

The obtain of digital glass decor using inorganic precursors

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Abstract Alkaline earth metal silicates as well as many polyvalent metal silicates can be obtained through aqueous solution's reactions between an alkaline silicate solution and the solutions of metal salts. The vitrification of the oxide compositions, established by the necessary molar ratios for the projected glass, is realized by calculating the concentration of chemical precursors, through their reaction directly on the substrate. The sodium silicate viscosity in aqueous solution and the viscosity of nitrogenated compounds or oxalates necessary in the silicates synthesis are compatible with the necessary viscosity for ink-jet cartridges. The necessary silicates forming reactions were studied directly on the deposition support, so that the functional characteristics of the multicompartment ink-jet cartridges were used. Compositions were realized, in which the coloring effect was obtained with molecular colorants. The vitrification and the quality of the obtained thin films were studied through Optical Microscopy and Scanning Electron Microscopy.

Keywords: glass decor, sodium silicate, ink-jet, nanometric pigments.

1. Introduction

Decor glass forming method through grinding, followed by the transformation of the vitreous powder into a stable suspension is a worldwide studied method [1, 2, 3]. The suspension is deposited on the support layer with special designed piezo cartridges. The results concerning the image resolution and also the productivity are better than those acquired by serigraphy technique.

Technological limitations are set by the nozzle sprayer with large dimensions, imposed by the granulometry of grinded vitreous material [4, 5].

Now, the digital printing technology uses fine ground colored glasses, applied on the ceramic support using industrial printers which work with 3-5 atm pressurized cartridge.

An advanced method is the synthesis of silicates directly on the substrate through the wet method. The deposited silicates are vitrified in the stage of decor fixing on the substrate, which is a necessary technological stage in conventional serigraphy techniques and also in the nonconventional decor digital deposition.

The silica matrix used in decoration must be carefully chosen in order to insure the maximum compatibility with the glass substrate and the decor

layer [7]. The experiments were directed toward the removal of the resulted suspension segregation. The main idea is that the alkaline-earth silicates and the silicates of many other polyvalent metals can be obtained through aqueous reactions between an alkali-silica solution and the solutions of some metallic salts.

Our purpose was to obtain a manufacturing technique of the forming reaction of necessary silicates directly on the deposition support, exploiting the functional characteristics of multicompartment ink-jet cartridges which can release simultaneously more ink drops. In this way the precursors used in the synthesis of necessary silicates can be isolated, without the apparition of precipitate.

The viscosity of sodium silicate in aqueous solution, as well as the viscosity of nitrates or oxalates necessary in the silicates synthesis is compatible with the one necessary for ink-jet cartridges.

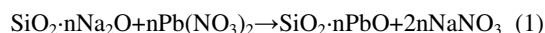
Thermal expansion coefficient of deposited decor must be closer to the coefficient of substrate material in order to prevent the tensions in decor glass or in substrate which can lead to cracks and finally can destroy the material. The highest recommended coefficient difference between glass

and substrate is $\pm 5 \times 10^{-7} / ^\circ\text{C}$. Thermal expansion coefficient of lead silicate glasses can be compatible with thermal expansion coefficient of a soda-lime silica glass layer.

Table 1. The thermal expansion of the linear expansion coefficient (α) of different glasses

Nr. crt.	Glass type	α (20°C) [$10^{-6}/\text{K}$]
1	Soda-lime silica glass	9.0
2	Borosilicate glass	3.2
3	Lead-silicate glass	8.5
4	Aluminosilicate glass	4.0

Basically, the reactions are:



It is mentioned that the replacement of alkaline oxide with lead oxide or other metallic oxide is equivalent, so that in order to obtain a lead silicate with a certain $\text{SiO}_2 / \text{PbO}$ ratio, an alkaline silicate with the same ratio between SiO_2 and the alkaline oxide must be used. Also, other soluble metal salts can be used. Their silicates and also the sulphates, chlorides, acetates, oxalates, etc., must be prepared. The starting alkaline silicate has a $\text{SiO}_2/\text{M}_2\text{O}$ ratio equal to the ratio $\text{SiO}_2/\Sigma \text{M}_2\text{O}$ because the needed result is a silicates mixture.

2. Experimental

For the use of the presented technique the alkali silicate with the most similar molar ratio was chosen, but greater than the desired one, and for the necessary compositions a correction was made.

Table 2. The compositions of the samples

Glass composition	R2 (weight %)	R3 (weight %)
Na_2O	20.7	18.53
SiO_2	54.28	39.73
PbO	16.6	24.31
$\text{ZnO}_x\text{S}_{1-x}$	8.42	0
$\text{CdO}_x\text{S}_{1-x}$	0	17.43
Total	100	100

A sodium silicate solution, with 8% Na_2O , 27% SiO_2 , with the density of 1370 g/l and the molar ratio

$\text{Rm}_{\text{SiO}_2/\text{Na}_2\text{O}} = 3.49$ was used. Compositions with the next molar ratio were calculated: $\text{Rm}_{\text{SiO}_2/\text{Na}_2\text{O}+\text{PbO}+\text{ZnO}_x\text{S}_{1-x}} = \text{Rm}_{\text{SiO}_2/\text{Na}_2\text{O}+\text{PbO}+\text{CdO}_x\text{S}_{1-x}} = 2.22$. The compositions of the samples are presented in table 2. The ZnS and CdS were added in the silicate mixture as molecular coloring. The calculated composition and the desired color was obtained after the thermal treatment.

We obtained the zinc and cadmium sulphide from nitrate solution by precipitation with sodium sulphide, at room temperature. The precipitation agent was added drop by drop with the purpose to obtain small precipitated particles. The obtained particle size distribution is about $0.67 \mu\text{m}$ without any influence of Zn/Cd ratio. The precipitated particle size decreased at 5-10 nm in aqueous solutions (Fig. 1 and Fig. 2) by using 100% additional acetone in reaction environment and at 1.23 nm if we use 100% additional styrene and maleic anhydride. (Fig.3).

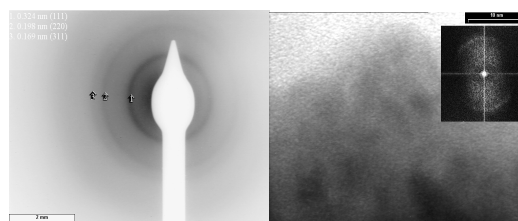


Fig. 1. SAED and HRTEM image and Fourier transform of the precipitated ZnS

SAED image presented in the Fig. 1 shows diffraction diffuse rings which indicate a crystalline order on nanometer scale. The corresponding interlayer distances have small deviations from the displayed values on the image. These distances correspond to ZnS particles with cubic crystalline structure (cfc). HRTEM image shows that dark crystalline clusters (about 5 nm) are dispersed in a thin film which seems to be an amorphous material. However, Fourier transform shows high level of local disorder.

Electron diffraction pattern from the Fig. 2 presents some pronounced diffraction rings which certifies the existence of a small size crystalline phase. The interplanar distances between the diffraction rings indicate the presence of CdS compound with cubic crystalline structure. The crystalline plane families have Miller index (111),

(220), (311), (331), (422), in accordance with CdS compound with cubic crystalline structure. HRTEM images exhibit crystallites of 10 nm dimensions. Fourier transform of areas from image shows that crystalline networks have an interplanar distances equal to 3.37 Å (planes 111) belong CdS compound.

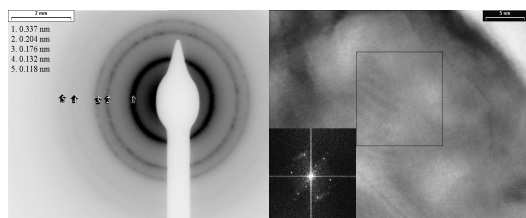


Fig. 2. SAED, HRTEM image and Fourier transform of the precipitated CdS

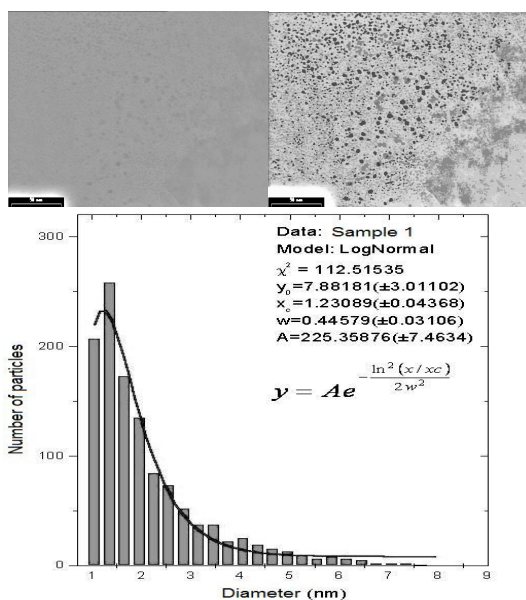


Fig. 3. BFTEM image and the particles diameter distribution for $\text{Zn}_{0.75}\text{Cd}_{0.25}\text{S}$ sample

Supposed particle size distribution is an lognormal type function where A is an arbitrary value depending of particles number, x_c represent the maximum of distribution and w represent the diameters dispersion. Diffraction image show the presence of a polycrystalline substance. The very small dimension of particles (determined on TEM images) $d = 1.23$ nm, going at some bands

formation. We suppose, based on this image, the existence of two phases, having similar structure.

Comparing the obtained results with those obtained in other experiments we can conclude that the particle size of precipitated pigment can decrease at nanometric dimensions in stable suspensions by decrease of concentration of reagent solutions and by use of dispersant agents in reaction environment.

Because the ordinary printer cartridges have 50nm diameter nozzles, the synthesized pigments may be used for the digital decor deposition. We have realized digital deposition of $\text{SiO}_2\text{-nNa}_2\text{O}$, $\text{nPb}(\text{NO}_3)_2$, ZnS and CdS and we have treated this deposition with the purpose to obtain vitrified décor.

Glass forming oxide compositions were set, established as a function of linear thermal expansion coefficient of the glass which is the support for decoration, the soda-lime silica glass with a coefficient of linear thermal expansion between $9 - 13 \times 10^{-6} \text{ K}^{-1}$. We chose the samples R2, R3, thereupon the thermal expansion coefficient value, calculated based on chemical composition is the same (equal to $11.776 \times 10^{-6} \text{ K}^{-1}$).

The researches regarding the behavior at thermal treatment of silica matrix and the compatibility with the support layer were made with the help of high temperature microscope – Carl Zeiss Jena.

3. Results and Discussions

The temperature at which the deposited silicates form vitreous phase was determined. Between 100°C and 340°C the decomposition of unreacted precursors and the elimination of polyvinyl alcohol from the deposited layer takes place. The visualized exfoliations are consolidated starting at the temperature of 580°C . The temperature of 670°C is the temperature at which the deposited silicates are forming the vitreous phase.

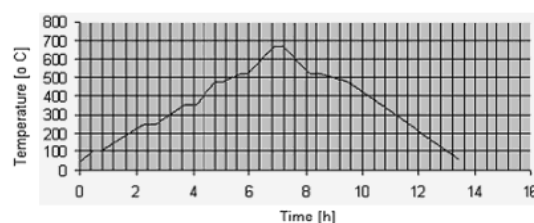


Fig. 4. Vitrification diagram

In conformity with the determinations made on the high temperature microscope we chose the vitrifying temperature (Fig. 4) and the vitrification diagram form.

An optical microscopy study was realized in order to study the forming of silicates in green film from the reaction of the deposited precursors on the support layer, as well as the glass forming tendency of the projected compositions.

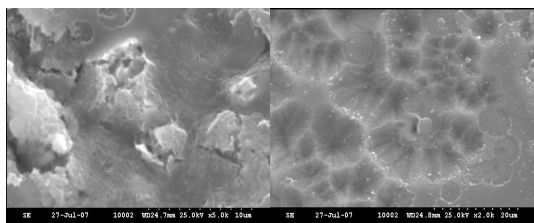


Fig. 5. Green film

Fig. 6. Vitrified decor

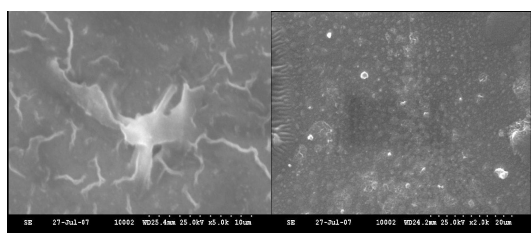


Fig. 7. Green film

Fig. 8. Vitrified decor

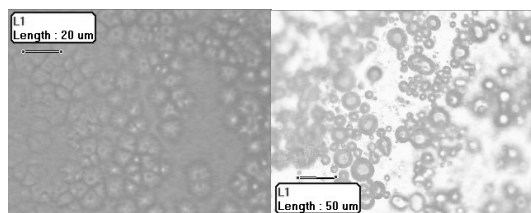


Fig. 9. R2 sample
vitrified decor

Fig. 10. R3 sample
vitrified decor

Samples' characterization was effectuated also by scanning electron microscopy (SEM). Silicates agglomerations are observed in decor green film, Fig.5. In Fig.6 the vitrification of silicate agglomerations is shown. The samples with the same composition, but deposited in a thicker layer, has a smaller exfoliation tendency than the one of obtained green film (Fig.7). Through vitrification, an accentuated uniformization is acquired (Fig.8, 9, 10).

4. Conclusions

The experiments have shown that, generally speaking, the silicates necessary for the glass decors can be obtained through chemical synthesis, directly on the deposition surface. The necessary chemical precursors have the similar viscosity with the ink needed for the ink-jet cartridges. The deposited silicates were vitrified in the decor fixing stage on the substrate. This is the technological stage necessary in conventional serigraphy techniques and in non-conventional digitalized decor deposition techniques. Precursor's concentration calculus was made in order to realize the oxide composition imposed by the molar ratios necessary for the glass type projected for the decor, with a thermal expansion coefficient compatible with the coefficient of the glass substrate. Through experiments other compositions can be realized, in which the coloring effect can be obtained with ionic colorants and with molecular colorants, in order to realize a wider coloring spectrum for the decor. $Zn_xCd_{1-x}S$ samples with different x were obtained at 5 nm in water – acetone solutions and in water – styrene – maleic anhydride solutions.

5. References

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