Research Reports of the National Institute
of Industrial Safety, NIIS-RR-2005 (2006)
UDC 537.24:667.612

静電粉体塗装用塗料の着火性に関する研究（その1）*

崔　光石**, 山隈　瑞樹**,　鄭　載喜***

Study on Ignitability of Coating Powder Used in Electrostatic Powder Coating System (Part 1)*

by Kwang-Seok CHOI**, Mizuki YAMAGUMA** and Jae-Hee JOUNG***

Abstract; Electrostatic powder coating has been successfully implemented in the painting industry as an environmentally friendly process. However, there have been many accidents involving dust fires and/or explosions in electrostatic powder coating systems using corona discharge. One of the methods for avoiding fires and/or explosions in electrostatic powder coating plants is to investigate the Minimum Ignition Energy (MIE) of coating powders due to the capacitive discharge, such as the electrostatic discharge. This paper reports the experimental results dealing with MIEs of the coating polymer powders (polyester, epoxy, epoxy-polyester co-polymer, nylon, and polyacrylonitrile). The MIEs of five kinds of polyester powders, which were also investigated in this study, differed with respect to pigment type, non-combustible mass fraction, and particle size. The Hartman vertical-tube (1.2 l) apparatus (MIKE-3) was used for the ignitability (MIE) testing of dust clouds.
The important results were found as follows: (1) the ignitability of epoxy powder related to the thermal decomposition and surface conditions was higher than that of other powders used in this study, (2) the particle size of coating powders is more important than other factors, such as the pigment type and a non- combustible mass fraction, with regard to their ignitability, (3) some of the sample was so sensitive that even a spark with very low energy, such as 2 mJ, could ignite them. The values of the discharge spark energy of ignition testing set by the BSI standards and the FM regulations related to safety of the electrostatic powder coating system are high enough to result in the ignition of some of the coating powders. Therefore, it is imperative that more appropriate discharge spark energy values in testing be defined for safety assessment in electrostatic powder coating systems.

Keywords; electrostatic discharge, minimum ignition energy, coating polymer powders

---

* JJAP (Japanese Journal of Applied Physics, Vol. 44, No. 19, 2005, pp.L.599-602, 2005)で一部誌上発表

** 物理工学安全研究グループ Physical Engineering Safety Research Group

*** ソウル産業大学校 安全工学科Seoul National University of Technology, Department of Safety Engineering

1. INTRODUCTION

The Electrostatic Powder Coating (EPC) system was first introduced to the industrial process in the early 1960s. Thereafter, since the EPC system has offered significant environmental benefits compared to its conventional solvent-based counterparts, it has been widely adopted for many industrial processes. Particularly, many countries have taken a hard line in the regulation of Volatile Organic Compound (VOC) emissions, which has encouraged the shift to powder coatings or water based coatings in the industrial finishing field.

However, accidents involving fires and/or explosions with EPC systems using a corona discharge of high voltage still occur even though the ignition hazards arising from an electric spark are reduced in comparisons with those at liquid paint plants. From the viewpoint of safety engineering related to this EPC system, the Minimum Ignition Energy (MIE) of coating powders is a very important aspect of technical safety indices.

Various reports have been published on the ignitability of dust clouds over a long period of time [1,2]. However, the MIEs of coating powders due to a spark have not been sufficiently investigated.

Therefore, in the present study, experiments were conducted dealing with MIEs of several kinds of coating powders, which differed with respect to polymer type, pigment type, non-combustible mass fraction, and particle size. In addition, a detailed discussion is presented, which deals with the reasons that the ignitability of epoxy coating powder is higher than that of other powders used in this study. A primary objective of this paper is to publish information regarding the ignitability of coating polymer powders for the benefit of individuals working to prevent and mitigate dust fires and related explosions.

2. BRIEF SURVEY OF STANDARDS RELATED TO SAFETY OF EPC SYSTEMS AND MIE OF DUST CLOUDS

There are a large variety of standards from country to country governing the safety of EPC systems and testing methods associated with the MIE of powder. The standards, regulations, and research have been screened and are presented in this Section.

Initially, safety regulations and standards related to spray finishing operations were prescribed by the following: (1) the National Fire Protection Association (NFPA) Nos. 33 and 68, (2) Factory Mutual (FM) Class Nos. 7261 and 7264, (3) Occupational Safety and Health Standards (OSHA) CFR 1910.107, (4) American National Standards Institute (ANSI) Z9.3, (5) British Standards Institution (BSI), EN 50050-2001, (6) DMT 03 ATEX E092, (7) National Swedish Board of Occupational Safety and Health, Safety Regulations No. 12:2, (8) *Hauptverband der gewerblichen berufsgenossenschaften* in Germany, ZH 1/444, (9) Korea Occupational Safety and Health Agency (KOSHA) Code E-3-2002, (10) Occupational Health and Safety Regulation 2001, New South Wales in Australia, and (11) Uniform Fire Code (UFC), Part V, Article 45. In general, these standards deal with safety from a variety of viewpoints. However, several aspects of these standards have not been evaluated quantitatively and systematically.

The second part is devoted to the standards relating to the testing methods for assessing the MIE of dust clouds as follows: (1) the International Electrotechnical Commission (IEC, 1994), 1241-2-3, (2) the National Fire Protection Association (NFPA, 1993), 77, (3) the Draft European Standard (DES, 1998), (4) CENTC 305/WG1/SG:1.2, (5) the British Standards Institution (BSI, 1991), BS5958, (6) the American Society for Testing and Materials (ASTM, 2001), 2019-99, and (7) The Research Institute of Industrial Safety, Japan, RIIS-TR-87-1. These standards emphasize the use of the MIE of dust clouds as very important safety indices in practice and provide basic information about dust clouds ignition processes.

In the third part, important researches related to prevention and mitigation of dust explosions are specifically addressed as follows: (1) Eckhoff (1994, 1996 and 2000) reviewed a large number of studies on dust explosions. His papers reviewed in detail three aspects of dust explosions: basic research, applied research and prevention and mitigation of dust explosions in industry. Furthermore, his work covered the testing of the ignitability and explosibility of dusts 3-5). Gibson (1993) presented a valuable summary of methods for preventing the ignition of powders and dusts in drying operations 6). Electrostatic hazards in connection with industrial use of big flexible bags were discussed by Rogers (1994) and Dahn et al. (1994) 7,8). Pratt (1994) presented three case histories in which an electrostatic spark discharge was generated during pneumatic transport of powders 9). Matsuda (1995) gave an account of ignition hazards of combustible dusts and their prevention 10). Siwek et al. (1995) summarized the ignition behavior of dust clouds. Test apparatus and procedures were introduced, including the significant parameters on the safety indices 11). Jaeger et al. (1998, 2001) described the determination, prevention and mitigation of potential hazards due to the handling of powders during transportation, charging, discharging and storage. They also outlined a "risk analysis" to ensure and maintain safety in the chemical industry 12,13). Kodama (1999) gave an overview for MIE and the incendiary potential of gases and powders exposed to ESD 14). These kinds of research emphasized the use of the minimum ignition energy (MIE) of dust clouds as very important safety indexes in practice and also provided basic information about dust cloud ignition processes.

3. EXPERIMENTAL

3.1 Apparatus and method

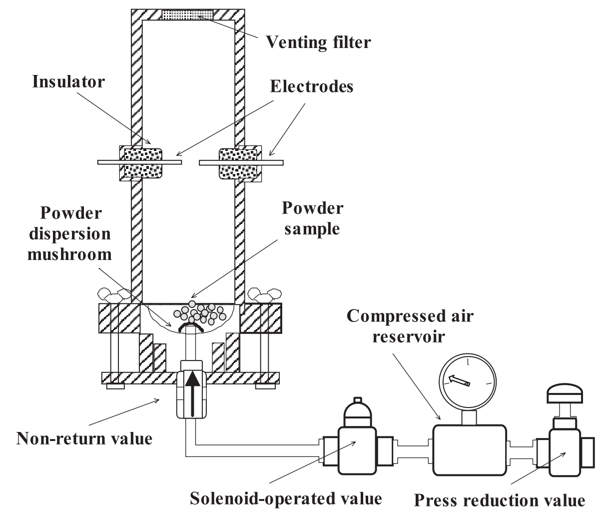


Fig.1 Schematic drawing of the MIE measurement apparatus (MIKE-3) for coating powder.

The Hartman vertical-tube (1.2 *l*) apparatus (MIKE-3), which is illustrated in **Fig. 1**, is one of the pieces of equipment used for the general ignitability (MIE) testing of dust clouds mentioned in Section 2 above 15). The control range of the dust concentrations of the MIE apparatus used in this study is from 0.125 kg/m^3 to 3 kg/m^3. For MIE measurements, a single electric spark from a capacitance is carried via a transformer to pass between the two electrodes with a diameter of 2 mm. The energy of the spark is varied by changing the values of the capacitor and the applied voltage in the discharge circuit. The dust is dispersed by means of air stored in the reservoir (0.7 bar), which is suddenly released into the chamber by means of a solenoid valve. Observations are made until the lowest possible energy at which the flame propagates through dust clouds is found under a constant condition of testing (inductance, 1mH; ignition delay time, 120 ms; and electrode spacing, 6mm). This test conditions were described in the international standard of IEC 15). In the case of the capacitive-inductive (*LC*) sparking circuit used in this study, since virtually all the stored energy on the capacitor appears in the spark, the net energy (in J) was given by 1/2 CV^2, where C is the capacitance in the circuit (in F) and V is the potential at the moment of discharge (in V).

In this experiment, "ignition" was acknowledged to have taken place when the dust cloud caught fire by electric sparking within 10 successive attempts. All the test conditions were 26 ± 2 °C and 35 ± 5 % RH.

3.2 Coating polymer powder

In general, a coating powder consists of a polymer, such as, polyester, epoxy, nylon, or acrylic, and a small amount of pigment. Thus, the coating powders used in the experiment were polyester, epoxy, epoxy-polyester co-polymer, nylon, and polyacrylonitrile. Five kinds of polyester powders, which were also used in this study, differed with respect to pigment type, non-combustible mass fraction, and particle size. Before being subjected to the testing, the coating powders were dried in a desiccator at 25 °C for 24 hours.

4. RESULTS AND DISCUSSION

Figure 2 shows the ignition energy as a function of the dust concentration of coating powders. Each data point in the figure indicates the lowest energy at which ignition occurs within 10 successive attempts to ignite the dust/air mixture.

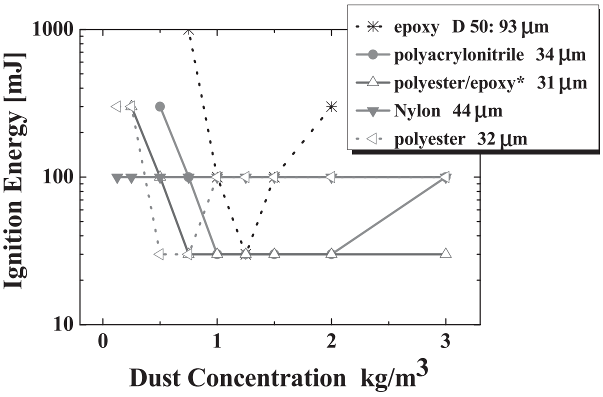


Fig.2 Ignition energy as a function of the dust concentration in coating powders (*:epoxy-polyester co-polymer).

Table 1 Median particle size, *D* 50 and MIE among the five kinds of coating powder used in this study.

Specimens	Color	*D* 50 [µm]	MIE* [mJ]	Manu-facturer
Polyester	Black	32.45	17	A
Epoxy	Black	93.16	24	B
Epoxy-Polyester co-polymer	White	31.85	13	A
Polyacrylonitrile	White	34	15	C
Nylon	Black	44	35	D

*: value estimated by the use of the probability of ignition within 10 successive attempts.

The mean particle size distribution, *D* 50 measured by the laser diffraction method (LDA Win 1.21, Wet type) and the MIE values estimated by the use of the probability of ignition are listed in **Table 1**. It should be noted that the MIE is usually quoted as a range; the lower value represents the highest energy at which no ignition is found in at least 10 experiments. The higher value, on the other hand, is the lowest energy at which the dust air mixture is just ignited: no ignition (W_1) < MIE <ignition (W_2) 11). The MIE value can be estimated by the use of the probability of ignition as follows16): $\mathrm{MIE} = 10\,\hat{}\,(\log W_2 - I\,[W_2]\ \cdot \log W_2 - \log W_1/(NI+I)\,[W_2] + 1))$, where, I is number of tests with ignition at the energy W_2, $(NI+I)$ is total number of tests at the energy W_2.

The first noteworthy point in the experimental results in **Fig. 2** and **Table 1** is that coating powder was so sensitive that even a spark with energy as low as several tens of mJ could ignite them. Another interesting point is that, nevertheless, *D* 50 of the epoxy powder, 93 µm, was almost three times as large as those of the other powders. Its MIE, 24 mJ, was similar to those of the other powders. This value was much smaller than expected. It is well known that epoxy powder has high ignitability. This is evident from previous papers by Eckhoff et al. and Pidoll et al. 1,2). It remains to be demonstrated why the ignitability of epoxy powder is higher than that of other powders. This is discussed in detail later. First, as to the ignition phenomena of dust clouds, the increased temperature of particles is initiated by spark discharge, and, subsequently, the combustion reaction of particles starts and forms a kernel for flame propagation, leading to ignition. From this point of view, the thermal decomposition of coating powder has an effect on the ignitability of dust clouds.

Thermal analysis of the coating powders under atmospheric pressure was conducted with a differential scanning calorimeter (DSC 2920). The heat-increasing rate and the mass of the coating powder in the test were 10 ℃/min and 1.5 mg, respectively. A sample pan (aluminum, open type) and a GPIB interface for communication with the controller were used for this testing.

The heat flow associated with transition for three kinds of coating powders as a function of the temperature is shown in **Fig. 3**. As indicated in the figure, it is clear that epoxy coating powder has a lower exothermic onset temperature, T_a [°C], and a higher heat of the decomposition, Q [J/g], than the other powders. The value, 8362 J/g of Q, for epoxy coating powder was almost twice as large as the 4099 J/g of polyester powder. These characteristics result in the acceleration of the combustion reaction of epoxy coating powder particles. In addition, in case of the epoxy-polyester co-polymer, the values of T_a and Q lie between the values of epoxy and polyester, as expected. Strictly speaking, the MIE for epoxy-polyester co-polymer is lower than that of polyester in almost the same size as that given in **Table 1**. This experimental result is also related to the values of T_a and Q.

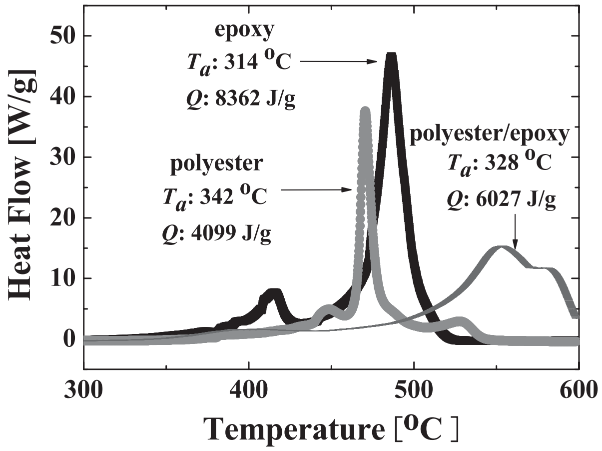
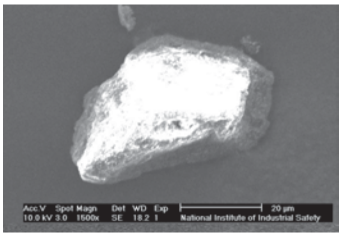
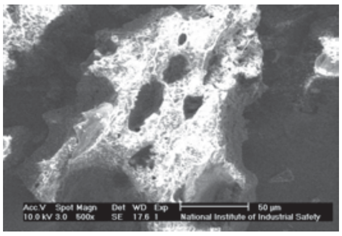


Fig. 3 Heat flow associated with the transition for coating powder as a function of temperature.

Second, the surface conditions and the shape of the coating powder particles could be responsible for its ignitability. Coating powders (polyester and epoxy) observed with scanning electron microscopy (SEM) are shown in **Fig. 4**. The epoxy-polyester co-polymer had almost the same surface condition as polyester powder; thus, the SEM image was omitted in **Fig. 4**. As shown in **Fig. 4** (a), the polyester particles were almost spherical. However, epoxy particles (see **Fig. 4** (b)) were irregular in shape. It was also found that the surface of epoxy coating powder had innumerable variety in the size of holes from several µm to several ten µm, which does not occur in the surface of other powders.



(a) polyester



(b) epoxy

Fig. 4 Surface conditions of the polyester and epoxy coating powders observed with SEM.

Both of these characteristics, irregular shape and surfaces with holes, suggest that the combustion rate increases because the total contact surface area between the particle and air has increased, resulting in a very small amount of energy required for the ignition of epoxy powder.

There are two possible explanations with regard to the holes. First, with the rapid progress of powder technologies in recent years, these holes may improve the performance of the charge of coating powder and the high-quality decorative finish. Secondly, the holes may occur unexpectedly due to problems during the manufacture of the coating powder. Accordingly, the MIE for the same types of coating powder may differ according to the technology used by the manufacturer.

The ignition energy with dust concentrations of polyester coating powder (specimen taken from the E company) in various colors is shown in **Fig. 5**. **Table 2** gives the fundamental characteristics, such as pigment type, particle size, and non-combustible mass fraction of coating powder used in **Fig. 5**, including MIE values.

Black polyester had the smallest MIE value, 2.4 mJ, the smallest one being 7.5 μm. Other coating powders, except for the black one, gave approximately the same MIE values in a similar particle size irrespective of the pigment type as well as a non-combustible mass fraction. This result suggests that the particle size of coating powders is more important than other factors with regard to their ignitability. However, it was also found that the minimum ignition dust concentrations (MIC) decreased as the content of non-combustible material decreased. This result agreed with the data obtained by Eckhoff 1). A more detailed discussion will be presented concerning several tests in another report.

Concerning the relationship between the particle size of the coating powders and their ignitability, we assumed that the epoxy coating powder mentioned in **Fig. 2** included some particles that were similar in size to those in the polyester coating powder shown in **Fig. 5**.

The dependence of the ignition behavior (MIE) on *D* 50 can, thus, be described by the following equation: $MIE_2=MIE_1 \times (M_2/M_1)^{2.5}$ ---(1), where Index 1: measured, Index 2: estimated, MIE_1: 24 mJ, M_1: 93 μm (*D* 50), and M_2: 7.5 μm (*D* 50). As estimated, the MIE_2 of epoxy coating powder with 7.5 μm was far lower than 1 mJ.

The previous data obtained by Pidoll et al. indicate that the MIE for epoxy coating powder with a mean particle size of 30 μm was 1.7 mJ 2). Besides, the MIE for epoxy powder (*D*50; 58 μm, color; green) taken from another company (F) was 7 mJ depending strongly on the particles size.

These values generally agreed with the data calculated in Equation (1) above as 1.4 mJ and 8 mJ, respectively. Moreover, Eckhoff showed that the true MIE for sensitive dusts, such as epoxy coating powder, was considerably lower, by at least one order of magnitude, to below 3 mJ 1). In this sense, it could be argued that extreme low energy below 1 mJ could ignite fine epoxy coating powder with several μm.

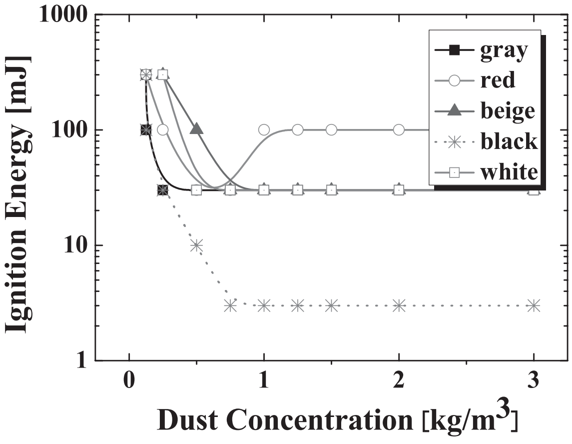


Fig. 5 Ignition energy with polyester dust concentrations in various colors.

Table 2 Fundamental characteristics of polyester powders with various colors.

Specimens	Pigment Type	*D* 50 [μm]	NCMF* [%]	MIE** [mJ]
Black	Carbon black	7.5	16	2.4
Gray	Iron oxide	28	28	14
Red	Iron oxide	38	27	24
Beige	Titanium oxide	34.2	44	17
White	Titanium oxide	33.9	44	14

*:Non-combustible mass fraction. **: value estimated by the use of the probability of ignition within 10 successive attempts.

A fatal accident with an EPC system using epoxy powder paint occurred in Japan 17). For the safety of spray-finishing operations and in accordance with BSI (BS EN) standards, a test gas mixture with a discharge spark energy of 2 mJ should be used for ignition tests on electrostatic spray apparatuses for flammable coating powders with an electrical high-voltage generator 18). In FM regulations, the value of the energy of the discharge spark mentioned above is defined as 5 mJ 19). The values of the energy of the discharge spark with both standards and regulations were higher than the MIE values of some coating powders. Therefore, it is important that the most appropriate value of a discharge spark be determined for assessing the safety of an EPC system.

5. CONCLUSIONS

To improve the understanding of the ignitability of coating powders due to a spark, such as an electrostatic spark, their MIEs were investigated experimentally. The results are summarized as follows:

(1) The ignitability of epoxy powder related to the thermal decomposition and surface conditions was higher than that of other powders used in this study.

(2) The particle size of coating powders is more important than other factors, such as the pigment type and a non-combustible mass fraction, with regard to their ignitability.

(3) As powder technologies have been rapidly progressing, a variety of new fine powders has been produced and used in various industrial processes. Therefore, it is imperative that the most appropriate discharge spark energy value in testing for the safety assessment in an EPC system be renewed as soon as possible.

ACKNOWLEDGEMENTS

We thank Mr. Shin Dae-Sung of Department of Safety Engineering, Seoul National University of Technology, Korea, for his assistance in the experiments. We gratefully acknowledge helpful discussions with Dr. T. Ando, Dr. M. Yashima, and Dr. M. Kumasaki of Chemical Safety Research Group in NIIS, on several points in this paper. We also wish to thank the coating powder companies for providing powder specimen to us. They want to remain anonymous.

REFERENCE

(1) Rolf K. Eckhoff, Geir H. Pedersen, Tommy A rvidsson: J. of Hazardous Materials, 19, p.1 (1988)

(2) U. Von Pidoll, H.Kramer: J. of Electrostatics, 30, p. 103 (1993)

(3) R. K. Eckhoff: Proc. 6th Int.Coll. Dust Explosions, Shenyang, P.R.China, 29 Aug.-2 Sept., eds Deng Xufan and Wolanski, P., pp.5-34 (1994)

(4) R. K. Eckhoff: J. Loss prev. Process Ind., Vol.9, No.1, pp.3-20 (1996)

(5) R. K. Eckhoff: 3th Int. Sym. on Hazards, Prevention, and Mitigation of Industrial Explosions Proc., pp.7-20 (2000).

(6) N. Gibson: Paper given at the European Summer School on; Dust Explosion Hazards; Their Assessment and control, Cambridge, UK, organized by IBC technical Services Ltd. In association with BMHB and IELG (1993).

(7) R. L. Rogers: Preprints for seminar on Explosion Safety and Related Risk Control, Gent. Belgium, organized by Technological Inst.〓KVIV, in cooperation with EuropEx (Kontich, Belgium), pp.169-179 (1994).

(8) C. J. Dahn, B.N. Reyes and A. Kashani: Proc. 28. AIChE Ann. Loss Prev. Sym., Session No. 12 on Electrostatic Hazards, Atlanta, USA, April 17-21. American Institution of Chemical Engineers, 345 E. 47. Street, New York (1994).

(9) T. H. Pratt: Proc. 28. AIChE Ann. Loss Prev. Sym., Session No. 12 on Electrostatic Hazards, Atlanta, USA, April 17-21. American Institution of Chemical Engineers, 345 E. 47. Street, New York (1994).

(10) T. Matsuda: J. Insti. Electrostatics Japan, Vol.19, No.1, pp.35-40 (1995)

(11) R. Siwek: Process safety progress, Vol.14, No.2, pp.107-118 (1995)

(12) N. Jaeger: Process safety progress, Vol.17, No.1, pp.74-81 (1998)

(13) N. Jaeger: J. of Loss prev. Process Ind., Vol.14, No.1, pp.139-151 (2001)

(14) T. Kodama: J. Insti. Electrostatics Japan, Vol.23, No.5, pp.227-233 (1999) (In Japanese)

(15) IEC, International standard (1241-2-3) (1994)

(16) A. D. Kuhner: Instruction Manual of MIKE-3(1999)

(17) Countermeasure for Accident due to Electrostatic Discharge (In Japanese), Japan Paint Manufacturers Association (JPMA) p.87 (2002)

(18) British Standard Institution (BSI), BS EN 50050 (2001)

(19) Factory Mutual (FM) Class No. 7260 (1996)

（平成17年10月23日受理）

Research Reports of the National Institute
of Industrial Safety, NIIS-RR-2005 (2006)

抄　　録

静電粉体塗装用塗料の着火性に関する研究（その1）

崔　光石，山隈瑞樹，鄭　載喜

近年、静電粉体塗装は一般の吹付塗装に比べ，生産効率が高く，環境にやさしいという大きなメリットから普及率が極めて高い。しかし，静電粉体塗装は高電圧印加により塗料を帯電させ，接地した被塗物に向かって移動させる工程であり，放電による粉塵爆発・火災の発生が危惧されていることから，粉体塗料の最小着火エネルギー(MIE)を測定した。測定には，国内外で標準的に用いられているIEC規格に準拠した吹上げ方式着火試験装置（ハルトマン式、MIKE-3）を使用し，着火試験用粉体塗料としては，ポリマーを主成分とする粉体塗料（ポリエステル，エポキシ，ポリエステル/エポキシ, アクリル, ナイロン）及び5種類(色別)のポリエステル粉体塗料の計10種類を用いた。その結果，粉体塗料は数mJの小さい放電エネルキーでも着火する危険性が明かとなった。特に，粉体塗料の粒径を考慮すると、エポキシ粉体塗料の方が他の粉体塗料に比べて，着火しやすいという結果が得られた。また，粉体塗料に含まれている顔料などの成分によっては，MIEはほとんど変化しないことが明らかになった。

（図5，表2，参考文献19）

噴霧・噴出帯電の静電気危険性評価法の検討

大澤　敦

配管やノズルなどから液体が噴出すると液体および液滴に静電気が帯電して着火源となることがあるので，各種工程の現場において簡便に噴霧・噴出帯電の静電気危険性を評価する方法を構築することは工程の安全化と静電気による着火の防止対策の指針を与え，安全工学の立場からも重要である。本研究では噴霧・噴出の静電気危険性を評価するための測定技術とこの測定データを元に評価する手法を構築することを目標としている。測定技術として接地円筒ケージと電界計による空間電荷密度の測定，吸引ファラデーチューブによる空間電荷密度の測定またはフローティングプローブによる電位測定の３つの方法を検討した。また，評価手法としては，各測定データを元にポアソンの方程式と$\mathbf{E} = -\nabla V$を用いて噴霧空間の電界強度分布を求め，静電気放電の可能性を評価する方法を検討した。圧搾空気ドライフォグ２流体ノズルを用いた噴霧帯電のモデル実験により，これらの３つの測定方法を検討して，接地円筒ケージ・電界計と吸引ファラデーチューブの測定が妥当な結果を導き，現場で簡便に測定できることを考慮すると接地円筒ケージ・電界計による方法が適していることを示した。また，静電気放電の可能性を評価するための簡便なモデルも提案している。

（図7，参考文献4）

破砕を伴う落石現象の物理モデル化に関する研究

伊藤和也，豊澤康男，日下部治

落石は道路，鉄道，住宅等へ影響を及ぼす斜面災害の中でも発生頻度が比較的高い災害現象の一つである。また，落石に起因する労働災害について調査したところ，過去10年間で40件程度報告されていた。中には落石が突破・跳躍して落石対策工により保護されている箇所にいた労働者が被災する事例も報告されており，落石の運動形態や衝突現象など，落石対策の計画・設計に必要な事柄についても未だ十分には解明されていないのが現状である。そこで本研究は，多くのパラメーターが自明となり，応力条件を等価にすることが出来る遠心模型実験手法を用い，破砕を伴いながら衝突と跳躍を繰り返すような落石現象について物理モデル化を行い，その運動形態・衝突現象の解明を試みた。本報では，新たに開発した遠心場落石発生装置の概要と，それを用いて行った落石実験の落石軌跡および落石の破砕状況を確認した。その結果，球形タイプの落石形態は回転運動が主であるが，破砕を伴うと回転運動から跳躍運動に変化し，破片は大きな跳躍をすることが確認された。　（図4，表5，写真12，参考文献28）