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Abstract

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ON TEMPERATURE PROFILES DURING THE COMBUSTION OF AMMONIUM PERCHLORATE

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The study of the regularities of ammonium perchlorate combustion is of great interest in connection with the anomalies that have been discovered in investigations of its combustion. Friedman, Nugent, and others (^{1}) discovered the phenomenon of an upper and lower pressure limit of combustion, and also measured, with the aid of thermocouples (junction ~50 μ), the maximum flame temperature, which proved to be 930° and increased only slightly with increasing pressure up to 150 atm. Later, Levy and Friedman (^{2}), continuing the study of perchlorate combustion, eliminated the upper-limit phenomenon by using an asbestos sheath.

However, experiments by one of the authors of the present paper (^{3}) showed that the combustion of perchlorate is very sensitive to changes in experimental conditions and, in particular, to the sheath; for unarmored specimens 7 mm in diameter, in the pressure region above 150 atm, in contrast to the 4 mm specimens used by Friedman, combustion occurs, but proceeds unstably, with pulsations, and the dependence of the burning rate on pressure has an unusual form: increasing the pressure above 150 atm entails a decrease in the burning rate*.

A decrease in the burning rate with increasing pressure was also observed in experiments by A. F. Belyaev and A. I. Korotkov (^{4}) for potassium picrate.

This phenomenon is unusual. A tentative explanation of this fact was put forward by K. K. Andreev and Sun Quan-tsae (^{5}), who associated it with the phase transformation characteristic of perchlorate at 240°; it was assumed that such a temperature must be reached by the surface of the burning perchlorate at a certain pressure (at this temperature the orthorhombic modification transforms into the cubic one, which, according to Birkumshaw (^{6}), decomposes at a considerably lower rate).

In light of the above, measurement of the temperature distribution in the condensed and gas phases during the combustion of ammonium perchlorate is important, since temperature measurements may shed light on its mechanism. Ar-

Fig. 1

Figure 1: Fig. 1

den, Polling, and Smith ([6]) attempted to determine the surface temperature of burning perchlorate by means of an infrared pyrometer and the maximum flame temperature by the method cited above ([1]). They established that at atmospheric pressure $T_p = 450 \pm 30^\circ$ and does not depend on the burning rate or on the nature of the combustible additive; they suggested that sublimation is the leading mechanism in combustion.

We studied the temperature distribution during the combustion of ammonium perchlorate using the thin-thermocouple method developed by A. A. Zenin ([8]).

For the measurements, Π-shaped thermocouples W + Re ÷ W + Re (5 and 20% Re), round, 15 and 30 μ in diameter, and ribbon thermocouples, 3.5 and 7 μ thick respectively, were used.

The experiments were carried out with 7 mm specimens of unsieved ammonium perchlorate (pressed to a density close to the specific gravity–1.93-1.94 g/cm^3), for which the decrease in burning rate with pressure is most pronounced. The experiments were conducted at constant pressure in the range 30-350 atm in a nitrogen atmosphere. During the experiments, the rate and character of combustion were simultaneously recorded on film with a photorecorder, and the temperature profile was recorded on an N-700 oscillograph.

* A decrease in the burning rate with increasing pressure was also observed for 12 mm specimens, which is considerably larger than the critical combustion diameter under these conditions (see ([3])).

It was found, in particular, that at pressures above 150 atm, along with cessations of combustion, regular temperature oscillations occur in the gas phase with a period of ∼ 50 μsec and an oscillation amplitude up to 500° (1000—500°). It should be emphasized here that the oscillations in the flame temperature and the plateau on the temperature record agree well with the decrease in the brightness of the glow and with the cessations in photographs of combustion. This gave

Fig. 1. Typical combustion oscillograms. *a* –in the stable region, $P = 50$ atm; *b* –in the unstable region, $P = 250$ atm

us grounds to call the pressure range 160–350 atm the region of unstable combustion.

Figure 1 presents the most characteristic oscillograms for stable and unstable combustion, and Fig. 2 the temperature profiles obtained by processing oscillograms in the stable region. The oscillograms in the region of unstable combustion (160–350 atm)* are characterized by the presence, on most oscillograms, of a plateau with a stable temperature of ∼ 270° and of a pulsating temperature

Fig. 2

Figure 2: Fig. 2

Figure 3

Figure 3: Figure 3

in the flame. We note that in some experiments combustion went out upon reaching the thermocouple; in these cases the surface of the extinguished pellets was strictly horizontal, and the maximum recorded temperature was $\sim 270°$, which we took as the surface temperature.

Fig. 2. Temperature profiles at $P = 50$ (1), 100 (2), 150 (3) atm

In the region of stable combustion, the surface temperature was determined both by the method of (8)—from the maximum intensity of heat release in the condensed phase when processing oscillograms—and by direct measurements according to the method proposed by P. F. Pokhil (9), using thermocouples with weights.

The graph in Fig. 2 shows the dependences on pressure of the total heat release, the heat release in the condensed and gas phases, and also the heat input from the gas phase (4).

In the pressure interval 40—150 atm (stable regime) an increase in total heat release (1) is observed, which is associated with its strong increase in the gas phase (2), since the heat release in the condensed phase (3) decreases with increasing pressure. However, it would be incorrect to consider that the increase in burning rate is caused only by the increase in heat release in the gas phase, since heat transfer from the gas phase is small (4) and changes only weakly with pressure. The heat release in the condensed phase, although greater by an order of magnitude, decreases sharply with increasing pressure and therefore cannot explain the observed increase in burning rate by the usual thermal mechanism. The explanation of this phenomenon should probably be sought in the chemical nature

* At present, final processing of oscillograms for unstable combustion is not possible, since recording the rate with a photoregister does not allow its values to be calculated accurately in sections of deceleration and during cessations of combustion; the oscillograms will be processed after additional experiments have been carried out.

···of the reactions proceeding in this case, the mechanism of which may vary with pressure. In principle, a sharp increase in dispersion is also possible; however, in our experiments it was greater at the lower burning rate (at 50, 250-350 atm)*.

Fig. 3. Dependence of the total heat release (1), the heat release in the gas (2) and condensed (3) phases, and also of the heat input from the gas phase (4),

Figure 4

Figure 4: Figure 4

during combustion of ammonium perchlorate, on pressure.

The assumption mentioned above (7) concerning the decisive role of sublimation of solid perchlorate in the combustion process, but in the condensed phase during combustion of ammonium perchlorate a considerable amount of heat is liberated (80–120 cal/g) (Fig. 3), whereas sublimation should have been accompanied by its absorption. In addition, during sublimation the surface temperature should have increased with pressure, and not the reverse, as follows from our experiments: as is seen from the graph in Fig. 4, the surface temperature of burning perchlorate decreases with increasing pressure and, in the region of unstable combustion, approaches the temperature of the phase transition. It should be noted in passing that on some oscillograms in the region of temperatures of the order of 250° a small break was observed, with an effect that was practically thermoneutral; this is possibly connected with the temperature of the phase transition (Fig. 4, 2).

It was noted above (see Fig. 3) that heat release in the condensed phase decreases with increasing pressure, which had not previously been observed for any of the substances studied. At 150 atm the heat release is 80 cal/g. In experiments in the region of unstable combustion, cases were observed of extinction of specimens with a surface temperature of ~270°. If one calculates the amount of heat required to heat the condensed phase to this temperature, it is likewise equal to 80 cal/g. In this connection the supposition arose that this amount of heat is critical and is the threshold separating the region of stable combustion from that of unstable combustion: if the condensed phase receives more than 80 cal/g, combustion proceeds steadily; at the boundary it becomes pulsating; and with a smaller amount of heat it is extinguished. Heat release in the condensed phase is determined by the surface temperature, which in because of a mechanism as yet unknown to us, decreases with pressure (see

Fig. 4. Dependence of the surface temperature of burning ammonium perchlorate on pressure. 1 –T_p, determined from the spike on the oscillogram; 2 –the same, determined with thermocouples with weights; 3 –the same at 200 atm, obtained during stable combustion of specimens preheated (to 40–50°); 4 –temperatures of the break in the temperature distribution in the condensed phase in certain experiments on combustion of ammonium perchlorate

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* In connection with this observation, P. F. Pokhil noted that, apparently, the combustion mechanism of ballistite powders can be extended to the combustion of ammonium perchlorate, i.e., combustion involving dispersion and formation of a smoke-gas phase.

Fig. 4), and on approaching the temperature of the phase transition the heat release in the condensed phase must fall still more sharply, since the phase transition occurs with absorption of heat. This circumstance may be the cause of a decrease in the rate and, in certain unfavorable cases, the cause of extinction of combustion.

The results presented in Fig. 4 in the interval 50–150 atm are surprising not only because of the decrease in surface temperature with increasing pressure, i.e., with increasing burning rate, but also because of the low value of the temperature. The known data on the kinetics of decomposition of perchlorate, obtained at temperatures up to 280° (5), and also extrapolated to 420°, give a gasification rate of perchlorate several orders of magnitude smaller than the measured rate of decrease in the amount of perchlorate during combustion. Apparently, the kinetics and mechanism of gasification at the relatively low temperature in experiments on the decomposition of perchlorate differ from the kinetics and mechanism of gasification of perchlorate occurring at the same or a higher temperature on the surface of burning perchlorate. One of the authors has suggested that, perhaps, during combustion there is catalysis of the decomposition of perchlorate at the surface by reaction products and active centers coming from the flame zone to the surface of the condensed phase. The point is that the presence of a heat flux from the flame zone to the surface automatically implies the presence of diffusion of molecules (including radicals) from the flame zone to the surface. These active reaction products can exert an effective catalytic action.

This supposition naturally applies not only to the combustion of perchlorate, but also to the combustion of any condensed system in which there is a heat flux from the reaction zone in the gas phase to the surface of the condensed phase: heat conduction in the gas is accomplished by diffusion of “hot” (including active) molecules. This supposition obviously also contains a possible mechanism by which the gas phase controls the decomposition of the condensed phase. This is especially important in those cases where the heat input from the gas phase is small, while the heat release in the condensed phase is large and almost ensures maintenance of the required surface temperature.

The maximum combustion temperature initially increases with increasing pressure, passes through a maximum value of 1060° at 100–150 atm, and then begins to decrease, although the pressure continues to rise.

As a result of the work, temperature profiles were obtained in the pressure range 40–350 atm, which show the existence of two regimes of combustion of ammonium perchlorate: stable (40–150 atm) and unstable (160–350 atm).

Anomalous dependences of the surface temperature and heat release in the condensed phase on pressure have been established—a decrease as the latter increases.

Suggestions have been advanced concerning the reason for the decrease in burning rate with increasing pressure and concerning the catalytic influence of products diffusing from the reaction zone in the gas phase to the surface on the gasification reactions of the condensed phase.

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