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Combustion Characteristics of Coated Nano Aluminum in Composite Propellants

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ABSTRACT

The effects of coated nano-sized aluminum (*Al*) powder (*n-Al*) and micron-sized *Al* powder (g-*Al*) in propellants on the burning rate and pressure exponent have been investigated. The results show that the burning rates of propellants increase as the *n-Al* content increases, but the burning rate pressure exponents tend to decrease. Compared with propellant containing μ-*Al*, the increments of burning rates of propellants containing *n-Al* powder reduce gradually with increase in the pressure because of the differences of the combustion characteristics and ignition performances of *n-Al* powder and *g-Al* powder. Single short distance photograph, scanning electron microscopy, x-ray fluorescence analysis were used to characterise the flame image, combustion phenomena, the quenched surface image, and surface elements. A substantial difference in combustion characteristics of *n-Al* powder has been found in comparison with μ-*Al* powder. In addition, oxygen-bomb combustion heat, ignition temperature, and recovery ratio of residues were measured.

Keywords: Nanotechnology, nanostructured materials, aluminium powder, micron-sized aluminium powder, combustion, nano-sized aluminium powder, composite propellants

1. INTRODUCTION

Nanotechnology is a frontal crossing subject developed gradually since late 1980's. Nanostructured materials have been used in the area of defence, military, space, and aviation. It is well known that solid propellants are the fuels of the solid rocket motors. If nano-sized materials are added to the solid propellants, the performance of propellants dramatically enhances. For fabricating the higher burning rate and the higher energy propellants, nano-sized materials have tremendous latent energy. The new generation of missiles and propellants for space flight application requires higher performance, so this provides widespread perspectives for the application of nanostructured materials. Thus, the study of nano-sized materials as a component of propellants is considered important.

In 1994, Daizo Fukuma[1] used the 1.5 μm superfine ammonium perchlorate (AP), 100 nm superfine *Al* and silver wire into the hydroxy-terminated polybutadiene HTPB-based propellants, and 150 mm/s super-burning rate was achieved. American company MACH I produced a kind of nanocat superfine iron oxide (SFIO) with particle size of 3 nm. The burning rate of HTPB-based propellants increases from 22.10 mm/s to 27.69 mm/s and the pressure exponent decreases from 0.5 to 0.46 with a mass addition of 10 per cent SFIO. Moreover, the safety and the stabilised performance of SFIO are far better than conventional Fe_2O_3, catocene and other ferrocene derivative[2].

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In 1990's, American Argnide Corporation produced alex by electro-explosion of metal wire. Ivanov and Tepperv[3] had found that propellants containing alex powder exhibit burning rates 5 to 20-time greater than the same propellant formulations containing regular *Al* powder. At the same time, they had found that propellants containing 40 per cent or more regular *Al* powder generally cannot burn successfully, but propellants containing from 42 to 75 weight per cent of alex were shown to burn at very fast rates.

Chiaverini,[4,5] *et al*. showed that the mass burning rate of HTPB-based propellants can be increased by 70 per cent by the addition of 20 per cent alex powder. However, for the same weight per cent of conventional *Al* powder, the increase of mass burning rate is far less than 70 per cent. Mench[6], *et al*. studied the effects of alex on the burning rate temperature sensitivity, and the pressure exponent of propellants by replacing 30 μm conventional *Al* powder with 180 nm alex powder. It had been found that the pressure exponent and the burning rate temperature sensitivity increase with initial temperature increasing. Nanopowders added to propellants not only show beneficial effects but also show adverse effects, and therefore, their merits and demerits have been considered in details.

Although a lot of work has been carried out recently with *n-Al* powder increasing burning rate of propellants, it is not clear why the increments of burning rate are different at different pressures. The present study aims to examine the effect of replacement of conventional *Al* powder with coated *n-Al* powder of different contents in HTPB-based propellants on combustion performance and to investigate and compare the combustion behaviour of propellants containing coated *n-Al* powder and analyse the possible combustion mechanism.

2 EXPERIMENTAL

2.1 Propellant Formulations

To study the effect of *Al* size particles on the combustion performance, the propellant formulations investigated include coated nano-sized *Al* powder (*n-Al*), in addition to micron-sized *Al* powder (μm-*Al*). In particular, two grades of powder: *n-Al* (coated aluminum nanopowder, 20~50 nm) and *g-Al* (conventional aluminum powder, 31~37 μm) were considered.

Typically, the composite propellants consist of 14.5 per cent mixture of HTPB+TDI (toluene diisocyanate)+DIOS (diisooctyl sebacate), 65.5 per cent AP and 20 per cent *Al* powder. Each propellant is based on a trinal AP size distribution. The formulations of propellants studied have been reported in Table 1.

Table 1. Propellant compositions studied

Sample	Propellant compositions Wt (%)			
	HTPB+TDI +DIOS	AP	*g-Al*	*n-Al* (coated)
N-1	14.5	65.5	20	0
N-2	14.5	65.5	17	3
N-3	14.5	65.5	14	6
N-4	14.5	65.5	11	9

2.2 Burning Rate and Pressure Exponent Measurement

Propellant samples were burned in nitrogen atmosphere at 20 °C. The burning rate was measured in the range 3~7 MPa using a strand burner, and the pressure exponent (n) defined as

$$n = \ln(\text{burning rate})/\ln(\text{pressure})$$

2.3 Flame Images of Propellants

The experimental setup used for the flame image of a propellant consists of a combustion chamber fitted with two quartz side windows. Propellant samples of size 2×4×10 mm were ignited by a hot nickel-chrome wire. The combustion flame was obtained by single-short distance photograph camera. Propellants were allowed to burn in nitrogen atmosphere at pressure ranging from 0.49 MPa to 4.9 MPa

2.4 SEM and XFS Measurement

To study the effects of *n-Al* powder and *g-Al* powder on the quenched surface, the experiments were carried out only for N-1 and N-4 propellants. The quenched surfaces of propellants were acquired by slack water. The quenched surface images were observed by SEM.

XFS (x-ray fluorescence) analysis was carried out to measure the quenched surface composition and to quantify the atomic concentration on the quenched surface.

2.5 Oxygen-bomb Combustion Heat, Ignition Temperature and Recovery Ratio of Residues Measurement

A comparison of the chemical latent energy of propellants N-1 and N-4 was performed by oxygen-bomb combustion experiment. The oxygen-bomb combustion heat was measured by GR-3500 oxygen-bomb combustion calorimeter at nitrogen pressure of 1.96 MPa using benzoic acid as the standard substance.

The ignition temperature measurement was carried out in a tube furnace. Propellants N-1and N-4 with the same volume were heated using suitable heating voltage at 1.0 MPa atmospheric pressure, respectively. The ignition temperature was monitored using a thermocouple, placed on the top of the sample.

The combustion residues obtained from the oxygen-bomb combustion experiments were collected by ethanol and were treated, dried, and weighted to determine recovery ratio of residues quantitatively.

3 RESULTS AND DISCUSSION

3.1 Characteristics of Burning Rate and Pressure Exponent

The measured burning rate was shown as a function of pressure at the initial propellant temperature 20 °C. The burning rate increased linearly as the pressure was increased in a ln(pressure) versus ln(burning rate) for all samples tested, as shown in Fig. 1. It is clearly seen from Fig. 1 that *n-Al* powder enhances the burning rates of HTPB/AP-based propellants considerably. It is conspicuously seen that the burning rates increase with increasing *n-Al* powder contents at various pressures, especially for the propellant sample N-4. The effect of *n-Al* powder is evident in HTPB/AP-based propellants. *n-Al* powder not only enhances the burning rate, but also leads to a decrease in the pressure exponent.

It is well known that the burning rate is determined by the heat transferred back from the gas phase to the burning surface and the heat generated at the burning surface. Due to the decrease of the size of *n-Al* powder and increase of the reaction's surface area, these are directly ignited on the burning surface of the propellants, and burned completely on or near the burning surface[7]. This enhances the heat feedback to the unburned solid fuel. In addition, due to the huge surface area of *n-Al* powder, there are a lot of active sites on the surface. Thus, these can adsorb the gaseous reactive molecules from decomposition of AP, and catalyse their reactions. At the same time, the average distance between *n-Al* particle and oxidiser particle in the propellant is dramatically reduced as compared to the propellant containing *only g-Al* powder. So *n-Al* powder has been shown to be a very effective burning rate accelerator for solid propellants. When the pressure increases, the diffusion distance decreases, and the location of combustion flame is brought closer to the burning surface which leads to accelerate reaction and increase the heat transferred back from the gas phase to the burning surface, so that the burning rates increase.

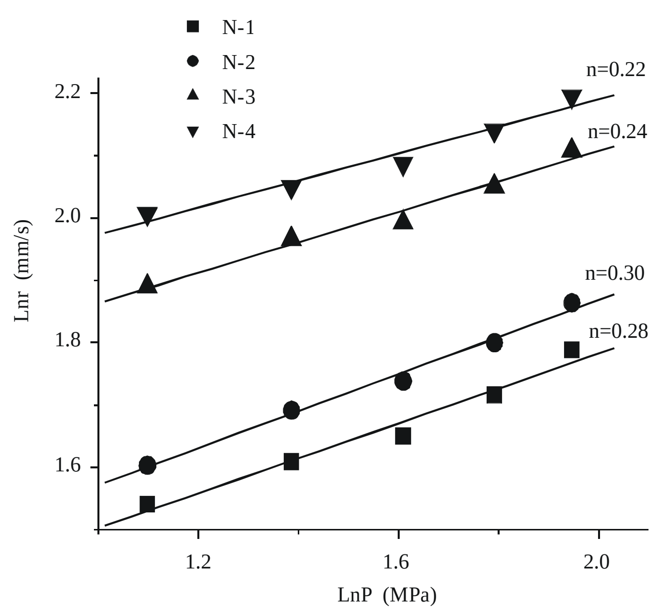


Figure 1. Burning rate and pressure exponent characteristics for propellants N-0~N-4.

To clearly understand the effect of *n-Al* powder on the burning rates at various pressures, the relationship between pressure and the increasing percentage of burning rate compared to N-1 propellant is shown in Fig. 2. It is found that the increment of burning rate is a function of pressure and *n-Al* powder content. With increasing *n-Al* powder content, increments of burning rate tend to increase sharply at low pressure, whereas at high pressure, there are relative small increases in increments of burning rate. To explain these phenomena, it should be taken into account that at low pressure, the diffusion phenomenon is rapid and the burning rate is controlled by the chemical reaction rate[8]. In these propellants, combustion performance of *n-Al* powder and *g-Al* powder plays a crucial role for burning rate.

The burning behaviour of *g-Al* powder added to solid propellants is different from that of *n-Al* powder. Most of the *g-Al* powders do not vapourise on the burning surface, but agglomerate into large particles. The energy for igniting the large particles on the burning surface comes from the diffusion flame of AP and the binder. The construction of the diffusion flame of a single particle surface of AP is related to pressure[9]. The lower the pressure; the more difficult is the ignition, so the conglomeration of *Al* is severe.

So, it can be concluded that the ignition performance of *g-Al* powder depends intensively on pressure.

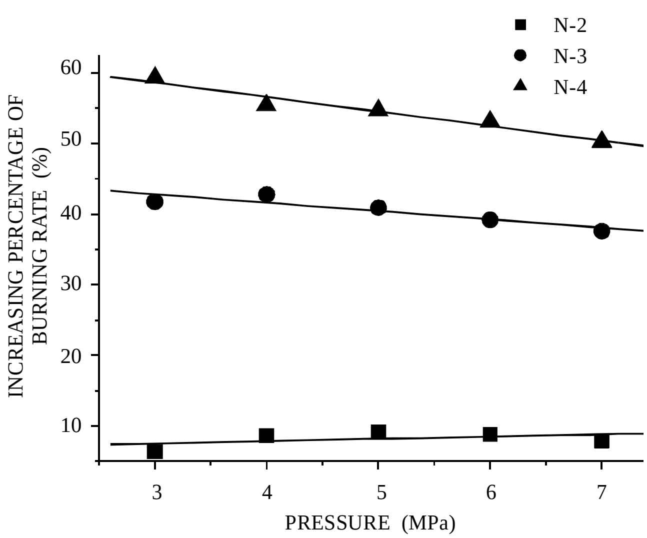


Figure 2. Increasing percentage of burning rate for propellants N-2~N-4 compared with propellant N-1.

The energy of igniting *n-Al* powder is low due to the small particle size. The energy coming from the diffusion flame of AP and binder is enough to ignite the *n-Al* powder. Due to the low ignition threshold, the *n-Al* powders expand lower-pressure ignition limit, and improve the ignition performance at low pressure. The above-mentioned facts indicate that the increments of burning rate of propellants containing *n-Al* powder at low pressures are large.

When the pressure increases, the ignition performance of *g-Al* powder is improved and the diameters of *Al* agglomerates decrease, so the combustion effect gradually improves. On the other hand, with the pressure increasing, recessional rate of the burning surface is accelerated. Temperature gradient near the burning surface becomes large and conductive heat feedback plays an important role. The heat conduction of large-sized particles is better than those of small-sized particles. So, heat conduction of *g-Al* powder is more than that of *n-Al* powder. So, it can be demonstrated that the increments of burning rate of propellants containing *n-Al* powder gradually decrease with increase in the pressure. Of course, due to increments of burning rate at low pressure gradually larger than those at high pressure with increasing *n-Al* powder contents, the pressure exponents of HTPB/AP-based propellants tend to decrease.

3.2 Characteristics of Combustion Flame

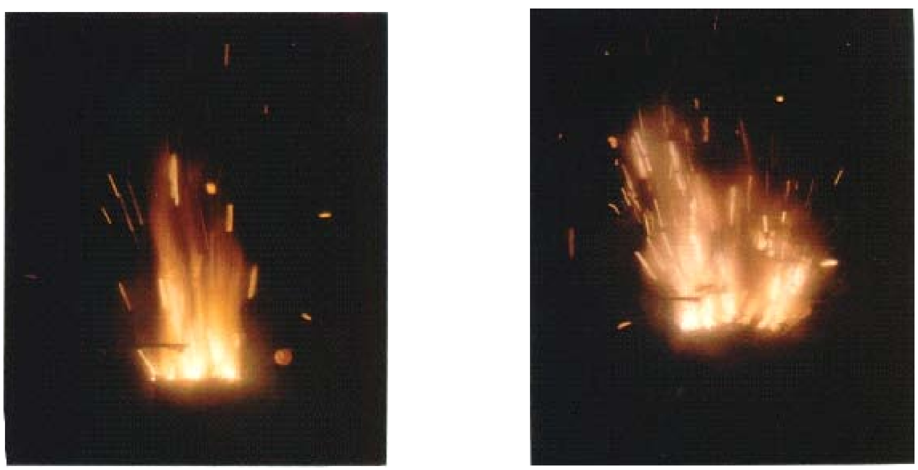
Figure 3 shows flame images of N-1 propellant containing *g-Al* powder at two pressures. The multiple bright streaks represent the trajectories of burning *Al* particles during the recording interval of 1/1000 s. It can be seen clearly that the *Al* particles burn far from the propellant surface, reducing heat feedback from the metal-oxidiser combustion to the unburnt propellant zone. This leads to lower combustion efficiency and higher two-phase flow losses.

Figure 4 shows flame images of N-4 propellant with addition of *n-Al* powder at two pressures. It can be noted that the bright streaks are very few in the flame. In Fig. 4 (b), flame is especially bright near the burning surface. On comparison of these pictures, it is evident that *g-Al* particles burn far from the burning surface, whereas *n-Al* particles directly ignite on the burning surface, and burn on or near the burning surface. This attributes to the large surface area and the short ignition delay time of *n-Al* powder.

The influence of pressure on gas-phase combustion is also depicted in Figs 3 and 4, respectively. It is seen that increase in the pressure causes a violent combustion on comparison of Figs 3 and 4. The corresponding change in combustion phenomenon is evident. In the case of propellant N-1 sample, the number of bright streaks and the flame luminance increase with increase in pressure. Furthermore, the bright streaks turn smaller. But for propellant N-4 sample, the bright streaks appear not to be observed at 0.49 MPa. When the pressure increases to 4.9 MPa, the area of flame becomes large and uniform. The recorded particles burning trajectories show pronounced jetting phenomena. These could be caused by decomposition gas from the molten liquid and ejected through the oxide lobe. This phenomenon appears not to be obvious in N-1 propellant at 4.9 MPa.

3.3 Analysis of Quenched Surface

In Figs 5 (a) and 5 (b), the surfaces of unburned N-1 and N-4 propellants were covered with binders. Oxidiser and metal fuel were connected by binder. Figure 6 (a) shows the surface structure of the burned N-1 propellant recovered. The surface was very coarse and there were many spherical particles. The diameters of the particles were about 22~74 μm.



(a) (b)

Figure 3. Flame images of N-1 propellant at (a) 0.49 MPa and (b) 4.9 MPa.

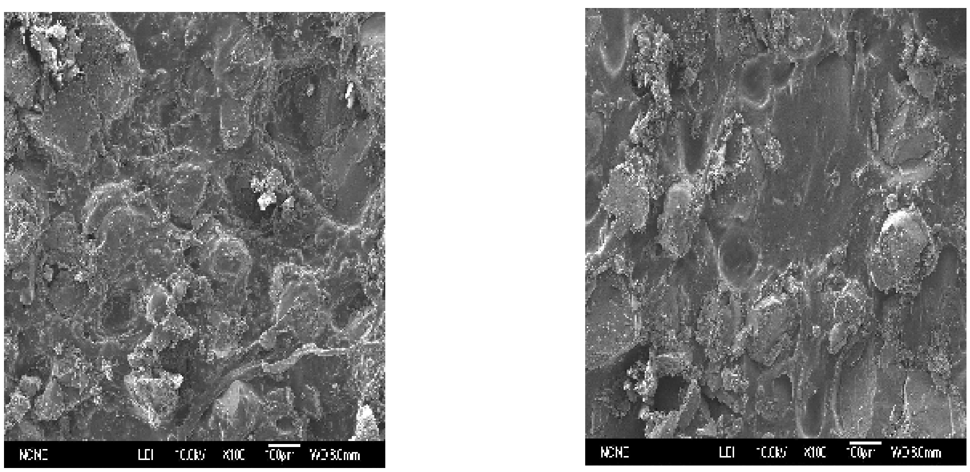
(a) (b)

Figure 4. Flame images of N-4 propellant at (a) 0.49 MPa and (b) 4.9 MPa.

It was analysed that the spherical particles were the agglomerated *Al*. The surface structure of the burned N-4 propellant recovered is shown in Fig. 6 (b). It can be seen that the spherical particles were few on the surface. This can be proved by XFS analysis. The XFS experiments showed that the *Al* contents of quenched surface in both N-1 and N-4 propellants were 0.8082 per cent and 0.4779 per cent, respectively. It can be explained that conglomeration degree of the coated *n-Al* powder is very low. The quenched surface of N-4 propellant is relatively smoother than that of N-1 propellant. This phenomenon was also observed by Mench,[6] *et al*. This is attributed to the same receding rate of both *n-Al* powder and the binder. The phenomenon further shows that *n-Al* powder ignites on the burning surface and tends to burn on the burning surface of propellant. However, as discussed in previous sections, *g-Al* powders are related to the processes of accumulation, agglomeration, ignition, departure of aluminum from the burning surface of the propellant, and its entry into the region of flame to burn. Due to the large *Al* agglomerates tending to burn far from the burning surface, these lead to the quenched surface quite coarse.

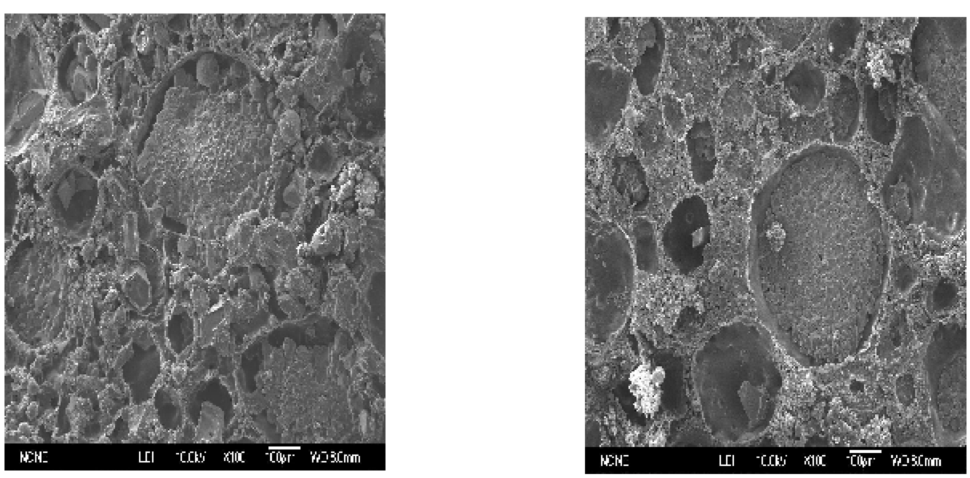
3.4 Analysis of Ignition Temperature,Oxygen bomb Combustion Heat and Recovery Ratio of Residues

The average ignition temperature of N-1 propellant is 309.5 °C, but for N-4 propellant it is 286.5 °C.



(a) (b)

Figure 5. SEM of (a) N-1 propellant surface before combustion, and (b) N-4 propellant surface before combustion.



(a) (b)

Figure 6. SEM of the burning surface of (a) N-1 propellant quenched at 1 MPa, and (b) N-4 propellant quenched at 1MPa.

Their relatively standard deviations are 3.63 per cent and 5.94 per cent, respectively. It is evident that the addition of *n-Al* powders to the propellant makes the ignition temperature decrease. This illustrates that propellant containing *n-Al* powder is easier to ignite than propellant containing *g-Al* powder only. The ignition threshold of *Al* powder increases many orders of magnitude with the size of particle increasing[10]. At the same ignition energy-flux density situation, it is considered that the ignition threshold[3] is directly proportional to d_0. The ignition threshold of *n-Al* powder is 10^{-9} times as that of *g-Al* powder. It can be concluded that the low ignition threshold of *n-Al* powder leads to decrease in the ignition temperature of the propellant.

As shown in Table 2, the oxygen-bomb combustion heats of N-1 and N-4 propellants are 9555 J/g and 8130 J/g, respectively. The value of oxygen-bomb combustion heat of propellant containing *n-Al* powder is lower than that of propellant containing *g-Al* powder only. It is believed that the coated *n-Al* powders contain some proportions of coating material and which lead to the decrease of the real content of *n-Al* powder, so oxygen-bomb combustion heat decreases.

The recovery ratios of residues of N-1 and N-4 propellants are 15.20 per cent and 12.11 per cent, respectively. It is reported[11] that the amount of residues is the same for both HTPB/AP and HTPB decomposition, so the decomposition residues are not relative to the content of AP. It is well known that the decomposition product of AP is gas. Of course, the amount of residue depends on HTPB. The amount of residue also depends on the activity of Al in the HTPB/AP/*Al* propellants. It is reported[6] that AP-based propellants containing alex elementally have no residues after combustion, but propellants containing *g-Al* powder have a large number of conglomeration particles and surface residues, which is in agreement with the experimental results obtained.

4. CONCLUSIONS

- In this study, the burning rates of propellants containing coated *n-Al* powder increase as the *n-Al* content increases.
- The pressure exponents tend to decrease. The better ignition performance and directly igniting and combustion on the burning surface of *n-Al* powder, and the improvement of combustion and ignition performance of *g-Al* at high pressure lead to the decrease of the pressure exponent.
- The better ignition performance of *n-Al* powder also makes the ignition temperature of propellant decrease. At the same time, characteristics of combustion flame and quenched surface further support that *n-Al* particle directly ignites on the burning surface and tend to burn in a single particle. Due to these, *Al* trajectories are very few in combustion flame of propellant and combustion is violent near the burning surface. Aluminium content of the quenched surface dramatically reduces, and the quenched surface of propellant containing *n-Al* powder is relatively smoother than that of propellant containing *g-Al* powder only.
- Propellants with *n-Al* powders increase combustion efficiency and decrease recovery ratio of residues.

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Table 2. Data on oxygen-bomb combustion heat, ignition temperature, and recovery ratio of residues

Sample	Oxygen-bomb combustion heat		Ignition temperature		Recovery ratio of residues (%)
	Average value (J/g)	RSD (%)	Average value (°C)	RSD (%)	
N-1	9555	3.63	309.5	0.47	15.20
N-4	8130	5.94	286.5	0.99	12.11

(RSD= relatively standard deviation)

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