Investigation of the mechanism of mercury removal from a silver dental amalgam alloy

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Abstract: An investigation of silver dental amalgam decomposition and the mercury removal mechanism was performed. The decomposition process was analysed during thermal treatment in the temperature interval from 400 °C to 850 °C and for times from 0.5 to 7.5 h. The chemical compositions of the silver dental amalgam alloy and the treated alloy were tested and microstructure analysis using optical and scanning electron microscopy was carried out. The phases were identified using energy disperse electron probe microanalysis. A mechanism for the mercury removal process from silver dental amalgam alloy is suggested.

Keywords: silver amalgams, mercury removal, thermal treatment.

INTRODUCTION

Silver dental amalgams have been the most commonly used material in restorative dentistry for over 150 years. The wide use of Ag-Sn-Cu amalgams as dental restorative materials makes them important biomaterials. Their physical and mechanical properties, stability, and ease of use and relatively low cost have made amalgams the preferred choice in many clinical situations when compared with other direct restorative materials. One of their major components, mercury, is of particular concern due to its potential adverse effects on humans and the environment.[1–3] The mechanism of the amalgamation process in dental amalgam alloys has been studied in the literature.[4,5] However, the process of mercury removal is not well analysed, especially the recycling of in dental amalgam alloy scrap. The only component of the amalgam scrap likely to be hazardous is mercury in the form of dust or, particularly, vapours, as mercury is extremely mobile due to its high vapour pressure and low affinity for oxygen.

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The objective of this investigation was to analyse dental amalgam alloy decomposition and mercury removal during the thermal treatment which could be applied during the recycling process. Also, an attempt was made to understand the mechanism and suggest the effects of process variables on this process with the aim of protection of the environment.

EXPERIMENTAL

Material

The investigated material was dental amalgam scrap in a shape of ellipsoidal granules, with rough surfaces and a silver grey colour. It was collected from dental surgeries. The granules weighed about 1 g. Their outer dimensions were defined by a screening process and by measuring the two perpendicular ellipsoid axes, d_1 and d_2. The results are presented in Table I.

TABLE I. Granulometric analysis and dimensions of the dental amalgam scrap

Mash size/>mm		6.68	4.69	3.32	1.65	0.59
Percentage/%		21	48	18	8	5
Measured elipsoid	d_1	9.46	5.51	5.80	3.01	1.62
axes/mm	d_2	6.15	3.91	2.03	1.12	0.39
	d_{mean}	7.81	4.71	3.91	2.01	1.00

The material contained approximately 50 wt. % (Ag + Sn + Cu) and 50 wt. % Hg. The chemical composition was determined by wet chemistry and the results are presented in Table II.

TABLE II. Chemical composition of the silver amalgam scrap

Chemical composition/wt. %			
Ag	Sn	Cu	Hg
35.22	12.16	2.45	50.17

The alloy density was 11510 kg/m^3, which was determined by the picnometric method in water. Hardness measurements by the Vickers method (HV$_{0.05}$) were also carried out. Five hardness measurements yielded a mean value of 79 HV$_{0.05}$.

Thermal process of Hg removing

The decomposition mechanism of the dental amalgam alloy and the removal of Hg on heating was analysed. The experiments were performed under laboratory conditions in a temperature-controlled tube furnace with a water-cooled condenser for mercury. A controlled, continuous flow of nitrogen gas through the furnace was maintained. The gas was crubbed by a solution of nitric acid at the exit of the furnace tube exit. The samples in ceramic ladles were placed deposited in the furnace and heated for 0.5 h to 7.5 h at temperature from 400 °C to 850 °C. During the process, mercury evaporated from the amalgam and was transported by the carrier gas to the cooler at the end of the furnace where it condensed. Six groups of experiments were performed each at a different temperature for various periods of time. Each sample was weighed before and after the thermal process. One sample from each group was chemically analysed after the thermal treatment.

Microstructure examination

The microstructure of the alloy was analyised by optical microscopy. The samples were prepared by standard metallogarphic techniques, following grinding and polishing. The alloys were

etched for 60 s in Aqua Regin contanuing glycerine (50 ml glycerine, 30 ml HCl and 15 ml HNO_3) or by two stage etching in the following solutions: a) 20 g CrO_3 and 100 ml distilled H_2O, and b) 10 g NH_4NO_3 and 100 ml distilled H_2O for 60 s.

The samples were also analysed by scanning electron microscopy (SEM) and by the application of an energy disperse spectrometer (EDS). Quantitative chemical analysis was performed with the ZAF factor correction.

RESULTS AND DISCUSSION

The thermal treatment conditions as temperatures and times for the six groups of experiments are presented in Table III. The weights of the amalgam alloy samples before and after thermal treatment, as well as the calculated weights of the removed Hg are also summarised in the same Table.

TABLE III. Parameters for the silver amalgam thermal treatment process

Group of experiments	Temperature °C	Time	Sample weight g	Sample weight after process g	Calculated weight of Hg g
1	400	2 h	54.27	27.11	27.16
	400	3 h	60.00	30.62	29.38
2	800	30'	68.03	30.75	37.28
	800	45'	60.00	27.49	32.51
3	800	1 h 20'	60.00	27.77	32.23
	800	1 h 30'	60.03	28.50	31.53
	800	1 h 30'	60.00	28.45	31.55
	800	1 h 30'	60.00	29.65	30.35
4	850	1 h	60.00	27.67	32.33
	850	1 h	60.00	27.38	32.62
	850	1 h	60.00	27.55	32.45
	850	1 h 5'	60.00	27.21	32.79
5	850	1 h 30'	60.00	28.50	31.50
	850	1 h 30'	60.00	30.25	29.75
	850	1 h 30'	60.00	28.27	31.73
	850	1 h 30'	60.00	29.05	30.95
	850	1 h 30'	60.00	29.20	30.85
	850	1 h 35'	60.00	27.06	32.94
6	850	7 h 25'	60.00	24.19	35.81

The chemical composition of one sample from each group of the treated amalgam alloy is presented in Table IV. An additional test was performed to detect the

presence of mercury in the alloy treated at 850 °C. This was done by using biphenylcarbazone (ditizone), which is known to react with mercury at concentrations higher than 5×10^{-7} g, and no mercury was detected.

TABLE IV. Chemical composition of the treated amalgam alloy

Group of experiments	Process parameters	Chemical composition/wt. %			
		Ag	Sn	Cu	Hg
1	400 °C2/h	70.40	24.06	2.43	3.11
2	800 °C/0.5 h	72.90	23.80	2.39	0.91
3	800 °C/1.5 h	75.40	21.73	2.16	0.70
4	850 °C/1 h	74.71	22.85	2.44	n.d.[*]
5	850 °C/1.5 h	73.70	22.73	3.57	n.d.[*]
6	850 °C/7.5 h	72.23	23.84	3.93	n.d.[*]

Comment: [*]n.d. – not detected, content of Mg = 0.02 – 0.03 % and Ca = 0.01 – 0.02 %

The results of the chemical analysis presented in Table II show that the investigated allyo was a traditional dental amalgam alloy. The applied thermal treatments result in the elimination of mercury to a great extent, as shown in Table IV. At the temperature of 400 °C (which is significantly above the boiling temperature of mercury $T_b = 357$ °C), most of mercury from the dental amalgam scrap is removed. The quantity of mercury decreased from 50.17 wt. % in the raw material to 3.1 wt. % Hg in the alloy heat treated at 400 °C. Increasing the temperature up to 800 °C resulted in a further decrease in the mercury. The mercury content decreased to undetectable levels after treatment at a temperature of 850 °C. It is obvious that at this temperature a treatment time of one hour is sufficient for complete mercury removal.

Visual analysis of the treated alloy samples showed no change in the sample shapes and dimensions but the recovered alloy was porous and the density of the samples after thermal treatment was approximately 5600 kg/m^3, as compared to 11510 kg/m^3 before treatment. With respect to the density, the 51.5 wt. % loss can be attributed to mercury removal. The hardness measurements showed that the treated alloy was 25 % softer than the raw material. It could be concluded that there were no mercury microconstituents in the microstructure of the hard phases.

The results of metallographic investigations performed by optical microscopy show that the silver dental amalgam alloy microstructure consisted of a homogeneous distribution od different phases in a matrix phase, with the existence of some light grey interdendritic phases, as presented in Fig. 1a. A uniform distribution of pores of different sizes is evident as dark areas. The microstructure of the treated alloy is shown in Fig. 1b. The increase in porosity is the result of mercury removal. By comparison of the microstructures, it is evident that the area fraction of pores in
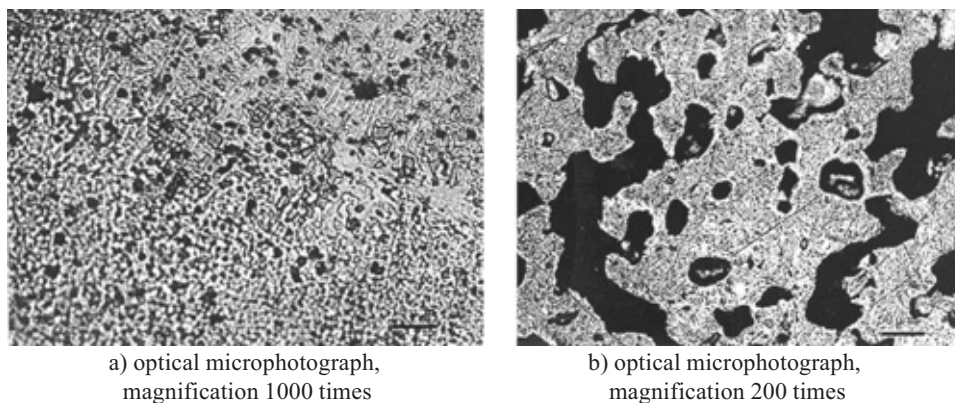
<table>
<tr><td>a) optical microphotograph,
magnification 1000 times</td><td>b) optical microphotograph,
magnification 200 times</td></tr>
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Fig. 1. Microstructure of dental amalgam alloy a) and treated alloy b).

the treated alloy was approximately 50 %. The microstructure was non-homogenous and consisted of different dark microconstituents located in a lighter matric.

The microconstituents in the microstructure of the raw and treated alloy were different. The amount and distribution of the phases and pores in the amalgam depend not only on the alloy composition, but also on the manufacturing process, the alloy particle size distribution and shape, the mercury concentration, the trituration conditions and the condensation practice.[3] The microstructure in traditional amalgam alloys consists of the intermetallic compound Ag_3Sn, the γ-phase of the binary Ag–Sn system and the reaction matric of γ_1 - Ag–Hg (Ag_2Hg_3) and γ_2-Sn–Hg ($Sn_{7-8}Hg$). A small quantity of β-(Ag–Sn) solid solution may also be present. Some investigators suggest that the γ_1 phase corresponds to $Ag_{22-23}Hg_{26-27}Sn$. Small amounts of minor phases may also be present in the γ_1 matrix. For example instance, β_1-(Ag–Hg) with $\approx$ 60 wt. % mercury may appear. Also, depending on the copper content and the thermal histories of the alloy, some phases such as ε-Cu_3Sn and η'-(Cu_6Sn_5) may also be present.[4–7] In the recovered alloy, phases which do not contain mercury, such as: γ-phase, Ag_3Sn, β-(Ag–Sn), and some phases containing Cu, such as ε-Cu_3Sn, η'-(Cu_6Sn_5), can be expected.

A SEM micrograph and typical EDS spectrums of various phases of the dental silver amalgam aloy are given in Fig. 2. The light areas show the present of pores. The quantitative compositions of the phases are given in Table V. Characteristic SEM micrographs of thermally treated alloy (a and b) and the EDS spectrums (c – f) of the analysed phases are given in Fig. 3. The chemical compositions of the analysed phases and the approximate phase composition are presented in Table VI.

From the presented results, it could be concluded that three phases with the approximate compositions $Ag_{22-23}Hg_{26-27}Sn$, Ag_2Hg_3 and ($Sn_{7-8}Hg$) were identified in the raw dental amalgam. The γ phase of the binary Ag–Sn system was not evidenced. Some Cu was detected combined with Ag or Sn, but it was not possible to distinguish a corresponding phase composition. In the thermally treated alloy,
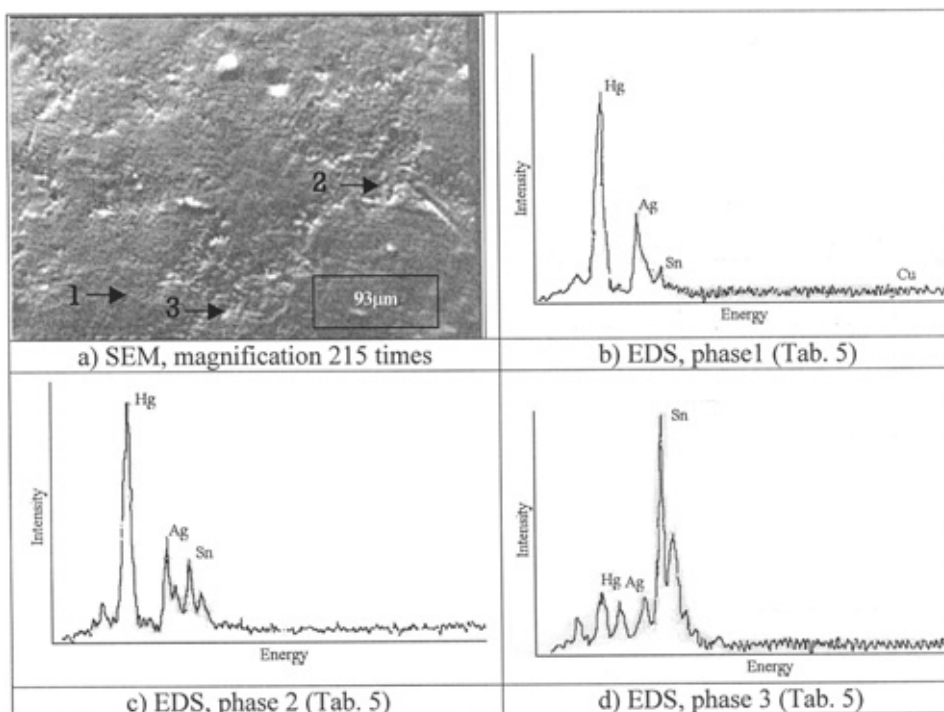
Fig. 2. Silver dental amalgam scrap microstructure (SEM) a) and EDS analysis (b–d).

phases not containing mercury, such as: γ-Ag$_3$Sn, ε-Cu$_3$Sn, η'-(Cu$_6$Sn$_5$), were identified.

TABLE V. EDS analysis of the dental silver amalgam alloy

Analysed phase	Chemical composition/w. %				Approximate phase composition
	Ag	Sn	Cu	Hg	
1	29.68	6.34	0.32	63.66	Ag$_{22-23}$Hg$_{26-27}$Sn+Ag–Cu
2	25.12	13.79	0	61.09	Ag$_2$Hg$_3$+Sn$_{7-8}$Hg
3	3.64	82.11	0	14.25	Sn$_{7-8}$Hg

Based on the obtained results, the reaction of mercury removal from the silver amalgam alloys during thermal treatment at temperatures above 400 °C could be decribed as:

$$Ag_{22-23}Hg_{26-27}Sn+Ag_2Hg_3+Sn_{7-8}Hg+Ag_3Sn+(Ag–Cu) \rightarrow \quad (1)$$
$$\rightarrow Hg+Cu_3Sn+Cu_6Sn_5+Ag_3Sn$$
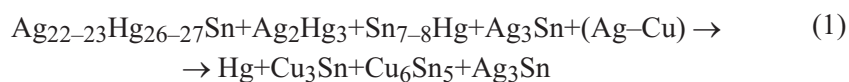
The reaction starts at temperatures below the boiling point of mercury (357 °C) by diffusion of mercury to the grain boundaries of the Ag and Sn rich phases and to the pores of the amalgam alloy. It is likely that the pores represent free space
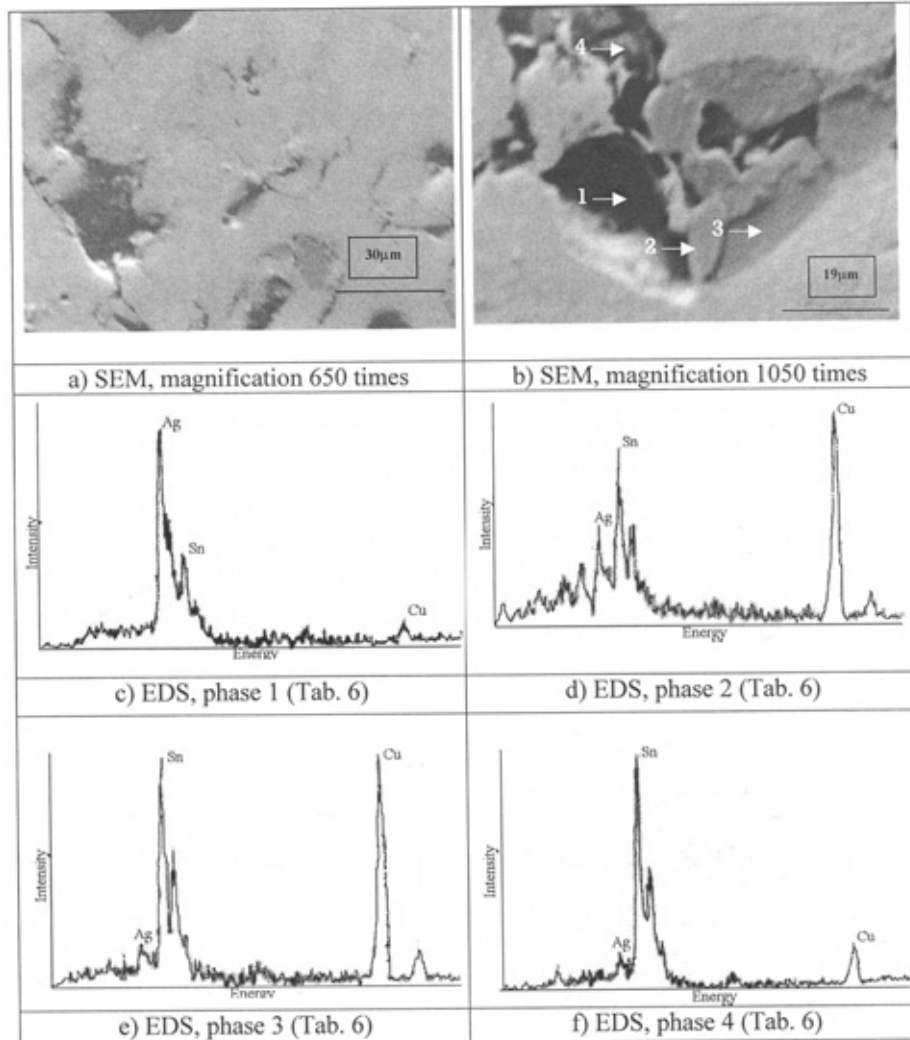
Fig. 3. Treated alloy microstructure by SEM a–b and EDS analysis c–f.

for mercury collection. When the temperature exceeds 375 °C, mercury first commences to vaporise which increases the vapour pressure in the pores. Based on data from the literature[8] and our calculations, at this temperature the partial pressure of Hg is slightly higher than those of the other elements in the amalgam alloy, as presented in Fig. 4 fo the tested temperatures. At higher temperatures, the values of the volume and grain boundary diffusion coefficients of mercury in the Ag–Sn alloy are higher.[6] Also, at these temperatures, the vapour pressure of Hg is significantly higher in comparison with the other alloying elements.[8] When the vapour pressure becomes higher than the forces between the phase boundaries, coalescence of the pores begins and the boundaries between the pores crack. The pores eventually be-
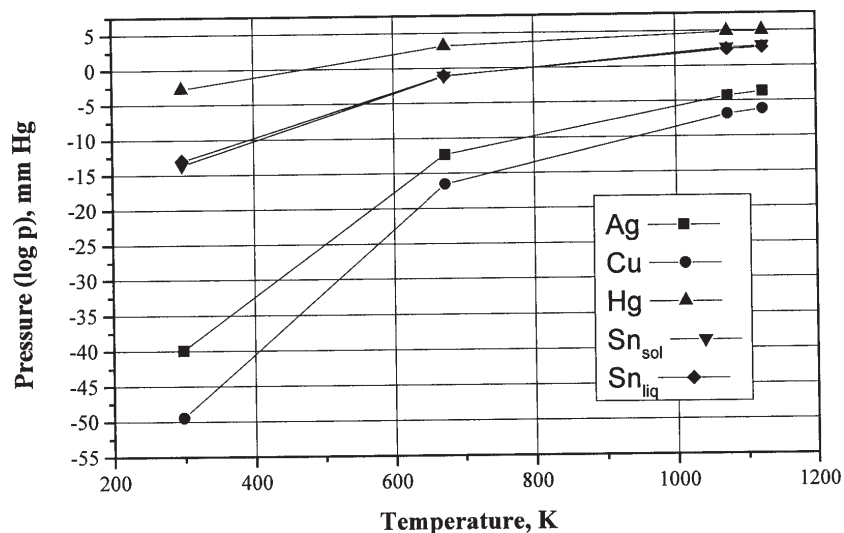
Fig. 4. Calculated partial pressures for the elements present in the alloy.

come connected with the granule surface and the mercury vapours flow outside of the alloy. The crushing of the walls between the pores is illustrated by the sharp edges of the pores presented in Fig. 1. As a result, the mercury vaporises and leaves the bulk material of the amalgam alloy, and the treated alloy has a spongy structure. The opinions in the literature concerning the rate of dissolution between Ag, Sn, and Cu in liquid mercury are contradictory. According to our experimental and calculated results, as well as results from the literature, it is assumed in this work that the removal sequence of the mercury from amalgam alloy occurs from the phases in the following order: Sn, Ag and Cu phases. Our experimental results also indicate that the temperature is the main factor influencing the removal rate of mercury, while the time factor is less significant. This could be a result of the significantly higher partial pressure of Hg, which is directly dependent on temperature.

TABLE VI. EDS Analysis of the treated alloy (850 °C/1.5 h)

Analysed phase	Chemical composition/wt. %				Approximated phase composition
	Ag	Sn	Cu	Hg	
1	66.43	27.18	6.39	0	$Ag_3Sn+Cu_6Sn_5$
2	12.13	38.74	49.13	0	Cu_3Sn+Ag_3Sn
3	0	32.40	67.60	0	Cu_3Sn
4	4.70	56.20	39.1	0	Cu_6Sn_5

As shown in Table IV, some mercury is still present in the allyo after 1.5 h at 400 °C. This suggests that some phases with low solubility (most likely the Cu phases) are not freed of mercury. At higher temperatures, the solubility increases and the rest of mercury is removed.

Based on the experimental results, a mechanism of silver amalgam decomposition during thermal treatment is suggested. This study may be taken as a first step in this direction. The performed experiments and the applied techniques were not sensitive enought for a clear definition of the amalgam decomposition mechanism. Therefore, more sensitive submicroscopic method or/and alternatively *in situ* observations should be applied in future research.

CONCLUSIONS

Based on the obtained results the following conclusions could be made:

– The decomposition of dental silver amalgam alloy and the removal of Hg by thermal treatment was analysed. The experiments were performed under laboratory conditions. The process was analysed at the temperature interval from 400 °C to 850 °C for the heating time from 0.5 to 7.5 h.

– Dental amalgam alloy decomposition was studied by chemical composition analyses, property testing, microstructural investigations and phase identification *via* EDS analysis.

Based on the obtained results, an attempt to explain the silver amalgam decomposition mechanism is made. It is presumed that this process results in mercury removal during thermal treatment and in the formation of Cu_3Sn, Cu_6Sn_5 and Ag_3Sn phases.

ИЗВОД

ИСТРАЖИВАЊЕ МЕХАНИЗМА УКЛАЊАЊА ЖИВЕ ИЗ АМАЛГАМА СРЕБРА

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У раду су приказани резултати истраживања механизма разлагања и уклањања живе из амалгама сребра који се користи у стоматологији. Процес разлагања је анализиран за време термичког третмана у температурном интервалу од 400 до 850 °C у трајању од 0,5 до 7,5 сати. Испитан је хемијски састав амалгама и добијене легуре након процеса и извршена је микроструктурна анализа применом светлосне и скенирајуће електронске микроскопије. Идентификација присутних фаза је урађена енерго дисперзионом анализом. Предложен је могући механизам уклањања живе из амалгамске легуре.

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