ZENON MICHAŁOWSKI,
Assist.Prof.,D.Sc.,Chem.E.
KAROL BARCEWICZ, M.Sc.Chem.
Gdynia Maritime Academy

A new proposal for assignment criteria of the oxidizers into 5.1 class and packaging categories of IMDG Code

SUMMARY

Derivatographic tests (based on DTA method) were carried out on wood flour - oxidizer mixtures to determine new criteria for assignment of the oxidizers to the class 5.1 and appropriate packaging categories of IMDG Code. It was demonstrated that DTA method can be applied to elaborating the criterion of classification of oxidizing substances into 5.1 class and appropriate packaging categories on the basis of the temperature change and time value for a reactive mixture after its self-ignition. As the criterion the temperature change rate, in °C/s, counted from the self-ignition instant to that of obtaining the maximum temperature value, is proposed.

On the basis of the criterion new principles of classifying the oxidizers and assigning to them a packaging category were formulated.

INTRODUCTION

In sea transport various chemicals are often shipped, deemed hazardous because of their physical, chemical or toxic properties which form different dangerous situations not only in seaway but also during cargo handling operations (storing, loading and unloading etc).

To avoid risk of the hazards a special code (International Maritime Dangerous Goods Code - IMDG Code) was elaborated in which most chemicals shipped by sea were grouped into nine hazard classes divided into sub-classes. The Code comprising the characteristic physical and chemical properties of particular substances forms guidelines for all operations connected with the transportation of dangerous chemicals by sea (selection of packaging, segregation during stowage etc). The Code is continuously updated and supplemented.

The class 5.1 comprises oxidizing substances. Oxidizers are defined as the substances, not neccesserily 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. The oxidizer is any substance able to absorb electrons by the atoms of its elements, located at a higher stage of oxidation and able to absorb the electrons. The chromates and bichromates contain Cr atoms at the oxidation stage +6 and are the oxidizers as they lower, by absorbing the electrons, the oxodation stage of Cr to +3.

In sea transport the chromates are not assigned at all to the dangerous oxidizing goods of the class 5.1, basing on multi-year experience with them. Out of all Cr compounds only CrO_3 oxide and $(NH_4)_2Cr_2O_7$ ammonium bichromate are at the +6 stage of oxidation, but all remaining bichromates e.g. $K_2Cr_2O_7$ have been eliminated from the IMDG Code, as the substances accelerate to an insuficient extent the burning process of combustible materials e.g. wood flour, which is the basis for assessing the hazards formed by an oxidizer during its sea shipping.

In the Department of Chemistry, Gdynia Maritime Academy, derivatographic tests were carried out on wood flour - oxidizer mixtures to determine new criteria for assignment of the oxidizers to the class 5.1 and appropriate packaging categories.

OUTLINE OF DERIVATOGRAPHY - DIFFERENTIAL THERMAL ANAYSIS (DTA)

The derivatographic tests called also the differential thermal analysis (DTA) make it possible to demonstrate effects which accompany the physical changes (e.g. melting, sublimation) or the chemical ones (exo-or endothermic reactions). During measurements the test sample and the standard one in which no thermal changes occur, are simultaneously heated in an oven, in the same conditions. Heating rate of the oven should be constant to obtain the linear relationship between oven temperature and time. Thermoelements are installed in the test sample and neutral substance, which make measuring and recording the temperature difference ΔT of the sample and substance possible.

As long as no processes occur in the sample, which could absorb or emit heat, the test sample and standard sample temperatures are equal, $T_p = T_w$, and the measuring device does not indicate any temperature difference as $\Delta T = T_p - T_w = 0$ (Fig.2). If endothermic reaction is taking place in the sample, the test sample temperature T_{pl} is lower than the standard sample temperature T_{wz}, $T_{pl} < T_{wz}$, and the device shows the temperature difference $\Delta T_1 = T_{pl} - T_{wz}$.

In the case of exothermic reaction the tested sample temperature $T_{p2} > T_{wz}$, $\Delta T_2 = T_{p2} - T_{wz}$.

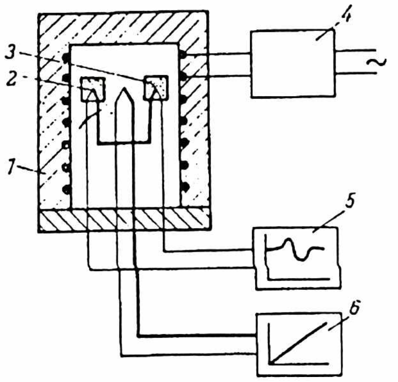

Fig.1. Scheme of DTA device
1- oven, 2 - test sample, 3 - standard substance (sample), 4 - oven constant heating rate control system, 5 - temperature difference recording system, 6 - temperature recording system

Detection of the exothermic and endothermic effects which proceed in a tested system is possible by using DTA method. Derivatograph's indications are automatically recorded to form the temperature - time relationship curve, T = f (t) and the curve ΔT = f (t).

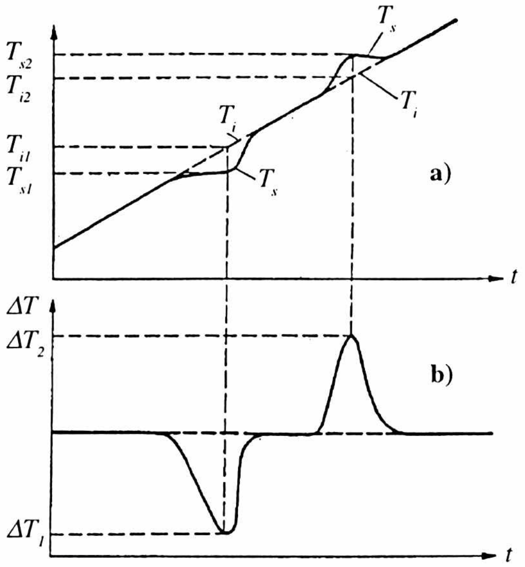

Fig.2. Formation of DTA curve
a) T_s - the curve of test sample temperature changes versus time, T_i - the curve of standard substance temperature changes versus time
b) The curve of temperature differences versus time (DTA curve); it is obtained by deducting the appropriate values of T_s and T_i curves and scaling-up the result

Raemy and Lolinger [1], by using the method, determined self-ignition temperatures of different powdered nutriment substances. Dust explosion and fire are especially hazardous in food industry. They used the DTA method for determining the proneness of nutriment powders to self-ignition to fix safety conditions for high temperature technological processes. On the basis of test results they concluded that it is possible to precisely determine self-ignition conditions by using the DTA method.

The method was also applied to testing the explosives. The materials are thermally labile and disintegrate, when heated or fired, revealing a highly exothermal effect. For explosive materials the temperature at which the disintegration originates, is of special importance. They heated different nutriment powders in the derivatograph, in the oxygen atmosphere and under the pressure of 2.5 mPa, to determine their self-ignition temperatures. They succeeded to get temperature change versus time record for wheat flour which is similar to that presented in Fig. 2. Thus DTA method makes determining the temperature possible, additionally informing on the physical processes (phase transformations, melting) which occur just before the disintegration or directly after it.

DERIVATOGRAPHIC TESTS OF MIXTURES OF OXIDIZERS AND WOOD FLOUR

The above reviewed tests led to expectations that DTA method could be applied to assigning the oxidizers to 5.1 class of dangerous goods shipped by sea, and to a relevant packaging category, I ,II or III, in respect to a hazard level of their properties.

Mixtures of the dried wood flour of grain diameter less than 0.3 mm, as the flammable substance, and oxidizers of the same grain size, were tested in a MOM Budapest Q 1100 derivatograph, in the temperature range of 20 to 1000°C. Oxidizer content in the mixtures was of 40 to 80 % . The following oxidizers were tested :

- ammonium proxy sulphate, $(NH_4)_2S_2O_8$
- potassium perchlorate, $KClO_4$
- sodium nitrate, $NaNO_3$
- potassium bromate, $KBrO_3$
- nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$
- potassium dichromate, $K_2Cr_2O_7$
- sodium dichromate, $Na_2Cr_2O_7 \cdot 2H_2O$
- magnesium nitrate, $Mg(NO_3)_2 \cdot 6H_2O$
- ammonium nitrate, NH_4NO_3
- sodium peroxy borate, $NaBO_3 \cdot H_2O_2 \cdot 3H_2O$.

Aluminium oxide was used as the standard substance. The tests were carried out in argon atmosphere, with simultaneous extraction of the decomposition products by means of a pump. The argon atmosphere was applied to prevent oxidizing effect of air. Measurements were performed at the heating rate of 10°C/min. The samples tested within the temperature range of 20 to 250°C were heated at the rate of 5°C/min.

The test mixture was weighed on the derivatograph's balance. The mixtures which contained violently reacting oxidizers, were weighed in the amount of several dozen to 200 mg and placed in a platinum cell. Mixtures with less active oxidizers were placed in a ceramic cell (300 to 600 mg). An amount of substance and way of sample preparation was such as not to cause throwing away the substance from the cell due to the violent effect of starting the combustion, i.e. in the self-ignition moment. Therefore when testing the mixtures containing very active oxidizers, they were thinned with aluminium oxide. For sodium chlorate the mixture/aluminium oxide ratio was 1:3; for sodium nitrate 1:1.3; for potassium dichlorate and potassium bromate 1:1.

The following outputs were recorded during measurements :

- the temperature change curve T which is a straight line till the mixture flash point is reached, with a distinct peak in the self-ignition region, especially during reaction of very active oxidizers
- DTA curve
- TG curve of mixture mass change during reaction.

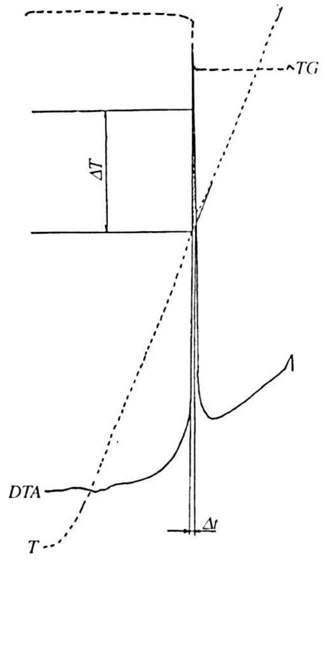

Fig.3. Derivatogram for potassium bromate
t - time

Test conditions

Test mixture content : 80 % of $KBrO_3$ and 20 % of wood flour
Oxidizer weighed amount: 0.124 g
The oxidizer-wood flour mixture thinned with Al_2O_3 at the weight ratio 1:1
Tests in argon atmosphere at 0.03 mPa pressure

Recorder's operating parameters :

T curve	-	500μV	Sensitivity : 500
TG curve	-	500μV	Paper speed : 2.5 mm/min
DTA curve	-	1mV	Temperature change rate : 10°C/min

Self-ignition temperature : 322°C
Maximum temperature increment : ΔT = 100°C
Temperature change time read from a stop-watch : Δt = 5.6 s

The samples were heated to 250, 500, or 1000°C in dependence on their self-ignition temperature values.

The temperature increment value was determined from the temperature change curve T on the basis of its deflection out of the straight line, in the peak region. At the moment when temperature began increasing the stop-watch was started to measure the time running until the maximum temperature value was obtained.

As the oxidizer mass, wood flour mass, temperature increment value and time of this increment were known, the following parameters could be calculated :

- the temperature increment value in °C per 1g of an oxidizer
- the temperature increment value in °C per 1 milimole of an oxidizer
- the burning time in seconds per 1 g of an oxidizer
- the burning time in seconds per 1 milimole of an oxidizer
- the burning rate of a mixture in °C/s, by dividing the maximum burning temperature per 1 milimole by the burning time in seconds per 1 milimole of an oxidizer in question.

On the basis of the above mentioned data the following diagrams were prepared :

- the temperature increment diagram in °C per 1 milimole for different oxidizers, Fig.4
- the temperature change rate diagram in °C/s for different oxidizers, Fig.5.

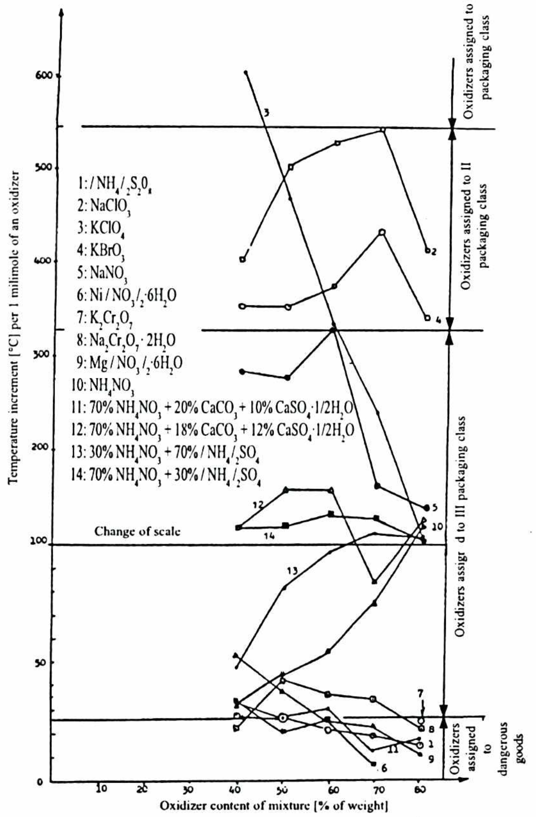

Fig.4. Measured temperature increment values in °C per 1 milimole of an oxidizer

Test conditions

Recorder's operating parameters :

T curve	-	500μV	Sensitivity : 500
TG curve	-	500μV	Paper speed : 2.5 mm/min
DTA curve	-	1mV	Temperature change rate : 10°C/min

Water content of oxidizers : 0%
Water content of wood flour : 0%
Size of oxidizer grains : < 0.3 mm
Size of wood flour grains : < 0.3 mm

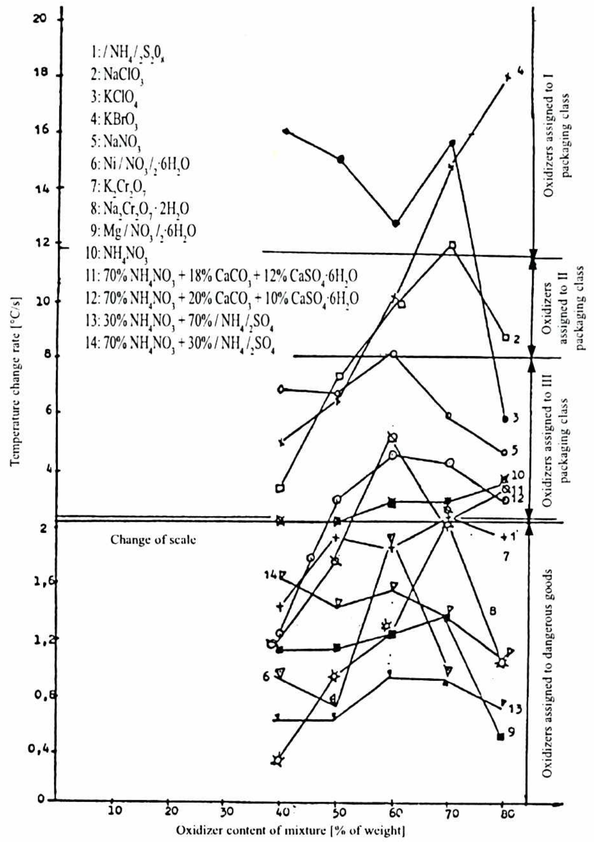

Fig.5. Measured temperature change rates [°C/s]

Test conditions see Fig.4.

CONCLUSIONS

The performed tests led to the following conclusions :

- DTA method can be applied to elaborating the criterion of classification of oxidizing substances into 5.1 class and appropriate packaging categories on the basis of the temperature change and time value for a reactive mixture after its self-ignition. As the criterion, the temperature change rate, in °C/s, counted from the self-ignition instant to that of obtaining the maximum temperature value, is proposed.

- On the basis of the criterion the following principles of classifying the oxidizers and assigning to them a packaging category are proposed :

- To ***I packaging category*** to assign the oxidizers with the maximum burning rates, in an arbitrary mixture with wood flour, greater than 11.9°C/s, i.e. the maximum temperature change rate of an arbitrary mixture of the flour with sodium chlorate.

- To ***II packaging category*** to assign the oxidizers with the maximum burning rates during derivatographic tests greater than 8, but equal or less than 11.9°C/s, i.e. the maximum burning rate of an arbitrary mixture of wood flour with sodium nitrate, but equal or less than the maximum burning rate of an arbitrary mixture of the flour with sodium chlorate.

- To ***III packaging category*** to assign the oxidizers with the maximum burning rate measured in the derivatograph, equal or greater than 2.1°C/s, but equal or less than 8°C/s, i.e. equal or greater than the burning rate of an arbitrary mixture of wood flour with ammonium peroxy sulphate and equal or less than the burning rate of an arbitrary mixture of the wood flour with sodium nitrate.

- To **5.1 class of dangerous oxidizers** it is proposed to assign the oxidizing substances which reveal during derivatographic tests the maximum burning rate equal or greater than 2.1°C/s, i.e. equal or greater than the combustion rate of an arbitrary mixture of ammonium peroxy sulphate with wood flour.

- Results of the performed assignment and classification of the tested substances are collected in Tab. and compared with the recent state in accordance with IMDG Code. The test results justify introducing the following amendment proposals of the packaging and 5.1 class assignment :

Assignment of oxidizing substances to 5.1 class and packaging categories on the basis of the maximum temperature change rate of their mixtures with wood flour, measured during derivatographic tests

Oxidizing substance	Mixture content [% : %]	Measured maximum temperature change rate [°C/s]	Assignment and classification according to:	
			test results	IMDG Code
Sodium chlorate $NaClO_3$ STANDARD	70:30	11.9	5.1/II	5.1/II
Sodium nitrate $NaNO_3$ STANDARD	60:40	8.0	5.1/III	5.1/III
Ammonium peroxy sulphate $(NH_4)_2S_2O_8$ STANDARD	70:30	2.1	5.1/III	5.1/III
Potassium perchlorate $KClO_4$	70:30	15.5	5.1/I	5.1/II
Potassium bromate $KBrO_3$	80:20	19.0	5.1/I	5.1/II
Nickel nitrate $Ni(NO_3)_2 \cdot 6H_2O$	60:40	1.8	not classified	5.1/III
Magnesium nitrate $Mg(NO_3)_2 \cdot 6H_2O$	70:30	1.3	not classified	5.1/III
Sodium dichromate $Na_2Cr_2O_7 \cdot 2H_2O$	70:30	2.0	not classified	not classified
Potassium dichromate $K_2Cr_2O_7$	80:20	1.9	not classified	not classified
Ammonium nitrate NH_4NO_3	60:40 and 70:30	2.7	5.1/III	5.1/III
Sodium peroxy borate $NaBO_3 \cdot H_2O_2 \cdot 3H_2O$	no temperature increment	no temperature increment	not classified	not classified
Fertilizer: 70% NH_4NO_3 + +18% $CaCO_3$ + +12% $CaSO_4 \cdot 1/2\ H_2O$	60:40	4.9	5.1/III	5.1/III
Fertilizer: 70% NH_4NO_3 + +20% $CaCO_3$ + +10% $CaSO_4 \cdot 1/2\ H_2O$	60:40	4.4	5.1/III	5.1/III
Fertilizer: 70% NH_4NO_3 + +30%$(NH_4)_2SO_4$	40:60	1.6	not classified	5.1/III/ A_3 type
Fertilizer: 30% NH_4NO_3 + +70%$(NH_4)_2SO_4$	60:40 and 70:30	0.9	not classified	not classified

- to change the potassium dichlorate packaging category from II to I category
- to change the potassium bromate packaging category from II to I category
- to exclude nickel nitrate II and magnesium nitrate from the dangerous oxidizers class 5.1, which is however in contrast to the test results of the substance, performed in different conditions [2].

● The derivatographic testing demonstrates many advantages when comparing it with other methods, because :

- it requires only a small amount of oxidizing substance
- applying the water solutions of oxidizing substances or wet samples is possible as the contained water evaporates during measurements.

● It should be possible to finally establish the assignment criteria to 5.1 class and packaging categories by carrying out further derivatographic tests of the remaining oxidizers, applying other combustible substances, and obtaining a better repeatability and accuracy of test results.

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Appraised by Stefan Kawiak, Assist.Prof.,D.Sc.,Chem.E.

Miscellanea

ANALYTICAL PROCEDURES OF HIGH-CYCLE FATIGUE ASSESSMENT OF STRUCTURAL STEEL ELEMENTS

Under this heading Technical University of Gdańsk issued a very valuable monography especially useful for structural designers.

The publication presents analytical procedures developed to evaluate the fatigue safety factor and the fatigue lifetime of structural steel members subjected to complex periodic loadings, as well as to estimate the fatigue damage and failure probability under complex random stress. The procedures include more data than those commonly used because each component of the stress tensor along with the corresponding σ-N curve is taken into account. In-phase loadings are treated by means of so-called σ-N surfaces (Wähler surfaces). The functional of fatigue safety and the strain power of elastic distortion per unit volume are defined which enable the influence of the phase shifts between individual stress components on the fatigue resistance to be examined. The Rice's concept of the equivalent frequency and the Cempel's theory of energy transforming systems are applied which made it possible to model complex stress patterns by much simpler equivalent ones. It is assumed that the stress components are physically and statistically independent of each other, and that they are given in the form of Fourier series or, respectively, that their power spectral densities are known. The case of linear relationship between magnitudes of individual stress components is also considered. Particular attention is focused on the assessment of fatigue under variable loading conditions expected during the service life. Closed-form solutions are obtained and fatigue design criteria are formulated without application of the conventional cycle counting technique and fatigue damage accumulation rule. The results of exemplary calculations are given. The ideas of stress modelling are extended onto the stresses under aperiodic and nonstationary random loading conditions.

The book was written in English by Prof. Janusz Kolenda, Chair of Mechanics and Strength of Ship Structures, Faculty of Ocean Engineering and Ship Technology.

Conferences

STRUCTURAL DESIGN AGAINST FATIGUE FAILURE

On 28 April 1997 the working seminar on „Design against fatigue" was held in the Faculty of Ocean Engineering and Ship Technology, Technical University of Gdańsk. During the Seminar specialists of Gdańsk scientific circle presented two groups of papers dealing with the problems.

The first group comprised the following experimental research themes:

- research on the fatigue life of complex ship structural elements and possible application of the „ fail safe" concept for its assessment
- research on the fatigue failure repair effectiveness of the ship girder cross joints
- measurements of the residual stress in complex structures with the use of the Barkhausen's effect
- research capability of the laboratory of Faculty of Ocean Engineering and Shipbuilding Technology.

The second group of papers was devoted to such theoretical problems and their applications in shipbuilding as:

- determination methods of the variable load spectra for ship structures
- background of the elaborating and functioning of PRS (Polish Register of Shipping) rules for the fatigue life assessment of ship structures
- analytical fatigue life determination of the structures under complex periodical loading.

In the Seminar representatives of the civil and military aviations, Polish Register of Shipping and physicists took part, having also an occasion to be acquainted with a fatigue research work just carried out in the laboratory of the Department of Shipbuilding Technology, Technical University of Gdańsk.

After disscusion the gathered gremium came to the conclusion that it would be reasonable to contain the fatigue research activity in a form of organization. In result the group on „ Structural design against fatigue" was established within the Machine Building Committee, Polish Academy of Sciences. Krzysztof Rosochowicz, Assoc.Prof.,D.Sc. was appointed as its chairman and Janusz Kozak, M.Sc., as its secretary.