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Compatibility of Thermobaric Mixtures Based on Isopropyl Nitrate and Metal Powders

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The compatibility of thermobaric mixtures based on isopropyl nitrate (IPN), magnesium (Mg) and aluminium (Al) powders are researched by microcalorimetry. Calculated (theoretical) and measured (experimental) curves of compatibility of the examined samples are presented. The heat of combustion of the IPN/ Mg composition is determined by adiabatic calorimetry.

Key words: **thermobaric mixture, isopropyl nitrate, metal powder, magnesium, aluminum, microcalorimetry, adiabatic calorimetry, compatibility.**

Used marks and symbols

T – temperature, (K)
τ_1 – time, (h)
τ_2 – heating period, (h)
τ_3 – "induction" time, (h)
Δp – developed pressure, (kPa)
Q – heat flow data, $(\mu W/g)$
Q_m – heat of combustion of thermobaric mixture, (J)
Q_c – heat of combustion of acetobutyrate capsule, (J)
Q_{iv} – heat of combustion of ignition wire, (J)
m_m – weight of thermobaric mixture, (g)
m_c – weight of acetobutyrate capsule, (g)
C – thermal capacity of the calorimetric system, (J/K)
ΔT_d – rise of temperature determined during test by digital thermometer, (K)
ΔT_B – rise of temperature determined during test by Beckmann thermometer, (K)

Introduction

THIS paper considers results of compatibility examination of thermobaric mixtures based on isopropyl nitrate and metal powders. The heat of combustion of thermobaric mixture, whose components were classified as compatible, was determined experimentally by adiabatic calorimetry. The paper gives a short overview of certain data found in references - physical properties and high temperature stability of IPN.

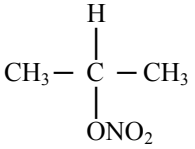
Production, manufacturing and storage of materials for special use [1, 2] very often poses a risk of potential hazards. The compatibility of two – phases systems (thermobaric mixture consists of solvent and metal powder - liquid and solid state of aggregation) have to be precisely known to prevent serious problems associated with the change of their characteristics and reduction of their stability. It is expected that the components of thermobaric mixtures do not react with each other even after long storage periods under various conditions. However, the characteristics of thermobaric mixture are changed and their functioning and safety become unacceptable. Therefore, the results of compatibility tests are very important for stability evolution of energetic materials.

One of compatibility tests based on accelerated ageing at higher temperature is available for measuring heat effects is microcalorimetry [3]. The microcalorimetric method is widely accepted in laboratories dealing with compatibility and stability examinations of energetic materials.

Microcalorimetry and calorimetry examinations, which are elaborated in this paper, were carried out in the laboratories of the Military Technical Institute.

Properties of isopropyl nitrate

Isopropyl nitrate is colourless liquid with an ethereal odour and the following physical properties and chemical structure:



- nitrogen percentage 13.33 %
- oxygen balance (to CO_2) -98.93 %
- melting temperature 191 K
- boiling temperature 374.5 K

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- specific gravity $1.049\ 10^3$ g/cm^3
- heat of combustion ~ 1015 J/g

Minimal spontaneous ignition temperature in the air measured on heated brass, Al, stainless steel or mild steel plate 518 – 533 K.

The ignition temperatures obtained by passing IPN vapour/air mixtures through a heated glass tube [4] are shown in Table 1.

Table 1. IPN vapor – air igunition temperature

Composition (% vol. IPN)	Ignition temperature T (K)
3.2	No ignition up to 773
3.8	513
4.6	493
12.6	473
28.2	463
46.2	473

Stability of isopropyl nitrate

The following data is the result of a series of high temperature storage (stability) experiments conducted on isopropyl nitrate [4]:

1. A summary for a series of **pressure development tests, developed pressure -** $\Delta p\,(\mathrm{kPa})$, involving a steel vessel of 100cm^3 capacity, half filled with IPN, and maintained at the given temperature for four hours is shown in Table 2.

Table 2. Stability of IPN

Temperature T (K)	Heating period τ_1 (h)	Δp (kPa)
373	4	82.74
393	4	103.42
408	4	158.58
415	4	515.58
423	4	689.48
433	2	Explodes

2. In another series of tests on IPN involving 500cm^3 steel vessels, the rate of temperature rise was recorded at the temperatures shown in Table 3. The **elapsed time required before decomposition, "induction" time -** τ_2 (h)**,** occurred at each.

Table 3. "Induction" time and reaction

Temperature T (K)	Time τ_2 (h)	Reaction after "induction" time
393	3	decomposition
403	2	decomposition
423	< 0.5	decomposition

Compatibility test

Microcalorimetry is a powerful tool for solving compatibility and stability problems for explosives and their components. It is a very general method due to the fact that practically all physical and chemical processes are accompanied by sligh heat exchange (sensitivity of the micro calorimeter is approximately 0.1 μW).

In compatibility studies, the heat flow is measured separately for all the constitutional materials and a mixture of these [3]. The measured (experimental) heat flow curve for the mixture is compared with a calculated hypothetical curve for the same mixture with no physical and chemical interactions. The interaction energy is defined via dependences $Q(\mu\mathrm{W/g})$ of time τ_3 (h), where Q is the heat flow data recorded by the plotter at fixed time intervals. Measuring could be carried on within the temperature range of 313K–353K over a long period of time. Heat flow data, interaction energies and physical and chemical properties of the materials are considered in the interpretations of compatibility.

The compatibility of two thermobaric mixtures was examined by microcalorimetric method. Their compositions are given below.

mixture	**IPN** (weigh %)	**Mg** (weight %)	**Al** (weight %)
A	50	50	-
B	50	40	10

Thermobaric mixtures were prepared by the method described in reference [1], with isopropyl nitrate ("Fluka") and magnesium powder definite particle size distribution and quality according to references [5, 6].

Microcalorimeter apparatuses consist of:

- LKB 2277 Thermal Activity Monitor,
- Multitemp II Thermostatic Circulator,
- LKB 2210 Potentiometric Recorder and
- Clime chamber.

Approximately 3 grams of the samples were packed in 4.5cm^3 steel ampoules and in pair with standard ampoules, after heating on the work temperature, were stored in the cylinder of microcalorimeter. Heat flow data were recorded continuously by the plotter at definite time period.

All results have been normalized to unit sample weight.

Components of the mixture (IPN, Mg and Al powders) are stabile on usual ambient exploitation temperatures (253K–313K). Components of mixtures thermobaric mixtures were tested on temperatures as high as maximum summer ambient temperatures in our country. According to information found in the references physical and chemical characteristics and thermal stability of IPN, Mg and Al, it can be concluded that eventual instability of mixture may be caused by interactions between their components. Heat exchange, caused by this interactions within the thermobaric mixture, could be measured by microcalorimeter, and presented as dependences $Q(\tau_3)$ in a diagram.

The compatibility test for samples was performed over 210 hours at 323K and heat flow data were recorded continuously by the plotter.

Results and discussion

Measured (experimental) curves have been obtained for IPN, Mg, Al, mixtures A and B based on the measured heat flow data. Measured heat flow data for single components is shown in Tables 4 and 5.

Table 4. Measured heat flow data of IPN

Time τ_3 (h)	Q (μW/g)
60	-0.25
84	-0.59
108	-1.77
132	-0.77
156	-0.59
180	-0.18
204	-0.18

Table 5. Measured heat flow data of Mg and Al

Time τ_3 (h)	Q(μW/g)	
	Mg	Al
60	8.4	0.60
84	8.6	0.60
108	8.2	0.60
116	9.5	0.60
130	8.5	0.60
138	9.0	0.54
162	8.8	0.52
210	8.0	0.60

Measured heat flow data for mixtures A and B is shown in Table 6.

Table 6 . Measured heat flow data of mixture A and B

Mixture A		Mixture B	
Time τ_3 (h)	Q(μW/g)	Time τ_3 (h)	Q(μW/g)
48	18	60	17.3
60	10	72	14
72	8	100	13.3
96	1	128	12.0
120	-0.4	152	9.3
144	-0.4	176	9.3
168	-0.4	204	9.3

Calculated (theoretical) curves of mixtures A and B are drawn using the calculated flow data. The calculations are based on the measured heat flow data for single components and their weight ratio (content) in mixtures, without interactions between the components. Calculated data for thermobaric mixture is shown in Table 7.

Table 7. Calculated flow data for mixtures A and B

Mixture A		Mixture B	
Time τ_3 (h)	Q(μW/g)	Time τ_3 (h)	Q(μW/g)
60	2.95	60	3.30
84	4.0	84	3.20
108	3.22	108	2.40
132	3.87	132	3.08
156	4.10	156	3.36
204	3.10	210	3.17

The compatibility of mixture A is shown in Fig.1.

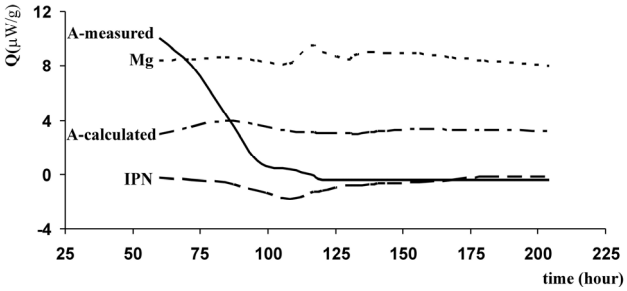

Figure 1. Compatibility of mixture A

The compatibility of mixture A is estimated by comparing the position of the measured curves of the mixture and curves of their single components (IPN and Mg). Measured curve of mixture A was located in the *zone of compatibility* – area between the curves of IPN and Mg in Fig.1. It is possible to conclude that the components of mixture A are compatible i.e. there was no interaction among the components during 210 hours on 323 K.

The compatibility of mixture B is shown in Fig.2.

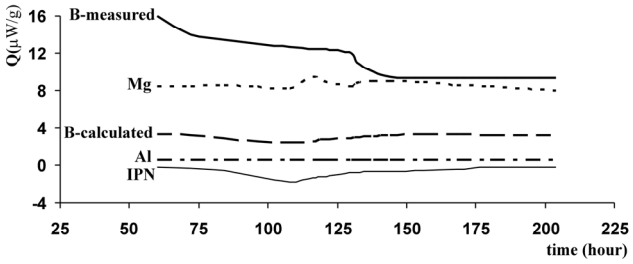

Figure 2. Compatibility of mixture B

The measured curve of mixture B is compared to curves of single components (IPN, Mg and Al). Measured curve of mixture B is outside the *zone of compatibility* – area between the curves of IPN and Mg in Fig.2. A particular heat flow registered by the microcalorimeter is probably caused by interactions between the components of mixture B. Therefore, the components of mixture B are not classified as compatible.

Heat of combustion

Heat of combustion of mixture A, whose components are classified as compatible, was determined by adiabatic calorimetric method. Heat of combustion is determined by burning a weighed sample in an oxygen bomb calorimeter under controlled conditions.

The IKA calorimetric system consists of the following components:

- IKA Central cooling water supply type KV 400,
- IKA C 400 adiabatic calorimeter,
- IKA – TRON digital calorimeter thermometer type DKT 400 C and
- Beckmann thermometer.

Heat of combustion of the sample is determined by burning it inside a calorimeter bomb B – 3321 in pure oxygen with a pressure of 30 bar [7]. IPN is a volatile liquid substance and therefore the burning is done in acetobutyrate capsules. The combustion is initiated by an electrical impulse through the ignition wire.

The heat of combustion is computed from the temperature observed before and after combustion (rise of temperature - ΔT) by digital and Beckmann thermometer.

$$Q_m = \frac{C \cdot \Delta T - \left(Q_{iw} + m_c \cdot Q_c\right)}{m_m} \qquad (1)$$

where:

- Q_m (J) – heat of combustion of thermobaric mixture,
- C (J/K) – thermal capacity of the calorimetric system,
- ΔT (K) – the rise of temperature determined during testing by digital (ΔT_d) or Beckmann (ΔT_B) thermometers,
- Q_{iw} (J) – heat of combustion of ignition wire,
- Q_c (J) – heat of combustion of acetobutyrate capsule,
- m_c (g) – weight of acetobutyrate capsule,
- m_m (g) – weight of thermobaric mixture.

If the sample is to be burnt, it has to be weighed exactly to 4 decimal places after the point. The weight of mixture A

was approximately 0.4 g, and temperature of the outer vessel water was 278 K.

The observed values of the temperature rise, determined during the calorimetric test, and calculated heat of combustion (according to formula 1) are given in Table 8.

Table 8. Combustion heat of mixture A

	digital thermometer		Beckmann thermometer		Q_m (J/g)
	ΔT_d (K)	Q_m (J/g)	ΔT_B (K)	Q_m (J/g)	
1.	1.217	1173.02	1.213	1170.53	1171.77
2.	1.204	1170.18	1202	1170.47	1170.32
Combustion heat (average)					**1171.05**

The heat of combustion of mixture A is calculated by the formula given in reference [8]. Calculation is based on heat combustion data for single components (for IPN Q~1015J/g, and Mg Q~1409J/g) and their weight ratio (content) in thermobaric mixtures. The calculated (theoretical) heat of combustion was 1213J/g. The measured results of the heat of combustion are in good agreement with the theoretical data, with the difference of 3.7%.

Conclusion

The spontaneous ignition temperature range for IPN in the air is 518–533K. The mixtures of their vapour and air are inflammable in a wide range of concentrations in defined temperatures and pressures.

IPN is stabile during storage on temperatures below 323K. It is moderately stabile on 393K for 3 hours. Decomposition of IPN starts at 393K and above this temperature.

The compatibility of IPN with the metal powders (Mg and Al) was examined.

On the basis of the microcalorimetric examinations, it is possible to conclude that IPN is compatible with Mg powder (mixture A). IPN is incompatible with the mixture of Al and Mg powders (mixture B) and its compatibility should be additionally examined using other methods.

On the basis of the adiabatic calorimetric examinations, it is possible to conclude that the mixture A (IPN /Mg) is not easily inflammable in the air, and combustion was therefore done in pure oxygen.

The obtained measured values of combustion heat of mixture A shows good agreement between the calculated results and those found in the references.

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Kompatibilnost termobaričnih smeša na bazi izopropilnitrata i metalnih prahova

Mikrokalorimetrijskom metodom je ispitana kompatibilnost termobaričnih smeša na bazi izopropilnitrata (IPN), magnezijuma (Mg) i aluminijuma (Al) u prahu. Prikazane su teorijske i eksperimentalne krive kompatibilnosti ispitivanih sastava. Metodom kalorimetrije je određena toplota sagorevanja smeše IPN/Mg u prahu.

Ključne reči: **termobarična smeša, izopropilnitrat, metalni prah, magnezijum, aluminijum, mikrokalorimetrija, kalorimetrija, kompatibilnost.**

Совместимость термобарических смесей на базисе изопропилнитрата и металлических порошков

Микрокалориметрическим методом здесь испытана совместимость термобарических смесей на базисе изопропилнитрата (ИПН), магния (Мг) и алюминия (Ал) в порошке. Тоже показаны и теоретические и экспериментальные кривые совместимости испытыванных составов и эталонов. Методом калориметрии определена теплота сгорания смеси ИПН/Мг в порошке.

Ключевые слова: **термобарическая смесь, изопропилнитрат, металлический порошок, магний, алюминий, микрокалориметрия, калориметрия, совместимость.**

Compatibilité des mélanges thermobares à la base de l'isopropyle nitrate et des poudres de métal

La compatibilité des mélanges thermobares à la base de l'isopropyle nitrate (IPN), magnésium (Mg) et aluminium (Al) en poudre a été examinée au moyen de la méthode microcalorimétrique. On a présenté les courbes théoriques et expérimentales de la compatibilité des compositions testées.
A l'aide de la méthode calorimétrique on a déterminé la température de combustion du mélange IPN / Mg en poudre.

Mots clés: **mélange thermobare, isopropyle nitrate, poudre de métal, magnésium, aluminium, microcalorimétrie, calorimétrie, compatibilité.**