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DIFFERENTIAL THERMAL ANALYSIS OF POTASSIUM PERCHLORATE

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A study has been made of the differential thermal analysis of (i) potassium perchlorate in powdered form, (ii) potassium perchlorate in pelletized form, (iii) potassium perchlorate recrystallized from liquid NH_3, and (iv) potassium perchlorate preheated for 24 hours at 375°. Pretreatment of potassium perchlorate leads to a desensitization of both endothermic and exothermic processes. Additionally, the pretreatment tends to convert the symmetric exotherm into an asymmetric exotherm due to merging of the two exotherms. An analysis of the factors causing asymmetry in the exotherm has thrown fresh light on the mechanism of thermal decomposition of potassium perchlorate.

Potassium perchlorate ($KClO_4$) has gained importance as an oxidizer in solid composite propellants since 1950. Although the thermal decomposition of $KClO_4$ has been studied extensively with a view to understanding the mechanism of its decomposition [1—10], relatively little attention has been paid to clarifying the existing controversy on the differential thermal analysis (DTA) curve of $KClO_4$. The DTA of $KClO_4$ shows two endotherms, one at 300° corresponding to the phase transition from orthorhombic to cubic, and another around 600° corresponding to melting of the eutectic mixture. The two endotherms are followed by an exothermic reaction, around which is centred a controversy. Anderson and Freeman [8] studied the DTA of $KClO_4$ in air by taking 0.086 g of doubly recrystallized material. They located the thermocouples in the samples and reference standard. Their observations reveal that $KClO_4$ has two endotherms and two exotherms. The first exotherm appears after the "melting endotherm at 606°". Its exothermicity decreases as it reaches 636°. At 636°, a sharp rise in exothermicity occurs, with a peak at 641°, followed by the rapid decay of the exotherm. Markowitz and Boryta [9], on the other hand, observed a single exotherm, pointing to a reaction occurring in a single stage. The latter authors used shielded thermocouples and varied the sample size from 3 to 0.1 g, and observed only one exotherm. Further, the latter authors attributed the "resolved exotherm" of Anderson and Freeman [8] to the "possible catalytic effect of the chromel-alumel thermocouple". Later work [10] in this laboratory has confirmed the results of Markowitz and Boryta [9]. More recently, while studying the effect of precompression on the

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reactivity of $KClO_4$, we have observed that the symmetrical exotherm gives way to an asymmetric exotherm on precompression. Throughout the work the thermocouples were shielded and platinum cups were used. The asymmetry therefore did not arise from the instrumentation drawbacks. The present work deals with the possible causes of the asymmetry and its implications on the thermal decomposition of $KClO_4$.

Experimental

$KClO_4$ (Riedel, Hannover, Germany) was used as received in all the experiments. The crystals were graded through standard ASTM sieves and <37 μm particles were taken in the present investigation. The average particle size was determined using a scanning electron microscope, and was found to be 24 μm. Predetermined pressures (500, 1500 and 2500 kg/cm^2) were applied using a hydraulic press on 20 g of the sample to make 5 cm diameter cylindrical pellets. In all cases, the pressure was applied in an identical manner and the desired pressure was maintained for 5 minutes.

DTA's of the samples were carried out in air on a home-made apparatus. The DTA assembly was housed in a tubular quartz furnace which was programmed to a constant heating rate of 10°/min. Platinum cups were used as holders for the sample and the reference, ignited powdered alumina. The DTA curves were recorded on an Omniscribe two-pen recorder with an amplifier in circuit. In each case, 52.5 mg of the sample was taken. To avoid possible differences in thermal characteristics with density variations within a compact, the samples (one single piece of the pellet weighing 52.5 mg) were chosen from similar portions of presumably identical density (for example, 1 cm away from the edge of the pellet).

$KClO_4$ was dissolved in anhydrous liquid ammonia and recrystallized from the same solvent. Recrystallized $KClO_4$ was ground (avoiding circular motion) and <37 μm particles were taken in the present set of experiments. For pretreating, the $KClO_4$ pellet was heated at 375° for 25 h, and the DTA was taken within a few hours.

X-ray diffraction patterns were taken on a Philips diffractometer with a specimen thinner and a pulse height discriminator. The patterns were recorded with a copper tube run at 30 kV and 20 mA using a nickel filter. The diffraction peak profiles were obtained by step-scanning and taking the number of counts for 4 sec.

A few DTA runs were interrupted at 535°, for the quantitative estimation of chlorate contents. Estimation was carried out as indicated in reference [9].

Results

DTA

The DTA curves of uncompressed $KClO_4$, precompressed $KClO_4$ and pretreated $KClO_4$ are shown in Fig. 1. The DTA curve of uncompressed $KClO_4$ displays the first endotherm at 303°, a second endotherm at 573° and a large

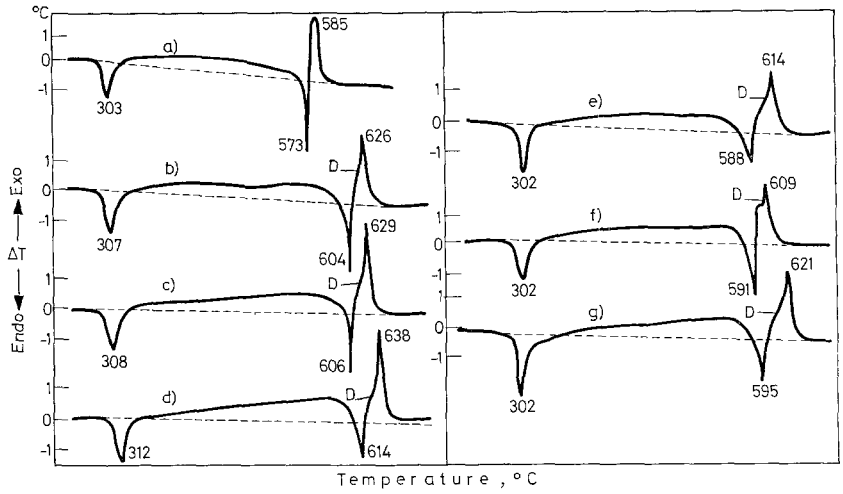

Fig. 1. DTA (10°/min) of untreated $KClO_4$ compared with that of pretreated $KClO_4$: (a) uncompressed, (b) pelletized at 500 kg/cm^2, (c) pelletized at 1500 kg/cm^2, (d) pelletized at 2500 kg/cm^2, (e) recrystallized in liquid NH_3, (f) preheated at 375°, (g) pelletized at 1500 kg/cm^2 and ground to <37 μm. (– – – Indicates baseline shift)

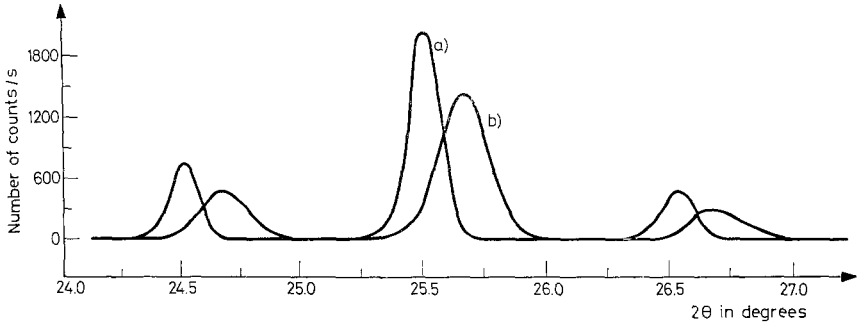

Fig. 2. X-ray diffraction peak profiles of (a) uncompressed $KClO_4$ and (b) $KClO_4$ precompressed at 1500 kg/cm^2

exotherm at 585°. The sharp exotherm at 585° indicates the decomposition of $KClO_4$, forming KCl as the final product. This DTA curve is in qualitative agreement with the DTA curves reported in references [9] and [10]. The DTA curve of $KClO_4$ precompressed at 500 kg/cm^2 shows that the endotherms have shifted to 307° and 604°, respectively. The exotherm at 585° for uncompressed $KClO_4$ has shifted to 626° and is asymmetric in nature, indicating the existence of two stages of decomposition. The single, symmetric exotherm of $KClO_4$ after melting changes into an asymmetric "resolved exotherm" on precompression at 500 kg/cm^2. The desensitization phenomenon of endothermic and exothermic peaks is seen more clearly at still higher pressures, as indicated in Fig. 2. At 2500 kg/cm^2

pelleting pressure, the asymmetry of the exothermic peak is seen distinctly where the slopes of the two stages of the exotherm are different. Further, the Figure reveals that the intensity of the second exotherm increases with the pelleting pressure. Also noticeable is the fact that the precompressed material shows an enhanced decomposition at low temperatures prior to fusion as compared to uncompressed $KClO_4$, signifying the increased defect nature of the sample, as observed by Pai Verneker and Rajeshwar [11].

It is known that pretreatments such as preheating of the material and recrystallization in liquid NH_3 increase the defect nature of NH_4ClO_4 [10, 12]. Therefore, DTA curves of recrystallized $KClO_4$ in liquid NH_3 and preheated $KClO_4$ (precompressed at 1500 atm) were taken and are indicated in Fig. 1. Both the pretreatments indicate a desensitization effect on the peak temperatures, with an asymmetry in the exothermic peak as compared to uncompressed NH_4ClO_4. The DTA of $KClO_4$ pelletized at 1500 atm and ground to the original particle size (<37 μm) also showed an asymmetry in the nature of the exothermic peak as compared with the uncompressed powder. Therefore, the results of pretreatment of $KClO_4$ indicate two stages of decomposition, immaterial of the kind of pretreatment given to the sample.

X-ray diffraction

A comparison of the X-ray diffraction patterns of uncompressed and precompressed $KClO_4$ shows a broadening of the peaks in the case of the precompressed material. Also, the peaks are shifted towards higher 2Θ values, due to the strain on the $KClO_4$ crystals bringing down the lattice parameters. Typical results are shown in Fig. 2. "Selective broadening" of the peaks due to pretreatment is shown in Table 1, for various *hkl* planes.

Table 1

Effect of pretreatment on the X-ray diffraction peak profiles of $KClO_4$

d, Å	*hkl*	Peak widths					
		$KClO_4$ powder <37 μm			$KClO_4$ precompressed at 1500 kg/cm² and ground to <37 μm		
		B_0	B	β	B_0	B	β
3.699	002	0.137	0.096	0.013	0.150	0.111	0.029
3.487	210	0.150	0.111	0.029	0.150	0.111	0.029
3.359	102	0.144	0.105	0.022	0.155	0.115	0.032
3.145	211	0.144	0.105	0.019	0.159	0.125	0.042
2.890	112	0.156	0.120	0.035	0.159	0.125	0.040
2.831	020	0.150	0.111	0.024	0.150	0.111	0.024

B_0 = Peak width at half maximum intensity.
B = Corrected peak width.
β = Pure diffraction breadth.

Estimation of chlorate content

Dynamic DTA's of uncompressed, precompressed and pretreated $KClO_4$ samples were interrupted much before the eutectic melting point of $KClO_4$ (535°) to estimate the chlorate content. The analytical results of these samples are presented in Table 2. The chlorate content increases depending on the pretreatment, and is maximum for $KClO_4$ pelletized at 1500 kg/cm^2 and ground to <37 μm.

Table 2

Chlorate contents of untreated and pretreated $KClO_4$

Sample	Chlorate content	
	at room temperature	after heating to 535°
$KClO_4$ powder <37 μm (as received)	trace	3.1×10^{-3} g
$KClO_4$ pelletized at 1500 kg/cm^2	2 to 3×10^{-4} g	5.3×10^{-3} g
$KClO_4$ recrystallized in liquid NH_3	trace	8.7×10^{-3} g
$KClO_4$ pelletized at 1500 kg/cm^2 and ground to <37 μm	2 to 3×10^{-4} g	9.3×10^{-3} g

Detection level: 1×10^{-4} g.

Discussion

The asymmetry observed in the exothermic reaction due to precompression or pretreatment is not due to experimentation or sample size, since the same DTA set-up and the same weight (i.e. 52.5 mg) of the sample were used throughout the investigation. Each experiment was repeated at least twice for accuracy, and a very close agreement in the temperatures and shapes was observed. The asymmetry is observed when the sample weight is increased to 105 mg. (Fig. 3a, reference weight 52.5 mg.) Therefore, the desensitization of endothermic and exothermic peaks and asymmetry caused in the exotherm is definitely due to precompression or pretreatment of $KClO_4$. Pai Verneker and Rajeshwar [11] studied the effect of precompression by applying very low pressures on $KClO_4$ and observed the desensitization of endothermic and exothermic peaks. They could not observe the asymmetric nature of the exotherm due to very low pelleting pressures.

Precompression or pretreatment in addition results in a broadening of the X-ray diffraction peaks. Keating and Krasner [13] and Bogardus and Roy [14] have observed a similar broadening of the X-ray diffraction peaks on grinding and precompression of sodium azide and polycrystalline barium titanite, respectively. Pai Verneker and Rajeshwar [15, 10, 11] have also observed a broadening of the IR bands and X-ray peaks on precompression of ammonium perchlorate and $KClO_4$. They have interpreted the line-broadening effect as being due to the production of strain and faulting caused by grinding and compression of the poly-

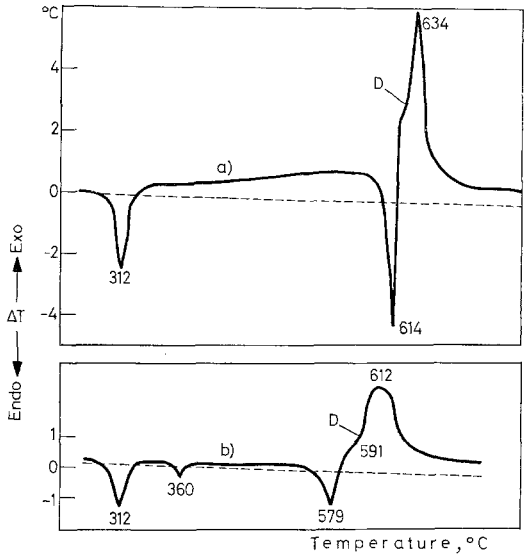

Fig. 3. DTA (10°/min) of (a) $KClO_4$ pelletized at 1500 kg/cm^2 (b) uncompressed 90% $KClO_4$ + 10% $KClO_3$ mixture. (– – – Indicates baseline shift)

crystalline materials. On this basis, the increased broadening of the X-ray diffraction peaks in $KClO_4$ on pretreatment shows an increase in the extent of disorder in the material and thus an increase in the dislocation density.

The desensitization observed in the endotherm (of phase change) temperature on pretreatment gives an indication of the average strain on the individual particles. In the case of chemical treatment such as recrystallization of $KClO_4$ in liquid NH_3, ammonia is adsorbed onto the $KClO_4$. Desorption takes place only after the phase transition [12] and consequently the physical defects will be present only after the phase transition. Hence, the phase transition temperature will not be affected but the latter process will be as observed in the present work.

The DTA's clearly show, prior to the melting endotherm, a broad exotherm which becomes pronounced after pretreatment such as pelletization, etc. This is in confirmation of what Pai Verneker and Rajeshwar observed earlier [11]. During this exothermic process $KClO_4$ produces $KClO_3$. This is shown to be the case by chemical estimation by arresting the DTA experiment prior to the melting endotherm (Table 2). As is seen from Table 2, the chlorate content produced is dependent on the nature and type of pretreatment (or precompression) given to the $KClO_4$ (resulting in the production of imperfections). The increase in the chlorate content of precompressed or pretreated material is brought about by the decomposition of $KClO_4$ at a temperature much lower than the eutectic melting point. As the $KClO_4$ content increases, the rate of decomposition of $KClO_4$ into KCl slows down because of a competitive reaction between $KClO_4-KClO_3$ and $KClO_4-KCl$. Under normal circumstances, $KClO_4$ contains a limited concentration of $KClO_3$

and the rate of production of KCl is in a sense uniform, and therefore the exotherm is symmetric in nature. In the case of precompressed or pretreated material the presence of $KClO_3$ in significant quantities slows down the process. $KClO_3$ powder (37 μm) was added intentionally to $KClO_4$ powder (<37 μm) and the DTA curve (Fig. 3b) of the mixture (90% $KClO_4$ + 10% $KClO_3$) confirms that $KClO_3$ slows down the decomposition of $KClO_4$. This can be seen from the peak temperature of the exotherm, which is around 612° as compared to 585° for pure $KClO_4$ powder. Also, the asymmetric nature is seen in the exotherm. Instead of a sharp endotherm after point 'D', as seen in the DTA's reported in Fig. 1, a broad endotherm is observed, indicating the decatalyzing effect of $KClO_3$. This agrees qualitatively with the decomposition behaviour of $KClO_4$ in the presence of $KClO_3$ [16].

The eventual production of KCl on the other hand enhances the rate of decomposition; and these two processes put together give rise to an asymmetry, i.e. once a sufficient amount of KCl is formed, the decomposition reaction becomes more exothermic, giving rise to an asymmetry in the DTA curve at point 'D' in Fig. 1.

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RÉSUMÉ — On a effectué l'étude par analyse thermique différentielle du perchlorate de potassium: (i) en poudre, (ii) sous forme comprimée, (iii) recristallisé dans NH_3 liquide, (iv) préchauffé à 375° pendant 24 heures. Le traitement préalable du perchlorate de potassium entraîne la désensibilisation des processus endothermiques et exothermiques. De plus, le traite-

ment préalable tend à convertir l'exotherme symétrique en un exotherme asymétrique, du fait de la fusion des deux exothermes. Une analyse des facteurs causant l'asymétrie de l'exotherme a donné une vue nouvelle du mécanisme de la décomposition thermique du perchlorate de potassium.

ZUSAMMENFASSUNG — Eine differentialthermoanalytische Untersuchung wurde an, (i) Kaliumperchlorat in Pulverform, (ii) Kaliumperchlorat in pelletisierter Form, (iii) Kaliumperchlorat, umkristallisiert aus flüssigem Ammoniak und (iv) Kaliumperchlorat, 24 Stunden bei 375° vorgeheizt, durchgeführt. Die Vorbehandlung von Kaliumperchlorat führt zu einer Verdichtung sowohl der endothermen als auch der exotherman Vorgänge. Ausserdem führt die Vorbehandlung zur Umwandlung der symmetrischen Exotherme in eine asymmetrische Exotherme durch Vereinigung der zwei Exothermen. Die Analyse der die Asymetrie der Exothermen verursachenden Faktoren zeigte den Mechanismus der thermischen Zersetzung des Kaliumperchlorats unter neuen Gesichtspunkten.

Резюме — Термический анализ по производной был использован для изучения перхлората калия в порошке, в таблетках, перекристаллизованного из жидкого аммиака, а также предварительно термически обработанного при 375° в течении 24 часов. Предварительная термическая обработка перхлората калия приводит к нивелированию эндотермических и экзотермических процессов. Кроме того, такая обработка приводит к превращению симметричной экзотермы до асимметричной, что обусловлено слиянием двух экзотерм. Анализ факторов, вызывающих асимметрию экзотермы, привел к новым представлениям о механизме термического разложения перхлората калия.