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Study of the stability of dispersed systems based on polyaluminosilicates for 3D aerosol printing of ceramic layers of printed circuit boards

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Abstract. A composite material based on polyaluminosilicate and highly dispersed filler powders of AlN and Al₂O₃ has been synthesized by means of the sol-gel synthesis. The pH effect on the Zeta potential of highly dispersed filler powders of AlN and Al₂O₃ has been investigated. The effect of the Zeta potential of filler powders on the sol polyaluminosilicate stability has been studied. Ceramic coatings for printed circuit boards have been obtained by 3D aerosol printing.

1. Introduction

The methods to manufacture products and devices and in particular the methods to apply dielectric and conducting coatings and layers on the bases of various chemical nature and having various geometric forms are currently of great importance in the electronic industry and medicine. The traditional methods to apply dielectric and conducting coatings and topologies such as paint and varnish technologies, roller rolling, screen printing, photolithography, milling, laser cutting with a focused ion beam, do not always allow obtaining the coatings and topologies necessary to solve technological and design problems in the development and manufacture of microelectronic and medical products and devices. The above mentioned methods have a number of limitations, for example:

- expensive and complex equipment;
- high manufacturing cost;
- slow manufacturing process;
- possible failure to use methods to produce coatings and topologies on complex-shaped parts.

Moreover, the above mentioned methods cannot be used to apply coatings and layers on an already manufactured part or device. The additive technologies based on 3D printing, which have received increased attention in the last decade, have been increasingly used to manufacture the parts and devices in electronic and medical industries to transcend these limitations.

Ink-jet printing eliminates many problems encountered when printing layers and topologies on complex-shaped parts. These technologies accelerate manufacturing of a part and then of a device and eliminate the problem of excessive material consumption. The methods of additive printing also suit better for making parts of a larger area in comparison with the commonly used methods. Thus, 3D printing allows manufacturing printed circuit boards of a large size, antennae, capacitive and resistive



sensors, photoelectric and optoelectronic devices and appliances, LEDs, and 3D structures with a high aspect ratio and a printing definition up to 0.5 microns. A printing definition of 0.5 microns clearly shows the importance of 3D printing methods for the development of the electronic and medical industries [1].

There are several types of 3D printing: FDM (fused deposition modeling), Polyjet technology, LENS (laser engineered net shaping), LOM (laminated object manufacturing), SL (stereolithography), LS (laser sintering), 3DP (three dimensional printing), extrusion through a die and 3D aerosol printing. Many of the above mentioned methods are adapted directly to the existing goals and objectives and to the properties of the used materials [2-6].

The 3D aerosol printing method based on additive production of coatings, layers, elements, and interconnects based on dielectric and conducting materials has been chosen in this study. The smallest droplets of the material are applied by an aerodynamically focused jet on a three-dimensional base selectively, and masks are not used. The advantages of 3D aerosol printing are in greater freedom in product design, production flexibility, absence of tooling costs (stencils, templates), and less adverse environmental impact in comparison with the other methods of additive printing, photolithography, and other methods to apply coatings and topologies.

Using only the modern 3D printing methods to manufacture layers and topologies is impossible without developing new dielectric and conducting composite materials that specify the necessary physicochemical, thermal, and structural properties of end products and microelectronic and medical devices due to the unique opportunity to form structural elements with the phase composition peculiarities.

Thus, to solve the problem of developing new composite materials is only possible with the use of the:

- modern methods to synthesize polymer binders;
- methods to obtain dispersed filler powders;
- modern methods to study the properties of materials.

The research purpose is to study the stability of the systems based on polyaluminosilicates filled with highly dispersed fillers for 3D aerosol printing of the ceramic layers of printed circuit boards.

2. Experiment

The system (composite material) based on polyaluminosilicates filled with highly dispersed fillers suits better for 3D aerosol printing of the ceramic layers of printed circuit boards, since this is a system, in which the highly dispersed particles of the solid phase are evenly distributed in a liquid dispersion medium. According to the research results, the most preferable method is a pneumatic method as an aerosol generator, which allows working with highly viscous materials without destroying the supramolecular structure of the polymer binder, i.e. polyaluminosilicate.

Stability is the most important parameter for aerosol printing. The aerosol stability, in its turn, depends on the physicochemical properties of the dispersed filler (the powders based on AlN and Al₂O₃ have been studied in this case) and on the polyaluminosilicate physicochemical properties.

One of the ways to increase the stability of the dispersed filler based on AlN and/or Al₂O₃ is to reduce its size. However, the problem that arises by the sol manufacturing based on polyaluminosilicate and smaller ceramic powders AlN and/or Al₂O₃ is that both the boundary area between the particles of the solid phase and a liquid carrier and the number of particles in this volume increase significantly. This leads to the strong physicochemical interaction between solid particles in the liquid phase and reduces workability, especially by aerosol generating. Therefore, one can expect that the need to reduce the loading volumes in the sol may counteract the advantage of smaller particles. The shape of the particles also plays an important role, since the sol viscosity strongly depends on the shape. The work [7] presents the viscosity dependence on the volume content of the solid phase and the shape of the particles (figure 1).

The problem that arises by the manufacturing of the sol with the highly dispersed powders of ceramic fillers is that both the boundary area between the particles of the solid phase and liquid carrier

and the number of particles in the given volume significantly increase with the particle size decreasing. This leads to the strong physicochemical interaction between the solid particles in the liquid phase and consequently results in the viscosity increase.

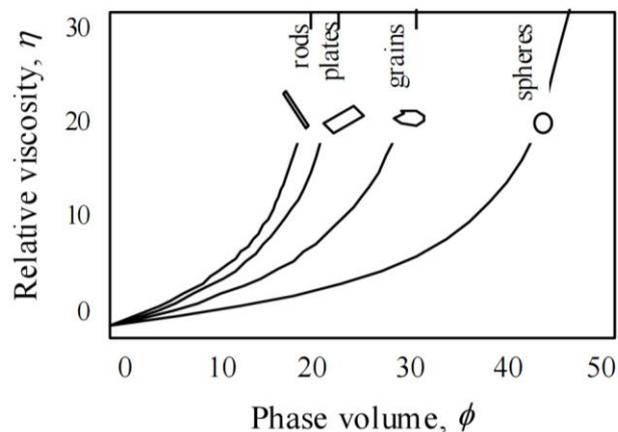


Figure 1. Viscosity dependence on volume content of solid phase and shape of particles [7].

The elemental and phase composition of the particles, their size, shape, and Zeta potential are the main parameters of the particles that allow characterizing them in the liquid phase. The Zeta potential arises at the boundary between the solid and liquid phases as a result of electrical charges accumulation. As a result, a double electric layer is formed at the phase boundary. The electric double layer arises when two phases come into contact, at least one of which is the liquid phase (figure 2). The electric double layer consists of the potential determining ions bound to the surface of the solid dispersed phase and an equivalent amount of counter ions. One part of the counter ions directly adjoins the interfacial surface under the action of both electrostatic and adsorption forces, and the other part is in a diffusion part due to thermal movement and is kept at the surface only by electrostatic forces. The Zeta (electrokinetic) potential corresponds to a glide plane and is the part of the diffuse layer potential [8].

The glide plane is formed because the dispersed particles move, and the furthest part of the diffuse layer does not participate in the movement but remains fixed. As a result, the surface charge of the particle becomes uncompensated, and the electrokinetic phenomena affecting the viscosity and resistance of the particles to aggregation become possible.

A schlicker made from wet powdered materials is more stable and have high Zeta potential. However, thicker solvation layers are formed due to the prolonged contact with the dispersant. This affects the porosity, consistently leads to an increase in the rate of weight gain, and increases the shrinkage factor by drying the layers after aerosol application. Therefore, it is more appropriate to use the powders obtained by the dry method.

The dissolved air presence in the carrier fluid and its presence in the adsorbed form on the particles surface are the negative factors affecting the schlicker viscosity and properties. One of the ways to solve this problem is the schlicker evacuation with considerable shear deformations while stirring (the nominal stirrer speed is 5000 rpm).

After the polyaluminosilicate sol has been mixed with the passivated ceramic powder, a dispersant is added in an amount of 3-4% to reduce the viscosity and increase the resistance to settling and agglomeration of the particles. The dispersant type depends on the types of the sol and dispersed filler. The criteria for choosing the dispersant are such that it should facilitate the uniform distribution of the dispersed filler along the polyaluminosilicate sol minimizing the phase separation. The uniform distribution of the passivated particles facilitates the coating of particles with a binder (the polyaluminosilicate sol), thus making it possible to use less binder.

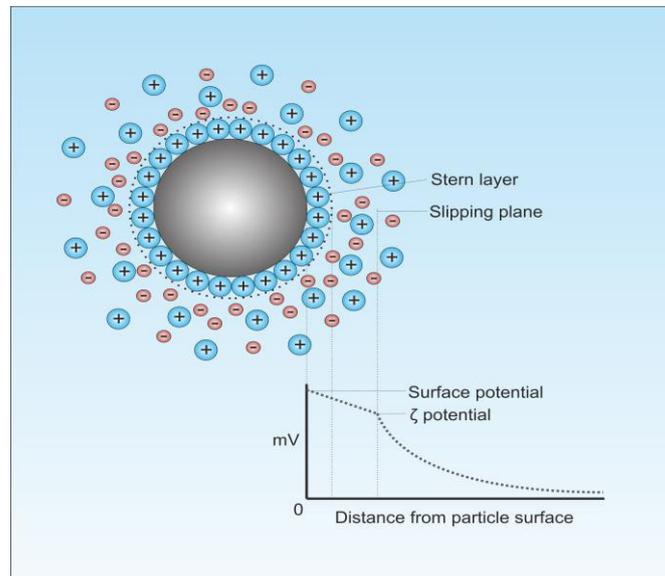


Figure 2. ζ -potential formation at phase boundary surface.

The state stability of the dispersed filler particles in the polyaluminosilicate sol is connected with the Zeta potential ζ that depends on pH and temperature. The ζ value determines the suspension structure formation, since it affects the aggregation and disaggregation of the particles. In this case, the most preferable value of ζ is in the range from plus 10 to plus 40 millivolts or in the range from minus 10 to minus 40 millivolts. The ζ value less than ± 10 millivolts leads to the suspension state in which electrostatic repulsion is insufficient to prevent the particle agglomeration [9, 10].

The Zeta potential of the particles has been measured with the *Malvern Zetasizer Nano-ZS* device characterizing nanoparticles.

3. Results and discussion

Figure 4 shows the Zeta potential distribution of the obtained and used Al_2O_3 powder (figure 3a). Figure 5 shows the dependence of the alumina powder Zeta potential on pH.

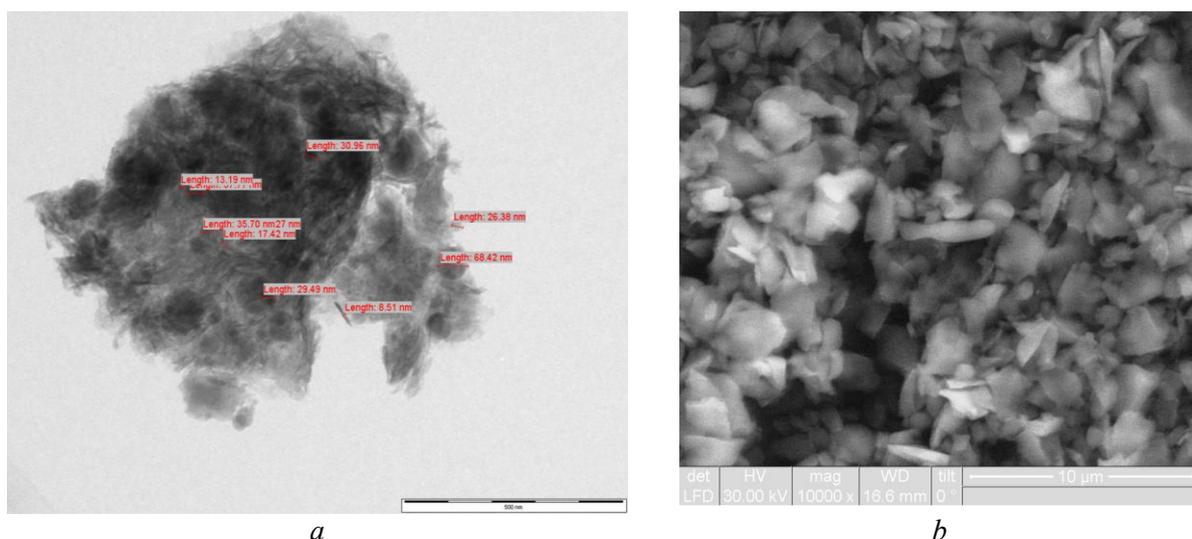


Figure 3. Microphotography of Al_2O_3 (a) and AlN (b) particles.

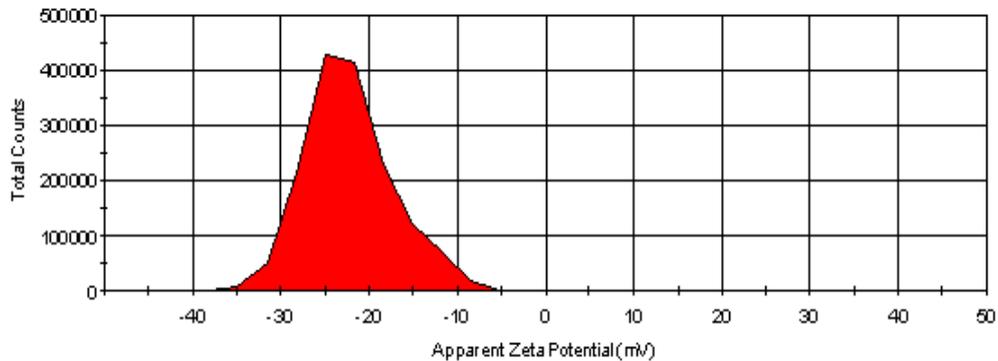


Figure 4. Zeta potential ζ distribution of Al_2O_3 powder by $\text{pH}=10$.

Figures 4 and 5 show that Al_2O_3 particles have the maximum Zeta potential ζ by $\text{pH} = 11$ and $\text{pH} = 3$. The particles are resistant to aggregation and settling by these pH values. When the pH is between 7 and 9, the potential forming layer is fully compensated for many mineral oxides. In other words, all the counter ions are located in the adsorption layer, and the ζ -potential is equal to zero. The point characterizing the similar state (when $\zeta = 0$) is called an isoelectric point ($\zeta = 0$ for Al_2O_3 particles by $\text{pH} = 8.7$).

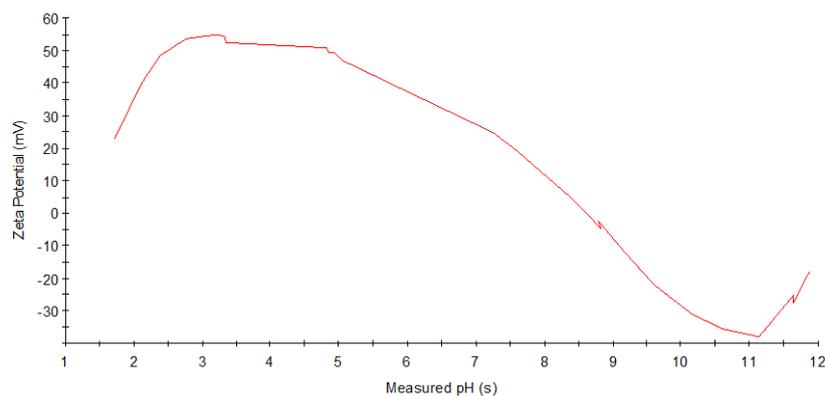


Figure 5. Dependence of Zeta potential ζ of Al_2O_3 powder particles on pH .

The study of the obtained AlN particles (figure 3b) with a d size of $(v, 50) = 1400$ nm (figure 6) has determined the pH effect on their Zeta potential ζ (figures 7 and 8).

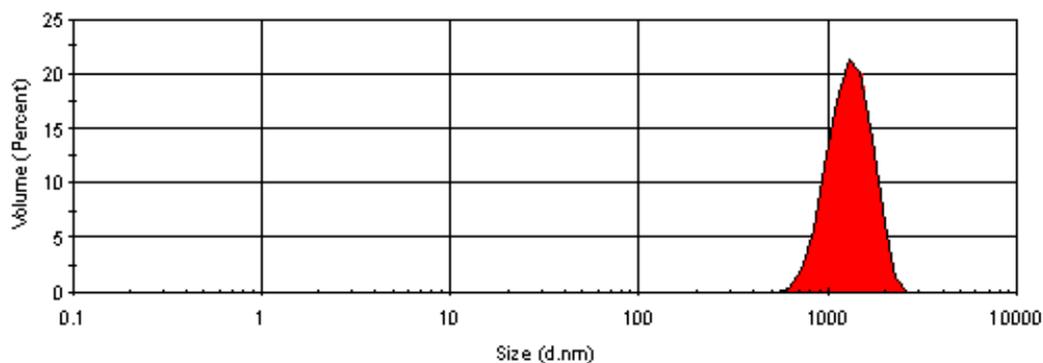


Figure 6. Volume distribution functions of AlN particles by size by $\text{pH} = 4$.

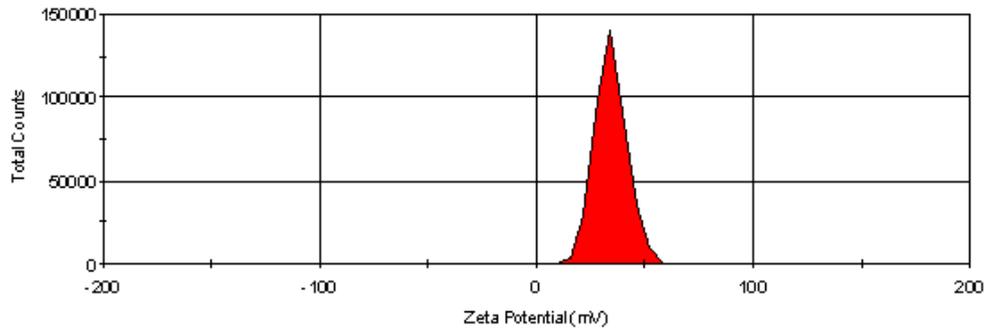


Figure 7. Zeta potential ζ of AlN powder distribution by pH = 4.

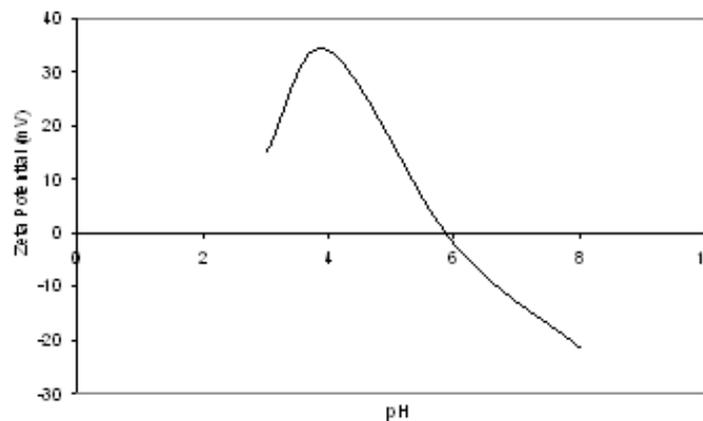


Figure 8. Zeta potential ζ of AlN powder distribution by pH = 4.

Figure 8 shows that a change in the AlN powder pH from 3 to 8 leads to a change in the Zeta potential ζ from plus 15 mV to minus 23 mV ($\zeta = 0$ by pH = 5.9).

The obtained data analysis has proved that temperature (the average kinetic energy of water molecules) has a significant influence. Figure 9 shows that an increase in temperature from 10 to 60 °C leads to an increase in the potential ζ from plus 17 to plus 34 mV by pH-2. ζ increases to plus 63 mV by pH-3, it changes slightly in the range from plus 10 to plus 50 °C, and the charge sign changes from plus to minus in the range from plus 50 to plus 60 °C (figure 10). Thus, an increase in temperature leads to an increase in pH. Therefore, it changes the Zeta potential ζ having the same isoelectric point where $\zeta = 0$ as in the case of a change in pH.

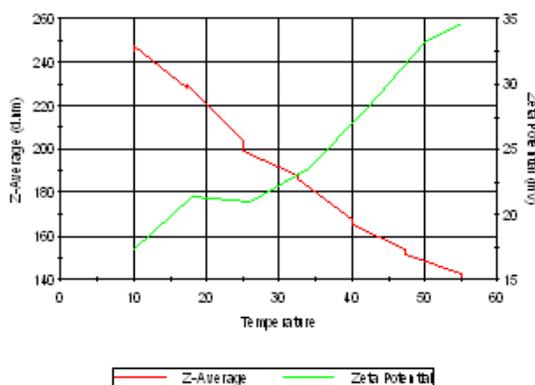


Figure 9. Dependence of Zeta potential ζ of Al₂O₃ on temperature by pH=2.

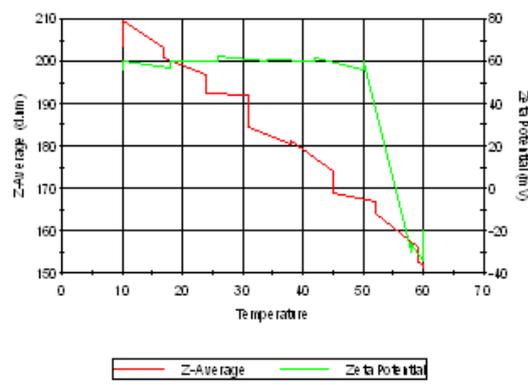


Figure 10. Dependence of Zeta potential ζ and size of Al₂O₃ on temperature by pH=3.

The maximum stability values and minimum viscosity values of the system of the polyaluminosilicate sol – highly dispersed Al_2O_3 or AlN powder, and, correspondingly, the minimum values of shrinkage and porosity when producing the ceramic layers of printed circuit boards correspond to the maximum values of the potential ζ [11].

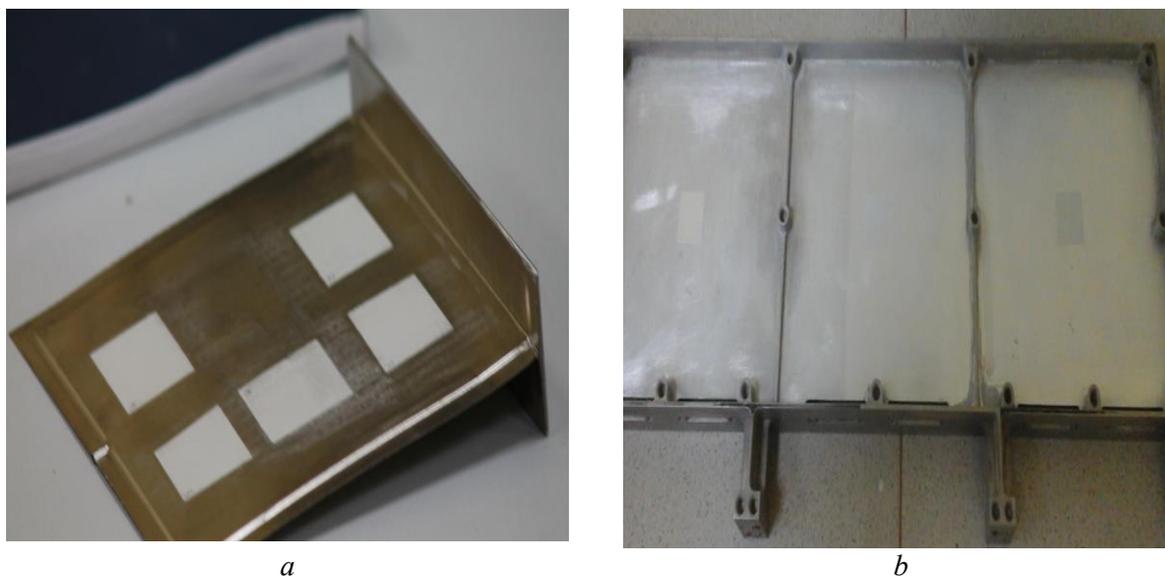


Figure 11. Photographs of microelectronic products of complex shape with applied dielectric layers in structurally specified areas.

4. Conclusion

Thus, it is possible to use temperature and pH as a tool for structuring particles by changing the heterocoagulation systemic stability and ultimately to adjust the performance characteristics (thermal conductivity, electrical strength, adhesion, degassing, and so forth) applied by 3D aerosol printing of the ceramic layers of printed circuit boards to produce the systems of the polyaluminosilicate sol - highly dispersed filler powder (figure 11 *a* and *b*).

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