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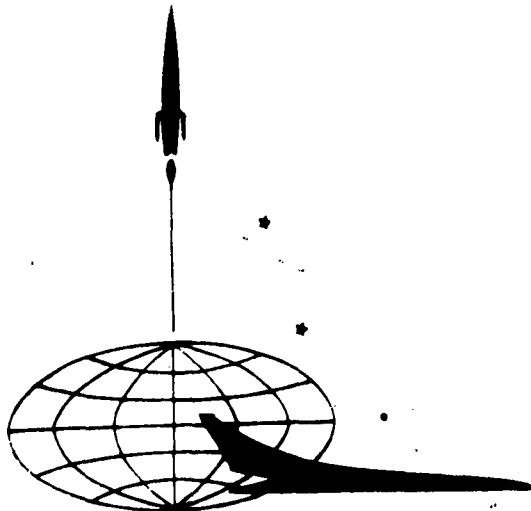
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INVESTIGATION OF THE SURFACE
STRUCTURE OF BURNING MODEL
MIXTURES OF SOLID FUELS

Translation

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INVESTIGATION OF THE SURFACE STRUCTURE OF BURNING MODEL
MIXTURES OF SOLID FUELS

Translation

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FOREWORD

This translation was prepared in response to ATD Work Assignment No. 70. The article was originally published as follows:

Pokhil, P. F., and L. D. Romodanova. Issledovaniye struktury poverkhnosti goreniya model'nykh smesevykh tverdykh topliv. Zhurnal fizicheskoy khimii, v. 39, no. 2, 1965, 294-299.

INVESTIGATION OF THE SURFACE STRUCTURE OF BURNING MODEL MIXTURES OF SOLID FUELS

To understand the burning mechanism of composite solid propellants, we investigated the structure formed during the burning of stoichiometric model mixtures containing the following oxidants: ammonium perchlorate, which does not melt, but is self-inflammable at $360-380^{\circ}\text{C}$; potassium perchlorate, which melts with decomposition at 610°C ; and sodium perchlorate, which melts at 482°C and decomposes at 505°C .

The following fuels having different physicochemical properties were selected: graphite, which does not melt and does not decompose; tungsten, which melts at $\sim 3200^{\circ}\text{C}$; naphthalene, which melts and sublimates at 80°C ; starch, which melts and decomposes at 260°C ; succinic and malonic acids (succinic acid melts at 185°C and decomposes at 235°C ; malonic acid melts at 135.6°C).

Experimental Part

The investigation of the structure of the surface formed during the burning of these mixtures was carried out with the aid of a microscope (magnification, $10-80$ times). Surfaces formed by burning the mixtures in vacuum, in air, and under pressures were investigated. The mixtures were pressure-molded to a maximum density; the diameter of the charge was 5 mm .

None of the compositions studied, except the composition KClO_4 +tungsten, burned steadily in vacuum (pressure $p \cdot 10^{-2}\text{ mm Hg}$) and at room temperature; combustion ceases after the hot spiral is removed.

At atmospheric pressure the mixtures were extinguished with compressed air. The mixtures burning under pressure were extinguished by a rapid pressure drop in the bomb. The experiments, in vacuum and under pressure, were carried out according to a method described previously [1, 2].

Mixtures with NH_4ClO_4 as the oxidant. Investigation of the structure of the surface formed during the burning of stoichiometric model mixtures with NH_4ClO_4 as the oxidant (having a particle size from 4μ to 30μ) and malonic and succinic acids and starch as the combustibles, showed that in a vacuum ($p \cdot 10^{-2}\text{ mm Hg}$) under the action of an hot spiral, while the oxidant crystals remain on the surface and therefore protrude over the surface. The depressions between the protruding oxidant crystals contain the fuel, as is shown in Fig. 1a. In addition to separate crystals, crystal aggregates $\sim 0.4\text{ mm}$ in size were observed on the surface.

The larger the crystals the more they protrude over the burning surface. The protruding crystals are partially covered with combustion products (e.g., carbonized starch particles).

A similar picture was observed during burning in air. As the pressure increases, the oxidant crystals which are protruding over the surface

decrease in size, and at a pressure exceeding $p \sim 30$ atm abs., depressions are formed on the places where the crystals were located, as shown in Fig. 1a.

The phenomenon is explained as follows. It is known from previous studies [3] that the pressure below which ammonium perchlorate does not burn steadily at room temperature is equal to 20-30 atm abs. Therefore, during the burning of mixtures at low pressures, when ammonium perchlorate itself does not burn and its decomposition temperature is higher than that of the fuel, the crystals of NH_4ClO_4 are observed on the surface.

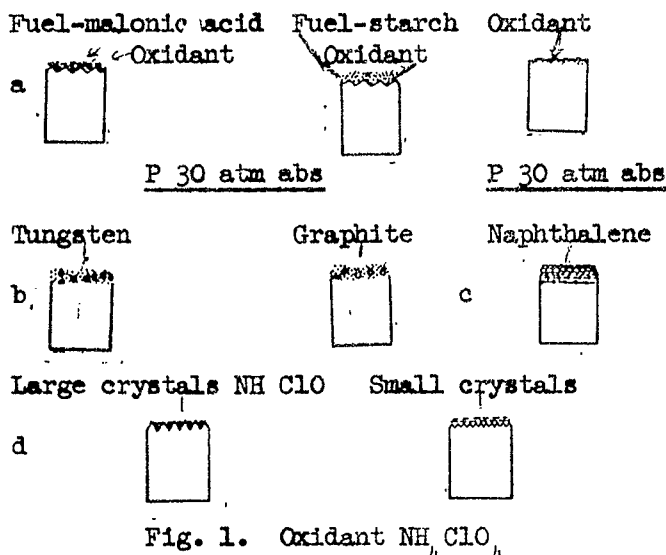


Fig. 1. Oxidant NH_4ClO_4

At pressure higher than the limiting value, when ammonium perchlorate itself is capable of steady combustion (without the binder), it disappears faster than the binder, and craters therefore appear on the surface (in place of the NH_4ClO_4) crystals.

On the extinguished surface of the NH_4ClO_4 +naphthalene mixtures, as shown in Fig. 1c, the oxidant is accumulated on the surface. The accumulation of the oxidant on the surface due to

the big difference in the melting and sublimation temperatures of naphthalene and the temperature of the thermal decomposition of NH_4ClO_4 . Therefore, during the burning of the mixture, when the surface temperature is $\sim 450^\circ\text{C}$, naphthalene disappears from the surface layer faster than the oxidant.

It is significant that on the surface and in the surface layer, between the NH_4ClO_4 crystals, products of various degree of decomposition of naphthalene were observed, which probably are formed as a result of the reaction of the gaseous decomposition products of the oxidant with the liquid phase of the fuel, i.e., with naphthalene.

The study of the burning of mixtures of ammonium perchlorate with tungsten showed that this mixture ignites and burns steadily when ignited with an incandescent spiral at room temperature in the pressure region of $p > 5$ atm abs. On the surface of the extinguished specimen, as shown in Fig. 1b, are accumulated tungsten and products of its oxidation. The NH_4ClO_4 -graphite mixtures does not burn steadily in the pressure range studied, up to 100 atm abs. Visual observation of the surface after the application of the incandescent spiral showed accumulation of graphite on the surface (Fig. 1b).

For mixtures of ammonium perchlorate with the fuels studied--malonic and succinic acids, naphthalene, starch, graphite, and tungsten--limiting pressures (below which the mixture does not burn steadily and ceases to burn) were determined as a function of the particle size of the oxidant. Ammonium perchlorate had a particle size of 40--50 μ and 200--300 μ (table).

From the results given in the table, it is evident that the limiting pressure for mixtures with a melting fuel of the type of malonic and succinic acids increases with decreasing particles size of the oxidant.

This phenomenon is probably due to the fact that fine particles are easily covered with a film of the molten fuel which protects and hinders the heating of the oxidant to the temperature of vigorous decomposition as shown schematically in the Fig. 1d.

Large particles of NH_4ClO_4 , as shown in Fig. 1d, are partially covered with a film of the fuel, but their upper part is free. During the burning of the NH_4ClO_4 +naphthalene mixture, NH_4ClO_4 is accumulated on the mixture surface and the limiting pressure of steady burning is independent of the particle size of the oxidant.

Starch, as is known, melts only slightly when heated to decomposition temperature, and the limiting pressure of the steady burning of the NH_4ClO_4 +starch mixture is therefore independent of the size of the oxidant particles.

The limiting pressure of steady burning is also independent of the size of the oxidant particles in mixtures of ammonium perchlorate with tungsten and graphite.

Mixtures with KClO_4 and NaClO_4 as oxidants. In burning of mixtures containing KClO_4 or NaClO_4 as oxidants, the formation of a molten layer on the charge surface was observed in all cases. The reaction between the oxidant and the fuel originates either in the liquid layer or on its surface.

In vacuum ($p \sim 10^{-2}$ mm Hg) at room temperature, the KClO_4 +tungsten mixture burns steadily with a velocity of ~ 0.22 cm/sec.

We were not able to extinguish this mixture either in vacuum or at high pressures. NaClO_4 was used as an oxidant to study surfaces formed during the burning. Mixtures with this oxidant burn less intensively and are extinguished at pressure $p > 1$ atm abs, but these oxidants have similar properties.

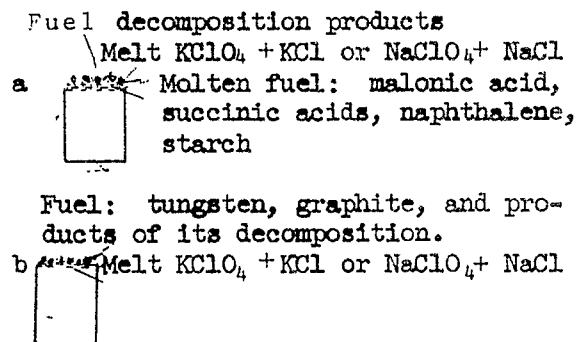
During the burning of this mixture, a melt of NaClO_4 and NaCl , a decomposition product of the former, is formed. Tungsten and products of its oxidation are located on the surface of the melt, i.e., heat-resistant fuel is accumulated on the melt surface (owing to a big difference between the decomposition temperatures of the fuel and the oxidant).

Under the action of an incandescent spiral, on the surfaces of the KClO_4 +graphite and NaClO_4 +graphite mixtures, accumulation of graphite was also observed, as is schematically shown in Fig. 2b.

Mixtures of $KClO_4$ with graphite and $NaClO_4$ with graphite do not burn steadily in the pressure range studied, up to 100 atm abs. The mixtures of $KClO_4$ +naphthalene and $NaClO_4$ +naphthalene do not burn at $p \sim 10^2$ mm Hg. They burn steadily in air and at elevated pressures.

On the burning surface, which consists of molten $KClO_4$ and KCl or $NaClO_4$ and $NaCl$, dark-brown naphthalene decomposition products are located.

Molten naphthalene is located under the molten $KClO_4$ layer, and a dark-brown layer of naphthalene decomposition products is located at the interface of the two molten layers. A similar picture was observed on the burning surface of mixtures of $KClO_4$ and $NaClO_4$ with succinic acid and starch, as is shown schematically in Fig. 2a. With all mixtures with melting ($KClO_4$) and nonmelting (NH_4ClO_4) oxidants and a melting fuel, fine bubbles were observed in the surface layer of the melt which are formed from the gaseous products of the oxidant and the fuel and the liquid-phase oxidation of the fuel as a result of the reactions occurring in the condensed phase.



In the surface layer of the melt reactions are possible not only between the gaseous decomposition products of the oxidant and the gaseous decomposition products of the fuel, but also between the gaseous products of the oxidant and the molten fuel in the reaction layer of the condensed phase, i.e., a liquid-phase oxidation take place.

Fig. 2. Oxidants $KClO_4$ and $NaClO_4$

When the mixture consists of a melting oxidant and nonmelting fuel or a nonmelting oxidant and nonmelting fuel, the reaction between the oxidant decomposition products and the fuel occurs on the surface of the condensed phase of the fuel.

In [4] it is shown that the mechanism of burning of NH_4ClO_4 is similar to the mechanism of burning of powders and mixed solid fuels [1, 2] While 95% of the heat needed for heating the NH_4ClO_4 charge comes from the heat generated in the reaction layer of the condensed phase, 5% comes from the heat generated in the gaseous burning zone of the mixture.

Mixtures containing $KClO_4$ and $NaClO_4$ as oxidants burn more intensively than mixtures containing NH_4ClO_4 . This difference is due to the temperature being higher (equal ~ 600 — $700^\circ C$) on the surface of mixtures containing $KClO_4$ and $NaClO_4$ than on the surface of the mixtures with NH_4ClO_4 , where it is equal

to $\sim 500^\circ\text{C}$, and in addition to that, the sodium and potassium chlorides which are formed during the decomposition of KClO_4 and NaClO_4 act as catalysts of the burning process [5].

Thus, it is evident from the results obtained that the initial stage of the burning of various mixtures of solid fuels occurs in the reaction layer of the condensed phase and is completed with the formation of the smoke phase.

CONCLUSIONS

1. In the pressure region of $p < 30$ atm abs, oxidant crystals appear on the surface of burning mixtures containing the nonmelting oxidant NH_4ClO_4 and fuels melting or decomposing at temperatures close to the oxidant decomposition temperature. The larger the oxidant crystals, the more visible do they become on the surface. At pressures of $p \geq 30$ atm abs, the picture is the converse, i.e., craters are formed on places where the ammonium perchlorate crystals were located.
2. Heat-resistant fuels (graphite, tungsten) are accumulated on the surface of the mixtures during the burning process. When the decomposition temperature of NH_4ClO_4 is higher than the sublimation or decomposition temperature of the fuel, e.g., naphthalene, the oxidant is accumulated on the surface.
3. In the surface layer of the melting oxidants or melting fuels, bubbles were observed which are formed from the gaseous decomposition products of the oxidant and the fuel and by liquid-phase oxidation of the fuel.
4. For mixtures containing the nonmelting ammonium perchlorate, the pressure below which the mixture does not burn steadily (ceases to burn) depends on the size of the oxidant particles and the physical properties of the fuel.
5. The mixture KClO_4 +tungsten burned steadily in a vacuum of $p \sim 10^{-2}$ mm Hg at $t \geq 5^\circ\text{C}$. The mixture NH_4ClO_4 +tungsten burned steadily at room temperature and pressure in the region of $p \geq 5$ atm abs. The mixtures KClO_4 +graphite and NH_4ClO_4 +graphite do not burn steadily in the range of pressures studied up to 100 atm abs.
6. The initial stage of burning of mixtures of solid propellants occurs in the reaction layer of the melt of the condensed phase or on the surface of heat-resistant fuels (graphite, tungsten) with an overall positive thermal effect and is completed by the formation of a fuel-smoke mixture which burns in the zone above the mixture surface to form the final combustion products.

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Mixture	Oxidant particle size 40--50 μ										Oxidant particle size 200--300 μ									
	P, atm abs					P, atm abs					P, atm abs					P, atm abs				
	vacuum, 10 ⁻³ mm Hg	in air	inert	5	10	20	40	80	100	vacuum, 10 ⁻³ mm Hg	in air	inert	5	10	20	40	60	80	100	
NH ₄ ClO ₄ + tungsten	1	2	3	4						1	2	3								
NH ₄ ClO ₄ + graphite	1	1	1	2						1	1	1								
NH ₄ ClO ₄ + malonic acid	1	1	2							1	5	6								
NH ₄ ClO ₄ + succinic acid	1	1	2							1	3	3								
NH ₄ ClO ₄ + naphthalene	1	3	4							1	3									
NH ₄ ClO ₄ + starch	1	3	4							1	3									
KClO ₄ + tungsten	5		6																	
NaClO ₄ + tungsten	5	3	4							5	3									
KClO ₄ + graphite	1		2							1										
KClO ₄ + malonic acid	1	5	3	4						1	3									
KClO ₄ + succinic acid	1	3	4							1	3									
KClO ₄ + naphthalene	1	5	3	4						1	5	3								
KClO ₄ + starch	1	3	4							1	3									

1 - Does not burn; 2 - burns unsteadily; 3 - burns steadily; 4 - is not extinguished; 5 - burns; 6 - burns well, is not extinguished; 7 - burns very well, is not extinguished.

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