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Application of Thermal Analysis and Trough Test for Determination of the Fire Safety of Some Fertilizers Containing Nitrates

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ABSTRACT: The studies on how a fire on board accidents may be prevented have been actively carried out at both the national and international levels. This paper provides an outlook on fire safety assessment concerning nitrates fertilizers in sea transport. The investigation was aimed at comparison two methods of classification and assignment to a packing group of solid fertilizers of class 5.1 of International Maritime Danger Goods Code. First research was conducted in accordance with the test method described in the United Nations Recommendations on the Transport of Dangerous Goods, Manual of Test and Criteria, Part III, 34.4.1 "Test for oxidizing solids". The second method was the differential thermal analysis (DTA) where the basis was the determination the temperature change rate during thermal reaction. According to two used tests, the investigated fertilizers belong to 5.1 class and require to packaging group III of the International Maritime Danger Goods Code. The DTA method gives more quantitative information about fire risk on the ship than method recommended in International Maritime Danger Goods Code.

1 INTRODUCTION

The range of materials, which must be transported by sea and stored, is gradually increasing. Today we need observe more consideration of aspects of transportation of large quantity of dangerous goods. The term dangerous is limited to substances which have the potential to cause major accident risk from fire, explosion or toxic release. Including also oxidizing and explosives materials, which during transport might be initiated by fire, impact, resulting from badly packed or was out of specification explosives. In the International Maritime Dangerous Goods Code the information concerning various aspects of sea handling of hazardous materials is contained. Official regulations and supplementary documentation of the hazardous properties of materials can be found in this code. It is an important source of basic information and a guide to shipping of hazardous goods for a ship staff.

Oxidizers are dangerous goods in accordance with International Maritime Dangerous Goods Code (IMDG Code), belong to 5.1 class, they are not necessarily flammable, but able to intensify the fire by emission oxygen. Oxidizers may be elements, acids, or solid substances (e.g. nitrates salts). Some oxidizing substances have toxic or corrosive properties, or have been identified as harmful to the marine environment. They will react in contact with reducing reagents. Hence oxidizing agent will invariably accelerate the rate of burning of combustible material. The National Fire Protection Association in United Stated classified oxidizing substances according the stability [Burke, 2004]:

Class1 – Solid or liquid that readily yields oxygen or oxidizing gas or that readily reacts to oxidizer combustible materials.

Class 2 – Oxidizing material can cause spontaneous ignition when contact with combustible materials.

Class 3 – Oxidizing substances that can undergo vigorous self sustained decomposition when catalyzed or exposed to heat.

Class 4 – Oxidizing articles that can undergo an explosive reaction when catalyzed or exposed to heat, shock or friction.

Among the fertilizers mentioned in the IMDG Code the most dangerous are nitrates(V), belong to oxidizers of class 5.1 of danger goods and ammonium salts [IMDG Code]. Pure ammonium nitrate, the base of fertilizers, belong to compounds transported in limited quantities (UN 0222 –ammonium nitrate, with more than 0,2% combustible substance) Ammonium nitrate UN 1942 with not more than 0,2% total combustible substances including any organic substance calculated as carbon during transport the temperature of material should not be above 40^{0}C. Do not ventilate this cargo.

Ammonium nitrate based fertilizers UN 2067, UN 2071,UN 2067 may transported in bulk. Fertilizers: potassium nitrate – UN 1486, sodium nitrate UN 1498 and sodium and potassium nitrate mixtures UN 1499, calcium nitrate UN 1454 may be also transported in bulk [BC Code]. Nitrates fertilizers are highly hygroscopic and will cake if wet. They belong to cargo group A and B (Group A consists of cargoes which may liquefy if shipped at a moisture content in excess of their transportable limit. Group B consists of cargoes which possess chemical hazard which could give rise to dangerous situation on the ship) [Appendix A and B BC Code, 2001].

A major fire aboard a ship carrying these materials may involve a risk of explosion in the event of contamination by combustible materials or strong confinement. An adjacent detonation may also involve a risk of explosion. During thermal decompose nitrate fertilizers giving toxic gases and gases which support to combustion. Dust of fertilizers might be irritating to skin and mucous membranes.

Classification of oxidizing substances to class 5.1 is based on test described in the IMDG Code and Manual of Tests and Criteria [UN Recommendations Part III]. In this test, the investigated substances were mixed with cellulose, which is a combustible material, in ratios of 1:1 and 4:1, by mass, of substance to cellulose. The mixtures were ignited and the burning time was noted and compared to a reference mixture, in ratio 3:7, by mass, of potassium bromate(V) to cellulose.

The assignation criteria to the packaging groups are based on a physical or chemical property of goods. There are at present no established good criteria for determining packaging groups. (To packaging group I belongs substances great danger, II - medium danger, or III, minor danger).

If a mixture of test substance and cellulose burns equal to or less than the reference mixture, this indicates that the combustion of the combustible material (cellulose) is enhanced by the test substance and the test substance has oxidizing (fire enhancing) properties and is classified in class 5.1. This also means that oxidizing substance is assigned to a packing group III (if the criteria of packing group I and II are not met). Next the burning time is compared with those from the packing group I or II reference standards, 3:2 and 2:3 ratios, by mass, of potassium bromate(V) and cellulose. Any substance which, in both the 4:1 and 1:1 sample-to-cellulose ratio (by mass) tested, does not ignite and burn, or exhibits mean burning times greater than that of a 3:7 mixture (by mass) of potassium bromate(V) and cellulose, is not classified as class 5.1.

Using these criteria we test a big mass sample of component which involve larger volumes of toxic gases, as opposed to a differential thermal analysis, where the basis is the determination the temperature change rate during thermal decomposition.

Using differential thermal analysis (DTA) we can registration quality and quantity changes during dynamic heating of investigated materials in time.

The self-heating or thermally explosive behavior of individual chemicals is closely related to the appearance of thermogravimetry-differential thermal analysis (TG-DTA) curve with its course.

In previous examinations of mixtures of oxidizers with cellulose and flour wood [Michałowski, Barcewicz 1997, Michałowski Barcewaicz 1998, Michałowski, Rutkowska, Barcewicz 2000, Kwiatkowska-Sienkiewicz et al 2006, Kwiatkowska-Sienkiewicz 2008] the temperature change rates [^{0}C/s] were calculated into 1 milimole of an oxidizer and tested oxidizing substances were blended with combustible substance in mass ratio 5:1.

According to later experiments not classified to class 5.1 any substances which temperature change rate are lower than 0,2 [^{0}C/s].

To packaging group III should be assigned substances, which during thermal analysis mixtures oxidants with cellulose, the temperature change rate values are between 0,2 to 1,4 [^{0}C/s].

To packaging group II should be assigned substances blended with cellulose of with the temperature change rate values are between 1,4 to 5,0 [^{0}C/s].

To packaging group I belong of mixtures oxidizes with cellulose which temperature change rate values exceed 5,0 [^{0}C/s].

Later and now in experiments used cellulose as combustible material. Cellulose belongs to polysaccharides, develop free radicals on heating. The free radicals in cellulose thermolysates is cellulose variety dependent. The generation of free radicals on heating is time and temperature dependent whereas in termoanalitical studies exposure to heat is for relatively short time. All polysaccharides (e.g. starch) during heating generated free radicals [Ciesielski, Tomasik 1998, Ciesielski, Tomasik, Baczkowicz 1998].

In practice, during long transport combustible materials and commodities containing polysaccharides we can observe self-heating effect, specially, if polysaccharides are blended with oxidizers. Free radical exposed during thermal reaction polysaccharides mixed with nitrates (V) (nitrates(V) belongs to 5.1 class dangers goods), gives possibility self-heating and self-ignition chemical reaction.

In these paper fertilizers, containing sodium, potassium, calcium and ammonium nitrates, blended with cellulose was investigated.

This examinations whereas basing on potassium bromated (V) blends with cellulose (in mass ratio 2:3 and 7:7) as a standard shows that class 5.1 includes substances which temperature change rate was greater than temperature change rate of mixture of potassium bromated (V) with cellulose, in mass ratio 3:7 – 0,96 [ºC/s].

To the III packaging group should be assigned substances, which during thermal analysis mixtures oxidants with cellulose, the temperature change rate values are between 0,96– 1,82 [ºC/s].

II packaging group involves crossing value of the temperature change rate under 1,82 [ºC/s].

In this paper we concerned on comparison two methods of assignation to class 5.1 and classification to packing groups. The first one is recommended by United Nations [UN Recommendations] and second one, differential thermal analyze is using in chemistry.

2 EXPERIMENTAL

Determination according to IMDG Code and UN Recommendations test and DTA method were carried out using the same blends oxidants/fertilizer and cellulose.

The following substances were blended with cellulose in mass ratio 1:1 or 1:4

- sodium nitrate (V) pure for analysis,
- ammonium nitrate based fertilizer with 30% nitrogen,
- nitro-chalk with 27,5% nitrogen,
- calcium nitrate based fertilizer with 15% nitrogen,
- potassium nitrate based fertilizer with 14% nitrogen,
- as reference material - potassium bromate(V) pure for analysis blended with cellulose in mass ratio 3:7 and 2:3.

In experiments used microcrystalline cellulose, grade Vivapur type 101, particle size >250 µm (60

mesh), bulk density 0.26 – 0.31 g/ml.

Mean burn time of trials mixtures fertilizes and cellulose are presented in Table 1.

Chemical reaction course during the heating can be investigated by means of differential thermal analysis (DTA) method. Using thermal analysis (DTA), the changes of mass, temperature and heating effects curves are recorded.

Thermal decomposition with self-ignition effect is demonstrated in Fig.1:

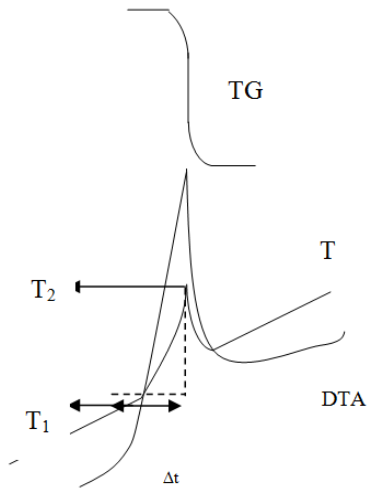

Figure 1. Self –ignition effect monitored by DTA method [Kwiatkowska-Sienkiewicz, Barcewicz 2001]

The following outputs were recorded during measurements using DTA method.

- T – the temperature change curve which is a straight line till the mixture flash point is reached, with a district peak in the self-ignition region, especially during reaction of very active oxidizers,
- DTA curve – gives information about heat effects,
- TG curve - of mass change during the reaction,

beginning of self-ignition process - T_1,

maximum of self-ignition reaction – T_2,

maximum temperature increase: T_2-T_1= ΔT,

temperature change time (from T_1 to T_2) Δt,

The temperature increase value was determined from the temperature change curve T on the basis of its deflection out of the straight line, in the peak region. On the ground of the above mentioned data following parameters could be calculated. The temperature change rates [^{o}C/s] were calculated by dividing the temperature increase (ΔT) by the time of self-ignition effect (Δt), counted into 1 g of a fertilizers/oxidizers. At first pure oxidants and fertilizers were tested. Then mixtures of fertilizers with cellulose and oxidizers substance with cellulose were tested. Thermal treatment of pure oxidizers or the blends were heated from room temperature to 500^{o}C. The procedure was run in the air under dynamic condition. The rate temperature increase was 10^{o}C/min. Ceramic crucibles were taken. Paulik-Paulik-Erdley 1500 Q Derivatograph (Hungary) was used. The measurements were carried out three times. Decomposition initiating temperatures of the compounds, and his blends with cellulose were read from the recorded curves.

The temperature change rates [^{o}C/s] were calculated from the curves DTA and T by dividing the temperature increase by the time of self-ignition effect, calculated into 1 g of an oxidizer or multicompound fertilizer.

3 RESULTS

The results of performed thermal reactions of oxidizers/fertilizers and cellulose are presented in Tables 1 and 2.

On the basis of results of the test described in Manual of Test and Criteria all examinated fertilizers, according to IMDG Code, belong to class 5.1 of Dangerous Goods and require packaging group III.

The results of second method of performed thermal reactions between cellulose and selected fertilizers are presented in Tables 2 and 3. Blends of potassium bromate(V) and cellulose in mass ratio 3:7 and 2:3 are the standards in classification using differential thermal analyses tests (we used the same standards like in Manual Test recommended by IMDG Code).

Table 1. Determination risk of fire oxidizers/fertilizers according to Manual Test and Criteria IMDG Code

Oxidizer	Sample to cellulose.	Burn rate [cm/min.]		Proposed	
		Samppl e	Stand ard	Class IMDG	Paca-ging-group
Ammonium nitrate fertilizer (30% N)	1:1	1,38	0,83	5.1	III
	4:1	1,08			
Nitro-chalk fertilizer (27,5% N)	1:1	0,93	0,83	5.1	III
	4:1	0,20			
Calcium nitrate based fertilizer (15% N)	1:1	0,92	0,83	5.1	III
	4:1	0			
Potassium nitrate based fertilizer (14% N)	1:1	2,18	0,83	5.1	III
	4:1	0			
Sodium nitrate (V) (p.a.)	1:1	2,71	0,83	5.1	III
	4:1	0			
Potassium bromate (V) (p.a.) (standard)	2:3	10	10	5.1	II
	3:7	0,83	0,83	5.1	III

Table 2. Thermal decomposition oxidizers/fertilizers and his blends with cellulose using DTA method

Oxidizers	Sample to cellulose	Ignition temperature [ºC]		Temperature change rate [ºC/s]		Egzo+ Endo-reaction
		Oxidizer	Ox. – cell.	Ox.	Ox.-cell.	
Ammonium nitrate based fertilizer (30% N)	1:1	335	205,4	1,67	1.68	+
	4:1		211,7		1,68	+
Nitro-chalk fertilizer (27,5% N)	1:1	338	197,3	0,5	1,7	+
	4:1		218,3		1,74	+
Potassium nitrate based fertilizer (14% N)	1:1	–	*	–		
	4:1	*	315,3		0,95	–
Sodium nitrate (V) (p.a.)	1:1	–	320	–	1,16	+
	4:1	*	326		1,44	+
Potassium bromate (V) (p.a.) (Standard)	3:7	455	329,3	2,6	0,96	+
	2:3		190		1.82	

*- (not observed ignitron until 500°C)
Ox. – oxidizer/fertilizer
cell. - cellulose

Table 3. Assignment of the fertilizers to the packaging group based on temperature change rate

Name of the fertilizer	Temperature change rate [°C/s]	Assigned packaging group	Proposed class of IMDG Code
Ammonium nitrate based fertilizer (30% N)	1,68	III	5.1
Nitro-chalk fertilizer (27,5% N)	1,74	III	5.1
Potassium nitrate based fertilizer (14% N)	0,96	III	5.1
Sodium nitrate (V)	1,44	III	5.1
Potassium bromate (V) (Standard)	0,96÷1,81	III	5.1

The ignition temperature and temperature change rate make it possible to assess packaging group of investigated fertilizers, belong to class 5.1 of danger goods.

The blends of fertilizers and cellulose had lower ignition temperature then pure oxidizers. Hence those fertilizers will invariably accelerate the rate of burning with combustible materials. Pure potassium and sodium nitrates, high ionic compounds, had thermal decompose in higher temperatures than 500^0C, but the mixtures with combustible material – cellulose were decomposed in temperature about 320^0C. All blends fertilizers and cellulose decomposed in lower temperatures than pure oxidizes.

During reactions observed generally exothermic processes and weight losses. It's very dangerous in shipping, especially of bulk cargo. Fertilizers containing nitrates and ammonium salts, during fire on the boat, lost stowage mass about 1/3 to ½ .

The results differential thermal analyze suggest similar effects like in the tests recommended by IMDG Code; all investigated fertilizers belong to 5.1. class of dangerous goods and require to packaging group III.

After comparison these two methods of assignation to class 5.1 and packaging group's data thermal analyze gives quantitative information about thermal effects (melting, self-heating, self-ignition) and loss mass during heating. During Manual Test (according IMDG Code) we have only qualitative data burning time of blends oxidizers with cellulose. In Manual Test was use big probe - 30g blends of oxidizer and cellulose, in DTA method only - 300 ÷500 mg.

Differential thermal analyze is objective chemical method which could make it possible to determine the criteria of assignment of oxidizers to packaging groups, required for sea transport. Data DTA method gives more information about fire risk assessment that Manual Test recommended by IMDG Code.

4 CONCLUSION

Manual Test recommended in IMDG Code informs only qualitative about burning time special trial form of oxidizer – cellulose blends.

The comparison two methods of classification and assignment to a packing group of solid substances of class 5.1 of IMDG Code indicate, that differential thermal analyze (DTA method) gives objective, quantitative information about fire risk on the boat.

Using this method, during heating we can registration changes of temperature, loss mass, melting point temperatures mixtures before self-heating, self-ignition and explosive effects.

Data based on the differential thermal analysis gives more information about fire risk assessment that Manual Test recommended by IMDG Code.

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