are shown below in table [7].

Table 1. Contents of ceramic enamels

Tablica 1. Sadržaj keramičkog emajla

			Organic medium / Organsko sredstvo	
	Glass frit / Staklo	Inorganic pigment / Anorganski pigment	Solvent / Otapalo	Polimer / Polimer
IR medium / Infracrveno sredstvo	64%	16%	17%	3%
UV medium / UV-sredstvo	64%	16%		20%

Glass frit allows adherence to glass, gives mechanical and chemical resistance and obtains opacity after firing. Inorganic pigments are a mixture of metal oxides calcined at high temperature and give colour. Organic medium is a mixture of organic compounds, such as solvents and polymers and gives fluid form to enamel which is needed for silk screen printing. Most of the organic medium is evaporated during drying and the rest is burned at tempering or laminating furnace. [2]

1.2. Functions and Contents of Silver Pastes

Conductive silver prints were introduced on automotive glasses to increase performance such as de-icing functions or antennas. The contents of silver pastes are shown below in table. [2]

Table 2. Contents of silver pastes

Tablica 2. Sadržaji srebrnih pasti

Silver powder / Srebrna prašina	Glass frit / Staklo	Solvent / Otapalo
40-88%	2-8%	9-50%

Inorganic additives / Anorganski aditivi	Organic additives / Organski aditivi	Organic resins / Organski resins
0-20%	0-10%	1-8%

2. Diffusion mass transfer

It is well know that temperature difference causes heat transfer. Similar to this, the concentration difference in a mixture causes mass transfer. While the temperature gradient is the major factor for heat transfer phenomenon, concentration gradient in a mixture is the major factor for mass transfer phenomenon [1].

2.1. Fick's Law

The rate equation for mass diffusion is known as Fick's Law, and for the transfer of species A in a binary mixture of A and B, it may be expressed in vector form as

$$\dot{J}_{\mathrm{A}} = -\rho D_{\mathrm{AB}} \nabla m_{\mathrm{A}}, \tag{1}$$

$$\bar{J}_{\mathrm{A}} = -C D_{\mathrm{AB}} \nabla x_{\mathrm{A}}. \tag{2}$$

Fick's Law defines an important transfer property, namely, the "binary diffusion coefficient or mass diffusivity, D_{AB}".

The quantity $\dot{J}_{\mathrm{A}}, \frac{\mathrm{kg}}{(\mathrm{m}^2 \cdot \mathrm{s})}$ is defined as diffusive mass flux of species A. It is the amount of A that is transferred by diffusion per unit time and per unit area perpendicular to the direction of transfer, and it is proportional to the mixture mass density, $\rho = \rho_{\mathrm{A}} + \rho_{\mathrm{B}}$, and to the gradient in the species mass fraction, $m_{\mathrm{A}} = \rho_{\mathrm{A}}/\rho$. The species flux may also be evaluated on a molar basis, where $\bar{J}_{\mathrm{A}}, \frac{\mathrm{kmol}}{(\mathrm{s} \cdot \mathrm{m}^2)}$ is the diffusive molar flux of species A. It is proportional to the total molar concentration of the mixture, $C = C_{\mathrm{A}} + C_{\mathrm{B}}$, and to the gradient in the species mole fraction, $x_{\mathrm{A}} = C_{\mathrm{A}} / C$. If the total mass density ρ or the total molar concentration C is a constant, the foregoing forms of Fick's law may be simplified as [1]

$$\dot{J}_{\mathrm{A}y} = -D_{\mathrm{AB}} \frac{\mathrm{d}}{\mathrm{d}y} \rho_{\mathrm{A}}, \tag{3}$$

$$\bar{J}_{\mathrm{A}y} = -D_{\mathrm{AB}} \frac{\mathrm{d}}{\mathrm{d}y} C_{\mathrm{A}}. \tag{4}$$

2.2. Mass Diffusivity

Considerable attention has been given to predicting the mass diffusivity D_{AB} for the binary mixture of two gases, A and B. Assuming an ideal gas behavior kinetic theory may be used to show that

$$D_{\mathrm{AB}} \cong p^{-1} T^{3/2}. \tag{5}$$

This relation applies for restricted pressure and temperature ranges and is useful for estimating values of the mass diffusivity at conditions other than those for which data are available. [1]

2.3. Evaporation of Water: Theoretical and Experimental Study

Before defining the drying properties of glass colour where the physical properties are not known, here the mathematical model of mass diffusion for evaporating water is defined and tested by experimental way.

Let us consider diffusion of water in the air as shown at Figure 1.

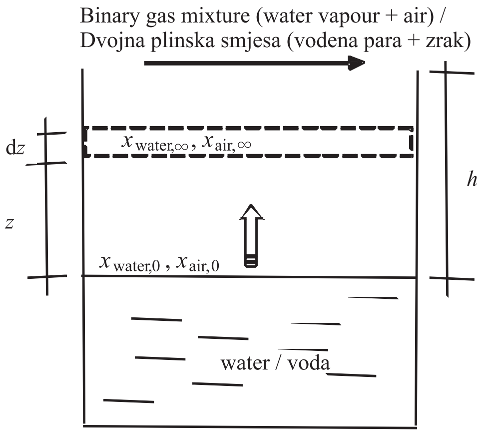

Figure 1. Evaporation of water

Slika 1. Ishlapljivanje vode

Water evaporates from the liquid interface and is transferred upward by diffusion. For steady, one dimensional condition with no chemical reactions, water cannot accumulate in the control volume of Figure 1. And molar flux of water may be defined as

$$\dot{n}_{\text{water}} = -\frac{CD}{1-x_{\text{water}}}\frac{\mathrm{d}x_{\text{water}}}{\mathrm{d}z}, \tag{6}$$

$$\dot{n}_{\text{water}}\int_0^h dz = -CD\int_{x_{\text{water},0}}^{x_{\text{water},\infty}}\frac{\mathrm{d}x_{\text{water}}}{1-x_{\text{water}}}, \tag{7}$$

$$\dot{n}_{\text{water}} = \frac{CD}{h}\ln\frac{1-x_{\text{water},\infty}}{1-x_{\text{water},0}}. \tag{8}$$

Water vapour may be adopted as an ideal gas and concentration and molar flux may be defined as

$$C = \frac{P}{\bar{R}T} \tag{9}$$

and

$$\dot{n}_{\text{water}} = \frac{PD}{\bar{R}Th}\ln\frac{1-x_{\text{water},\infty}}{1-x_{\text{water},0}} \tag{10}$$

Mass flux may be defined by means of molar flux and molar mass:

$$\dot{m}_{\text{water}} = \dot{n}_{\text{water}}M_{\text{water}}, \tag{11}$$

$$\bar{R} = M_{\text{water}}R_{\text{water}}, \tag{12}$$

$$\dot{m}_{\text{water}} = \frac{PD}{R_{\text{water}}Th}\ln\frac{1-x_{\text{water},\infty}}{1-x_{\text{water},0}}. \tag{13}$$

Concentrations of water vapour both at liquid film and top of container can be calculated by means of partial vapour pressure at given temperature and relative humidity.

$$x_{\text{water},\infty} = \varphi_\infty\frac{P_{\text{water}}}{P}, \tag{14}$$

$$x_{\text{water},0} = \varphi_0\frac{P_{\text{water}}}{P}. \tag{15}$$

The relative humidity at liquid film can be adopted as $\varphi_0 = 1$.

The equation (13) has been applied for three different temperatures and relative humidity condition and mass flux of evaporating water has been calculated. For each condition, mass flux of evaporating water has been measured also by experimental way. The results from both methods are given in Table 3. and Figure 2.

Table 3. Mass flux of evaporating water, g/(m^2·s)

Tablica 3. Gustoća masenog toka ishlapljene vode

	T=53°C, $\varphi_\infty = 0.25$	T=60°C, $\varphi_\infty = 0.24$	T=76°C, $\varphi_\infty = 0.20$
Equation / Jednadžba	0.40	0.56	1.21
Test / Test	0.30	0.57	1.30

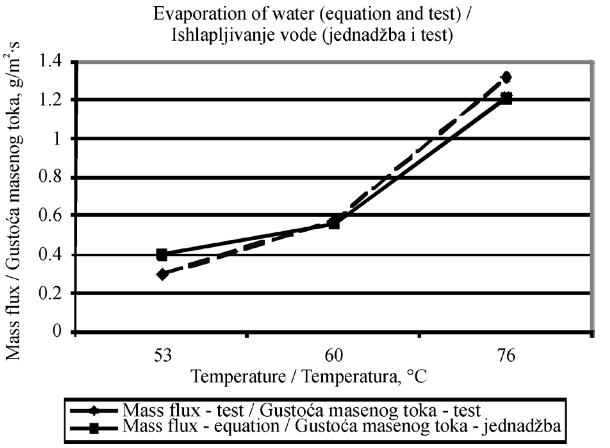

Figure 2. Mass flux of evaporating water

Slika 2. Gustoća masenog toka ishlapljene vode

As seen from Figure 2. there is a consistency between results from the equation and test.

The above result shows us that obtaining a mathematical model of evaporation will be helpful in designing the drying furnaces for the liquids where the physical properties are known.

2.4. Defining a calculation method for the partial vapour pressure of liquids

Evaporation of a liquid is dependent on physical properties of evaporating liquid (partial vapour pressure at given temperature, molar mass) and physical properties of environment (temperature, pressure, relative humidity).

Partial vapour pressure is given in tables for many liquids. Here, a method is defined to calculate the partial vapour pressure of a liquid by means of mathematical equation and results from an experimental study where the vapour pressure is not known.

The mass flux of evaporating liquid and known physical parameters are placed in equation (13) and a constant value (A) is obtained which is defined as

$$\ln\frac{1-x_{\mathrm{liquid},\infty}}{1-x_{\mathrm{liquid},0}} = A \text{ (constant)}, \tag{16}$$

$$e^{A} = \frac{1-x_{\mathrm{liquid},\infty}}{1-x_{\mathrm{liquid},0}}. \tag{17}$$

Equation (14) and (15) is placed in equation (17) and the following equation is obtained:

$$e^{A} = \frac{1-\varphi_{\infty}\dfrac{P_{\mathrm{liquid}}}{P}}{1-\varphi_{0}\dfrac{P_{\mathrm{liquid}}}{P}}. \tag{18}$$

Due to the complexity of equation (18) it is difficult to calculate P_{liquid}. This is why it is decided here to draw a graphic for different P_{liquid} values and calculated e^{A} values. By means of marking the calculated unique e^{A} value on the graph P_{liquid} is obtained as seen in Figure 3.

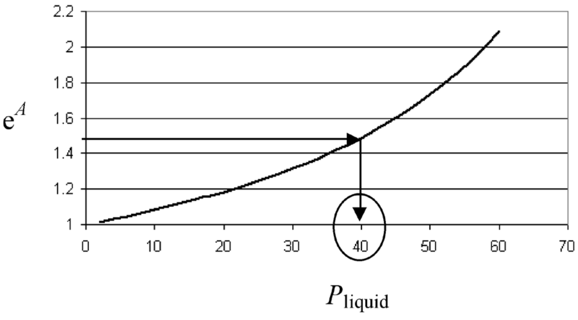

Figure 3. Obtaining partial vapour pressure of a liquid

Slika 3. Određivanje parcijalnog tlaka pare kapljevine

3. Determination of drying properties of automative glass colour by experimental study

There are certain producers for automotive glass colours in the world. Due to tough competition in the market, the chemical content of both ceramic enamels and silver pastes are kept secret and it is not possible to know the physical parameters (molar mass, partial vapour pressure etc…) of them.

Due to the above mentioned reasons, the only way to define the drying properties of glass colours is an experimental study.

It is well known that the drying speed of a glass colour is defined by evaporation speed of organic medium. In order to perform the evaporation test a certain amount of two different organic mediums denoted as 701 A and 702 A are found alone and heated up to certain temperatures in a test furnace and by measuring the weight change the mass flux is calculated.

Tests are repeated at two different temperatures (50 °C, 70 °C) and for stationary and non stationary mediums. Results are seen in Figures 4, 5, 6, 7.

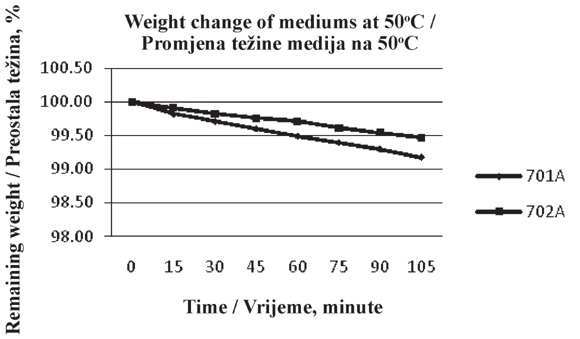

Figure 4. Weight change of mediums (50 °C / stationary drying atmosphere)

Slika 4. Promjena težine medija (50 °C / stacionarna atmosfera sušenja

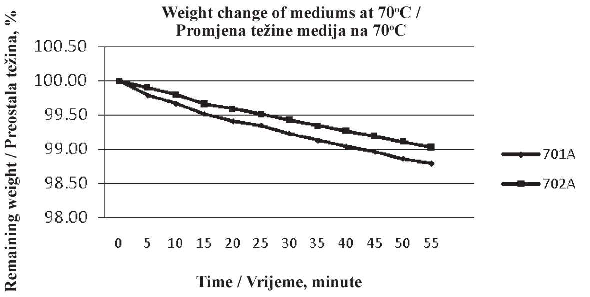

Figure 5. Weight change of mediums (70 °C / stationary drying atmosphere)

Slika 5. Promjena težine medija (70 °C / stacionarna atmosfera sušenja

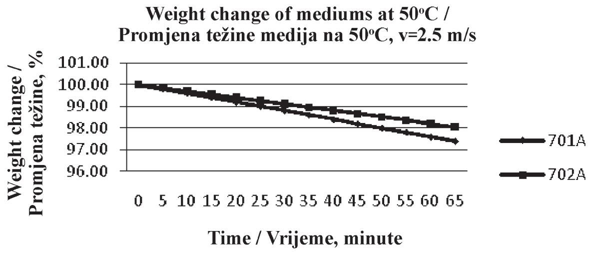

Figure 6. Weight change of mediums (50 ºC / nonstationary drying atmosphere)

Slika 6. Promjena težine medija (50 ºC / nestacionarna atmosfera sušenja

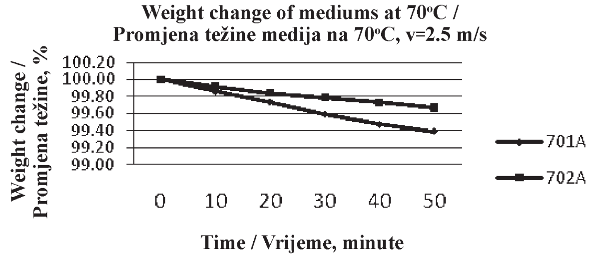

Figure 7. Weight change of mediums (70 ºC / nonstationary drying atmosphere)

Slika 7. Promjena težine medija (70 ºC / nestacionarna atmosfera sušenja

Considering the above results the surface area of evaporation mass flux for each organic medium may be calculated and is shown in Table 4.

Table 4. Mass flux of organic mediums

Tablica 4. Gustoća masenog toka organskih medija

Mass Flux	701A	702A
50 ˚C V=0 m/s	2.06 g/(m^2·min)	1.31 g/(m^2·min)
50 ˚C V=2,5 m/s	3.17 g/(m^2·min)	2.33 g/(m^2·min)
70 ˚C V= 0 m/s	5.72 g/(m^2·min)	4.59 g/(m^2·min)
70 ˚C V=2,5 m/s	14.15 g/(m^2·min)	10.60 g/(m^2·min)

Experimental study on the organic medium of glass colour shows us how evaporation speed is affected by temperature and air velocity in the test furnace. Increasing the drying temperature and air velocity will cause faster drying of glass colour.

Automotive glass printing process is a continuing process where the conveyor speed of drying furnace fits the cycle time of printing machine. This is why the needed drying time is only performed by length of the furnace. Since the evaporation is faster for nonstationary drying atmosphere, for a certain temperature the length of the drying furnace will be shorter, which will cause a decrease in the first investment cost and running costs.

4. Conclusions

Due to global competition in the market, we have to keep product costs at the lowest level. First investment costs and running costs have a highly increasing importance on the product costs. Energy costs have the biggest part in the running costs. This is why first investment costs and energy costs must be considered during the process design.

Shortage of energy sources in the world and environmental effects of using energy sources, force people to take effective precautions to decrease energy demand.

So, considering both global market situation and global energy policies, the optimum design of a drying process has a highly increasing importance in the industry. This study shows us that comparative studies, including both experimental and theoretical methods, are very important for design of a drying process.

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