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Research on reaction of the oxidizers and ammonium salts by using Differential Thermal Analysis (DTA)

SUMMARY

The presented investigations were aimed at finding objective magnitudes which could make it possible to determine the levels of separation of the oxidizers and ammonium salts, required for their transporting on ships. The levels for all chemically inconsistent substances are so far determined on the basis of multi-year experience in shipping of the goods.

In the investigations the temperature increment rate after initiation of chemical reaction of an oxidizer with ammonium salt, whose value can be determined from the thermogravimetric analysis curve, was proposed with this end in view.

INTRODUCTION

The investigations of the oxidizers of 5.1 class defined as dangerous goods in accordance with the International Maritime Dangerous Goods Code (IMDG) were earlier reported [1]. Oxidizers are defined as the substances, not necessarily flammable, but able to increase risk of fire of other materials with which they come in contact or are able to intensify the fire by emitting oxygen.

All oxidizing substances are deemed dangerous in shipping if they increase burning velocity of combustible materials such as e.g. wood flour, soot or metal dust. A list of the substances described in IMDG Code, forming combustible mixtures with combustible organic materials contains 103 items, all of 5.1 class.

New assignment criteria of the oxidizers into 5.1 class and packaging categories of IMDG Code were proposed on the basis of determination of the temperature increment rate during burning process [1÷3].

Information about oxidizer properties are given on their individual pages of IMDG Code. The data contained in the STOWAGE chapter of the Code are of special importance as they deal with oxidizer separation and determine the separation level 1 or 2: „far away from" or „separated from" other substances e.g. ammonium salts intended to be stowed in the same or neighbouring compartment or hold. The separation levels are explained in Fig.1.

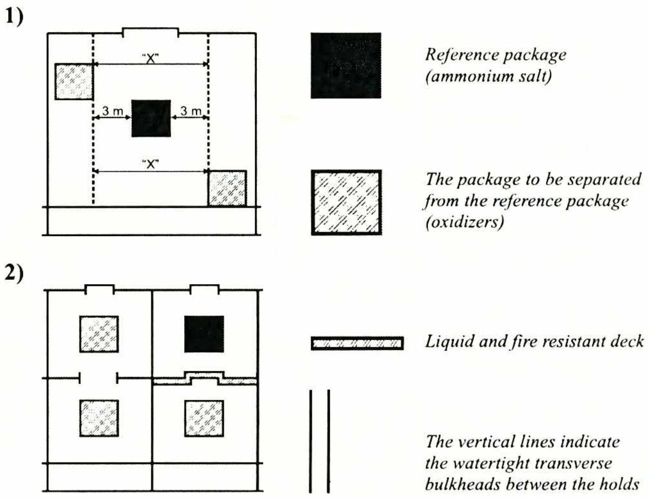

Fig. 1. Separation levels 1 (far away from) and 2 (separated from) to be applied for separation of ammonium salts from the dangerous oxidizers of 5.1 class

1) „Far away from" :

Effectively separated so that conflicting substances could not dangerously react in the case of accident, but they are allowed to be carried in the same hold, compartment or on the deck provided that the minimum horizontal distance „x" (space where stowing is not permitted) between them is 3 m (10 feet).

2) „Separated from" :

In separate holds when stowed under the deck. If the separating deck is fire and liquid resistant an equivalent stowage method can instead be applied by means of the vertical separation i.e. in separate compartments. This separation means „far away from" for stowing on the deck.

The presented investigations were aimed at finding objective magnitudes which could make it possible to determine the levels of separation of the oxidizers and ammonium salts, required for their transporting on a ship. The levels for all chemically inconsistent substances are so far determined on the basis of multi-year experience in shipping of the goods. In the investigations the temperature increment rate after initiation of chemical reaction of an oxidizer with ammonium salt, whose value can be determined from the thermogravimetric analysis curve, was proposed with this end in view.

APPLICATION OF THE DIFFERENTIAL THERMAL ANALYSIS (DTA) TO INVESTIGATION OF SOME CHEMICAL REACTIONS

Chemical reaction course during heating can be investigated by means of DTA method if the reaction occurs with a large exo-or endothermal effect. The method was earlier described in [1] and its different applications reported in [4÷9]. The attempts of its use for defining new classification criteria of the oxidizers and assigning them to the 5.1 class of IMDG Code was presented in [1].

DESCRIPTION OF EXPERIMENTS

Tests of pure oxidizers and ammonium salts

The following substances were tested by using the derivatographic method during heating :

Pure oxidizers :

Silver nitrate (V)	$AgNO_3$
Sodium dichromate	$Na_2Cr_2O_7 \cdot 2H_2O$
Ammonium dichromate	$(NH_4)_2Cr_2O_7$
Ferrum (III) nitrate (V)	$Fe(NO_3)_3 \cdot 9H_2O$
Barium chlorate (VII)	$Ba(ClO_4)_2$
Barium nitrate (V)	$Ba(NO_3)_2$
Lead (II) nitrate (V)	$Pb(NO_3)_2$
Sodium chlorate (VII)	$NaClO_4 \cdot H_2O$
Potassium chlorate (V)	$KClO_3$
Potassium iodate (V)	KIO_3

Pure ammonium salts :

Ammonium chloride	NH_4Cl
Ammonium nitrate (V)	NH_4NO_3

During derivatographic tests in air the following curves were recorded :

- TG curve of mixture mass change
- T curve of temperature change in compliance with the assumed change rate of 10°C/min
- DTA curve of temperature difference between the tested and standard sample.

The following recorder's operating parameters were applied :

T curve	-	500 μV
TG curve	-	500 μV
DTA curve	-	2.5 mV
Sensitivity	-	500

Paper speed - 2.5 mm/min at recording up to 1000°C
5.0 mm/min at recording up to 500°C

Decomposition temperatures and decomposition initiating temperatures of the compounds in question were read from the recorded curves and temperature change rates [°C/s] were calculated for their decomposition reactions. Results are presented in Tab.1. An example of derivatogram of pure ammonium chlorate is shown in Fig.2. Melting, boiling and decomposition temperatures of the pure compounds are given in Tab.2.

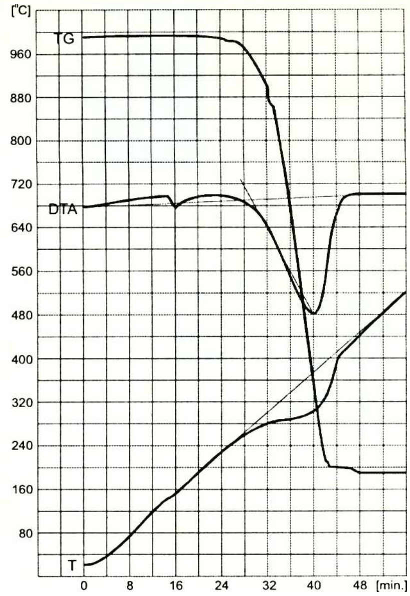

Fig.2. Derivatogram of pure ammonium chloride NH_4Cl

- *Sample weight : 420 g*
- *Heating range : 20 to 1000°C*
- *Initial decomposition temperature : 280°C*
- *Temperature change rate : 10°C/min*
- *Temperature difference read from DTA curve : Δt_{DTA} = 30°C*
- *Height of the peak on DTA curve : H = 52 mm*
- *Temperature difference read from T curve : Δt_T = 70°C*
- *Height of the peak on T curve : h = 28 mm*
- *Temperature change time : 648 s*

Tests of chemical reactions of oxidizers and ammonium salts

DTA tests of reactions of the earlier specified oxidizers and the ammonium salts : NH_4Cl and NH_4NO_3 were carried out, maintaining 1:1 weight ratio. The same operating parameters of the recorder as above were used. Lowering of an overly high peak of the temperature change was obtained by applying lower weight values of the substrates.

Measurement results are presented in Tab.1 where decomposition reaction initiating temperature of the pure oxidizers and ammonium salts, initiating temperature of the reaction between an oxidizer and ammonium salt, temperature change rates of the reactions of the pure substances as well as of an oxidizer and ammonium salt are given.

In Tab.3 results of measurements of the temperature change rates during reaction of the oxidizer and the salt NH_4Cl or NH_4NO_3 are presented , together with ranking them on the basis of the measured values.

An example of derivatogram of the reaction of potassium chlorate and ammonium nitrate is given in Fig.3.

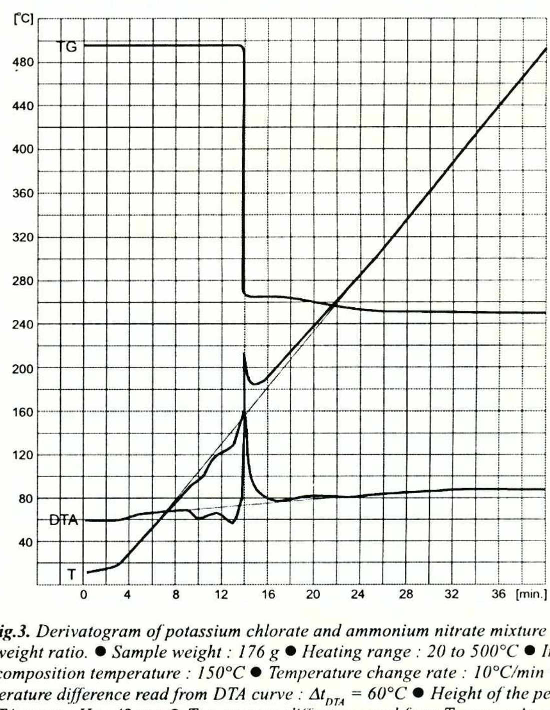

Fig.3. Derivatogram of potassium chlorate and ammonium nitrate mixture of 1:1 weight ratio. ● Sample weight : 176 g ● Heating range : 20 to 500°C ● Initial decomposition temperature : 150°C ● Temperature change rate : 10°C/min ● Temperature difference read from DTA curve : Δt_{DTA} = 60°C ● Height of the peak on DTA curve : H = 42 mm ● Temperature difference read from T curve : Δt_T = 57°C ● Height of the peak on T curve : h = 28 mm ● Temperature change time : 18 s

Tab.1. Measurement results: Thermal decomposition temperature of pure oxidizers, ammonium chloride and ammonium nitrate. Reaction initiation temperature, temperature change rate and post-initiation temperature of the reaction of oxidizer and ammonium salt

No	Oxidizers	Reacting substances	Thermal decomposition temperature or initiation temperature [°C] of :			Temperature change rate [°C/s] during :		Reaction character: „+" exothermic „-" endothermic
			oxidizer decomposition	decom-position of NH_4Cl or NH_4NO_3	oxidizer--ammonium salt reaction	thermal decom-position	oxidizer--ammonium salt reaction	
1.	Silver nitrate (V) $AgNO_3$	1) $AgNO_3$	500	-	-	-0.155	-	-
		2) NH_4Cl	-	345	-	-0.045	-	-
		3) NH_4NO_3	-	200	-	0.275	-	+
		4) 1+2	-	-	247	-	0.29	+
		5) 1+3	-	-	308	-	0.71	+
2.	Sodium dichromate $Na_2Cr_2O_7 \cdot 2H_2O$	1) $Na_2Cr_2O_7 \cdot 2H_2O$	349	-	-	-0.075	-	-
		2) NH_4Cl	-	345	-	-0.045	-	-
		3) NH_4NO_3	-	200	-	0.275	-	+
		4) 1+2	-	-	221	-	1.49	+
		5) 1+3	-	-	195	-	2.12	+
3.	Ammonium dichromate $(NH_4)_2Cr_2O_7$	1) $(NH_4)_2Cr_2O_7$	237	-	-	-0.075	-	-
		2) NH_4Cl	-	345	-	-0.045	-	-
		3) NH_4NO_3	-	200	-	0.275	-	+
		4) 1+2	-	-	246	-	0.59	+
		5) 1+3	-	-	181	-	7.37	+
4.	Ferrum (III) nitrate (V) $Fe(NO_3)_3 \cdot 9H_2O$	1) $Fe(NO_3)_3 \cdot 9H_2O$	138	-	-	-0.065	-	-
		2) NH_4Cl	-	345	-	-0.045	-	-
		3) NH_4NO_3	-	200	-	0.275	-	+
		4) 1+2	-	-	240	-	1.41	+
		5) 1+3	-	-	222	-	0.43	+
5.	Barium chlorate (VII) $Ba(ClO_4)_2$	1) $Ba(ClO_4)_2$	490	-	-	1.97	-	+
		2) NH_4Cl	-	345	-	-0.045	-	-
		3) NH_4NO_3	-	200	-	0.275	-	+
		4) 1+2	-	-	444	-	3.13	+
		5) 1+3	-	-	308	-	0.83	+
6.	Barium nitrate (V) $Ba(NO_3)_2$	1) $Ba(NO_3)_2$	758	-	-	0.21	-	+
		2) NH_4Cl	-	345	-	-0.045	-	-
		3) NH_4NO_3	-	200	-	0.275	-	+
		4) 1+2	-	-	360	-	0.19	+
		5) 1+3	-	-	350	-	0.40	+
7.	Lead (II) nitrate (V) $Pb(NO_3)_2$	1) $Pb(NO_3)_2$	425	-	-	-0.09	-	-
		2) NH_4Cl	-	345	-	-0.045	-	-
		3) NH_4NO_3	-	200	-	0.275	-	+
		4) 1+2	-	-	248	-	8.48	+
		5) 1+3	-	-	282	-	1.18	+
8.	Sodium chlorate (VII) $NaClO_4 \cdot H_2O$	1) $NaClO_4 \cdot H_2O$	580	-	-	0.44	-	+
		2) NH_4Cl	-	345	-	-0.045	-	-
		3) NH_4NO_3	-	200	-	0.275	-	+
		4) 1+2	-	-	448	-	8.48	+
		5) 1+3	-	-	282	-	1.18	+
9.	Potassium chlorate (V) $KClO_3$	1) $KClO_3$	548	-	-	0.225	-	+
		2) NH_4Cl	-	345	-	-0.045	-	-
		3) NH_4NO_3	-	200	-	0.275	-	+
		4) 1+2	-	-	178	-	7.37	+
		5) 1+3	-	-	140	-	7.67	+
10.	Potassium iodate (V) KIO_3	1) KIO_3	655	-	-	0.225	-	+
		2) NH_4Cl	-	345	-	-0.045	-	-
		3) NH_4NO_3	-	200	-	0.275	-	+
		4) 1+2	-	-	310	-	0.10	+
		5) 1+3	-	-	183	-	3.23	+

RESULTS AND CONCLUSIONS

- The tests of chemical reactions between 10 selected oxidizers and ammonium chloride or ammonium nitrate, performed with the use of DTA method, revealed that separation criteria of the oxidizers from ammonium salts can be established by determining the temperature change rate during the reactions.
- It was assumed that the compounds will require 2nd separation level, i.e. „separated from"if the temperature change rate during reaction of the oxidizer and ammonium salt exceeds 2°C/s.
- Therefore the following tested oxidizers require to be separated from ammonium salts in accordance with 2nd separation level :
  - Potassium chlorate (V) $KClO_3$
  - Sodium chlorate (VII) $NaClO_4 \cdot H_2O$
  - Barium chlorate (VII) $Ba(ClO_4)_2$
- It was revealed that if an ammonium salt itself is of oxidizing character then also less active oxidizers require to be separated in compliance with 2nd separation level. Namely, the following oxidizers should be separated from ammonium nitrate (V) with observing the 2nd level :
  - Ammonium dichromate $(NH_4)_2Cr_2O_7$ intended to be stowed together with ammonium nitrate but not ammonium chloride.
  - Potassium iodate (V) KIO_3 intended to be stowed together with ammonium nitrate but not ammonium chloride.
  - Sodium dichromate $Na_2Cr_2O_7 \cdot 2H_2O$ intended to be stowed together first of all with ammonium nitrate.
- Reaction hazards are very great first of all from the side of chlorates and perchlorates mixed with ammonium chloride. They are somewhat lower for their mixtures with ammonium nitrate (V).

It mainly concerns sodium chlorate (VII) and barium chlorate (VII). Potassium chlorate (V) is dangerous when mixed both with ammonium nitrate and ammonium chloride.

- The below specified oxidizers do not at all require to be separated from ammonium salts or 1[st] separation level can be applied to, i.e. the „far away from" level :

Silver nitrate (V)	$AgNO_3$
Ferrum (III) nitrate (V)	$Fe(NO_3)_3 \cdot 9H_2O$
Barium nitrate (V)	$Ba(NO_3)_2$
Lead (II) nitrate (V)	$Pb(NO_3)_2$

- The requirement of 2[nd] separation level for chlorates (V) and perchlorates is in compliance with IMDG Code provisions. Similarly, absence of requirements concerning the separation of silver (V), ferrum(III), barium and lead nitrates fully complies with the Code.
- Test results of sodium dichlorate and ammonium dichlorate as well as potassium iodate (V) justify to carry out further tests of the salts during reactions with the ammonium salts containing the oxidizing anion e.g. ammonium chlorate (VII) as well as with that containing the non-oxidizing anion e.g. ammonium orthophosphate (V).

Tab.2. Melting, boiling and decomposition temperatures of the tested oxidizers acc. [18]

No	Compound name	Temperature [°C]		
		melting point	boiling point	decomposition
1.	Silver nitrate (V) $AgNO_3$	212	-	444
2.	Sodium dichromate $Na_2Cr_2O_7 \cdot 2H_2O$	$-H_2O$ 100	-	400
3.	Ammonium dichromate $(NH_4)_2Cr_2O_7$	170	-	170
4.	Ferrum (III) nitrate (V) $Fe(NO_3)_3 \cdot 9H_2O$	47.5	-	125
5.	Barium chlorate (VII) $Ba(ClO_4)_2$	505	-	-
6.	Barium nitrate (V) $Ba(NO_3)_2$	592	Decomposition	-
7.	Lead (II) nitrate (V) $Pb(NO_3)_2$	470	-	470
8.	Sodium chlorate (VII) $NaClO_4 \cdot H_2O$	130	482	482
9.	Potassium chlorate (V) $KClO_3$	356	-	400
10.	Potassium iodate (V) KIO_3	560	-	R-100
11.	Ammonium chloride NH_4Cl	340	520	-
12.	Ammonium nitrate (V) NH_4NO_3	71.5	-	260

Note : „R – 100" - initiation of decomposition

Tab.3. The tested oxidizers ordered in accordance with their behaviour during reaction with the ammonium salts NH_4Cl and NH_4NO_3, expressed by the temperature change rate [°C/s] after reaction initiation

No	Name of the oxidizer tested during reaction with ammonium salts	Present level of separation from ammonium salts acc. to IMDG Code	Temperature change rate during reaction: oxidizer – ammonium salt [°C/s]		Separation level proposed in result of DTA tests
			NH_4Cl	NH_4NO_3	
1.	Potassium chlorate (V) $KClO_3$	2	7.37	7.57	2
2.	Sodium chlorate (VII) $NaCl_4 \cdot H_2O$	2	8.48	1.18	2
3	Barium chlorate (VII) $Ba(ClO_4)_2$	2	3.17	0.83	2
4.	Ammonium dichromate $(NH_4)_2Cr_2O_7$	Not required	0.59	7.37	2
5.	Potassium iodate(V) KIO_3	Not required	0.10	3.23	2
6.	Sodium dichromate $Na_2Cr_2O_7 \cdot 2H_2O$	Not required	1.49	2.12	2
7.	Silver nitrate (V) $AgNO_3$	Not required	0.29	0.71	No separation
8.	Ferrum(III) nitrate (V) $Fe(NO_3)_3 \cdot 9H_2O$	Not required	1.41	0.43	No separation
9.	Barium nitrate (V) $Ba(NO_3)_2$	Not required	0.19	0.49	No separation
10.	Lead(II)nitrate (V) $Pb(NO_3)_2$	Not required	0.27	0.63	No separation

Note: Separation level 2 - „Separated from"

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Conference

SYMPOSIUM ON FIRE PROTECTION

On 17 November 1998 a symposium was organized by the Institute of Ship Electrotechnics and Automation, Maritime University of Szczecin. The symposium was devoted to :

„Fire protection - fire spreading limitation - remedies"

Four out of all presented papers directly dealt with ship technology and shipping, namely :

- „Insulation failures in ship electric installations as a fire source" by J.Hrynkiewicz, Institute of Ship Electrotechnics and Automation, Maritime University, Szczecin
- „Fire- and electric-shock protecting system" by J.Hrynkiewicz, idem
- „Fire fighting on ships at sea" by K.Górka, Polish Shipping Company, Szczecin
- „Ship power plant fires" by G.Kidacki, Institute of Ship Power Plant Technical Exploitation, Maritime University of Szczecin.

A representative of Günther Klein Industriebedarf GmbH, Germany, taking part in the symposium, presented its own concept of leading the cables and pipes through watertight and fireproof bulkheads, which assures the required level of ship safety.

The symposium met with great interest (70 participants) of ship officers and engineers as well as students of the maritime universities at Szczecin.