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Processing of Fine Scale Multilayer Dielectric with Thermal Inkjet Printing

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The aim of this research deals with the thorough selection of the optimal ceramic inkjet ink composition and its detailed physicochemical. The most significant barium titanate nanopowder stabilization in the butyl alcohol has been observed for the dispersion with presence a lowmolecular linear saturated aliphatic alkanediol. The findings of physicochemical investigation suggest that optimized sample have exhibited non-structural type of sedimentation and also revealed dilatancy with a pronounced minimum viscosity of Newtonian flow. In order to understand the influence of operational performances on the printed image quality, have been studied surface properties of non-sintered single-layer dielectric films deposited on the different resolution modes.

Keywords: Inkjet Printing; Ceramic Ink; Barium Titanate Nanopowder; Dilatancy; Roughness Parameter

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1. INTRODUCTION

Successful implementation and introduction of inkjet printing in the production of various electronic devices is crucially depends on the quality and composition of the consumables. Composition of the functional material is of crucial importance because it determines the ability of ink to jetting, image resolution, formation mechanism and surface profile properties of the printed object and its degree of adhesion to the substrate [1-4]. Moreover, formulated functional material must have physicochemical properties that are accurately fulfill operational equipment requirements, which are specific for each particular inkjet printhead. In connection with this, selection of the optimal thermally jettable ink composition as well as thorough analysis of their physicochemical properties is actual issue.

2. MATERIALS AND METODS

$BaTiO_3$ nanopowder with a mean particle size of 20 nm has been used as green material for the preparation of ceramic inks by the mechanical mixing method. Reagent-grade n-butyl alcohol (Lab-Scan.) without further purification has been used as the liquid carrier. Several lowmolecular aliphatic polyalcohols with symmetrically located hydroxyl groups have been used as dispersants.

Investigated suspensions were prepared according to methodology that is described in detail in [4]. Obtained ceramic inks have been studied by sedimentation and rheological viscosity analyzes.

Dielectric multilayer structures have been fabricated through printing several layers of functional inks on a polymer substrate. The printing operation was performed using a Cannon PIXMA IP2700 printer. This printer used thermal drop-on-demand inkjet technology. Films thickness and roughness parameters have been identified by optical profilometry.

3. RESULTS AND DISCUSSION

3.1 Sedimentation Behavior

Tailoring of the ink vehicle was performed in order to obtain a good affinity between solvent career and barium titanate nanopowder. In previous works we have reported that most effective modification of nanosized $BaTiO_3$ particles has been observed for samples dispersed in ethanol media [6]. The most significant stabilization of the modified pigment was observed for formulated on n-butyl alcohol samples. Such type inks have a lower surface tension and evaporation rate of a volatile solvent with a slight increasing of viscosity. As a consequence, ink has a higher spreading coefficient. Also, formulated samples had good sedimentation stability during 30 days.

Table 1 – Some characteristics of the dispersants

Substance	Density, g/cm³	Viscosity, mPa·s	Functional groups	
			type	amount
[D_1]	1.052	52.0	–OH	2
[D_2]	1.017	84.9	–OH	2
[D_3]	1.118	42.0	–OH –O–	2 1
[D_4]	1.125	58.3	–OH –O–	2 3

Selection of optimal dispersant has been performed from several low molecular weight nonionic dispersants that are classified as symmetric aliphatic glycols with terminal hydroxyl groups. Some properties of the investigated dispersants are represents in table 1. Furthermore, compounds [D_1] and [D_2] also belong to linear saturated aliphatic alkanediols, and carbon backbone chain in the molecule [D_2] is one methylene group longer than [D_1]. At the same time, structure of the [D_3] and [D_4] is represented by a set of certain alkoxy group, in particular, [D_3] refers to the monoeters and [D_4] – to the trieters.

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Sediment dependences obtained for the barium titanate dispersions based on n-butanol media in the presence of investigated stabilizing agents are illustrated in fig. 1. It is interesting to note that ceramic suspensions with addition of saturated linear alkandiols, in general terms, provide better stabilization efficiency than corresponding systems in the presence of oligoalkylene glycols. This behavior is quite consistent with the Rehbinder's "rule of polarity equalization", according to which the autocoagulation of the particles increases with increasing polarity between the solid and liquid phases [7]. In keeping with the foregoing statement, it could be argued that the stabilizing effect of the compounds [D_1] and [D_2] (curves 2 and 3 respectively) could be attributed to formation of negative inductive effect on both sides of the carbon chain. And since accumulated inductive effect is damped during transfer along the carbon skeleton, it is obviously in that dispersant [D_2] is marked by weakening of a dispersive ability as compared with [D_1]. Meanwhile, presence of electronic acceptor ether bonds in the structural configuration of glycol oligomers [D_3] and [D_4], leads to localization of electron density around these oxygen bridges, that is evenly spaced along the backbone chain and this leads to reducing their deflocculation ability. It should also be stated that for these two surface active agents, disaggregating properties is primarily improves with the increasing of backbone chain dimension. That is to say, the dispersion ability of the weakly polar stabilizers [D_3] and [D_4] is qualitatively subject to a Duclot-Traube rule.

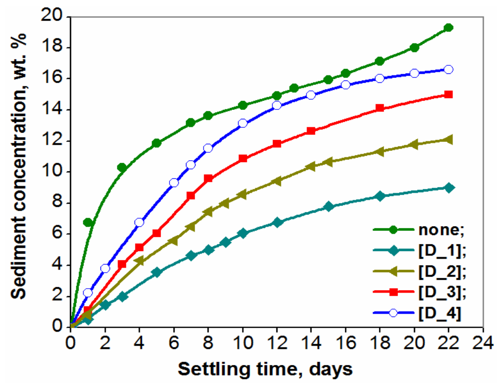

Fig. 1 – Kinetic curves of sedimentation for $BaTiO_3$ suspensions with the addition different dispersants

In order to define optimal dispersant content, extensive analysis of the impact of its concentration on final sedimentation and structural and flow parameters of inkjet inks based on barium titanate nanopowder. Kinetic sedimentation curves obtained ceramic inkjet inks with different dispersant concentration are depicted in fig. 2. The findings of sedimentometric analysis suggest that samples with a high dispersant concentration (15–20 wt.%) exhibit non-structural type of sedimentation, that is inherent for highly stable systems. In these dispersions, particle deposition is held independently of each other without any formation of the continuous coagulation structures. Simultaneously, barium titanate inks with low dispersant content (0–10 wt. %) show numerous signs of the semi-structural sedimentation mechanism. Structural configuration of such colloidal systems is peculiar the creation of the aggregative unstable flocculated system and obtained $BaTi0_3$ associates are binded by strong phase contacts, which are resulted in accelerating sedimentation rate [8].

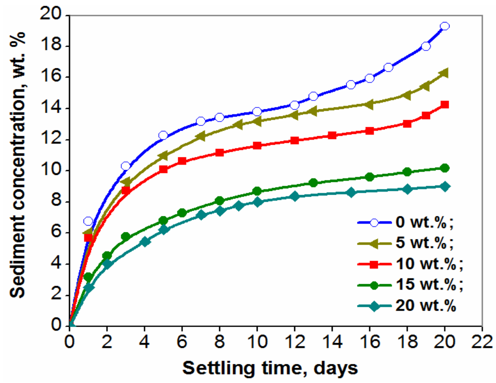

Fig. 2 – Kinetic curves of sedimentation for $BaTiO_3$ inkjet inks with different concentration of [D_1]

3.2 Rheological Properties

Resulted flow curves Table 1 shows that all ceramic inks based on $BaTiO_3$ nanopowder demonstrate dilatant flow with an established rate of dilatant deformation. It means that all systems flow as completely deflocculated dispersions after attaining the established equilibrium level of strain rate [5].

In general, such rheological behavior can be explained by physicochemical and molecular-kinetic interactions between components of the system. The determining factor of structure formation is powder-dispersant ratio which determines the composition and shape of the structural elements and their interaction conditions. Thus, in the case of Ink_5 high dispersant content leads to the formation of large adsorbed solvate shells on the highly developed surface of barium titanate nanopowder. In connection with the decreasing of kinetically free hydroxyl groups leveling couple fluctuation and the consequent degeneration of the ability of the structure to the applied shear stress relaxation is take place. This promotes a considerable duration initial Newtonian segment. Decreasing of stabilizer content on the interval Ink_4 resulted in the growth of specific effective volume of the dispersed phase and the gradual constriction of adsorption layers. In turn, vacancy volume expansion results in more unrestricted conditions of structure deformation that makes easily relaxation of the applied stress. This causes displacement of the beginning dilatant area flow curves in the region of higher shear rates and smaller pressures and also the gradual reduction of starting newtonian flow range. In addition, there is a gradual decrease in viscosity and degree of dilatancy values. With further reduction of the dispersant concentration on the interval Ink_3 – Ink_1 is causes crucial thinning of the solvent protective layers take place and, correspondingly, that enhances the processes of stepwise aggregation and coagulation.

It is nescessary to note that the foregoing statements about sedimentation stability are in good agreement with derived rheological characteristics of investigated samples (table 2). Thus, corresponding rheological curves of non-structured systems reveal dilatant flow with a pronounced minimum viscosity of Newtonian flow. The resulting flow curves of investigated specimens suggest that reducing dispersant concentration in the ink volume lead to displacement of flow parameters towards more dilatant values and also restriction initial Newtonian flow region. The dilatant regime in the deformation of inks explained by constrained conditions of the interaction between constituent elements. In terms of structure formation, derived form of the flow curves means that studied highly filled ceramic inks behaves as a periodic colloidal structure of the second type (PCS_2), in which a positive disjoining pressure $\pi_2>0$ operates. Stabilization of the finely disperse structural elements is achieved by appearance of the adsorption-solvate layers, that is significantly improve resistant to aggregation [9]. Herewith, barium titanate inks with low dispersant content indicate flow regimes with a complex dilatant-thixotropic mechanism of structurization. It is evident that such type of the colloidal systems has been classified as PCS_1. Observable dilatant thickening is related to rearrangement of colloidal structure under the influence of the flow. On a theory, in the PCS_1 volume occurs active development of numerous of coagulative contacts between enlarged particles and ultimately leads to the creation of "friable" spatial coagulative network. Stated differently, all PCS_1 systems are characterized by the formation of flocculative, i.e. aggregative unstable, structure. Summing up the aforecited results, has been substantiated the ability of a qualitative assessment of the sedimentation stability according to the relevant flow parameters. However, it should be emphasized that implementation of an assay procedure is crucially depends on establishing the nature of the solvate shells adsorbed on the surface of barium titanate nanoparticles.

Table 2 – Composition and rheological properties of investigated inks

Sample	**Dipersant content, wt. %**	**Viscosity at 2 Pa, mPa·s**	**Boundary shear stress, Pa**	**Dilatancy degree, a.u.**	**Sediment amount, wt. %**
Ink_1	0	1.57	10.76	4.63	18.70
Ink_2	4.75	1.44	10.93	4.45	16.59
Ink_3	9.5	1.48	11.55	4.19	14.45
Ink_4	14.25	1.90	13.31	3.75	10.18
Ink_5	19.0	2.01	13.81	3.67	9.01

Final content of the functional additives in formulated ceramic suspensions has been clarified according to the physicochemical properties of aqueous industrial Canon C11/B Black ink. Obtained parameters of the ceramic and commercial inks are compared in table 3.

The findings of the present study suggest that commercially available inkjet ink (table 3) was exhibited slightly dilatancy with a pronounced minimum viscosity of Newtonian flow. Such rheological regime is observed in weakly dilatant systems and is characterized by a large section of nonstructurized (Newtonian) flow. On attaining the boundary value of shear stress Pnd of 11 Pa, the flow transforms from Newtonian into structurized (dilatant) state [10]. The viscosity of the studied ink in the region of shear stresses close to the resting state (1 Pa) is 2.38 mPa·s and in terms of structural flow (under the intensity of deformation of 22 Pa), corresponding value increases to 8.10 mPa·s. At the same time, the value of minimum viscosity ηdm, that is characterized by absence of the dilatant structure formation, is 6.04 mPa·s. Meanwhile, rheological curves obtained for Ink_1 are demonstrating dilatant behavior that is similar to dependences of the industrial sample. Comparatively to a Canon C11/B, prepared barium titanate ink has been observed shifting of flow curves with simultaneously degeneration of certain minimum value of Newtonian viscosity to ηdn of 5.84 mPa·s. However, as clearly shows table 2, differences in density and viscosity are comparatively small. Thus, it can be argued that according to a given properties, optimal flow parameters for a chosen inkjet printhead corresponds to sample with dispersant concentration of 19 wt. %.

Table 3 – Physicochemical properties of the ceramic and industrial inkjet inks

Property		**Canon C11/B**	**Ink_5**
Solid concentration, wt. %		1.0	5
Density, kg·m-3		1010	920
Viscosity, mPa·s	at 1 Pa	2.38	2.26
	at 22 Pa	8.37	8.10
Newtonian viscosity, mPa·s		6.04	5.84
dilatancy parameter		1.94	2.49

3.3 Optimization of Printing Parameters

In order to understand the influence of operational factors on the quality of printed image has been analyzed surface properties of dielectrics deposited at a different printing resolution. Thus, average thickness of a non-sintered single-layer dielectric film deposited on the lowest printing regime has thickness is equal to 750.1 nm. At the same time, barium titanate films printed on a medium and high mode resolution inkjet printing are distinguished by thinning to a 640 and 611.4 nm respectively. Also it should be noted that obtained dielectric films have surface roughness parameters that are changing quite ambiguously (table 4). It must also be considered that relatively high relief heterogeneity of the printed layers primarily explained due to significant initial surface irregularity of the selected substrate. The findings of the optical profilometry analysis suggest that inkjet printing of planar dielectric structures is optimally performed on highest resolution mode.

Tailored ink composition has been printed into the flexible polymer substrate through thermal inkjet printhead on a "high" resolution option. Optical profilometry of the investigated films indicated that deposited structures have exhibited essential thinning after printing of each subsequent layer. In particular, thickness of the single-layer non-sintered film had been estimated of about 600 nm (fig. 3). Total thickness of the double-layer structure had decreased to 270 nm (fig. 4) and after printing the third layer this parameter had been amounted to 260 nm (fig. 5).

Table 4 – Properties of the printed structures

Resolution mode	Thickness, nm	Ra, nm	Rz, nm
bad	751	49.7	248.7
medium	640	21.2	75.4
high	611	38.1	82.9

Also decreasing of the roughness parameters had been observed for the deposited dielectric films after each subsequent reprinting. In particular, arithmetical mean deviation of the roughness profile (Ra) for the single-layer coating had amounted to 39.8 nm and maximum height of the roughness profile (Rz) had equal to 119.9 nm. Simultaneously, these values for the three-layer structure had been equal to 20.3 and 70.6 nm respectively.

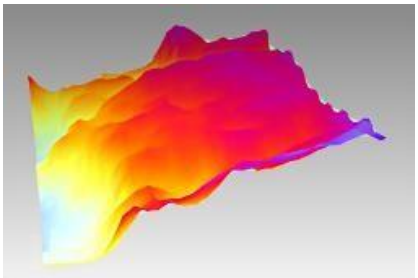

Fig. 3 – 3D surface profile of deposited one-layer dielectric structure

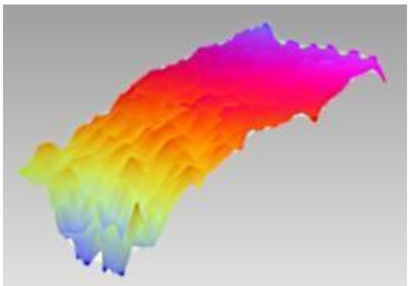

Fig. 4 – 3D surface profile of deposited two-layer dielectric structure

Spontaneous thinning and planarization that were observed during increasing the layers number could be substantiated in terms of structure rheological and colloid-chemical behaviors of the printed ceramic ink. As the jetted droplet impacts with substrate, spreading liquid volume along solid surface take place. However, significant evaluating of the evaporation area is accompanied by evaluating of the evaporation rate of volatile organic solvent. This leads to a sharp densification of the liquid functional material and as a result, its spreading is quickly suppressed. In fact, the progress of the spreading is not full, so during the deposition of the first dielectric layer there is a formation so-called "loose" irregular structure takes place. As investigated ink is characterized by the latency (as was noted earlier), during the deposition of the next layers, some part of precipitated pigment goes into the bulk liquid ink, that flows into the cavities and leads to spontaneous seal of the printed patterns and smoothing its surface.

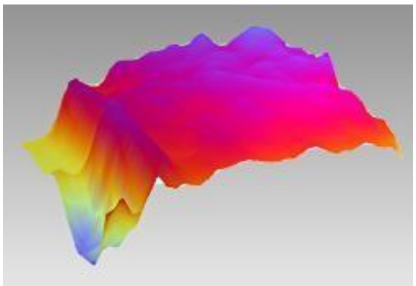

Fig. 5 – 3D surface profile of deposited three-layer dielectric structure

4. CONCLUSIONS

In the course of the work has been developed optimal dielectric ink formulation to meet the requirements of the thermal Canon IP2700 inkjet printer. Several lowmolecular aliphatic glycols with terminal hydroxyl groups have been used in order to obtain proper dispersing efficiency of barium titanate nanopowder in butyl alcohol suspension. It was shown that the most significant dispersion stabilization has been observed in the presence lowmolecular linear saturated aliphatic alkanediol. Optimal flow parameters for a chosen inkjet printhead correspond to ink with solid phase and dispersant concentration of 5 and 19 wt. % respectively. The findings of physicochemical investigation suggest that this sample exhibited non-structural type of sedimentation and also revealed dilatancy with a pronounced minimum viscosity of Newtonian flow. Observed dilatant regime was explained by constrained conditions of the interaction between constituent elements. Besides, in terms of structure formation, this ink behaves as a periodic colloidal structure of the second type (PCS_2).

In order to understand the influence of operational performances on the printed image quality, have been studied surface properties of non-sintered single-layer dielectric films deposited on the different resolution modes. The findings of the optical profilometry analysis suggest that inkjet printing of the thinnest layers is optimally performed on highest resolution mode. At the same time, deposition of the smoothest dielectric structures has been performed on medium printing quality.

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