

## PROPOSAL OF A NEW TEST METHOD FOR THE CLASSIFICATION OF OXIDIZING SUBSTANCES

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### Summary

Supplementary tests to the test method proposed by the United Kingdom to the International Maritime Organization (IMO) for the classification of oxidizing substances were carried out to investigate whether or not it was reproducible in Japan where high humidity occurs in summer. Results from these tests made it clear that to produce data in Japan which are almost equal to those obtained in the U.K., the proposed method required that the temperature and humidity of the testing place be controlled. Furthermore, a new burning test method using a pot was proposed, which is easy to perform and enables the classifying of oxidizing substances in accordance with the International Maritime Dangerous Goods (IMDG) Code. The method was proven to be competent enough to allow appropriate evaluation of the hazards of oxidizing substances.

### 1. Introduction

Oxidizing substances easily decompose and emit oxygen when heated. They are dangerous because the oxygen facilitates ignition and combustion. It is, however, not very easy to evaluate the oxidizing ability of those substances. Meyer [1] arranged oxidizing substances in order of oxidizing power as follows:

fluorine, ozone, hydrogen peroxide, hypochlorous acid, metallic chlorates, lead oxide, metallic dichromates, nitric acid (conc.), chlorine, sulfuric acid (conc.), oxygen, metallic iodates, bromine, ferric salts, iodine, sulfur, stannic salts

This order, perhaps resulting from past accumulated experiences, does not allow quantitative evaluation of the hazards of the substances. On the other hand, the United Nations Recommendation on the Transport of Dangerous Goods and the International Maritime Dangerous Goods (IMDG) Code have already listed dangerous oxidizing substances. They have classified

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those substances into three packaging groups according to their degree of hazard. However, there still do not exist definite regulations on the specific method for determining oxidizing substances as those which are subject to the regulations and those which are not, and for classifying those oxidizing substances which are designated as hazardous into packaging groups.

One method for the classification of the hazards of oxidizing substances is that of the U.S. Bureau of Mines [2]. In this method, a sample bed — one inch high, two inches wide, and seven inches long — made of a mixture of an oxidizing substance and a combustible substance, is ignited at one end. Its hazard level is determined from its burning rate. This method employs red oak sawdust as the combustible substance and the hazard of the oxidizing substances is grouped within the following four classes:

- Class 1 (least hazardous): Oxidizing substances which have a burning rate of less than 10 inches per min.
- Class 2 (moderately hazardous): Oxidizing substances which have a burning rate of 10 inches per min or more.
- Class 3 (greatly hazardous): Oxidizing substances which ignite automatically at less than 200°C.
- Class 4 (most hazardous): Oxidizing substances which detonate by heating or shock.

The method recently proposed by the United Kingdom to the International Maritime Organization (IMO) has been developed so that oxidizing substances, whose hazards may exist but are not listed in the IMDG Code, can be classified to correspond with the contents of the current IMDG Code [3].

The suggested method is persuasive and contains much data. The outline of this method is that a mixture of an oxidizing substance and a combustible substance is molded into a heap sample in a 250 mm long triangular prism with 14 mm sides. After the heap sample is ignited at one end, the burning rate of the sample is measured. This test is carried out with various percentages of oxidizing substance to the combustible substance. Plotting a graph of the burning rate against those mixture percentages provides the maximum burning rate for the substance. Oxidizing substances are grouped within three packaging groups by comparing the maximum burning rate with that of each standard substance:

- Packaging Group I: Substances which present oxidizing properties greater than that of sodium chlorate.
- Packaging Group II: Substances which present oxidizing properties greater than that of sodium nitrate.
- Packaging Group III: Substances which present oxidizing properties greater than that of anhydrous sodium dichromate.

Figure 1 illustrates an example of the plotting and is obtained from the data presented by the U.K. In this figure, the data for surface burning are included but most of them are for the burning of oxidizing substances.

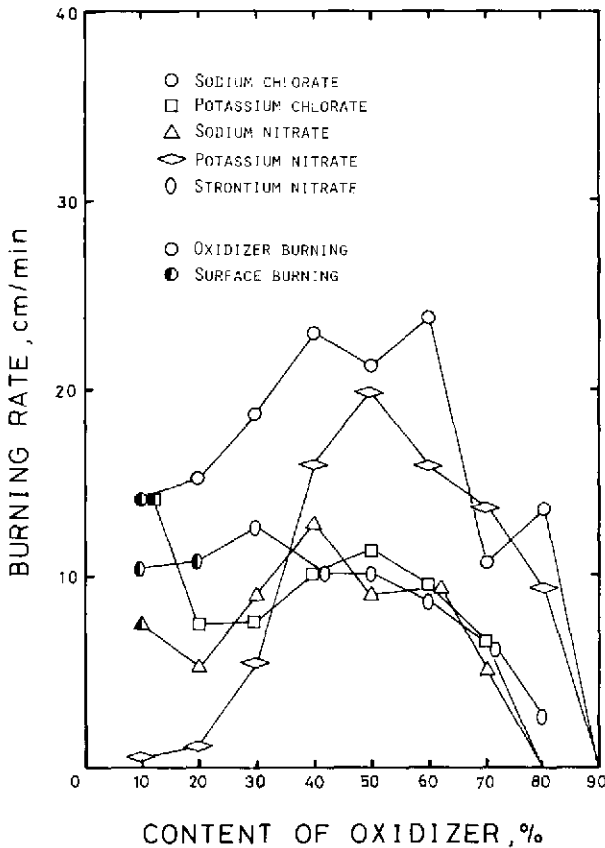


Fig. 1. A sample plot of U.K. (IMO) data [3].

The former mode of burning should be excluded because it is not characteristic of oxidizing substances. The results of this test will be examined in detail elsewhere.

This paper intends first to examine, by conducting a supplementary test of the U.K.'s proposal, whether or not this method is capable of yielding identical data in any place in the world and, second, to make a proposal for a new test method which is easier to perform.

## 2. Test method proposed by the United Kingdom and results of the supplementary test

### 2.1. Test method proposed by the United Kingdom [3]

The principle of this method (hereinafter referred to as the U.K. (IMO) method), which is similar to the above-mentioned methods of the U.S., is to mix an oxidizing agent under study with a combustible material and to subject the mixture to combustion. Sawdust or cellulose is designated as the combustible substance.

### 2.1.1 Preparations of samples

The oxidizing substance to be tested is dried at 65°C for eight hours and is stored in a desiccator with silica gel. If selected as a combustible substance, sawdust is dried at 105°C for four hours and is also allowed to cool in a desiccator. Oxidizing substances with sawdust are prepared with combustible substances ranging from 10 to 90 in 10% increments. The mixing should be done adequately to make the mixture homogeneous. The mixture is formed into a heap sample of a 250 mm long triangular prism with 14 mm sides by using a mold as shown in Fig. 2, that is:

- (1) Pile the mounted mold with loosely packed sample mixture until a slight heap is formed.
- (2) Drop the mold and the mounting from a height of 20 cm onto the base.
- (3) Level the surface of the mixture with a thin object, such as a paint scraper.
- (4) Remove the mounting from the mold and level the surface of the mixture by rolling a small roller along the length of the mold.
- (5) Place a board which is neither combustible nor conductive on the mold. Turn the mold and the board upside-down and remove the mold.

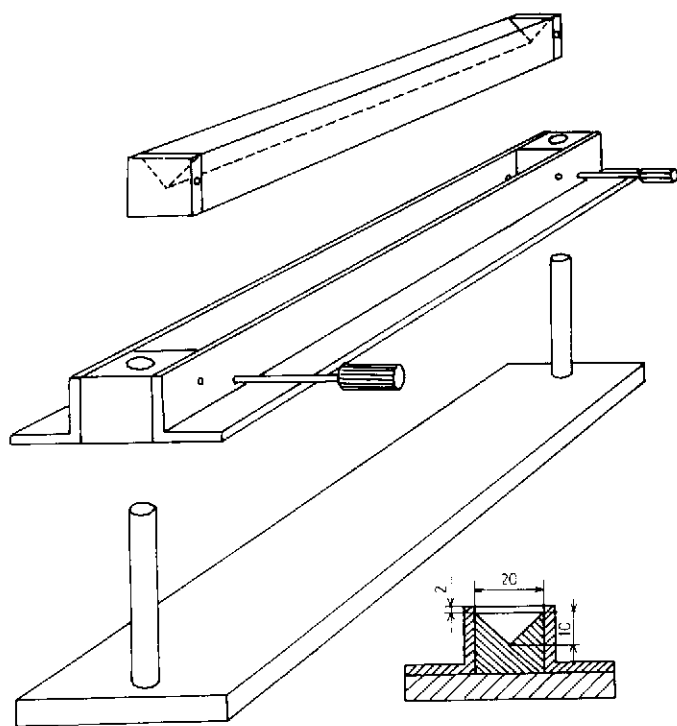


Fig. 2. The mount and mounting for the burning test proposed by the U.K. [3].

### 2.1.2 Test method

The heaped mixture is set in as draught free a position as possible. One end of the heap is touched with the tip of a flame for not more than 15 s. The time was measured using a stopwatch, from then until the reacting portion advances a further 100 mm from the 120 mm mark. Modes of combustion take place in two ways — one is an “oxidizing agent” made in which combustion develops in the entire mixture, and the other is a “surface-burning” made, where only the surface of the mixture burns. Classification is made of only the former type.

### 2.1.3 Results of the test

Results are plotted on a graph with the percentage of each oxidizing substances to the combustible substance as the abscissa, and the maximum burning rate for each mixture percentage as the ordinance. The graph provides the maximum burning rate of the substance under study.

### 2.1.4 Classification method

In accordance with the U.K. proposal which evaluates the hazards of oxidizing substances by using anhydrous sodium dichromate, sodium nitrate and sodium chlorate as the standard substances, the maximum burning rate of the substance under test should be compared with that of each standard oxidizing substance. The mean burning rate of sawdust, described only in the U.K. (IMO) method, is 10.9 cm/min.

The U.K. (IMO) method has 43 detailed sets of data relating to various oxidizing substances. Figure 1 gives an example from these data, that is, data on a group of substances whose names have an “ate” group ending. It is evident from the figure that the burning rate of sodium chlorate and sodium nitrate is faster than that of the substances under test, and that the maximum burning rates for both are 24.0 cm/min and 20.0 cm/min, respectively. The maximum rates for most of the substances are recorded when the percentage of each substance contained in the samples ranges from 40 to 60. The datum also mentions the maximum burning rate of 600 cm/min for sodium chlorate (as received) at its 40 percent mixture without any detailed information.

In the Federal Republic of Germany (F.R.G.), cellulose is used as the combustible material for the burning tests of oxidizing substances proposed by the U.K., and barium nitrate is used as the standard. A proposal has been made that substances burning faster than this are to be classified as oxidizing substances [4].

## 3. Supplementary test of the test method proposed by the United Kingdom

### 3.1 Test method and results of the test (U.K. (YNU-1))

In order to investigate the U.K. (IMO) method's ability to produce the same results in Japan (as those in the United Kingdom), a supplementary

test was designed using the same method (hereinafter referred to as the U.K. (YNU-1) method). Not only was the U.K. (IMO) method followed, but a mold of samples was similarly prepared in the pretreatment of oxidizing substances and the test procedure. A combustible material needs to be readily available and as its quality has to be as uniform as possible; soft chips of white birch, which are used as bedding for laboratory animals, were selected. For the test, the chips were ground and those which passed through a 16-mesh sieve were employed. The chips were laid 25 mm deep or less, dried at 105°C for four hours, and stored in a desiccator which had silica gel inside until just before use. In mixing the sample, great care was taken to ensure it was homogeneous.

The F.R.G. proposal recommends cellulose as a combustible substance [4], but the U.K. (IMO) method mentions cellulose as an alternative combustible substance. A trial with powdered cellulose for liquid chromatography manufactured by Toyo Roshi Ltd., however, failed to produce the combustibility desired for the test owing to the smallness of the particle size. Hence, for the tests performed thereafter, soft chips were used as the combustible substance.

Listed in Table 1 are the results of the test done in a non-airconditioned laboratory room on the Pacific coast of Japan in winter, when the area is in its dry season. The numbers quoted in parentheses are the values obtained in the U.K. (IMO) method. The mean burning rates of the ground soft chips measured six times were 10.9 cm/min, satisfyingly almost equal to the value in the data provided in the U.K. (IMO) method. Part of the burning rates of oxidizing substances, however, tended to become slower in comparison with the U.K. (IMO) method data. As it was a matter of relativity, the classification of hazards of oxidizing substances, based on the criteria given at the beginning of this paper, could be performed. The resultant classification corresponded to that under the IMDG Code, except for ammonium persulphate. Since anhydrous sodium dichromate, one of the standard substances, is not available in Japan, it was produced from a hydrated substance by heating. However, it reverted soon after the heating, hampering stable measurements and deeming it unusable. Potassium dichromate was then substituted. Therefore, in the tests described hereinafter, anhydrous sodium dichromate is replaced by potassium dichromate. As the burning rates measured by the U.K. (YNU-1) method test turned out to be not as fast as those in the data of the U.K. (IMO) method, further tests with more samples needed to be performed so that the former would agree with the latter as much as possible. Otherwise, burning rates would get faster or slower by chance, which would possibly mislead evaluation. To avoid this risk, measurement of the burning rates of standard substances was necessary for each test.

To raise the burning rates, the particle size of the oxidizing substances was pulverized to the size which passed through a 100-mesh sieve and the particle size of the ground soft chips was enlarged to the size which passed

TABLE 1

Burning rates of mixtures of oxidizers with soft tips (cm/min)

Substance	Percentage of oxidizer									
	10	20	30	40	50	60	70	80	90	
Ammonium dichromate	0.8 ss ( 9.7 s)	1.4 o ( 0.98 o)	2.8 o ( 1.6 o)	3.1 o ( 1.8 o)	3.0 o ( 3.5 o)	3.6 o ( 3.5 o)	4.2 o ( 5.9 o)	6.8 o ( 13.6 o)	12.8 o ( 15.0 o)	
Potassium chlorate	a ( 14.3 s)	0.9 ss ( 7.5 o)	2.1 o ( 7.6 o)	3.0 o ( 10.2 o)	3.0 o ( 11.5 o)	4.1 o ( 9.7 o)	5.3 o ( 6.7 o)	7.1 o ( a)	a ( a)	
Sodium nitrate	a ( 7.5 s)	6.8 ss ( 5.3 o)	1.9 o ( 9.0 o)	2.2 o ( 13.0 o)	5.4 o ( 9.1 o)	5.5 o ( 9.5 o)	4.1 o ( 5.2 o)	a ( a)	a ( a)	
Ammonium nitrate	8.6 s ( -)	10.0 s ( -)	6.7 s ( -)	4.6 o ( -)	5.3 o ( -)	3.5 o ( -)	2.7 o ( -)	a ( -)	a ( -)	
Ammonium persulphate	a ( 6.8 s)	a ( 6.8 s)	a ( a)	a ( a)	a ( a)	a ( 3.85 o)	2.1 o ( 5.9 o)	2.5 o ( a)	a ( -)	
Potassium dichromate	0.3 ss ( 9.7 s)	0.4 ss ( 8.8 s)	0.5 ss ( 8.1 s)	0.6 ss ( 0.47 o)	0.8 ss ( 0.54 o)	0.9 o ( 0.71 o)	1.6 o ( 4.5 o)	3.4 o ( 1.9 o)	a ( a)	
Manganese dioxide	0.5 ss ( 7.5 s)	1.5 ss ( 7.1 s)	1.6 ss ( 1.7 s)	2.0 o ( 0.9 o)	2.4 o ( 1.0 o)	1.9 o ( 1.2 o)	2.0 o ( 1.2 o)	2.0 o ( 1.5 o)	a ( 0.9 o)	

Upper line indicates UK (YNU) method. Lower line indicates UK (IMO) method. (Actual measurements)

a: no propagation

o: oxidizer burning

s: surface burning

ss: surface smouldering

through a 10-mesh sieve. Furthermore, air flow was given as 0.3 to 0.4 m/s at right angles to the length of the heap. The resultant maximum burning rates were 53.6 cm/min (70%) for sodium chlorate, 15.0 cm/min (50%) for sodium nitrate and 4.6 cm/min (70%) for potassium dichromate. This improvement was evidenced in the differences between the present test and the U.K. (IMO) method data.

### 3.2 Results of the test (U.K. (YNU-2))

The next test (U.K. (YNU-2)), which was carried out in June during the rainy season in Japan, where the temperature and the relative humidity frequently exceed 25°C and 90%, respectively, posed another major problem. That is, to what degree should the samples be dried prior to the tests, as samples were affected by the humidity at the time of testing. Illustrated in Fig. 3 are the results of a test with sodium nitrate under various humid conditions. As a result of a definite influence of the humidity, the maximum burning rate, 15.0 cm/min (50%) at the relative humidity of 54%, was 4.4

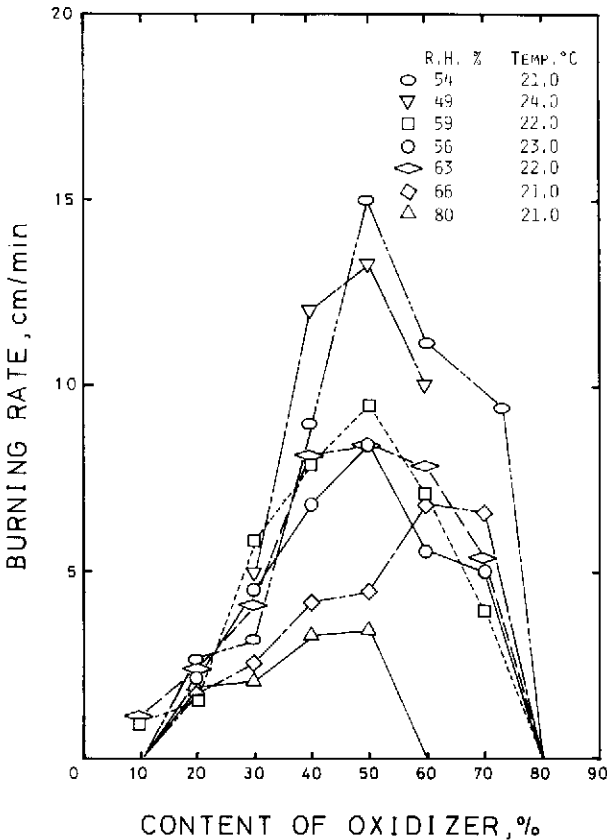


Fig. 3. Effect of humidity on the burning rate of sodium nitrate mixture.



times as fast as the minimum burning rate, 3.4 cm/min (50%) at 80% relative humidity. Likewise, such discrepancies were true with sodium chlorate (70% mixtures for both maximum and minimum burning rates) and 1.6 times with potassium dichromate. Tests conducted under the influence of humidity similar to this are meaningless. It is clear that the conditions of a test place should be controlled to low humidity.

### 3.3 Improvement of the test place and results of the test (U.K. (YNU-3))

Since the above-mentioned tests showed that the burning rates of the mixtures of oxidizing substances with ground soft chips were affected by the humidity to a great degree, an apparatus was devised which enabled control of the humidity at the test place. Figure 4 outlines the apparatus. Through it, moisture is removed from the air by a spot-type air-conditioner. Speed of the air flow is adjusted by an air flow controlling valve; the temperature of the air is adjusted by a local heater set up inside the pipe, and

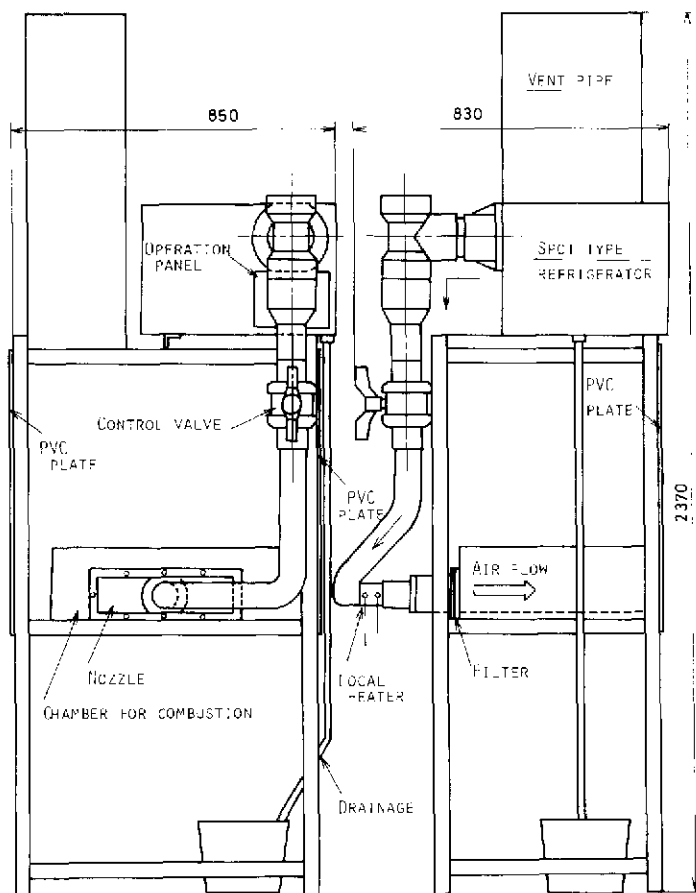


Fig. 4. Chamber for combustion used in U.K. (YNU-3) and pot methods.

later rectified with a filter. Air is then sent into a chamber of combustion. During this procedure, the temperature and humidity of the atmosphere inside the combustion chamber can be kept at  $20 \pm 5^\circ\text{C}$  and  $50 \pm 10\%$ , respectively. Further precautions were taken to prevent the samples absorbing moisture, and weighing and mixing of the samples were done inside a glove box containing silica gel. The particle sizes of oxidizing substances and soft chips were made equal to those described earlier in section 3.2.

Results of the tests using sodium nitrate are plotted in Fig. 5 as an example. The figure demonstrates that the low humidity of the atmosphere inside the combustion chamber, despite the high humidity of the test room, enabled the provision of data with less variation. The maximum burning rate obtained using sodium nitrate, 14.2 cm/min, with a' content of 50%, was nearly coincident with the 13.0 cm/min (40%) of the U.K. (IMO) data.

Tests with sodium chlorate and potassium dichromate conducted simultaneously also resulted in data with less variation, although the maximum burning rate of 76.0 cm/min (50%) for the former exceeded by a large

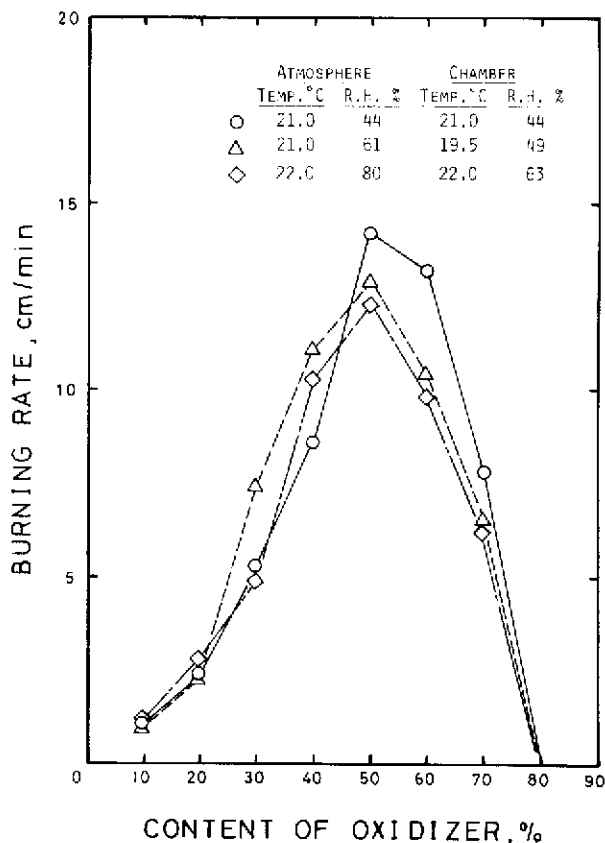


Fig. 5. Test results of U.K. (YNU-3) method.

margin that of 24.0 cm/min (60%) obtained in the U.K. (IMO) data. The maximum burning rate for the latter substance, 4.6 cm/min, almost equalled 4.5 cm/min as given in the U.K. (IMO) method.

Thus, the present test made it clear that with well-mixed homogeneous samples and the humidity controlled, the U.K. (YNU-3) method was able to yield results almost the same as those given in the U.K. (IMO) method, and to provide measures of the burning rates of solid oxidizing substances giving a base on which to evaluate their hazards. Problems of the present method are, however, that the method needs a special mold, that the preparation of prism-shaped samples is not simple and, most importantly, that the results produced by the method are not always consistent with the classification of the current IMDG Code. For those reasons, an easier and more precise method has been proposed.

#### 4. Proposal of a new test method — Pot method

##### 4.1 Outline of the test method

A mixture of an oxidizing substance and ground soft chips fills a metal pot and is ignited with a gas flame on the upper side. The time taken from this ignition to the burning out of the mixture is measured and based on this burning period the oxidizing substances are classified.

##### 4.2 Test method

###### 4.2.1 Samples

Basically, samples are used with their particle sizes as received. If necessary, samples were ground to pass through a 20-mesh sieve. Ground soft chips are prepared as in the previous tests. The samples are also pretreated as directed in the U.K. (IMO) method. Substances with a melting point of less than 65°C are made into samples after being left inside a vacuum desiccator for 12 hours. Since the results of the earlier conducted tests indicate that the maximum burning rate of each oxidizing agent was obtained within the range of 50–80% content of the agent, the percentage of the agent for ground soft chips is limited to two kinds of 50 and 80. Only in cases where the two contents do not suffice should further testing at another content be carried out.

###### 4.2.2 Test place

By employing the apparatus described in 3.4, the test is conducted in a chamber for combustion, the temperature and relative humidity of which are controlled at  $20 \pm 5^\circ\text{C}$  and  $50 \pm 10\%$ , respectively.

###### 4.2.3 Pot

A metal (nickel) pot with a diameter and height of 36 mm and a capacity of 30 ml is used. Ignition is made on contact with a 10 cm diffused flame by employing a 5 mm gauge gas burner.

#### 4.2.4 Test method

In the case of solid oxidizing substances, the mixed sample is heaped up in the pot and then made level with the brim using a thin object, such as a paint scraper. The pot should be immediately placed inside the chamber for burning and touched with a flame on the upper side. The time taken from ignition to the burning out of the sample is measured by a stopwatch.

With liquid oxidizing substances, the pot is filled with the prepared ground soft chips to heaping fullness and the heap is flushed at the level of the brim. Move the pot into the chamber for burning and evenly pour a liquid oxidizing agent into the pot from above with an injector until the content of the oxidizing agent reaches 50 or 80%. Upon the infiltration of the oxidizing agent into the combustible substance, the sample should be ignited and its burning time measured with the same procedure as for solid oxidizing substances. The test is conducted three times at 50% and at 80% content of the oxidizing agent, respectively. A comparison of the results of the two contents, either in the case that the mean burning rate is faster and also where the sample burnt out completely, should be carried out as regards the burning time of the substance. If the sample does not burn even at a content of 80%, a 90% sample should be tested in the same way.

#### 4.3. Results of the test

Modes of combustion of representative oxidizing substances were observed as follows:

Of those substances included in the Packaging Group I of the IMDG Code, sodium peroxide burns very violently. Its flames are white, tinged with orange, and reach a height of up to 60 cm. Likewise, perchloric acid (70%), a liquid oxidizing agent, presents a fierce combustion with flames of similar color to the above, and emits a light too strong for the naked eye.

Of the oxidizing substances which come under the Packaging Group II, sodium bromate has characteristics of violent combustion with reddish-white flames and also gives out strong light. Similarly intense in its burning, potassium bromate has a purplish-white flame. Calcium hypochlorite burns with flames of white tinged with orange, but burns five seconds longer than potassium bromate. Also classified into the Packaging Group II, ammonium dichromate gives off a reactive substance without glow and strikes sparks. Potassium perchlorate burns with a purple-white flame (Fig. 6).

Ammonium nitrate, grouped under the Packaging Group III, burns with orange flames for 30 seconds after ignition but thereafter smoulders. The same phenomenon occurred with sodium percarbonate.

However, the method under study was not able to ignite hydrogen peroxide (30% peroxide) and zinc nitrate in the Packaging Group III, and aluminium nitrate, calcium nitrate, sodium persulphate and strontium nitrate in the Packaging Group II which, therefore, did not allow the measurement of their burning times either. This problem remains to be further studied.

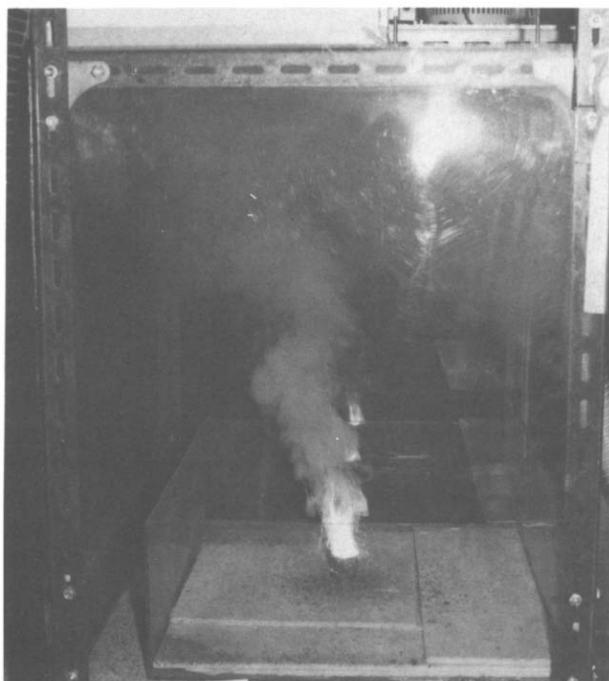


Fig. 6. The burning of potassium perchlorate mixture.

#### 4.4 Classification of the hazards

Evidently, oxidizing substances exhibit modes of combustion characteristic to each Packaging Group in which they were included. Moreover, the fact is closely associated with their burning times. Therefore, it is suggested that to determine the assignment of oxidizing substances to the Packaging Groups the following criteria be used in considering the test results and the classification of oxidizing substances under the IMDG Code:

- Packaging Group I: Substances whose burning time is 10 seconds or less.
- Packaging Group II: Substances whose burning time ranges from 10 to 60 seconds.
- Packaging Group III: Substances whose burning time ranges from 60 to 180 seconds.

Here, burning means combustion with flames. Substances which exhibit just burning without flames, that is, smouldering, should be left out.

#### 4.5 Discussion

The results of the various tests described are shown in Table 2. The substances are in Packaging Group and alphabetical order. Test results of substances that are not listed as hazardous substances in the IMDG Code are also given at the bottom of the table as they were included in the U.K. (IMO) data, and were also performed by the present pot method for comparison.

TABLE 2

Classification of oxidizers according to pot method

Substance	U.N. No.	Class	Pack. Group	Pot method Obs. (s)	U.K. (YNU-3) method Obs. (cm/min)	U.K. (IMO) method Obs. (cm/min)	Bur. Mines Obs. (cm/min)
Perchloric acid (58-78%)	1873	5.1	I	6	I	-	-
Sodium peroxide	1584	5.1	I	3	I	388.8	I 2158
Ammonium dichromate	1439	5.1	II	26	II	15.8	II
Barium nitrate	1446	5.1	II	76	III	13.8	III
Barium perchlorate	1447	5.1	II	3	I	-	-
Calcium hypochlorite dry (>39%)	1748	5.1	II	14	II	58.8	I 385
Lead nitrate	1469	5.1	II	48	II	9.8	III
Potassium bromate	1484	5.1	II	9	I	-	292
Potassium chlorate	1485	5.1	II	24	II	11.5	III
Potassium nitrate	1488	5.1	II	9	I	24.8	I
Potassium perchlorate	1489	5.1	II	51	II	-	-
Potassium permanganate	1498	5.1	II	16	II	158	I 38.5
Sodium bromate	1494	5.1	II	7	I	-	-
Sodium chlorate	1495	5.1	II	19	II	24.8	II 48.3
Sodium nitrate	1588	5.1	II	18	II	16.2	II
Sodium perchlorate	1582	5.1	II	19	II	2.8	-
Ammonium nitrate (combustible >8 2%)	1942	5.1	III	96	III	5.3	III
Ammonium persulphate	1444	5.1	III	167	-	2.5	III
Caesium nitrate	1451	5.1	III	16	II	35.3	I
Potassium nitrate	1486	5.1	III	26	II	28.8	I 71.1
Potassium persulphate	1492	5.1	III	163	-	9.1	III 18.2
Sodium nitrate	1498	5.1	III	35	II	5.5	III
Sodium percarbonates	2467	5.1	III	91	III	2.3	III
1,3-dibromo-5,5-dimethylhydantoin	-	-	-	86	III	-	-
Cerium nitrate	-	-	-	96	-	5.7	-
Iodine pentoxide	-	-	-	64	III	4.35	-
N-bromo succinic imide	-	-	-	287	-	6.1	III
Nitric acid, fumed	-	-	-	33	II	3.3	-
Periodic acid	-	-	-	9	I	25	I
Potassium dichromate	-	-	-	267	-	158	I
Potassium iodate	-	-	-	25	II	4.5	-
						25	I 8.9

#### 4.5.1 Correspondence of the results of the test with the classification under the IMDG Code

*Packaging Group I.* The present test by the pot method of Packaging Group I was performed only with perchloric acid and sodium peroxide. However, their characteristic mode of combustion and burning time were identical with the classification under the current IMDG Code. It is deemed there is no particular problem with this group.

*Packaging Group II.* Of the 14 tested substances in Packaging Group II, nine corresponded to the IMDG Code classification. Of those which did not correspond, four came under Packaging Group I: barium perchlorate, potassium bromate, potassium nitrate and sodium bromate. Taking into consideration their fierce mode of combustion, all of them are considered to have hazards as great as Packaging Group I. In the testing of Packaging Group III. Considering the fact that this substance is designated as the standard substance in the FRG proposal [4], this result should be considered reasonable. Hence it can be said that testing using the pot method of Packaging Group II yielded, as a whole, appropriate results.

*Packaging Group III.* In this group, seven substances were examined. Agreement to the IMDG Code classification was found in only two substances — ammonium nitrate and sodium percarbonate. Three of the other substances — caesium nitrate, potassium nitrate and sodium nitrate — resulted in a Packaging Group II classification. They were all nitrates. The remaining two — ammonium persulphate and potassium persulphate — could be classified in Packaging Group III in terms of burning time, but came to be excluded from hazardous substances because of their mode of smouldering combustion.

*Other substances.* Of eleven substances which do not appear in the IMDG Code but underwent testing by the U.K. (IMO) method, eight were examined by the present pot method. The result was that periodic acid was assigned to Packaging Group I, nitric acid (fumed), potassium iodate was assigned to Packaging Group II, and 1,3-dibromo-5,5-dimethylhydantoin to Packaging Group III. As is seen in Table 2, the remaining three, which also burnt, could be classified as Packaging Group III, but their mode of smouldering combustion led them to be exempt from classification as hazardous substances.

#### 4.5.2 Comparison of the U.K. (IMO) data and the classification under the IMDG Code

*Packaging Group I.* Only results of the test with sodium peroxide are described; they correspond to the classification given.

*Packaging Group II.* Four of the eleven substances tested are in accordance with this classification. They are ammonium dichromate, sodium chlorate (as this is a standard substance, it is natural), potassium nitrate and sodium nitrate. Of the remaining seven, three substances were assigned to Packaging Group I: potassium permanganate, calcium hypochlorite

(mixture, dry) and sodium chlorite. Three substances went to Packaging Group III: barium nitrate, lead nitrate and potassium chlorate. Potassium perchlorate was excluded from classification as a hazardous substance.

*Packaging Group III.* Eight substances from this Packaging Group were subjected to the test. Of them, five were in agreement with the Packaging Group III classification: sodium nitrate, strontium nitrate, sodium percarbonate, sodium persulphate and potassium persulphate. Caesium nitrate was classified in Packaging Group I, and ammonium persulphate and potassium nitrate in Packaging Group II.

*Other substances.* As mentioned earlier, the test was carried out with eleven other substances. Nitric acid (fumed), periodic acid and potassium iodate turned out to belong in Packaging Group I, none in Packaging Group II, and iodine pentoxide in Packaging Group III. Tests of the other substances resulted in classification as non-hazardous substances.

#### 4.5.3 Comparison of the present pot method and the U.K. (IMO) method

In the tests on substances from Packaging Group I, under the IMDG Code, both methods gave equally correct results. With regard to substances from Packaging Group II, a percentage of correct comparisons between the pot and the IMDG Code classification was 64%, but between the U.K. (IMO) method and the IMDG Code classification, the percentage was not more than 36%. Though the differences between the substances tested do not permit simple comparisons, the former method appears to be superior to the latter in yielding corresponding results in Packaging Group II. The results of both methods have in common the grouping of potassium nitrate under Packaging Group I and barium nitrate under Packaging Group III. Contrary to the results in Packaging Group II, percentages in Packaging Group III of corresponding results with the IMDG Code were reversed, showing the pot method to be 30% or less and 63% for the U.K. (IMO) method. The pot method seems likely to classify substances in Packaging Group II. None came under Packaging Group I with the former method, but the latter placed caesium nitrate in the group. In most other substances, both methods agree favorably with each other; periodic acid was equally classified as Packaging Group I, but the classification of potassium iodate differed only slightly.

An overall comparison between the two methods reveals that the present pot method seems inclined to classify substances in Packaging Groups I and II but is able to deal with a sufficiently wide variety of substances by excluding without hesitation substances which smoulder. On the other hand, U.K. (IMO) method displayed a tendency to assign oxidizing substances to Packaging Groups I and III, while its exclusions of substances from classification as hazardous substances tended to be similar to the pot method. A problem of the U.K. (IMO) method is that substances classified as Packaging Group II become small in number despite it being the leading group in the IMDG Code classification. Therefore, the pot method can be



said not only to be as competent as, or more competent than, the U.K. (IMO) method, but also easier to apply.

## 5. Conclusions

- (1) A supplementary test of the U.K. (IMO) method was conducted. The results of the test revealed that the method was not capable of generating sufficiently reproducible data if employed in a usual laboratory where the humidity of the atmosphere was not controlled.
- (2) To improve it, a chamber for combustion was prepared where the temperature could be maintained at the normal level and the relative humidity at 50–60%. The sample substances were also mixed in a glove box with silica gel inside. The measures proved effective in enabling the U.K. (IMO) method to produce reproducible data.
- (3) The data obtained from the U.K. (YNU-3) method and from the U.K. (IMO) method corresponded well with each other. Therefore, in applying the U.K. (IMO) method, full consideration should be given to high humidity areas. As anhydrous sodium dichromate is practically impossible to make use of, standard substances would be selected cautiously.
- (4) The U.K. (IMO) method requires a special mold to form heaped triangular prism samples and the forming method is inconvenient. Hence, we proposed the easy to operate pot method and used this method to carry out the tests.
- (5) A criterion has been proposed for classifying the hazards of oxidizing substances which was provided by observing their modes of combustion and recording the time it took them to burn. Comparison of the results of the test with the classification under the IMDG Code demonstrated that the pot method was able to rightly classify a wide variety of substances ranging from those in Packaging Group I to those considered not dangerous. On the other hand, the U.K. (IMO) method was good at evaluating substances in Packaging Groups I and III but was likely to classify a smaller number of substances into Packaging Group II, which is primary under the IMDG Code classification.
- (6) More advantageously, the pot method can easily deal with liquid oxidizing substances as well. In this respect also the pot method is considered to excel over the U.K. (IMO) method.
- (7) Although appearing in the IMDG Code as oxidizing substances, some substances were not ignitable using the pot method. More in-depth studies need to be carried out into whether it should be attributed to substantial properties of those substances or to the ignition method.

## References

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