研究論文

The thermal reaction and combustion of titanium hydride-boron- potassium perchlorate mixtures

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The titanium hydride-boron-potassium perchlorate mixture has been used as an igniting agent in some pyrotechnic devices. However, there have been few reports about its thermal reactivity and combustion mechanism, especially the effect of the addition of boron on its reactivity. In this report, thermal analysis, elementary analysis, combustion calorimetry and the burning rate measurement were carried out in order to clarify the mechanisms of its thermal reaction and the combustion reaction. The results obtained are as follows.

Though the mixture of titanium hydride with potassium perchlorate had a low thermal reactivity under normal pressure, its reactivity was enlarged if external pressure was applied or boron was added. Its burning rate increased with increasing titanium hydride content up to equiweight mixtures. The burning characteristics were significantly affected by the surrounding pressure, but the addition of boron caused a decrease in its pressure dependence.

1. Introduction

Titanium hydride- potassium perchlorate (TiH_2-$KClO_4$) pyrotechnic compositions are well-known as chemicals in actuators and igniters. These compositions have the advantages of relatively good ignitability, low sensitivity to an electrostatic discharge initiation compared to the one containing titanium and producing high heat content condensed species for combustion. Many studies, whether theoretical or experimental, have been reported on these pyrotechnic compositions[References 1 through 5].

Titanium hydride- boron- potassium perchlorate (TiH_2- B- $KClO_4$) pyrotechnic compositions are also utilized in actuators and igniters as well as the TiH_2-$KClO_4$ binary mixtures. However, there are few studies, which deal with these ternary mixtures. In this study, thermal analysis, elementary analysis, combustion calorimetry and burning rate measurements were carried out in order to clarify the mechanisms of the thermal reaction and the combustion reaction of the titanium hydride- boron- potassium perchlorate mixtures.

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2. Experimental

2.1 Materials

The sample titanium hydride obtained from DEGUSSA JAPAN CO., Ltd., contained 3.84wt.% hydrogen (TiH_x, $x = 1.92$) and had an average particle diameter of 21.2 μ m. Boron from DEGUSSA JAPAN CO., Ltd., was a 90/92% grade having an average particle size under 1 μ m. Potassium perchlorate was prepared by pulverizing and sieving a reagent grade material, and its average particle size was about 200 μ m. Binary mixtures of TiH_2- $KClO_4$ and B- $KClO_4$, and ternary mixtures TiH_2- B- $KClO_4$ were prepared using an ordinary ball-mill mixer after weighing the ingredients according to Eqs.(1) and (2).

$$4TiH_2 + 3KClO_4 \rightarrow 4TiO_2 + 3KCl + 4H_2O \quad (1)$$

$$8B + 3KClO_4 \rightarrow 4B_2O_3 + 3KCl \quad (2)$$

2.2 Analysis

Thermal analysis was performed using a RIGAKU DTA-TG simultaneous analyzer and high pressure

DTA, in which the sample weight was 5mg and the heating rate was 20℃/min under an argon gas flow.

Crystallinity was examined using an ordinary X-ray powder diffractometer. Hydrogen content was determined by ordinary elemental analysis.

2.3 Combustion experiment

A Shimadzu Autocalculating Bomb Calorimeter was used to measure the heat of combustion for a 1g sample in an argon gas atmosphere.

The binary and ternary mixtures were burned in an aluminum cylindrical tube, and the time for 10 mm burning was recorded using a digital memory with optical fiber signals. The mixtures were loaded nine times, and the bulk density was 65% to 80% of the theoretical maximum density.

3. Results and discussion

3.1 Titanium hydride/potassium perchlorate binary mixtures

Figure 1 shows the results of the thermal analysis of titanium hydride in air. DTA and TG curves in air shows a gradual and step-wise oxidation which started at about 600℃. This oxidation ranged up to above 850℃, and the final weight increase of about 60% corresponded well to titanium (IV) oxide formation. Other experiments under isothermal oxidation showed a large oxidation rate at its initial stage and a gradual decrease in the course of the oxidation, indicating that the diffusion-controlled processes exist.

Hydrogen in titanium hydride is strongly bonded and its liberation from titanium hydride commenced at the temperature of 400℃. This dissociation occurred ranging from 400 to 900℃ (Fig. 2). However, the reaction rate is the same in both air and argon.

As stated above, titanium hydride cannot be so easily oxidized by oxygen in air. Similarly, in argon, titanium hydride was gradually oxidized by potassium perchlorate at the temperature range of about 470 to 630℃ as shown in Fig. 5.

Generally, when a powder is pressed into a circular cylinder, the linear burning rate depends upon its diameter because of the conduction of heat to the atmosphere. However, preliminary experiments showed that the linear burning rate of titanium hydride-potassium perchlorate was independent of tube diameter above 4mm. Moreover, the linear burning rate also depends upon the bulk density. In the case of low bulk density, combustion is affected by the conduction of heat and hot gas flow through a vacancy. The sample which had a bulk density of above 65% real density showed the same mass burning rate. This tells us that there was no effect of hot gas flow on combustion above this loading density.

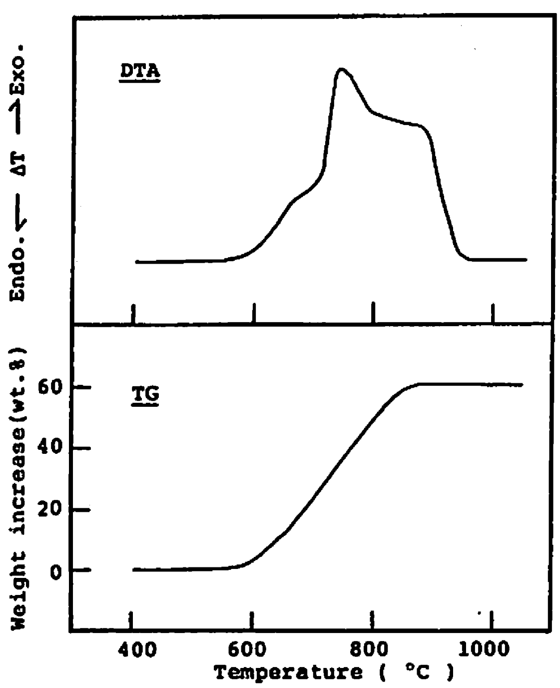

Fig. 1 Thermal analysis of TiH_2 in air

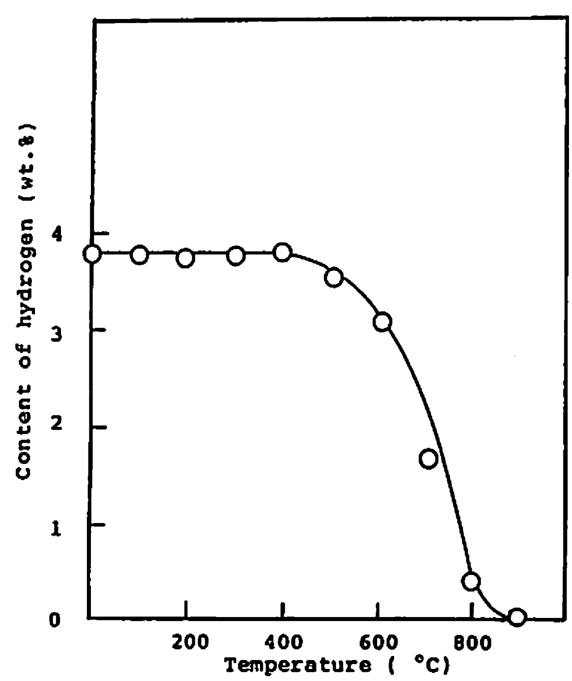

Fig. 2 Hydrogen content in titanium hydride on heating

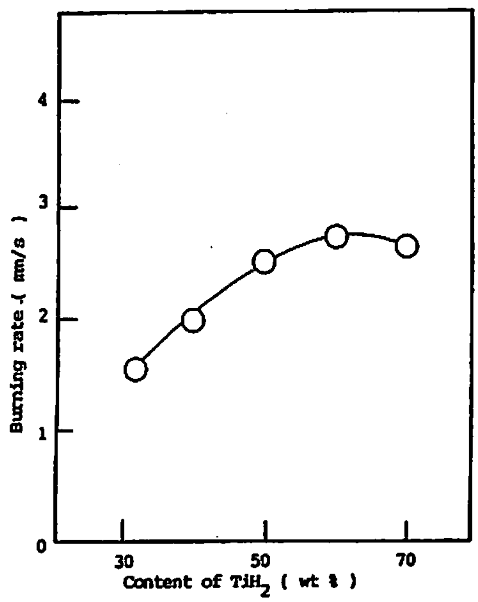

Fig. 3 Burning rate of TiH_2-$KClO_4$ mixtures

Figure 3 shows the result of burning rate measurements for the titanium hydride- potassium perchlorate binary mixtures. The maximum value of the linear burning rates is obtained with the composition of $TiH_2/KClO_4 = 65/45$ (by wt.) which corresponds to a fuel- rich condition according to Eq.(1).

Combustion calorimetry shows that the heat of combustion has a maximum value at $TiH_2/KClO_4 = 40/60$ (by wt.) (Fig.4). These results tell us that the condensed phase reaction is Eq.(3) rather than Eq.(1).

$$2TiH_2 + KClO_4 \rightarrow 2TiO_2 + KCl + 2H_2 \quad (3)$$

Figure 5 shows the results of thermal analysis of the titanium hydride- potassium perchlorate binary mixtures under various pressures. As above-mentioned, the TiH_2- $KClO_4$ mixture reacts not so vigorously under a normal pressure, but shows a intense exothermic reaction under pressurized conditions. Figure 6 shows the pressure dependence of the linear burning rate of titanium hydride - potassium perchlorate binary mixtures. The linear burning rate increases with increasing pressure and gives a large pressure index n in the following Vieille's equation,

$$V = a P^n \quad (4)$$

where V is the burning rate, P the pressure, n the pressure index and a the constant.

3.2 Titanium hydride/boron/potassium perchlorate ternary mixtures

Figure 7 shows the results of thermal analysis of the TiH_2- $KClO_4$, B- $KClO_4$ and TiH_2- B- $KClO_4$ mixtures. As above-mentioned, the TiH_2- $KClO_4$ mixture reacts not so vigorously under normal pressure, but

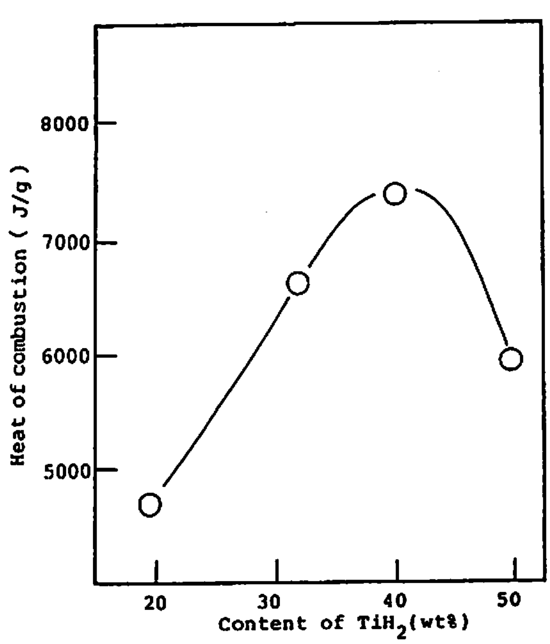

Fig. 4 Heat of combustion of TiH_2-$KClO_4$ mixtures

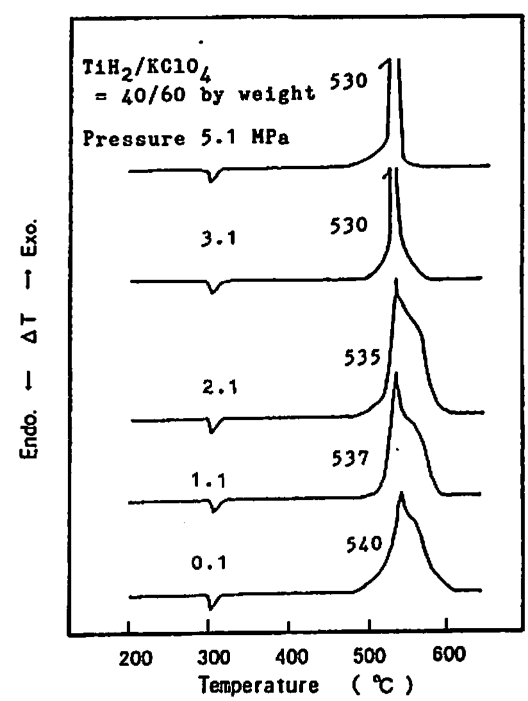

Fig. 5 Thermal analysis of TiH_2-$KClO_4$ under pressurized conditions

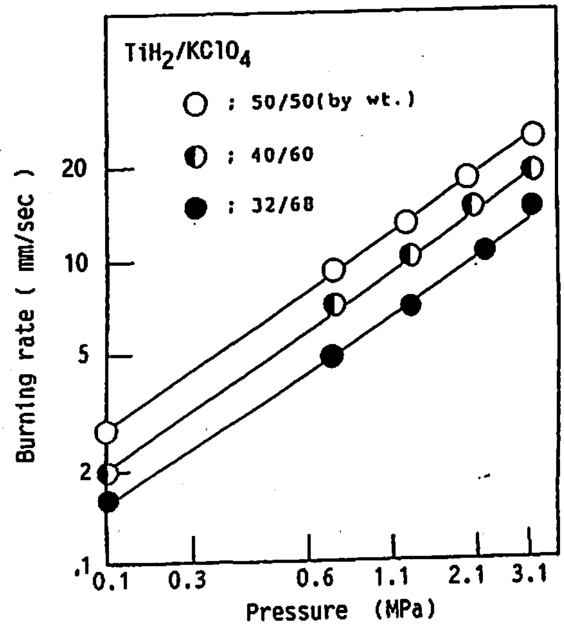

Fig. 6 Lineaer burning rate of TiH_2-$KClO_4$ under pressurized conditions

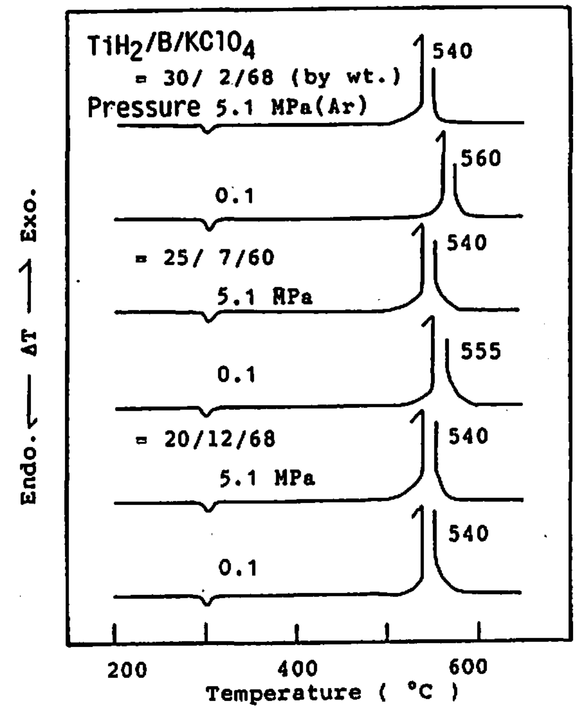

Fig. 8 Effect of pressure on the thermal analysis of TiH_2-B-$KClO_4$ mixtures

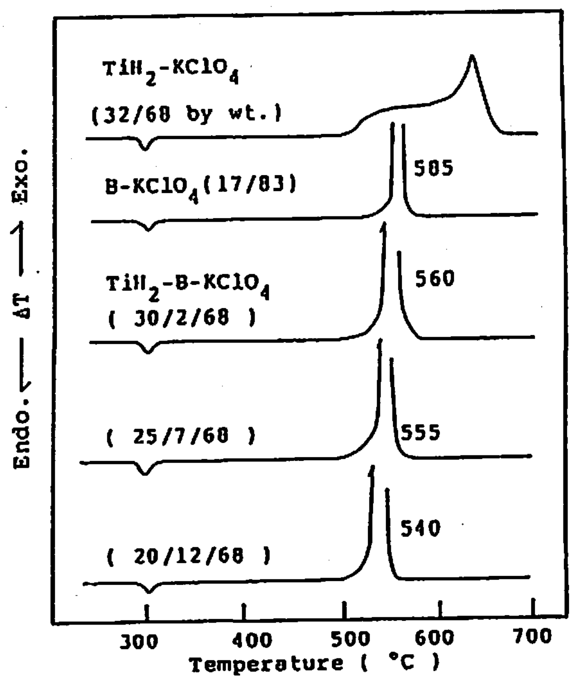

Fig. 7 Thermal analysis of TiH_2-$KClO_4$, B-$KClO_4$ and TiH_2-B-$KClO_4$ mixtures

the B-$KClO_4$ mixture shows a intense exothermic reaction at 585℃ even under normal pressure. The exothermic reaction of the TiH_2- B- $KClO_4$ mixtures occurred more vigorously at a lower temperature than that of the B- $KClO_4$ mixture. Moreover, the reaction becomes more intense with increasing boron content.

Figure 8 shows the results of thermal analysis of the TiH_2- B- $KClO_4$ mixtures under normal and pressurized conditions. Under atmospheric circumstances, the reaction temperature becomes lower with increasing boron content. Increase in pressure accelerates the reaction and the temperature at which an intense reaction occurs becomes lower if an external pressure 5.0MPa (gauge) is adopted. However, the larger the boron content, the smaller is the difference in this reactivity, and the sample which contains 12wt.% boron undergoes an intense exothermic reaction at the same temperature of 540℃, though under different external pressure. This is ascribed to a solid state reaction of the mixture of potassium perchlorate and boron, because a solid state reaction which proceeds between the surface of two solids contains none of the gas phase reaction which is affected by atmospheric pressure.

Figure 9 shows the result of the burning rate measurements for the TiH_2- B- $KClO_4$ mixtures, in which one part of titanium hydride is replaced by boron, keeping the potassium perchlorate content constant. Figure 10 shows one example of the effect of boron content on the linear burning rate of the TiH_2- B-

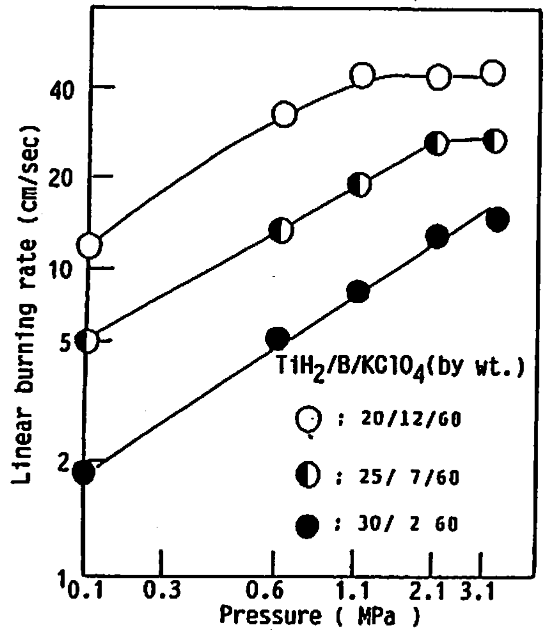

Fig. 9 Linear burning rate of TiH_2-B-$KClO_4$ mixtures under pressurized conditions

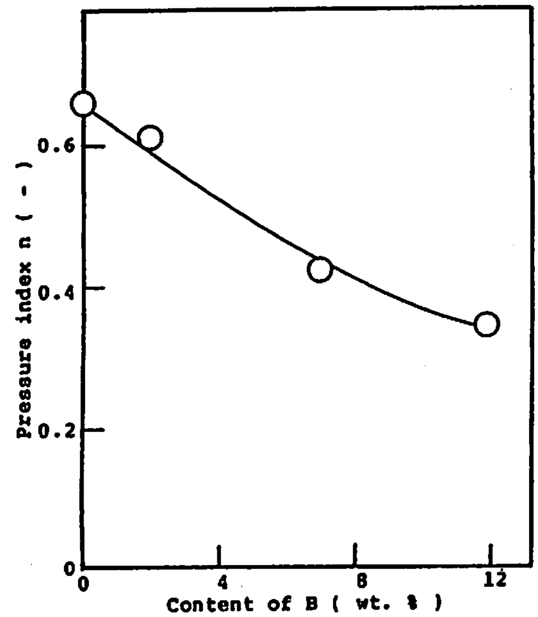

Fig. 11 Pressure index for the TiH_2-B-$KClO_4$ mixtures

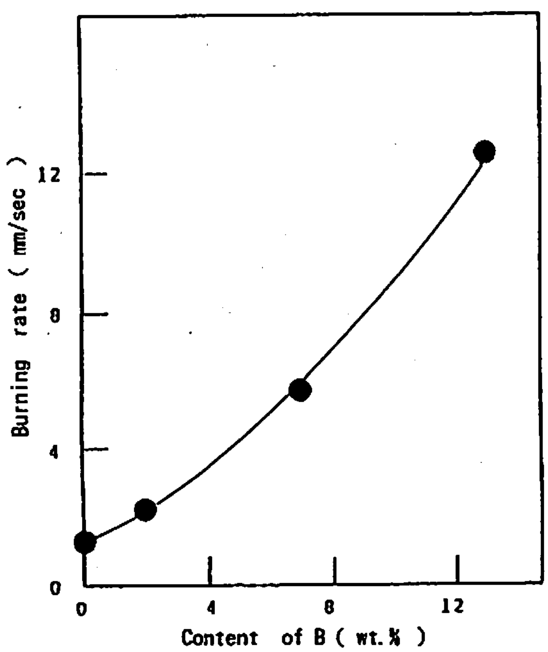

Fig. 10 Effect of boron content on burning rate of TiH_2-B-$KClO_4$ mixtures

$KClO_4$ ternary mixtures (under normal pressure). The linear burning rate increases with an increasing boron content. That is, addition of boron to the TiH_2-$KClO_4$ mixtures increases the combustibility as well as the thermal reactivity.

Figure 11 shows the pressure index of the combustions of TiH_2- B- $KClO_4$ ternary mixture. As previously mentioned, the TiH_2- $KClO_4$ binary mixtures give a large pressure index. However, if boron is added to this binary mixture, the pressure index becomes small with increasing boron content. This is ascribed to a combustion characteristics of potassium perchlorate - boron mixture, which shows plateau or minus pressure index under pressurized conditions (Fig. 12).

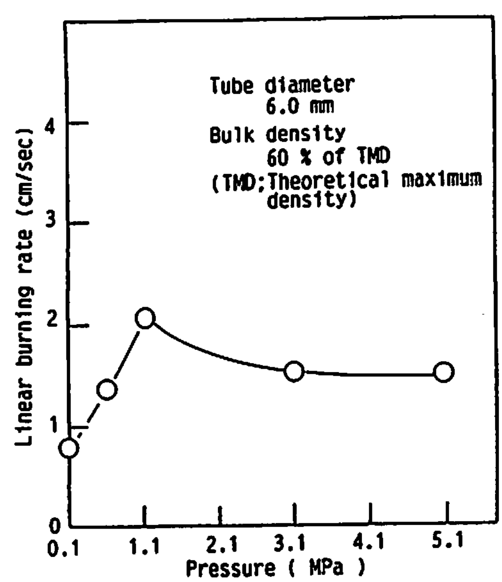

Fig. 12 Linear burning rate of B-$KClO_4$ mixtures under pressurized conditions

4. Conclusion

In this report, thermal reactivity and combustibility of the $TiH_2/KClO_4$ mixtures were studied, when boron was added to the $TiH_2/KClO_4$ mixtures in substitution for part of the TiH_2. Addition of boron caused the thermal reaction to become easier, especially under pressurized conditions. Burning characteristics were also improved by boron addition in accordance with its amount, and the pressure effect decreased with increasing boron contentt.

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水素化チタンーホウ素ー過塩素酸カリウム混合物の反応性

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水素化チタンーホウ素ー過塩素酸カリウム混合物の熱および燃焼反応性を熱分析、燃焼熱測定、燃焼速度測定等を行い検討し，以下の結果が得られた。水素化チタンー過塩素酸カリウム混合物の熱および燃焼反応性は常圧下では激しくないが，加圧下あるいはホウ素の添加で激しくなる。また，ホウ素の添加で水素化チタンー過塩素酸カリウム混合物の反応の圧力依存性は小さくなる。

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