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EFFECT OF IRON OXIDE ON COMBUSTION RATE  
OF MIXTURES WITH DIFFERENT PERCHLORATES

V. I. Avdyunin, et al

Foreign Technology Division  
Wright-Patterson Air Force Base, Ohio

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# FOREIGN TECHNOLOGY DIVISION



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OF MIXTURES WITH DIFFERENT PERCHLORATES

by

V. I. Avdyunin, N. N. Bakhman, et al.



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13. ABSTRACT  
The catalytic activity of Fe<sub>2</sub>O<sub>3</sub> in the combustion of mixts. of NH<sub>4</sub>ClO<sub>4</sub> with poly(Me acrylate), polystyrene, S, or carbon black was at a max. with 1-5% Fe<sub>2</sub>O<sub>3</sub> and fell off markedly for mixts. contg. greater than 20-35% Fe<sub>2</sub>O<sub>3</sub>. In all cases, the effectiveness of Fe<sub>2</sub>O<sub>3</sub> was less for mixts. of relatively higher uncatalyzed burning velocity than for those of lower velocity. Studies of the catalytic effect of Fe<sub>2</sub>O<sub>3</sub> in mixts. contg. Me<sub>4</sub>NC1O<sub>4</sub> instead of NH<sub>4</sub>ClO<sub>4</sub>, in the reaction of which NH<sub>3</sub> and HCl are presumably absent, indicated that a single mechanism of catalysis cannot account for the effect of Fe<sub>2</sub>O<sub>3</sub> on burning of perchlorate mixts. Mosk. Khim.-Tekhnol. Inst. Im. Mendeleeva, Moscow, USSR [AP1209459]

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7

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Combustion Rate Fuel Additive Combustion Catalyst Iron Oxide Ammonium Carbon Black Styrene Perchlorate Ammonia Catalyst Activity						

13  
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Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

\* ye initially, after vowels, and after ъ, в; e elsewhere.  
 When written as ё in Russian, transliterate as yё or ё.  
 The use of diacritical marks is preferred, but such marks  
 may be omitted when expediency dictates.

EFFECT OF IRON OXIDE ON COMBUSTION  
RATE OF MIXTURES WITH DIFFERENT  
PERCHLORATES

(Moscow Institute of Chemical  
Technology im. D. I. Mendeleev)

V. I. Avdyunin, N. N. Bakhman,  
V. S. Nikiforov, A. Ye. Fogel'zang,  
and Yu. S. Kichin

In this work we study the effect of the nature of a fuel and an oxidizer on the catalytic activity of  $Fe_2O_3$ .

The first series of experiments was conducted with mixtures of ammonium perchlorate (PKhA) [ПХА] with fuels of very different compositions: polymethylmethacrylate (PMMA) [ПММА], polystyrene (PS) [ПС], carbon black, sulfur, and guanidine nitrate (NG) [НГ]. The second series of tests was conducted with different perchlorates: of ammonium, potassium (PKhK) [ПХК], formamidine (PKhF) [ПХФ], and tetramethyl ammonium (PKhTMA) [ПХТМА].

The grades of these substances: PKhA - technically pure, PKhK - pure, PMMA - technically pure, carbon black - technically pure, sulfur - sublimed sulfur, NG - analytically pure,  $Fe_2O_3$  - analytically pure, PKhF and PKhTMA - synthesized and recrystallized from alcohol and water, respectively. All substances were desiccated; PKhA, PKhK, PKhTMA, and NG were ground in a vibration mill. By means of the PSKh-2 device  $S_{уд}$  was determined and the average particle dimension  $d$  was calculated, which for PKhA ~ 9  $\mu m$ ,

PkhK ~ 10  $\mu\text{m}$ , PkhTMA ~ 10  $\mu\text{m}$ , FMMA ~ 3  $\mu\text{m}$ , PS ~ 20  $\mu\text{m}$ , carbon black ~ 3  $\mu\text{m}$ , sulfur ~ 15  $\mu\text{m}$ , NG ~ 10  $\mu\text{m}$ , and  $\text{Fe}_2\text{O}_3$  ~ 1.8  $\mu\text{m}$ .

The components were mixed on tracing paper with a rubber cork and were pressed into brass cylinders with an inner diameter of 8 mm to a relative density of 0.92-1.0. The charges were combusted in a constant-pressure bomb in nitrogen at a pressure of 70 atm. A piezoelectric crystal pressure sensor was used to measure combustion time, and the average combustion rate was calculated. The effectiveness of the catalyst is described by the value  $z = u/u_0$ , where  $u$  and  $u_0$  is the combustion rate of a composition with and without a catalyst.

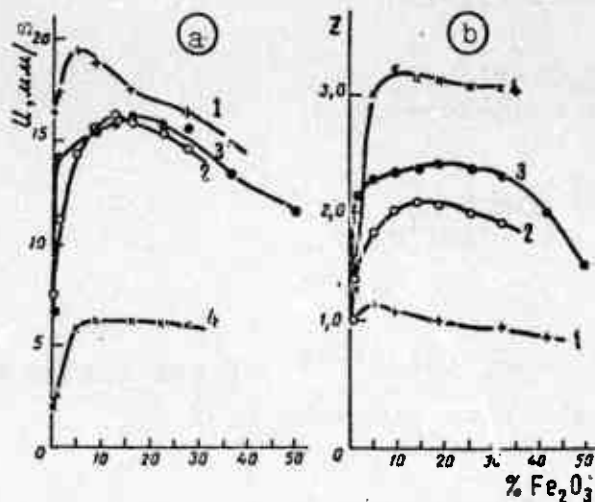


Fig. 1. Dependence of combustion rate (a) and effectiveness of catalyst (b) on per cent of iron oxide in mixture of PkhA + fuel ( $\alpha = 0.6$ ;  $P = 70$  atm). 1 - Sulfur; 2 - Carbon black; 3 - PMMA; 4 - NG.

In the first series of experiments we took curves  $u - \% \text{Fe}_2\text{O}_3$  and  $z - \% \text{Fe}_2\text{O}_3$  (see Fig. 1). The overall shape of the curves for all mixtures is the same, although on some curves there is a definite maximum (PkhA without fuel, all mixtures when  $\alpha = 2$ , and all mixtures with sulfur when  $\alpha = 1$  and  $\alpha = 0.6$ )<sup>1</sup>, while in other curves this shape represents a plateau (a mixture with carbon

<sup>1</sup> $\alpha$  - the stoichiometric coefficient:  $\alpha = \frac{m_0/m_2}{(m_0/m_2)_{\text{cmex}}}$ , where  $m_0, m_2$  ( $m_0$ )<sub>cmex</sub>, ( $m_2$ )<sub>cmex</sub> - are the parts by weight of the oxidant and the fuel in the given and the stoichiometric mixtures, respectively.



black,  $\alpha = 1$ ; a mixture with NG,  $\alpha = 0.6$ ). The increase in  $z$  with an increase in the % of  $\text{Fe}_2\text{O}_3$  is steep, while the decline (to the right of  $z_{\text{max}}$ ) is sloping. A catalyst effectiveness close to maximal ( $z \approx 0.9 z_{\text{max}}$ ) was reached at 1-5%  $\text{Fe}_2\text{O}_3$  and was maintained right up to a concentration of  $\text{Fe}_2\text{O}_3$  equal to 20-35%. However, values of  $z_{\text{max}}$  for mixtures with the studied fuels differ greatly. It seems that here the nature of the fuel does influence the effectiveness of the catalyst. Yet, if we plot the data for the different mixtures in coordinates  $z_{\text{max}} - u_0$  (see Fig. 2), all of the points are grouped around one curve<sup>1</sup>. In this case the higher the combustion rate of the initial (without catalyst) mixture, the lower will be the effectiveness of the catalyst<sup>2</sup>. This means that the effect of the nature of the fuel is not specific: if we equalize values  $u_0$  (for example, because of the oxidizer content), then the effectiveness of  $\text{Fe}_2\text{O}_3$  in mixtures with the fuels which we have studied is the same.

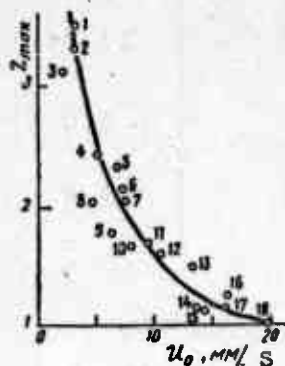


Fig. 2. Decline in effectiveness of  $\text{Fe}_2\text{O}_3$  with an increase in the combustion rate of the original mixtures: 1 - PKhA + carbon black,  $\alpha = 2.0$ ; 2 - 77% (30% PKhA + 70% PKhTMA) + 23% PMMA; 3 - PKhA + NG,  $\alpha = 0.6$ ; 4 - PKhA + carbon black,  $\alpha = 1.0$ ; 5 - PKhA + PMMA,  $\alpha = 0.6$ ; 6 - PKhA + PMMA,  $\alpha = 2.0$ ; 7 - PKhA + carbon black,  $\alpha = 0.6$ ; 8 - PKhA + PS,  $\alpha = 0.15$ ; 9 - PKhA (without fuel); 10 - PKhA + PS,  $\alpha = 2.1$ ; 11 - 77% (50% PKhA + 50% PKhTMA) + 23% PMMA; 12 - (10% PKhK + 90% PKhA) + PMMA,  $\alpha = 0.6$ ; 13 - PKhA + PMMA,  $\alpha = 1.0$ ; 14 - (50% PKhK + 50% PKhA) + PMMA,  $\alpha = 0.6$ ; 15 - PHhA + PS,  $\alpha = 0.3$ ; 16 - PKhA + sulfur,  $\alpha = 1.0$ ; 17 - PKhA + sulfur,  $\alpha = 0.6$ ; 18 - PKhK + PMMA,  $\alpha = 0.6$ .

<sup>1</sup> In Fig. 2 the curve corresponds to the dependence  $z_{\text{max}} \sim \frac{1}{u_0^{0.65}}$

<sup>2</sup> The value of  $z_{\text{max}}$  also declines with an increase in  $u_0$  due to an increase in the initial temperature  $T_0$  (for example, for a mixture of PKhA/PMMA when  $\alpha = 1$  at  $20^\circ\text{C}$  we have  $u_0 = 12.2 \text{ mm/s}$ ,  $z_{\text{max}} = 1.85$ ; and at  $150^\circ\text{C}$   $u_0 = 20 \text{ mm/s}$ ,  $z_{\text{max}} = 1.50$ ). The position of  $z_{\text{max}}$  has a relatively weak dependence on  $T_0$ , yet with a decline in the combustion rate to the right of  $z_{\text{max}}$  it becomes more sloping with an increase in  $T_0$  (Fig. 3).

Nevertheless, here we have a complicating factor: in any mixture based on PKhA the "total" fuel is a mixture of the "basic" fuel (for example, PS) and the ammonia<sup>1</sup>, where the molecular fraction of the ammonia is very significant. Therefore, the absence of a specific effect in the nature of the "basic" fuel could be explained by the fact that  $\text{Fe}_2\text{O}_3$  acts on the ammonia oxidizer.

We studied the effect of  $\text{Fe}_2\text{O}_3$  on the mixture  $\text{NH}_4\text{NO}_3$  + charcoal and the mixture PKhK + NG (pure and diluted  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{HCO}_3$ ). In all of these cases  $\text{Fe}_2\text{O}_3$  was not effective (see Table 1).

Table 1. Effect of  $\text{Fe}_2\text{O}_3$  on the combustion of mixtures whose gasification products contain ammonia but do not contain perchloric acid

Mixture	u, mm/s		
	without $\text{Fe}_2\text{O}_3$	1% $\text{Fe}_2\text{O}_3$	5% $\text{Fe}_2\text{O}_3$
$\text{NH}_4\text{NO}_3$ + charcoal, $\alpha = 1$	2.8	2.4	2.4
PKhK + NG, $\alpha = 0.6$	19.4	18.8	17.7
85% (PKhK + NG, $\alpha = 0.6$ ) + 15% $\text{NH}_4\text{Cl}$	6.9	5.2	3.8
80% (PKhK + NG, $\alpha = 0.6$ ) + 20% $\text{NH}_4\text{HCO}_3$	10.0	9.8	8.5

Hence it follows that  $\text{Fe}_2\text{O}_3$  either does not speed the oxidation of ammonia during combustion at all or speeds it, but only when the oxidizer is perchloric acid or its decay products. This is a problem which requires further study.

In the second series of experiments we tested the hypothesis that the effect of the catalysts on thermal decomposition and, possibly, on combustion of the perchlorates was related to the

<sup>1</sup>The drop in PKhA is according to the system  $\text{NH}_4\text{ClO}_4 \rightleftharpoons \text{NH}_3 + \text{HClO}_4$ .

accelerated decomposition of perchloric acid [1-4]. From this standpoint  $\text{Fe}_2\text{O}_3$  should be effective in compositions with PKhA and PKhF and should not be effective in compositions with PKhK and PKhTMA. Actually,  $\text{Fe}_2\text{O}_3$  substantially accelerated the combustion of PKhF (without fuel; plexiglass shell with  $d_{\text{внутр}} = 8 \text{ mm}$ ):

% $\text{Fe}_2\text{O}_3$	0	1	5	9.1	16.8	28.6
u, mm/s	13.5	26.4	27.7	26.0	24.0	19.9

The iron oxide had almost no effect on compositions with PKhK and PKhTMA, which, it seems, is in total agreement with the hypothesis concerning the role of the catalyst on the decomposition of  $\text{HClO}_4$ . Yet the combustion rate of these compositions is high, and judging from Fig. 2, this could be the reason for the low effectiveness of  $\text{Fe}_2\text{O}_3$ . Actually, when the value of  $u_0$  for mixtures based on PKhTMA was reduced due to dilution, the effectiveness of  $\text{Fe}_2\text{O}_3$  rose sharply (Table 2).

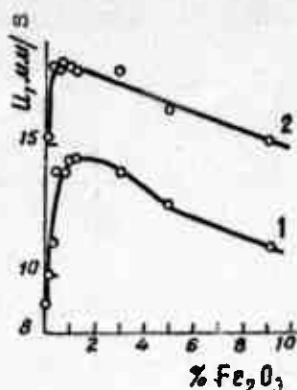


Fig. 3. Combustion rate of PKhA (without fuel) as a function of the per cent of iron oxide (tests with plexiglass shells at  $P = 100 \text{ atm}$ ).  $T_0, ^\circ\text{C}$ : 1 - 20; 2 - 100.

Since in the primary decomposition of PKhTMA neither perchloric acid nor ammonia are formed, we should turn our attention to other possible ways in which  $\text{Fe}_2\text{O}_3$  could be effective (for example, associated with reactions of chlorine oxides).

As for mixtures based on PKhK, when their combustion rate was reduced by introducing  $\text{KCl}$  or  $\text{Al}_2\text{O}_3$ , the addition of  $\text{Fe}_2\text{O}_3$

was, as before, not effective (see Table 3 for the composition of PKhK + PMMA).

Table 2. Effect of  $Fe_2O_3$  on combustion of mixtures based on tetramethyl ammonium perchlorate containing different diluents.

Composition, %			$u_{70atm}$ , mm/s		$Z$
PKhTMA	PKhK	Diluent	without $Fe_2O_3$	1% $Fe_2O_3$	1% $Fe_2O_3$
85	15	—	27.1	28.2	1.04
90	10	—	20.1	22.2	1.10
77.3	13.6	9.1 $NH_4Cl$	14.0	23.7	1.69
70.7	12.5	16.8 $NH_4Cl$	8.5	18.8	2.21
65.4	11.5	23.1 $Al_2O_3$	6.3	16.2	2.58
52.7	2.8	44.5 $KCl$	5.2	11.7	2.25
55.5	—	44.5 $KCl$	4.4	9.7	2.20

Table 3. Effect of  $Fe_2O_3$  on combustion of mixtures based on potassium perchlorate containing different diluents.

$\alpha$	Diluent	$u_{70 atm}$ , mm/s			
		without $Fe_2O_3$	1% $Fe_2O_3$	3% $Fe_2O_3$	5% $Fe_2O_3$
2.0	—	12.8	—	13.7	—
2.0	16.7% $KCl$	8.8	9.0	—	9.1
0.4	—	14.2	14.8	14.7	14.9
0.4	13% $KCl$	11.9	12.25	—	11.3
0.4	23.1% $KCl$	8.6	9.0	—	8.7
0.4	16.7% $Al_2O_3$	8.1	8.3	—	—
0.4	50% $Al_2O_3$	2.6	2.8	2.7	2.8

We note in conclusion that the results obtained confirm the ideas of [5] concerning the concurrence of a homogeneous reaction in volume and a heterogeneous reaction in the catalyst. With an

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increase in the rate of the homogeneous reaction<sup>1</sup> and, accordingly, with an increase in  $u_0$  the contribution of the heterogeneous reaction (which also means quantity  $z$ ) must decrease, which is observed experimentally.

One might think that the catalyst acts on one of the intermediate combustion stages. Actually,  $z_{\max}$  has already been reached with a relatively low per cent of  $\text{Fe}_2\text{O}_3$ . This is related to the fact that by accelerating the given stage the catalyst will accelerate the combustion rate only as long as one of the other stages does not become limiting.

#### CONCLUSION

*The authors*  
1. We have studied the catalytic effect of  $\text{Fe}_2\text{O}_3$  on the combustion of mixtures of ammonium perchlorate with five different fuels and of certain mixtures with perchlorates of formamidine, potassium, and tetramethyl ammonium.

2. For mixtures based on ammonium perchlorate the effectiveness of the catalyst, which is close to maximal, is reached with only 1-5%  $\text{Fe}_2\text{O}_3$ , while a substantial decline in its effectiveness is observed only at 20-35%  $\text{Fe}_2\text{O}_3$ .

3. In all cases the effectiveness of  $\text{Fe}_2\text{O}_3$  decreases with an increase in the combustion rate of the original composition. The nature of the fuel was not observed to have a specific effect on the effectiveness of  $\text{Fe}_2\text{O}_3$ .

4. An acceleration in the decomposition of perchloric acid and an increase in the oxidation rate of ammonia are not the only

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<sup>1</sup>As a result of the increased combustion temperature or the transition to a more active fuel (but not because of pressure, which can accelerate both the homogeneous and heterogeneous reactions).

possible ways in which  $\text{Fe}_2\text{O}_3$  can be effective, since  $\text{Fe}_2\text{O}_3$  effectively accelerates the combustion of dilute mixtures based on tetramethyl ammonium perchlorate, where perchloric acid and ammonia are absent.

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