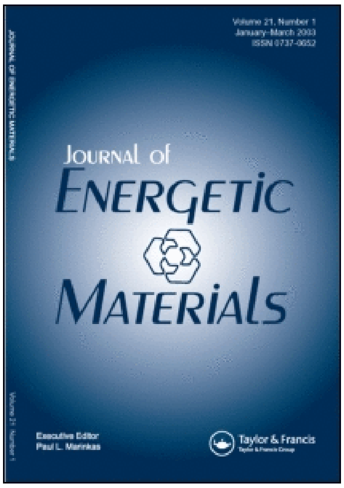

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Burning Rate Studies of Metal Powder (Ti, Ni)—Based Fuel-Rich Propellants

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This paper reports the burning rate results of titanium (Ti) and nickel (Ni)–based fuel-rich propellants with hydroxyl terminated polybutadiene (HTPB) and double-base (DB) matrix as binder. The results are discussed in comparison to aluminum (Al) and zirconium (Zr)–based formulations studied earlier by the authors. While 20% Ti containing composition with HTPB as binder gave burning rates comparable to those of aluminized formulation, superior burning rates were obtained for Ti-based formulations with higher metal loading (30–60%). 50–60% Ti-containing compositions gave higher burning rates than those for even zirconium (Zr)–based formulations. Fuel-rich formulations with a DB matrix produced much higher burning rates than corresponding HTPB-based compositions in the pressure range of 3.4–8.8 MPa. In these systems, Ti-incorporating formulations exhibited higher burning rates than aluminized compositions and lower than those for Zr compositions. Interestingly, Ni propellants gave burning rates close to those for Ti-based compositions and exhibited superior combustion characteristics in lower pressure ranges in systems with a DB matrix. Formulations with a GAP

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plasticized DB matrix exhibited 2–3 times higher burning rates than corresponding DEP plasticized compositions.

Keywords: propellant, rocket

1. Introduction

Fuel-rich propellants (FRPs) have emerged as an important class of solid propellant systems with the resurgence of the ramjet rocket concept, particularly for cruise missile applications demanding supersonic flights [1]. Unlike conventional rockets, ramjets utilize atmospheric air as an oxidant, and thereby maximum combustion potential of metals and other fuel components is exploited. Further, oxidizers that form 50–70% of conventional rocket propellant composition are not required to be carried along with the rocket, implying reduced missile weight. These features result in much higher performance of ramrockets employing FRPs than conventional propulsion devices based on high-performance composite and composite modified double-base (CMDB) propellants [2]. FRPs generally may offer improved combustion characteristics compared to polybutadine binders like hydroxyl terminated polybutadine (HTPB) polymers because of the presence of oxygen-rich nitrate ester substituents. Energetic azido polymers also find application as a binder/plasticizer of FRPs to achieve superior pyrolyzability, because of the presence of exothermally decomposing azido substituents [3, 4].

Researchers have evaluated various metals like Al, Be, B, and Mg as components of FRPs. Al, widely used in current CMDB and composite propellants, poses ignitability and combustion problems in highly metal-loaded FRPs because of a protective layer of alumina [5, 6]. In the case of Be also, combustion is sluggish because of an oxide layer barrier. Moreover, combustion products of Be (particularly BeO) are toxic [7, 8]. B is an attractive fuel for ramrockets in view of its superior air/fuel ratio, which is an outcome of the fact that its atomic weight is much less than that of candidate metals while it consumes an equal molar ratio of oxygen during oxidative combustion. However, high melting and boiling point of B cause serious ignition and combustion problems. Further, its combustion product B_2O_3 is a solid glassy liquid that can choke the exhaust nozzle. Attempts are ongoing to improve the pyrolyzability of these formulations to exploit the inherent potential of B. Although Mg has a low air/fuel ratio (3.3), FRPs based on it have found wide applications as fuel for ramjets in view of their high ignitability even at high metal loading, which is attributable to the pyrophoric nature or Mg [5, 9].

Zr and Ti are attractive fuels for ramjet rockets to achieve sustained combustion, particularly at very high metal loading because of the advantages of the solubility of their oxides in the molten metal and a moderate ignition temperature. Moreover, Zr and Ti-containing FRPs offer a high volumetric impulse because of a much higher density than those of Al and Mg-based compositions [6, 7]. Ni also appears to be an attractive candidate for FRPs in view of its high density and reactivity. However, information available on Zr-based FRPs is limited [10–12], and Ti/Ni are almost unexplored so far. We have reported earlier that Zr-based FRPs offer higher burning rates at low pressure at high metal loading both with HTPB (up to 70% Zr loading) and DB (up to 40% Zr loading) binders than aluminized compositions [13]. This paper reports burning rate behavior of Ti- and Ni-based FRPs in both HTPB and a double-base (DB) matrix. The effect of incorporation of a glycidyl azide polymer (GAP) to a DB matrix is also investigated. The results obtained during this work are compared with those of corresponding aluminized and Zr-based compositions reported earlier [13].

2. Experimental

Ni (average particle size $20 \pm 2\,\mu$), Ti (average particle size $20 \pm 2\,\mu$), Zr ($7 \pm 2\,\mu$), Al ($16\,\mu \pm 2\,\mu$), and AP (bimodal: $250\,\mu$ 70% and $10\,\mu$ 30%) of 99% purity were procured from indigenous sources. Their purity was checked before use with an Atomic Absorption Spectrophotometer (AAS) [Perkin Elmer, Model A-800]. Particle size was determined on a Malvern instrument. The spectrum obtained revealed that ~80% of the particles fall in the range of the average mean. The binder for composite formulations was composed of an HTPB prepolymer (number average mol. wt. $M\overline{n}$ 2,300–2,500, hydroxyl value 40 mg of KOH/g of sample, functionality 1.9–2.1, 1–4-trans 64%, 1–4 cis 16%, vinyl content 20%) cured with diphenylmethane diisocyanate (DDI) as per 1:1 OH:NCO ratio. Isodecyl pelargonate (IDP) was used as a plasticizer in a 40:60 ratio with HTPB. To process DB compositions, nitrocellulose (NC) partially plasticized with nitroglycerin (NG) was used as a binder. NC (nitrogen content 12.2%) was converted to spheroidal NC (SNC) at the HEMRL pilot plant. The process involved preparation of gel by adding ethyl acetate to NC corresponding to 90% by weight of SNC. NG (corresponding to 7% by weight of SNC) with carbamite (corresponding to 3% by weight of SNC) was incorporated to the gel in a mixer. SNC was obtained in a disperser mill. To ensure safe handling, NG was desensitized by adding diethyl phthalate (DEP) along with 2-nitro diphenyl amine (2-NDPA) used as stabilizer. The overall composition of desensitized NG referred to as a casting liquid (CL) was NG 80, DEP 18, 2-NDPA 2%. In GAP plasticized formulations, GAP of mol. wt. ~500 was added as replacement of the DEP. It was prepared by the authors adopting the single-step method for direct conversion of epichlorohydrin to GAP, on the lines of the process reported by Ahad [14].

Propellant compositions were prepared with a slurry cast technique [1, 15]. The method involved loading of a binder to the vertical planetary mixer. Fuel and oxidizers were added in installments, and the ingredients were mixed for 2 hr at ~40°C for CMDB formulations and at ~60°C for a composite propellant (CP). The curative (DDI) was added in a later case. The mix was deaerated during the mixing process to remove occluded air. Slurry thus obtained was cast in the evacuated molds. The propellant was cured at 70°C for 10 days and subjected to various tests after machining the samples to desired dimensions.

The base composition of composite formulation had 20% binder (HTPB 12%, isodecyl pelargonate (IDP) + diphenylmethane diisocyanate (DDI) 8%) and 80% filler (20–60%

metallic fuel and 60–20% AP). Double-base compositions composed of 30% SNC (NC ~27%, NG ~2%, carbamite ~1%), 30% desensitized NG (NG ~24%, DEP or GAP ~5.4%, and 2-NDPA ~0.6%), and 40% filler (20–40 metallic fuel and 20–0% AP).

The burning rates were determined by the acoustic emission technique in a 1–8.8 MPa range. The method involved combustion of the propellant sample in a nitrogen pressurized stainless steel bomb in a water medium. Water helps to maintain unidirectional burning and transfers acoustic emissions generated because of deflagrating propellant, which are sensed through a piezo electric transducer having a resonance frequency of 200 kHz. Burning rates were computed from the emission versus time record [16].

To understand the combustion behavior of fuel-rich propellants, extinguished propellant samples obtained by injecting liquid N_2 through nozzles on a propellant combusting in a chamber were subjected to SEM studies using a JEOL instrument (model JSM–J 200). DB formulations containing 30% metal with 10% AP were subjected to SEM studies. The samples were coated with a thin layer of gold under a vacuum and subjected to 25 kV acceleration voltage. The photographs were taken at a 750× magnification.

3. Results and Discussion

3.1. HTPB Binder

Burning rate results obtained for fuel-rich composite propellants are given in Table 1. A Ti-based formulation with 20% metal content gave burning rates of the order of 3.5–6.4 mm/s in the 1–8.8 MPa pressure region, which are more or less close to those for the corresponding aluminized formulation. 30–40% Ti-based formulations also gave stable combustion in this pressure range unlike corresponding aluminized compositions, which exhibited a low-pressure combustion limit (LPCL) of 3.4 MPa. Moreover, burning rates of these Ti formulations were 30–60% higher than those of aluminized compositions in the 3.4–8.8 MPa pressure range. 50–60% Ti-based FRPs gave

Table 1
Burning rates of HTPB-based fuel-rich formulations

Metal contents	Burning rates (mm/s) at MPa						Pressure index (n)
	1	2	3.4	4.9	6.9	8.8	
20% Al	3.9	4.2	4.9	6.1	6.4	6.8	0.25
20% Ti	3.5	4	4.5	.5	5.9	6.4	0.27
20% Ni	2.4	3.9	4.5	5	5.7	6.4	0.54
20% Zr	3.7	4.2	5.2	6.2	6.4	6.7	0.27
30% Al	Ext.	Ext.	2.9	3.1	3.3	3.7	0.26
30% Ti	2.9	3.5	3.9	4.2	5.1	5.8	0.32
30% Ni	2.1	3.3	3.8	4.2	4.8	5.6	0.45
30% Zr	3.1	3.8	4.7	5.3	5.9	6.6	0.34
40% Al	Ext.	Ext.	2.4	3	3.2	3.2	0.3
40% Ti	2.2	2.8	3.1	3.6	4.6	5.2	0.39
40% Ni	1.6	2.3	2.5	3.1	3.6	4.1	0.43
40% Zr	2.3	3.2	3.6	4.5	4.9	5.2	0.37
50% Al	Ext.	Ext.	Ext.	Ext.	2.1	2.3	0.36
50% Ti	2.1	2.7	3	3.5	4.6	5	0.39
50% Ni	Ext.	Ext.	Ext.	Ext.	1.5	1.6	0.26
50% Zr	2.2	2.5	2.8	3.1	3.4	4.2	0.29
60% Al	Ext.	Ext.	Ext.	Ext.	Ext.	Ext.	
60% Ti	2	2.2	2.3	3	3.8	4.2	0.34
60% Ni	Ext.	Ext.	Ext.	Ext.	Ext.	Ext.	
60% Zr	Ext.	Ext.	Ext.	2.1	2.3	2.9	0.55

Base composition: Binder 20%

Filler 80%: Metal [20–60%], AP [60–20%]

Composition with 60% Al did not undergo combustion Composition: Ext. = Extinguished (did not undergo stable combustion)

burning rates of 2–5 mm/s in the pressure range of 1–8.8 MPa. On the other hand, 50% Al-based composition did not produce stable combustion up to 4.9 MPa, and 60% Al-based formulation did not undergo combustion in the entire pressure range studied.

Compared to Zr-based formulations, 20–40% Ti-based formulations gave relatively lower (5–20%) burning rates while 50% Ti-based compositions gave marginally higher burning rates. A 60% Ti-formulation was found to be superior to a Zr formulation in terms of the LPCL as well.

As regards Ni-based FRPs, formulations containing 20–30% metal exhibited combustion characteristics almost close to those of Ti FRPs, while 40% metallized composition exhibited relatively lower burning rates. 50–60% Ni composition exhibited combustion problems more or less similar to those of corresponding aluminized propellants.

In general, a drop in burning rates was observed on the increase in metal content. Pressure index values for Al and Ti FRPs were in the range of 0.25–0.4. Zr-based FRPs gave a more or less similar pressure index up to 50% metal content. Increase of metal content in Ni FRPs resulted in a decrease in the pressure index. In general, Al, Ti, and Zr-based formulations gave a lower *n* value than Ni-based formulations.

3.2. Double Base Binder

Propellant composition containing 20% Ti and 20% AP dispersed in a DB matrix produced sustained combustion in the 3.4–8.8 MPa pressure range and gave burning rates of 8–16 mm/s like corresponding aluminized composition. 30% Ti formulation gave burning rates of 6.6–12.2 mm/s in the same pressure region, while aluminized formulations did not produce stable combustion up to 4.9 MPa and exhibited 20–30% lower burning rates in higher pressure zones. 40% Ti-based DB compositions like corresponding aluminized composition did not produce stable combustion in the pressure range studied (Table 2).

Incorporation of 20–30% Ni in DB FRPs led to extension of the LPCL to 1 MPa, suggesting superior combustion behavior than Ti formulations. This pattern is similar to that of 20–30% Zr-based formulations. As regards burning rates in the pressure range of 3.4–8.8 MPa, 20–30% Ni-based FRPs in a DB matrix were more or less similar to corresponding Ti

Table 2
Burning rates of DB matrix-based fuel-rich formulations

Metal contents	Burning rates (mm/s) at MPa 1	2	3.4	4.9	6.9	8.8	Pressure index (n)
20% Al	Ext.	Ext.	8.2	11.8	15.2	16.4	0.73
20% Ti	Ext.	Ext.	8	12	14.1	14.9	0.66
20% Ni	4.9	6.5	8	11.7	13.8	14.8	0.5
20% Zr	6.2	8.6	10.7	14.2	16.9	18.8	0.51
30% Al	Ext.	Ext.	Ext.	Ext.	7.3	10.2	1.33
30% Ti	Ext.	Ext.	6.6	8.2	9.7	12.2	0.65
30% Ni	5.8	4.8	6.8	8.8	10.2	12.4	0.54
30% Zr	5.6	7.4	9.8	13.6	15.1	17.9	0.53
40% Al	Ext.	Ext.	Ext.	Ext.	Ext.	Ext.	40% Al
40% Ti	Ext.	Ext.	Ext.	Ext.	Ext.	Ext.	40% Ti Ext.
40% Ni	2.9	3.8	5.4	7.3	9.3	11.7	0.63
40% Zr	Ext.	Ext.	7.8	12.2	15	17.4	0.85

Base composition: SNC 30%, desensitized NG 30%, filler (metal 20–40%), AP (20–0%) compositions with 40% Al & Ti did not undergo combustion.

FRPs, while Zr FRPs with similar metal content had superior burning rates than both of the former. Interestingly, 40% Ni DB FRPs also exhibited stable combustion in the pressure range of 1–8.8 MPa, while corresponding Zr formulations did not under go stable combustion at 1 and 2 MPa. However, burning rates of 40% Zr FRPs were on the higher side in the pressure range of 3.4–8.8 MPa (Table 2).

Replacement of DEP by GAP in the 20–30% Ti formulation extended the LPCL to 1 MPa and resulted in stable combustion of 40% Ti FRPs at 3.4 MPa. It also led to a 2–3 fold increase in burn rates of both Ti and Ni FRPs (Table 3). These trends are similar to these observed by authors for Al/Zr-based formulations during an earlier study [13]. Although the burning rates of Ni-based formulations were relatively lower than those of Ti FRPS, again it exhibited sustained combustion in a lower

Table 3
Burning rates of GAP-based fuel-rich formulations

Metal contents	Burning rates at Mpa pressures (mm/s)						Pressure index (n)
	1	2	3.4	4.9	6.9	8.8	
20% Al	Ext.	8.6	12.4	16.7	22.9	25.2	0.71
20% Ti	8.4	10.6	18.2	25.1	28	34	0.64
20% Ni	7.6	9	13.2	15.3	18.1	23.1	0.52
20% Zr	9.4	13.3	22.2	29.1	36	38	0.64
30% Al	Ext.	Ext.	7.9	12.2	17.5	21.9	1
30% Ti	6.9	7.9	11.2	23.8	27.3	29.3	0.66
30% Ni	6.4	7.6	10.7	14.7	16.9	22.5	0.57
30% Zr	8.3	12.6	21.4	26.4	28.2	31.2	0.6
40% Al	Ext.	Ext.	Ext.	9.2	12.2	13.4	0.64
40% Ti	Ext.	Ext.	9.4	12.5	17.4	19.6	0.78
40% Ni	4.6	6.2	8.8	11.7	13.3	16.2	0.57
40% Zr	6.8	10.2	19.6	25	27.6	30.8	0.68

Note: DEP in desensitized NG replaced by GAP

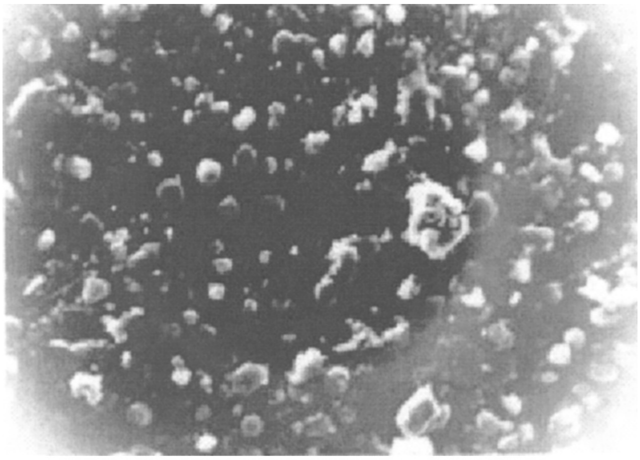
pressure range (1 MPa onward) even at 40% metal loading (Table 3).

Zr-based formulations exhibited overall superiority in terms of burning rates. The pressure index of FRPs with a DEP (0.5–0.85) and GAP (0.5–1) plasticized DB matrix was relatively higher than those for HTPB-based FRP formulations. However, a Ni-based formulation gave a relatively lower *n* value, probably because of relatively superior combustion behavior in the low-pressure region.

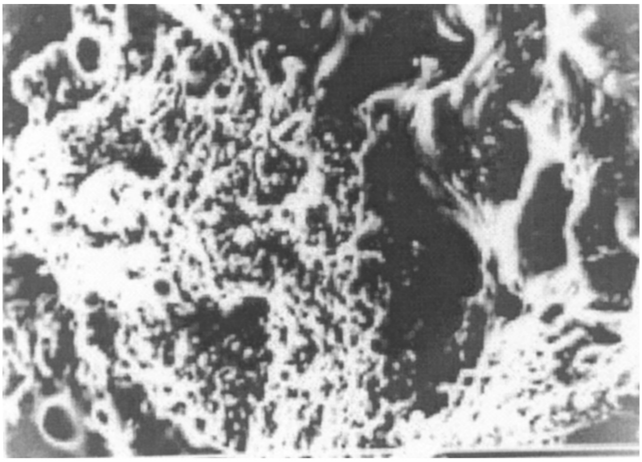
3.3. Combustion Mechanism

Poor combustion efficiency of aluminized formulations at low pressure and high metal content emanates from the fact that the oxide layer serves as an effective barrier to mass diffusion and energy transfer. The molten oxide retracts at the melting point of alumina and Al vapor flows out, leading to the formation of the detached flame envelope [17]. The Al combustion process occurs at a temperature around 2,500 K, which is generally achieved in the luminous zone of CP and CMDB propellants at a high standoff distance from propellant surface. Hence, Al combustion does not have much effect on propellant burning rates, and heat sink effects become more predominant at high metal content. Ti and Zr, on the other hand, get easily ignited at around 1,200 K [18]. This temperature can be achieved close to the burning surface of AP-based propellants. Thus, the energy released on Ti and Zr combustion can result in an increase in temperature of the propellant surface because of conductive/radiative heat feedback. An interplay between pyrophoricity and melting (mp)/boiling points (bp) of metal/metal oxide appears to be operative. Relatively superior combustion behavior of Ti FRPs beyond 40% metal content in HTPB-based systems may be an outcome of relatively lower melting and boiling points of both metal (Ti) and its oxide compared to those of Zr and Zr oxides. Ni is close to Ti in these respects. However, it is less pyrophonic than Ti and Zr. Superior combustion characteristics of Ni-based FRPs in a DB matrix at low pressure can be explained on the basis of Kubota and Hazama's findings [19]. They have reported that Ni catalyzes the reduction of $N_2O \rightarrow N_2$ in the dark/luminous zone of DB propellant leading to an increase in flame temperature, which stabilizes the combustion at low pressures. The higher burning rates of GAP-based compositions may be attributed to the fact that GAP decomposes exothermally at a propellant subsurface with the cleavage of the N_3 bond structure resulting in the liberation of energy on the order of 170 kcal/mole [20].

Additional information was obtained by subjecting the quenched propellant samples with a DB matrix to SEM studies. SEM photographs of an aluminized formulation with a DB matrix revealed unreacted Al particles on the surface in the form of accumulates, probably because of the concentration process (Figure 1). In the case of a Zr-based formulation, the expansion of metal particles and diffusion of metal out of the oxide skin could be clearly observed with the setting-in of the decomposition of the binder (Figure 2a). Ti and Ni-based



(a)



(b)

Figure 1. SEM pattern of (a) virgin and (b) extinguished aluminized propellant with DB matrix.

formulations exhibited a similar SEM pattern. The contribution of GAP towards burning rate enhancement of compositions was indicated by the absence of agglomerate formation even for an aluminized formulation (Figure 2b).

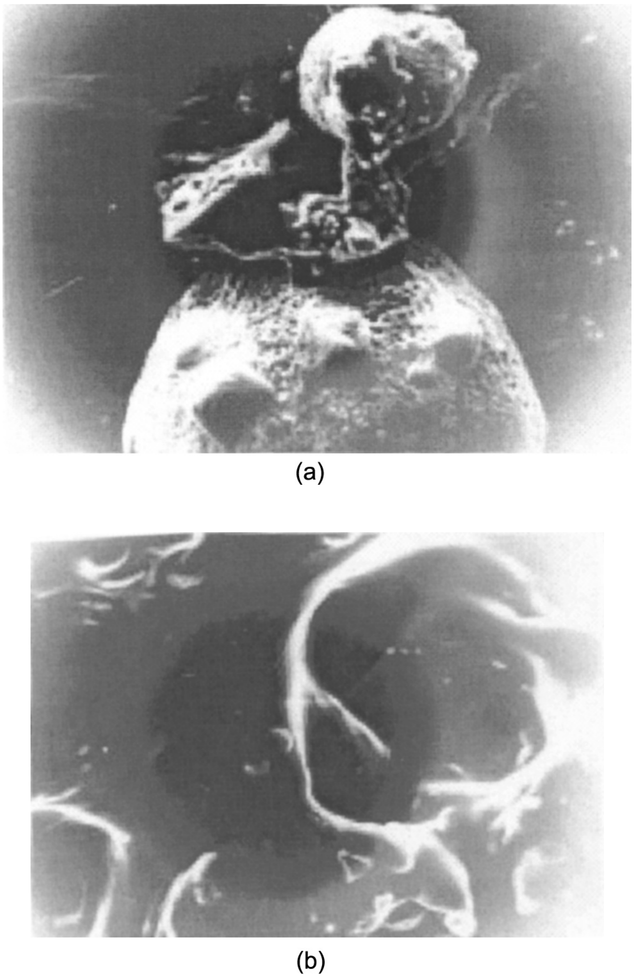


Figure 2. SEM pattern of extinguished surfaces of (a) Zn-based propellant with DB matrix and (b) aluminized propellant with GAP plasticized DB matrix.

4. Conclusion

This study brings out that fuel-rich propellants with a wide spectrum of burning rates and performance can be obtained by selecting an appropriate metal like Ti and Ni and a suitable binder like HTPB and nitroesters alone or in combination with an energetic plasticizer like GAP. In general, Ti-based formulations are superior to aluminized formulations in terms of burning rate and low-pressure combustion limit. Ni extends LPCL in the case of formulations with a DB matrix. SEM results suggest a significant role of metals and GAP in the combustion process. Both Ti and Ni, like Zr, have the potential to offer a superior density impulse over Al FRPs. However, detailed investigations need to be undertaken to exploit their potential in operational ramjet systems and to understand the mechanism.

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