Formation of Copper Sulfide–Copper Telluride Layers on the Polyamide Film Surface, Using Sodium Telluropentathionate

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The layers of copper chalcogenides – mixed copper sulfide–copper telluride, Cu_xS-Cu_yTe, were formed on the surface of semihydrophilic polymer – polyamide 6 using (0.01 – 0.10) mol/dm^3 solution of sodium telluropentathionate, $Na_2TeS_4O_6$, in 0.2 mol/dm^3 HCl as precursor of chalcogens. The concentration of sorbed tellurium and sulfur increased with the increase of the duration of treatment and concentration of $Na_2TeS_4O_6$ solution. The mixed copper sulfide-copper telluride, Cu_xS-Cu_yTe, layers were formed on the surface of polyamide 6 after the treatment of chalcogenized polymer with Cu(II/I) salt solution (10 min, 78 °C): the anions $TeS_4O_6^{2-}$ containing tellurium and sulfur atoms of low oxidation state react with the copper(II/I) ions. The conditions of a polymer initial chalcogenation determine the concentration of copper and composition of the chalcogenide layer. The concentration of copper in the chalcogenide layer increases with the increase of initial chalcogenization duration and the concentration of solution. The results of XRD confirmed the formation of mixed copper sulfide-copper telluride layers on the surface of polyamide 6: four copper sulfide phases, *digenite*, $Cu_{1.8}S$, *djurleite,* $Cu_{1.9375}S$, *anilite*, Cu_7S_4, *geerite*, $Cu_{1.6}S$, four copper telluride phases – *tetragonal* $Cu_{3.18}Te_2$, $Cu_{2.72}Te_2$, *hexagonal* Cu_2Te, and *orthorhombic vulcanite*, CuTe, were identified in the layers. At room temperature, electrical sheet resistance of the layers varied from ~ 2.0 kΩ/□ to 1.2·10^3 kΩ/□. Variation in the resistance of layers on the surface of PA shows an evident decrease with the increasing of the mass fraction of tellurium. The data determined enable formation of the layers of copper sulfide-copper telluride on the surface of PA of desirable conductivity by the sorption method using the solutions of sodium telluropentathionate as a precursor.

Keywords: telluropentathionate, polyamide, sorption-diffusion, copper chalcogenide layers.

INTRODUCTION

Copper chalcogenide Cu_xY (Y = S, Se, Te) thin layers have a number of applications in various devices such as solar cells, super ionic conductors, photo-detectors, photothermal conversion, electroconductive electrodes, microwave shielding coating, gas sensors [1 – 8], etc.

Over the last decade, a sorption-diffusion method for the formation of thin copper chalcogenide layers on the surface of polyamide 6 (PA) based on the initial treatment of a polymer with the solutions containing anions of polythionates, $S_nO_6^{2-}$, selenopolythionates, $SeS_nO_6^{2-}$ (n = 2, 4), has been under extensive investigation [9 – 16]: the polythionic compounds anions containing chains of divalent chalcogen atoms of low oxidation state [17 – 19] – the polythionates, $^-O_3S–S_x–SO_3^-$, selenotrithionate, $^-O_3S–Se–SO_3^-$, selenopentathionate, $^-O_3S–S–Se–S–SO_3^-$, are sorbed by a polymer. After chalcogenized polymer being treated with the solution of copper(II/I) salt, the copper sulfide, Cu_xS, [9 – 14], copper selenide, Cu_xSe, [15] or mixed copper sulfide-copper selenide, Cu_xS-Cu_ySe, [16] layers on the surface of a polymer are formed.

In our last work it was shown that using the solutions of potassium telluropentathionate, $K_2TeS_4O_6$, as chalcogenization agents of PA, semiconducting and electrically conductive mixed copper sulfide-copper telluride, Cu_xS-Cu_yTe, layers forms on the surface of this polymer [20]. By IR and UV absorption spectroscopy it was determined that the telluropentathionate ions, $^-O_3S–S–Se–S–SO_3^-$, are sorbed by a polymer from $K_2TeS_4O_6$ solution. After chalcogenized polymer being treated with the solution of copper(II/I) salt, the mixed copper sulfide-copper telluride, Cu_xS-Cu_yTe, layers on the surface of a polymer are formed; the phase composition of these layers was studied by X-ray diffraction analysis [20].

To confirm the results obtained using potassium telluropentathionate solutions as sulfur and tellurium precursors in the formation of copper sulfide-copper telluride layers, in the present work we studied the formation of these layers, sodium telluropentathionate, $Na_2TeS_4O_6$, solutions being used as precursors.

EXPERIMENTAL

The layers of mixed copper chalcogenide, Cu_xS-Cu_yTe, were deposited on polyamide 6 (PA) (manufacturer TY 6-05-1775-76, grade PK-4, (15×70) mm, 70 μm). The PA films were boiled in distilled water for 2 h to remove the monomer residues. They were dried with filter paper and then over anhydrous $CaCl_2$ for 24 h.

The PA films were chalcogenized in a thermostatic vessel using a continually stirred (0.01 – 0.10) mol/dm^3 solution of sodium telluropentathionate, $Na_2TeS_4O_6$, in 0.2 mol/cm^3 at 20 °C for up to 24 h. Previous studies using potassium telluropentathionate showed that sorption of polithionate anions from acidified solutions proceeds significantly more effective. At certain time intervals, samples were withdrawn, rinsed with distilled water, dried with filter paper, left over anhydrous $CaCl_2$ for 24 h and then used in analysis and further experiments.

Distilled water, reagents of the grades "especially pure", "chemically pure" and "analytically pure" were used in the experiments. The salt of sodium telluropentathionate, $Na_2TeS_4O_6·2H_2O$, was prepared and analyzed according to the published procedures [21].

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The samples of chalcogenized PA were treated with a solution of Cu(II/I) salts at 78 °C for 10 min. A Cu(II/I) salt solution was made from crystalline $CuSO_4{\cdot}5H_2O$ and hydroquinone as described in [22, 23]. It is a mixture of Cu salts, containing 0.34 mol/dm^3 of Cu(II) and 0.06 mol/dm^3 of Cu(I) [23]. After the treatment with the solution of Cu(II/I) salts, the samples of PA were rinsed with distilled water, dried over anhydrous $CaCl_2$ and used in further experiments.

The amount of tellurium and copper in a PA sample was determined using a "Perkin-Elmer 503" atomic absorption spectrometer. Before analysis, samples of PA with tellurium and sulfur containing films had been mineralized. Samples were treated with concentrated HNO_3 to destroy PA and to oxidize tellurium and sulfur compounds to tellurites and sulfates. Heating with concentrated hydrochloric acid removed the excess of nitric acid. For the conditions described above, the sensitivity of the AAS method is 1 μg/ml tellurium for the 1 % absorption.

The concentration of sulfur in PA, in the form of sulfates, was determined turbidimetrically. Sulfate ion in the range of concentration (1 – 15) mg/dm^3 may be easily determined by utilizing the reaction with barium chloride in a solution slightly acidified with hydrochloric acid to give barium sulfate. The intensity of the transmitted light as a function of the concentration of the dispersed phase of $BaSO_4$ was measured photometrically with a "KFK-4" photoelectric colorimeter (Russia) at $\lambda = 400$ nm. The standard deviation in the range of concentrations (5 – 10) mg/dm^3 was 8 %. The concentration of sulphur and tellurium were determined after the chalcogenization stage.

The phase composition of copper chalcogenides layers on PA surface was investigated by X-ray diffraction employing a "DRON-6" diffractometer equipped with a special device for beam limitation at low and medium diffraction angles using graphite-monochromatized Cu-K$_\alpha$ radiation source (λ = 1.54178 Å) under a voltage of 30 kV and a current of 30 mA. The XRD patterns were recorded with a step of 0.05° from 2θ = 30° to 70°. X-ray diffractograms of PA samples with layers of copper chalcogenides were treated using "Search Match", "ConvX", "Xfit" and "Excel" programs to eliminate PA maxima.

The sheet resistance of Cu_xS-Cu_yTe layers with different composition to the constant current was measured with an "MS8205F" constant current numerical measuring device with special electrodes. The electrodes were produced from two nickel-plated copper plates. The plates were fixed with a 1 cm spacing and the dielectric material was placed between them. The concept of sheet resistance is used to characterize thin deposited layers.

The morphology of the surface of Cu_xS-Cu_ySe layers and roughness measurements were performed using atomic force microscope "QUESANT QScope-250" (Quesant Corporation, USA) in the contact mode with ultra high resolution probes (Micromash Corp.). The data of measurements were analysed using the "Scan Atomic^{TM}, SPIP" (Scanning Probe Image Processor) programs.

RESULTS AND DISCUSSION

The results of earlier studies [20, 24] showed that under PA film treatment in acidified water solutions of potassium telluropentathionate, $K_2TeS_4O_6$, or telluropentathionic acid, $H_2TeS_4O_6$, the anionic particles containing tellurium and sulfur atoms of low oxidation state, ^-O_3S–S–Te–S–SO_3^-, do sorb-diffuse into the polymer. During in such a way chalcogenized PA films treatment with the solutions of Cu(II/I) salts, exactly these central divalent tellurium and sulfur atoms of low oxidation state react with the Cu(II/I) ions and form the layers of mixed copper sulfides-copper tellurides on the surface of semihydrophilic PA [20, 24].

Our experiments showed that, like in the case with $K_2TeS_4O_6$ solutions, the particles containing sulfur and tellurium (from analogy with $K_2TeS_4O_6$ solutions – the telluropentathionate anions) sorb-diffuse into PA films while keeping them in sodium telluropentathionate solutions. The concentrations of sorbed-diffused tellurium and sulfur increase with increasing the duration of polymer treatment in precursor solution and the concentration of this solution (Figs. 1 and 2). The highest concentrations of tellurium and sulfur in PA are reached after 24 h duration of PA chalcogenization; in most cases the saturation of the polymer is reched after 12 h. Maximum values of tellurium and sulfur concentrations are when sodium telluropentathionate solution of highest concentration (0.1 mol/dm^3) for the polymer chalcogenization has been used and they

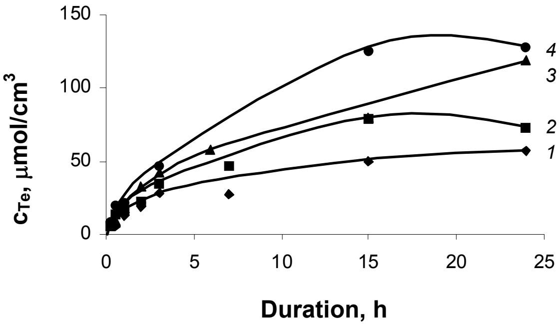

Fig. 1. Changes of tellurium concentrations in PA film chalcogenized at a temperature of 20 °C in $Na_2TeS_4O_6$ solution. Concentration of $Na_2TeS_4O_6$ solution, mol/dm^3: 1 – 0.01; 2 – 0.025; 3 – 0.05; 4 – 0.1

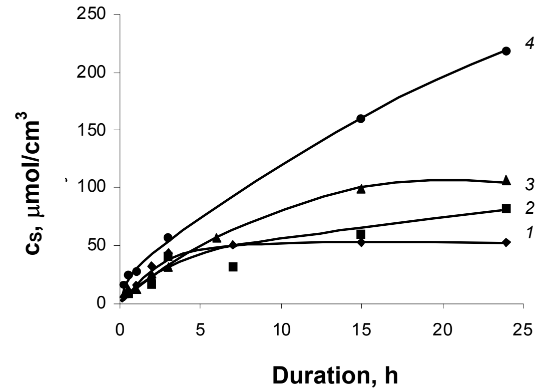

Fig. 2. Changes of sulfur concentrations in PA film chalcogenized at a temperature of 20 °C in $Na_2TeS_4O_6$ solution. Concentration of $Na_2TeS_4O_6$ solution, mol/dm^3: 1 – 0.01; 2 – 0.025; 3 – 0.05; 4 – 0.1

Table 1. The concentrations of tellurium (μmol/cm^3) in PA and the values of electrical sheet resistance (kΩ/□) of copper chalcogenide layers on PA surface formed using 0.1 mol/dm^3 $Na_2TeS_4O_6$ and $K_2TeS_4O_6$ solutions at a temperature of 20 °C at different duration of polymer chalcogenization

Chalcogenization duration, h	Te concentration, μmol/cm^3		S concentration, μmol/cm^3		Sheet resistance of Cu_xS-Cu_yTe layers, kΩ/□	
	$Na_2TeS_4O_6$	$K_2TeS_4O_6$	$Na_2TeS_4O_6$	$K_2TeS_4O_6$	$Na_2TeS_4O_6$	$K_2TeS_4O_6$
0.5	12.70	26.72	23.39	31.03	$1.19 \cdot 10^3$	256.43
1	21.16	37.70	28.06	25.83	360.40	41.44
2	35.60	58.70	18.71	30.86	623.90	9.85
3	47.02	78.40	56.13	45.48	5.30	9.89
12	125.39	143.28	–	46.97	–	1.57
24	127.74	162.49	218.27	23.31	2.07	2.92

are ~125 μmol/cm^3 and ~220 μmol/cm^3, respectively. We compared these data with the corresponding data obtained using potassium telluropentathionate solutions [20] (Table 1): tellurium concentrations obtained using $Na_2TeS_4O_6$ solutions were lower. The reason may be the fact, known in polythionate chemistry that the potassium salts are more stable compared with the analogous sodium polythionates [18].

In experimental conditions of the present work, during first 3 hours of PA chalcogenization Te concentrations using sodium telluropentationate solution are 1.5 – 2 times lower compared with those obtained using potassium telluropentathionate solution. But on prolongation of PA chalcogenization to 12 h – 24 h, concentrations of tellurium having used $Na_2TeS_4O_6$ solution are only slightly lower than having used $K_2TeS_4O_6$ solutions.

Semiconducting copper sulfide-copper telluride layers were formed on PA films if the films chalcogenized in $Na_2TeS_4O_6$ solutions had been treated with Cu(II/I) salts solution. The concentration of copper in PA increased with increasing in duration of polymer initial treatment in precursor solution and the concentration of this solution (Fig. 3). Thus, copper concentration in Cu_xS-Cu_yTe layers increases with increasing the concentration of chalcogens in the polymer. This is quite understandable since with a higher concentration of sulfur and tellurium sorbed-diffused into PA, a larger amount of Cu^+ and Cu^{2+} ions may be involved in the reaction with the sulfur-tellurium species. The highest concentration of copper after initial chalcogenization in 0.05 mol/dm^3 $Na_2TeS_4O_6$ solution at a temperature of 20 °C is ~360 μmol/cm^3, but about the same value of copper concentration was obtained using the solution of sodium telluropentathionate of twice lower concentration. That may be explained by decrease of $Na_2TeS_4O_6$ stability in solution with the increase in solution concentration. However in general, the largest copper concentration in our experiments was obtained using 0.025 mol/dm^3 $Na_2TeS_4O_6$ solution at a temperature of 20 °C and 24 h of chalcogenization (~740 μmol/cm^3).

In the Table 1 the values of electrical sheet resistance of copper chalcogenide layers, formed using 0.1 mol/dm^3 solutions of $Na_2TeS_4O_6$ and $K_2TeS_4O_6$ at the temperature of 20 °C and at different duration of a polymer chalcogenization are presented. The data presented show that the electrical sheet resistance of Cu_xS-Cu_yTe layers decreases with increasing the duration of the polymer initial treatment in chalcogenization solution, i. e. with increasing tellurium, sulfur and consequently copper concentrations in the layer. The value of sheet resistance after 24 h of chalcogenization in 0.1 mol/dm^3 $Na_2TeS_4O_6$ solution at 20 °C decreased from $1.19 \cdot 10^3$ kΩ/□ to ~2 kΩ/□. However, in this case, the values of electrical sheet resistance at a short duration of PA initial chalcogenization (up to ~2 h) were significantly higher compared with the values when the potassium telluropentathionate solution had been used [20]; at a longer duration of chalcogenization, the values of electrical sheet resistance in cases of both telluropentathionates were similar. The electrical resistance reduction of Cu_xS-Cu_yTe layers with increasing the duration of polymer chalcogenization may be explained by the increased concentrations of sorbed-diffused tellurium and sulfur and thus of the amount of copper that reacted in the stage of "copperizing".

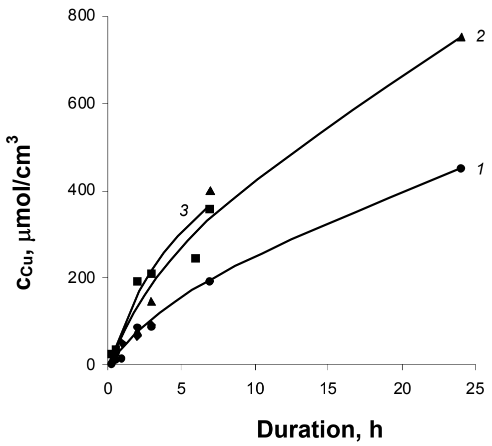

Fig. 3. Dependence of copper concentration in PA on chalcogenization duration when treating it with $Na_2TeS_4O_6$ solution at 20 °C and then in Cu(II/I) salt solution. The concentration of $Na_2TeS_4O_6$ solution, mol/dm^3: 1 – 0.01; 2 – 0.025; 3 – 0.05

The phase composition of copper sulfide-copper telluride layers formed using $Na_2TeS_4O_6$ solutions was studied by the X-ray difraction method. This method enables to identify the copper chalcogenides formed on the surface of PA, since the chemical composition and the crystal structure of most Cu_xS and Cu_yTe minerals has been studied [25, 26]. The results of our study are presented in the Fig. 4.

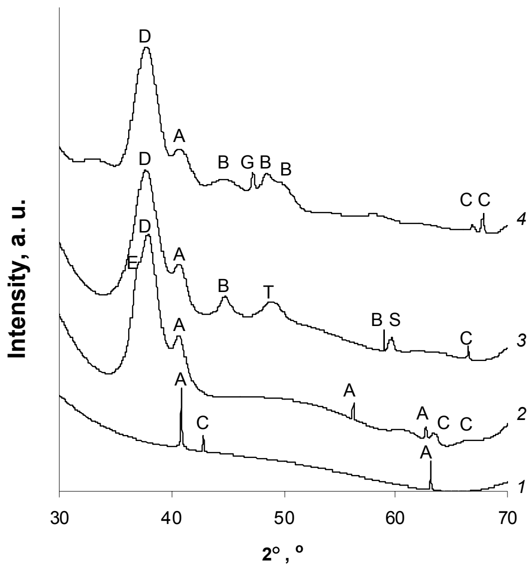

Fig. 4. X-ray diffraction patterns (A – *anilite*, Cu_7S_4, D – *djurleite*, $Cu_{1.9375S}$, S – *digenite*, $Cu_{1.8}S$, G – *geerite*, $Cu_{1,6}S$, C – hexagonal copper telluride Cu_2Te, T – tetragonal copper telluride $Cu_{3.18}Te_2$, B – *vulcanite*, CuTe, E – copper telluride $Cu_{2.72}Te_2$) of copper chalcogenide layers on PA treated for 3 h with $Na_2TeS_4O_6$ solution of different concentration at 20 °C and with Cu(II/I) salt solution. The concentration of $Na_2TeS_4O_6$ solution, mol/dm^3: 1 – 0.01, 2 – 0.025, 3 – 0.05, 4 – 0.1

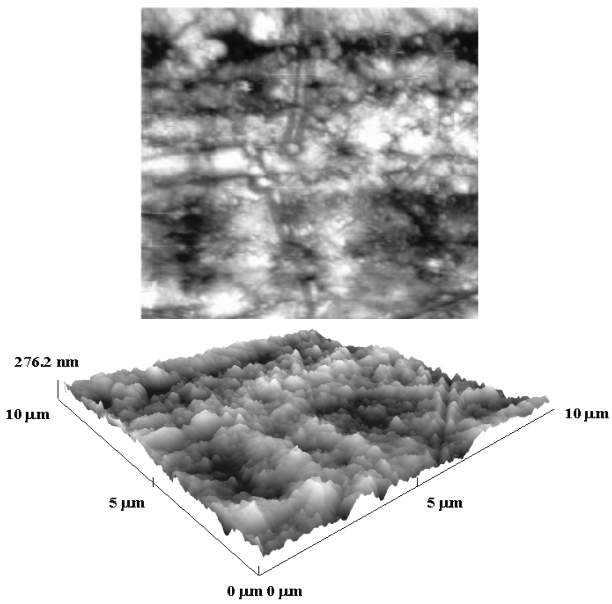

Fig. 5. AFM top view of copper chalcogenide layers on PA treated for 3 h at 20 °C in 0.1 mol/dm^3 $Na_2TeS_4O_6$ solution and with Cu(II/I) salt solution

According to the X-ray diffraction results all the samples of copper chalcogenide layers on PA are polycrystalline and many of them have some binary phases such as Cu_2Te, $Cu_{3\pm\delta}Te_2$ and $Cu_{2-\delta}S$. The four phases of copper tellurides, *tetragonal* $Cu_{3.18}Te_2$ (maximum at $2\theta = 47.6°$), $Cu_{2.72}Te_2$ (maximum at $2\theta = 37.2°$), *hexagonal* Cu_2Te (maximum at $2\theta = 42.9$, 63.5, 66.4 and 67.8°) and *orthorhombic* vulcanite, CuTe (maximum at $2\theta = 44.8$, 48.1, 50.0 and 58.3°), were found in films on the PA surface, among them four phases of copper sulfides such as *orthorhombic* anilite, Cu_7S_4 (maximum at $2\theta = 40.92$, 55.94 and 62.8°), *monoclinic* djurleite, $Cu_{1.9375}S$ (maximum at $2\theta = 38.3°$), geerite, $Cu_{1.6}S$ (maximum at $2\theta = 47.8°$) and *orthorhombic* digenite, $Cu_{1.8}S$ (maximum at $2\theta = 59.85°$) (Fig. 4).

The surface morphology of copper chalcogenide layers, formed using the solutions of sodium telluropentathionate, like the morphology of Cu_xS-Cu_yTe layers, formed using the solutions of potassium telluropentathionate [27] was studied by atomic force microscope (Fig. 5). Depending on the exposure in the precursor solution, chalcogenide layers of 180 nm – 560 nm height could be formed. The CuTe and CuS interface appeared to be graded with a substantial interdiffusion between the layers. The islands were observed due to surface roughness.

To sum up, we may state that, depending on the conditions of PA chalcogenization in $Na_2TeS_4O_6$ solution (duration, solution concentration), like in the case of $K_2TeS_4O_6$ solutions, on the surface of this polymer it is possible to form electrically conductive or semiconductive copper sulfide–copper telluride layers.

CONCLUSIONS

1. The layers of copper chalcogenides – mixed copper sulfide–copper telluride, Cu_xS-Cu_yTe, were formed on the surface of semihydrophilic polymer – polyamide 6 using (0.01 – 0.10) mol/dm^3 solution of sodium telluropentathionate, $Na_2TeS_4O_6$, in 0.2 mol/dm^3 HCl as precursor of chalcogens. The concentration of sorbed tellurium and sulfur increases with the increase of the duration of treatment and concentration of $Na_2TeS_4O_6$ solution.
2. The mixed copper sulfide-copper telluride, Cu_xS-Cu_yTe, layers are formed on the surface of polyamide 6 after the treatment of chalcogenized polymer with Cu(II/I) salt solution (10 min, 78 °C): the anions $TeS_4O_6^{2-}$ containing tellurium and sulfur atoms of low oxidation state react with the copper(II/I) ions. The conditions of a polymer initial chalcogenization determine the concentration of copper and the composition of chalcogenide layer. The concentration of copper in the chalcogenide layer increases with the increase of initial chalcogenation duration and the concentration of solution.
3. The concentration of copper in the chalcogenide layers increases with the increase of concentration of sulfur and tellurium in polyamide. The chemical and phase composition of copper chalcogenide layers depends on the conditions of the chalcogenization process. Four copper sulfide phases, *digenite*, $Cu_{1.8}S$, *djurleite,* $Cu_{1.9375}S$, *anilite*, Cu_7S_4, *geerite*, $Cu_{1,6}S$, four copper telluride phases – *tetragonal* $Cu_{3.18}Te_2$, $Cu_{2.72}Te_2$, *hexagonal* Cu_2Te, and *orthorhombic vulcanite*, CuTe, were identified in the layers by X-ray diffraction.
4. The use of 0.1 mol/cm^3 solution of sodium telluropentathionate as precursor enables the formation on the surface of PA electrically conductive layer of copper sulfides–tellurides with electrical resistance in the range of ~ 2.07 kΩ/□ to 1.19·10^3 kΩ/□.

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