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DRAFT AMENDMENTS TO THE MANUAL OF TESTS AND CRITERIA

Technical Information: Test Results Concerning on Test Conditions of Testing Methods for Oxidizing Solids

Transmitted by the Experts from Japan

1. SUMMARY

In this report some information is given concerning the test methods of oxidizing substances. It has been found that there are some points that need clarifying. That is; (1) Influence of humidity in the ambient atmosphere on burning time, (2) Materials of ignition wires and problems with wire breaking, (3) The size of cellulose for burning and water content, and (4) Others.

2. INTRODUCTION

The provisions regarding the testing methods for oxidizing solids in the United Nations Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria (Test Manual) were completely amended in 1995. Verification testing of the test conditions as provided in the Test Manual as amended, was carried out in the National Research Institute of Fire and Disaster, the Fire and Disaster Management Agency of the Ministry of Home Affairs, in conjunction with the experts from other Japanese laboratories and universities. Then the experimental results were examined by experts in the Fire and Disaster Management Agency.

3. TECHNICAL INFORMATION

Information provided by the test and discussion results are as follows.

(1) The significant influence of humidity in the ambient atmosphere on burning time

There are no provisions regarding the humidity of the testing environment in the Test Manual. The influence of humidity is related to the high hygroscopic property of cellulose, and the humidity influenced the test results of burning time (see Figures 1 and 2).

Figure 1 shows that when the humidity increased to over approximately 60 %, burning time increased and did not repeat well in testing Potassium bromate($KBrO_3$) with Merck 2331. Therefore the tests should be done with humidity lower than 60 %. The data in Figure 2 were from prof. Uehara of the Yokohama University, who examined different material (KMn_4) using different cellulose (Whatman CF-11), but gave similar results.

The Test Manual provides that the temperature should be maintained within 20 ±5°C. When the tests were carried out under different temperatures within this stipulated range, higher temperatures resulted in shorter burning times. However the influence of humidity was distinctly more obvious within the range of humidity of the tests (see Figure 3). Therefore the provisions regarding temperature need not be changed.

(2) Materials of ignition wires and problems with wire breaking

There are several kinds of ignition wires which comply with the provisions of the Manual of Tests and Criteria. Nichrome wire is employed widely for the experiments and it can be used ten times on average if it is new wire. Some testing wires, however, are severed after only one test, depending on the testing sample. It is possible that the severance occurs in the sample due to a low melting point of the sample. The melted portion of the sample fuses to the ignition wire and the fused portion can reach a temperature higher than the melting point of the ignition wire. Severance of the wire happened very often two minutes after ignition when stable energy was generated. In particular, nitrates frequently tended to cause severance (see Table 1).

When the ignition wire is broken, generation of thermal energy from the ignition wire stops. In many cases, however, the burning continues because enough thermal energy is produced from the ignition wire before it is broken to keep the flame alight, and the burning of the sample and the cellulose continues by means of the thermal energy from the flame. In this case, the burning time is longer and the deviation of burning time increases.

As a countermeasure, employing a thicker Nichrome wire or a high heat-resistant alloy, which contains Cr and Al, can solve this problem. For instance, a high heat-resistant alloy, produced by Kanthl Co. Sweden is recommended, but the electrical resistance in its specifications does not comply with the provisions of the Test Manual.

Table 1: The state of breaking by nitrate salts
(Probability of breaking of new Nichrome wire application, sample: cellulose = 2:3, Merck 2331, temperature 20 ±2°C humidity 45 ±5%)

Test materials	mp(°C)	Probability of breaking
Sodium Nitrate	308	5 / 10
Potassium Nitrate	339	7 / 10
Ammonium Nitrate	165	10 / 10

1) The test conditions and test methods were in accordance with the Test Manual
2) A new ignition wire was used for each test.
3) Burning generally continued after the ignition wire was broken.

(3) Provisions regarding the size of cellulose and water content, etc.

Shape and size of cellulose differ widely depending on type and manufacturer. Whatman CF-11, which is widely used among European and American countries in testing methods for oxidizing solids, is not appropriate to the provisions regarding size. Advan A which is made in Japan, was the only material that complied with the provisions of the Test Manual under the investigation by the laboratory of Nippon kaiji kentei kyoukai .

Therefore, neither CF-11 nor domestic products ‘except Advan A’ can be employed according to the provisions of the Test Manual. Under the provisions, if the length and thickness of cellulose employed were regulated to be, for example, in the range between 30 and 250 μ m in average length and in the range between 10 and 35 μ m in average thickness, Whatman CF-11, and W-100, W-200 and W-300 produced by the Japan Paper Co. would be suitable (see Table 2).

Burning time differs widely depending on the kind of cellulose. When tests are carried out using potassium bromate as a sample, Whatman CF-11 gives the longest burning time. This is possibly because the configuration and specific surface area (bulk specific gravity) are related. Evaluation of the level of danger is however only a relative evaluation compared with potassium bromate. Therefore, when cellulose, which comes under the above mentioned provisions, is employed, the evaluation results may not vary with other test conditions.

(4) Response to commercial products

Data vary widely when commercial products are examined, owing partly to their moisture content. According to the results using reference substances, as the moisture content increases, burning time increases and the data tended to be derived largely (see Table 3). When commercial products are tested as they are, it is proven that reduction of water content is necessary up to a certain degree, e.g., by stipulating that the sample should be kept in a desiccator for twenty-four hours in order to control the water content of various commercial products.

(5) Burning device

In Japan, a box-shaped burning device is constructed and burning tests are carried out in the burning device. If burning tests can be carried out in a draft etc., and still comply with the test conditions in the Test Manual, experimentation in a draft is adequate. When considering the easiness with which temperature, humidity and air velocity can be controlled. Therefore we believe that the box-shaped testing device is better.

Table 2: Test results of celluloses

List of celluloses used in the tests, and their average sizes, data on burning times and the results (pass or not) of each cellulose when the provisions of cellulose size is changed following the above size (range between 30 and 250 μ m in average length and between 10 and 35 μ m in average thickness). Sample: potassium bromate, Ratio of sample and cellulose = 2:3, Temperature and humidity are the same as in Table 1.

Manufacturers, Product name	Average size(μm) (Fibre length×thickness)*3	Burning time		Results of the above cellulose size changed
		in sec	Ratio *4	
Whatman CF11	90 ×15.0 *1	102.2 ±34.2	1	○
Merck #2331	110 ×12.0	75.7 ±12.0	0.74	○
Asahi Chemical PH101	40	-	-	○
Japan Paper W-100	120 × 20.0 112 × 14.0 *2	45.9 ±11.1	0.45	○
Japan Paper W-200	45.0 × 15.0	66.8 ±14.2	0.65	○
Japan Paper W-300	35.0 × 15.0	60.3 ±12.0	0.59	○
Merck #2330	15.0 × 3.1	40.7 ±11.6	0.39	
Aldrich	175 × 5.0	65.4 ±14.8	0.64	
Japan Paper W-50	-	34.7±10.0	0.34	
Japan Paper W-400	32.0 × 12.0	55.7 ±12.8	0.55	

* 1 Fibre length>90
* 2: Data provided by a manufacturer
* 3 Size data was obtained from electron microscope imaging
* 4 Ratio with burning time of CF-11set to 1

Table 3: Influence of aging time
(Potassium bromate and cellulose Merck 2301 were used.
Test conditions were the same as in Table 2)

Aging Time(min)	Burning Time(sec)	Increasing Rate of water contents (wt %)*
10	67.2 ±10.5	0.10
20	85.5 ±15.5	0.15
30	84.9 ±17.4	0.18
60	88.0 ±21.8	0.31

Figure 1 : Relationship between humidity and burning rate
Potassium Bromate and Merck # 2331 were used,
Sample : Cellulose = 2 : 3,
Temperature 20(±2)°C
Electrical power 150 ±5kW

Figure 2 : Relationship between humidity and burning rate
Potassium Permanganate and Whatman CF-11 were used,
Sample : Cellulose = 2 : 3,
Temperature 20(±2)$^\circ$C
Electrical power 150 ±5kW

Figure 3 : Relationship between temperature and burning rate
Potassium Bromate and Merck # 2331 were used,
Sample : Cellulose = 2 : 3,
Humidity 45(±5) %
Electrical power 150 ±5kW

Figure 4 : Schematic illustration of test device