Research paper

Development of a small-scaled drop hammer test for detoxifying adsorbents

Kosuke Yuasa*, Mieko Kumasaki**†, and Mitsuru Arai***

*Showa Denko k. k. Production Technology Center, 5-1, Okawa-cho, Kawasaki-ku, Kawasaki 210-0858, Japan

**Yokohama National University, 79-7 Tokiwadai, Hodogaya-ku, Yokohama, 240-8501, Japan
TEL : +81-45-339-3994
† Corresponding address : kumasaki@ynu.ac.jp

***Environmental Science Center, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Received : April 25, 2008 Accepted : February 24, 2009

Abstract

A small-scaled drop hammer testing apparatus has been developed and the applicability has been evaluated for an impact sensitivity test of used dry gas detoxifying absorbents which are applied in semiconductor manufacturing processes. As hazardous gases are concentrated and/or some reaction products may be formed on the surface of the absorbents during a detoxifying process, an impact sensitivity of the used absorbents could become higher than that of pure absorbents. The current impact sensitivity test, however, requires sample to be prepared in an atmospheric environment while used absorbents might change their properties during such preparation. In order to eliminate a risk of changes in the chemical properties and ensure a safety, an absorption process and a drop hammer test should be carried out under the same atmosphere, as is actually used in detoxifying process. Therefore, an apparatus providing hermetically-sealed condition has been developed to resolve the problem. In this research, results of a closed type apparatus were evaluated in comparison with existing data from conventional method. RDX (1, 3, 5-trinitroperhydro-1, 3, 5-triazine) was used as a test sample. The correlation between existing and new method was obtained and applicability was confirmed.

Keywords : drop hammer test, detoxifying absorbents, impact sensitivity, RDX

1. INTRODUCTION

Some hazardous gases are significantly used in semiconductor manufacturing processes as material gases. They usually exhibit flammable, explosive, corrosive, and / or toxic characteristics. Hazardous secondary gases also may be produced during the reaction between the manufacturing gases. Nevertheless, the industry has used them due to the market's demand. Therefore, they require special measures to avoid emission into the atmosphere.

One of the safety measures is a dry detoxifying system ; an adsorbent filled in column removes and stabilizes the hazardous exhaust gases. The system is available for a wide range of gases with a suitable adsorbent and allows easily replacing saturated cartridges with new ones. Due to the advantages of the low initial cost and high detoxifying capacity, this system has been applied in many plants and laboratories.

Despite these advantages, some accidents have been reported and many ignition or explosion hazards have been recognized. In 2004, for instance, one worker was killed and two were injured by an exploding cartridge during the treating process. As a result of an accident investigation, it has been indicated that an impact on the adsorbent in adsorbed phase may have caused the accident. This result suggests an impact sensitivity of the used adsorbents should be examined for safe treatment.

So far, many impact sensitivity apparatuses have been developed and applied for safe handling of chemicals. For example, BAM type drop hammer test is adopted as a recommended method in United Nations[1]. In Japan, drop hammer test and fall hammer test are authorized in JIS (Japanese Industrial Standards) as standard impact sensitivity testing apparatuses[2, 3]. For used detoxifying adsorbents, however, they are not suitable due to the open air sample chamber because used detoxifying adsorbents are at a gas−solid adsorption equilibrium. The chemical property of the samples may change if they are treated in air. In order to eliminate a risk of changes in the chemical properties and ensure a safety, an absorption process and a drop hammer test should be carried out under the same atmosphere of which is absorbed.

In this study, a closed type small−scaled impact sensitivity testing apparatus has been newly developed and the applicability has been examined through an measurement of RDX (1, 3, 5−trinitroperhydro−1, 3, 5−triazine). Experimental data have been analyzed statistically by a probit analysis method.

2. EXPERIMENTAL

2.1 Experimental apparatus

A newly developed apparatus mainly consists of a circular cylinder with top and bottom flanges (Fig. 1). A ball, which is held at the top of the cylinder, falls freely (70 cm) and delivers impact to a sample placed at the bottom flange. An Electrical magnet was used to hold the ball until just before falling. Various impacts can be given to the samples by changing a size of falling balls. In order to adjust the level of the apparatus, it was installed on a level adjustment table. A sample setting has referred to the existing methods[2]. An experimental sample was held between two cylindrical rollers (diameter 6 mm) and a guide ring (Fig. 2). Cylindrical rollers were replaced in each measurement. Before measurements, new falling balls and cylindrical rollers were washed out and dried so as to get rid of oil which was used to prevent rollers from rusting.

Applications such as gas cylinder, vacuum pump and pressure gauge can be connected to the circular cylinder through gas inlet / outlet. Falling balls and cylindrical rollers were made of steel. An adjusting table was made of iron. The other devices were made of SUS304.

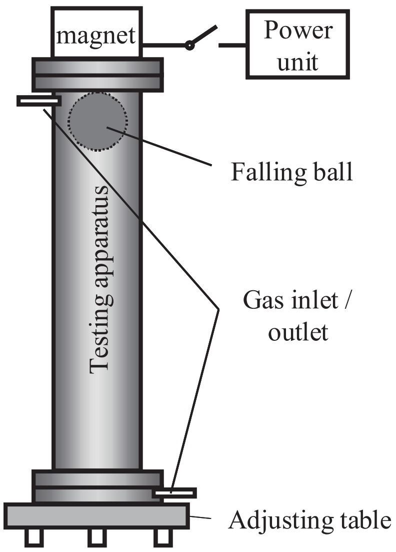

Fig. 1 An impact sensitivity testing apparatus

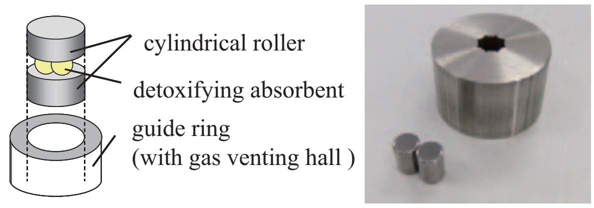

Fig. 2 Setting of samples

2.2 Experimental procedure and criteria of explosion /no explosion judgment

The experimental procedure was as follows: 1. Sample was placed at the bottom of the apparatus and the main unit was set up. 2. Level of the apparatus was adjusted. 3. Top flange holding falling ball was set up. 4. A test was conducted by turning off the electric magnet. In this research, four different balls were used and each trial has been conducted 18 times. Delivered energies to samples have been calculated from the potential energy of falling balls. Experimental results were analyzed by probit method[4].

The analysis has been used to calculate an effectiveness chemicals dosed to insects, human being and so forth. The dose−response curve should be sigmoid; as the concentration and the amount of chemicals are increased, the response approaches to 100%. Probit analysis transforms the sigmoid curve to a straight line by using of this equation so that it can be analyzed through least squares regression.

$$P = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{Y-5} e^{\frac{1}{2}u^2} du \qquad (1)$$

Probit number can be deducted from the response. The probit number−log (dose) should be a straight line and the point in log (dose) axis corresponding probit of 5 indicates the concentration or the amount of dose which causes 50% of response. In the research, log (E) are used instead of dose for calculation since the mechanical impact works in logarithmically. The significance was also tested by level of significance of the regression line.

A criteria of explosion / no explosion has referred to the existing methods[2]. Existence or nonexistence of explosion evidence on the surface of the two cylindrical rollers has been checked after each examination.

2.3 Chemicals

In order to examine an applicability of the developed apparatus, RDX (Type A Class C, Chugoku Kayaku Co., Inc.) was used as a standard testing sample based on the information that RDX exhibits stable impact sensitivity. Impact sensitivity of RDX has ever been examined with various apparatuses and pervious data enable availability of the apparatus by comparison with the result in this study. The experimental results with RDX are capable of validation for the apparatus. Furthermore, in case for a new material, it can be compared with the RDX and categorized in two classes: one which is more sensitive than the RDX and the other.

Before experiments, wet state sample had been dried in vacuum desiccator over 24 hours and then kept at 333K. From the experimental results of different sample mass (5.0−10.0mg), 7.0−9.0 mg had been adopted because of its producibility.

3. RESULTS AND DISCUSSION

Experimental results are shown in table1.This experiments obtained 2.72 J of E_{50} (50 percent explosion energy) while 8.1 J[5] and 1.6 J[6] of E_{50} were obtained in previous studies (Table 2).

Based on the results, the E_{50} is an overall result of complicated factors interacting each other. Since the energy applied to a sample is influenced by impact period, sizes of cylindrical rollers, energies lost in friction between parts, E_{50} strongly depend on apparatus shape and configuration. A lot of factors affecting on E_{50} value must be embedded and it is difficult to separate the effects.

Experimental results exhibited that explosion probability (number of explosions / number of trials) had risen according to the increase of given potential energies. This trend was the same as the results from existing methods.

Explosion probability of chemicals is empirically known to be log−normally distributed against provided energy. Hence, in order to evaluate the developed apparatus, probit analysis was adopted to judge whether experimental data from the developed apparatus had followed the tendency of the other research data.

Probit number was used for check the adequacy of the apparatus and a set of experimental results in this paper. Probit analysis itself can apply values obtained in experiments to normal distribution model. If the probit number and values have liner relation, the experimental results follows normal distribution. Since impact sensitivity is known to fit normal distribution against applied energy, probit number and log (logE) is subject to linear relation. Figure 3 represents the relationship between the logarithm of applied energy with drop hammers and probit numbers. Probit number can be calculated by adding 5 to cumulative frequencies corresponding to explosion probability in the normal distribution. The figure indicates 0.05 of significance level and represents validity for impact sensitivity as well as previous testing apparatuses.

Table 1 Results of measurements

Ball weight (g)	E (J)	Frequency (explosion / number of tests)
535	3.7	0.83(15/18)
441	3.0	0.67(12/18)
358	2.5	0.28(5/18)
287	2.0	0.11(2/18)

Table 2 Comparison of the explosion energy of RDX (*: carried out in this study)

Apparatus	E50 [J]
BAM type drop hammer test	9.8*
	8.1[5]
	1.6[6]
Small−scaled drop hammer test	2.7*

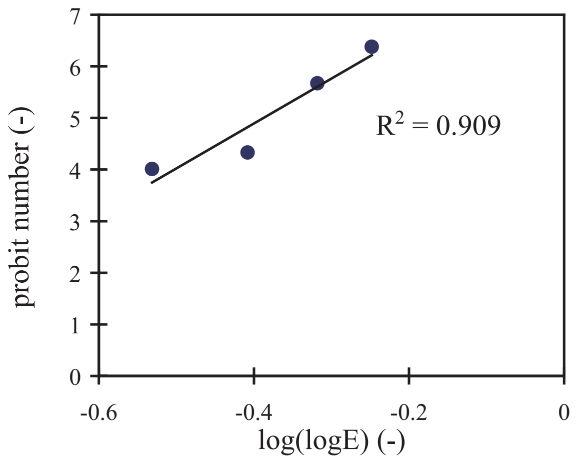

Fig. 3 Probit analysis of experimental data

4. CONCLUSION

A closed type drop hammer testing apparatus has been newly developed and the applicability has been evaluated to check an impact sensitivity of used dry gas detoxifying absorbents.

As a result of RDX experiments and the statistical analysis of data, it has turned out that explosion probability had risen according to the increase of provided energies. Also, it has become clear that explosion probability had been log−normally distributed against provided energy. From these results, it has been shown clearly that the apparatus was applicable as an impact sensitivity testing apparatus for detoxifying adsorbents.

5. Acknowledgement

The authors are grateful to Mr. Masataka Ogura of Chugoku Kayaku Co., Ltd. for his advice and discussions in developing the apparatus.

REFERENCES

1) United Nations, Recommendations on the Transport of Dangerous Goods : Manual of Test and Criteria, (1999)
2) JIS K 4810, "methods of explosives property test"
3) JIS K 4853, "percussion cap for match"
4) D. J. Finney, Probit Analysis, Cambridge University Press, (1977)
5) Y. Shitano, "impact sensitivity of energetic materials at low temperatures ", Kayaku Gakkai Autumn symposium, 2006
6) T. Matsunaga, Y. Kaneko, F. Yoshizawa, Y. Inoue, M. Tamura, I. Kuramochi, and T. Yoshida, "Mechanical sensitivities of high−sensitive materials using the drop ball tester", Kogyo Kayaku (Sci. Tech. Energetic Materials), 49, 13 (1988)

乾式除害剤のための小型密閉式打撃感度測定装置の開発

湯浅公輔*，熊崎美枝子**†，新井　充***

半導体産業に用いられる乾式除害剤の打撃感度試験に用いるため，小型落球感度試験を作成し，適用可能性について評価した。除害プロセスでは，有害ガスが除害剤上で濃縮される，あるいは除害剤との反応生成物が除害中に生成し，使用前の除害剤よりも感度が高くなるおそれがあるためである。既存の打撃感度試験器では試料を大気中で取り扱うが，吸着後の除害剤が変性してしまう可能性がある。実験者の安全を確保し，有害ガスを吸着した物性を保持したまま測定するため，落球感度試験を実際にプロセスで用いる場合と同様の雰囲気下で行う必要がある。この問題を解決するために，密閉式の装置を作成した。本研究では，密閉式の装置を既存の手法と比較することで適用可能性を評価した。試料としてRDXを用い，今回新たに作成した装置と既存の装置を比較して適用可能性を確認した。

*昭和電工株式会社　生産技術センター　〒210-0858　神奈川県川崎市川崎区大川町5-1

**横浜国立大学大学院環境情報研究院　〒240-8501　神奈川県横浜市保土ヶ谷区常盤台79-7
†Corresponding address : kumasaki@ynu.ac.jp

***東京大学環境安全センター　〒113-0033　東京都文京区本郷7-3-1