



ELSEVIER

Journal of Hazardous Materials A69 (1999) 245–256

**Journal of
Hazardous
Materials**

www.elsevier.nl/locate/jhazmat

The formation of explosive compounds in bitumen/nitrate mixtures

Ken Okada^{*}, Rifaid M. Nur, Yasuhiko Fujii

Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, 2-12-1, O-okayama, meguro-ku, Tokyo 152-8550, Japan

Received 5 January 1999; accepted 16 July 1999

Abstract

Ignition of various bitumen/nitrate mixtures was examined using a new method of thermal analysis, developed in the present study, in order to determine the self-ignition temperatures (SIT) of the sample materials. The effects on the SIT of transition elements, particularly silver, and the heating rates were examined. The same bitumen/nitrate mixtures were prepared by mixing bitumen, NaNO_3 , $\text{Ni}(\text{NO}_3)_2$ and either AgNO_3 or AgI . The sample heating rates were in the range from 0.5 to 4.0°C/min. In the present work, SIT was found to be independent on the heating rate when AgI is added, while SIT was found to depend on the heating rate when AgNO_3 was added. The activation energy E_a for the ignition of bitumen/nitrate mixtures has been calculated to be 30 kJ/mol. The suspected initiator of the ignition is thought to be silver fulminates or related compounds. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Low-level radioactive waste; Silver fulminate; Explosive compounds; Activation energy; Self-ignition temperature

1. Introduction

Incidents involving fires occurred at Eurobitum [1] in Belgium in 1981 and at the Tokai Works of PNC [2] in Japan in 1996. The fires occurred at both of these nuclear reprocessing plants involving the bituminization process. The bituminization facility makes solidification treatment on low-level radioactive liquid waste (LLW) from reprocessing plants. Although intensive investigation of the PNC accident has resulted in

^{*} Corresponding author. Tel.: +81-3-5734-2958; fax: +81-3-5734-2958; e-mail: okada@nr.titech.ac.jp

the release of an analysis report [3], analyses of the chemical reactions related to these accidents remain limited, because the chemical processes involved in bitumen related fires are very complicated.

After the above-mentioned accidents, the bituminization would not be used again as a low-level radioactive treatment for reprocessing; however, these accidents have shed light on the fire hazard involved when organic waste is mixed with nitrate salts. Generally speaking, treatment of organic waste should be handled carefully in PUREX reprocessing plants.

A similar chemical accident has been reported at the USDOE's Rocky Flats Environmental Technology Site (RFETS): an explosion occurred when leaded rubber gloves came into contact with nitric acid [4,5]. The analysis report indicated that the formation of explosive compounds must have played a role in this accident, which is another indication of the hazards involved when having organic materials, nitric acid and transition metal in close proximity.

In nuclear reprocessing plants, spent nuclear fuels are dissolved in nitric acid solutions. Some transition elements, such as Ni or Fe, may be dissolved from the vessel materials into the process streams, and nitrates of other transition metals, such as AgNO_3 , may exist in the process, because chemical reagents such as NaOH , NaNO_3 , $\text{K}_4[\text{Fe}(\text{CN})_6]$, NiSO_4 , AgNO_3 and $\text{Ba}(\text{OH})_2$, etc., are added to the waste solutions in order to immobilize long-life radioactive isotopes such as Cs, Sr and I during bituminization. If these mixtures of metal nitrates come into contact with organic materials, a fire may occur due to reactions similar to that described above, which caused the accident at RFETS.

In previous studies [6,7], the present authors reported that the combination of $\text{Ni}(\text{NO}_3)_2$ and AgNO_3 greatly reduces the self-ignition temperatures (SIT) of bitumen/nitrate mixtures. In the present work, thermal analysis is performed for bitumen/nitrate mixtures that include $\text{Ni}(\text{NO}_3)_2$, AgNO_3 or AgI . In the bituminization process, radioactive iodine is converted to AgI as an insoluble treatment. Most of the Ag ions added are expected to form AgI after waste treatment in reprocessing. In order to compare the effects of adding AgNO_3 or AgI to bitumen/nitrate mixtures, the SIT of bitumen/nitrate mixtures were investigated using AgNO_3 and AgI .

2. Experimental

2.1. Specification of bitumen and nitrates used

PNC type AD compound asphalt (abbreviated as ASP), was used to examine the SIT of bitumen/nitrate mixtures. Some characteristic properties [8] are given in Table 1. The specifications of this bitumen are expressed according to Japan Industrial Standard (JIS) regulations. Two types of samples were prepared for the present experiment: $\text{ASP} + \text{NaNO}_3 + \text{Ni}(\text{NO}_3)_2 + \text{AgNO}_3$ and $\text{ASP} + \text{NaNO}_3 + \text{Ni}(\text{NO}_3)_2 + \text{AgI}$. These chemical agents were mixed vigorously at 120°C . The sample was allowed to cool to room temperature and was then placed in the electric furnace.

Table 1
Specifications of the asphalt used in the present study

Testing	Methods	Results
Softening point [°C]	JIS K 2207	82
Penetration distance ^a at 25°C, 100 g, 5 s [mm]	JIS K 2207	3.6
Penetration index	–	3.8
Evaporation mass variation percentage [%]	JIS K 2207	0.02
Flash point, Cleveland Open Cup [°C]	JIS K 2265	316
Solubility in trichloroethane [%]	JIS K 2207	99.47
Ductility at 25°C [cm]	JIS K 2207	4
Density at 25°C [g cm ⁻³]	JIS K 2249	1.018

^a“Penetration” is defined as the penetration distance expressed by the unit of 0.1 mm. Thus the penetration of the present asphalt is 36.

2.2. Electric furnace with temperature measurement system

The electric furnace is illustrated in Fig. 1. Its temperature was controlled by a proportional integral derivative (PID) controlling power source, ULVAC Thermal Program Controller HPC-5000. The furnace containing the sample was a steel cylinder of 70-mm internal diameter and 130-mm internal height. The sample was heated at a

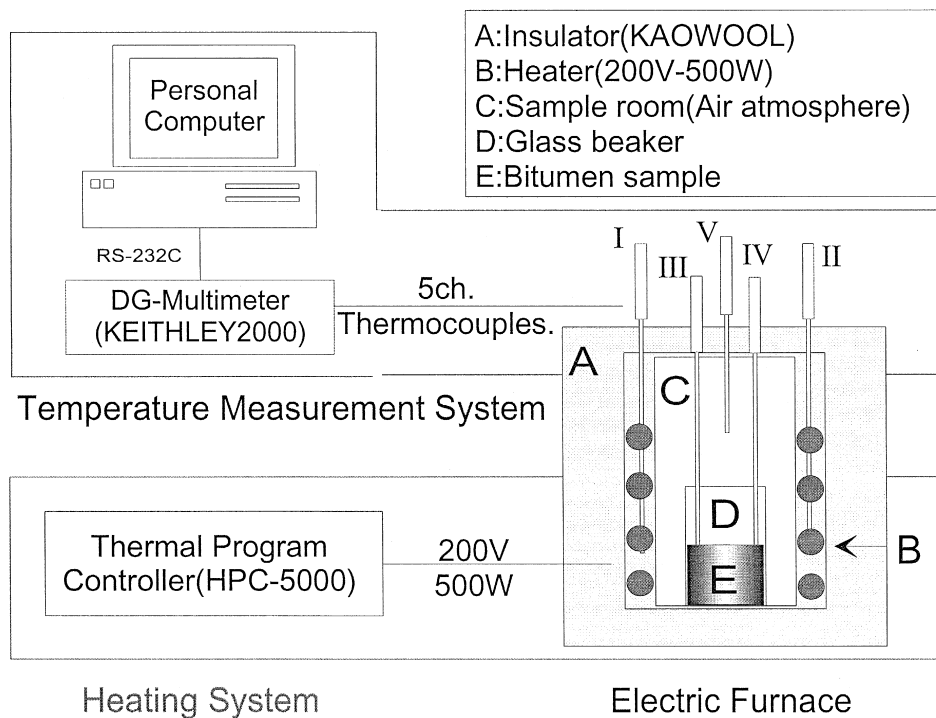


Fig. 1. Experimental apparatus.

constant rate by the heater surrounding the cylindrical sample room in which the sample beaker was placed. The heating rates varied within the range 0.5–4.0°C/min. The sample room was covered with KAOWOOL which is a short alumina–silica fiber product used as a thermal insulator. Temperatures in the heating apparatus were measured using five CA thermocouples covered with 316SS tubes (1.6 × 300 mm) as indicated in Fig. 1. Two of the thermocouples were attached to the outside surface of the sample room in order to measure the heater temperature. One of the thermocouples was placed just above the sample in order to monitor the temperature of the fire. The remaining two thermocouples were inserted at different places in the sample in order to make it possible to take into account the inhomogeneous temperature distribution in the sample. The thermocouples were connected to a digital voltmeter (Keithley multimeter 2000) in order to allow the temperatures to be read. All the temperature data were fed into a personal computer through an interface. The temperature was also monitored using analog recorders that were connected directly to the thermocouples. When the sample fired, the furnace source was switched off. The SIT was read as the initiating point of the rapid heating rate period. Two thermocouples were inserted in the sample. The lower temperature of them was determined as SIT. Self-ignition was also determined to have occurred when smoke was detected. The initial masses of bitumen, NaNO₃, Ni(NO₃)₂ · 6H₂O and AgNO₃ of the reagent were fixed as 25, 10, 5 and 1 g, respectively.

3. Results and discussion

3.1. Ignition temperature of bitumen / nitrate mixtures

Table 2 shows the SIT for the five samples. For the AgI additive, the SITs are independent of the 0.5 and 2.0°C/min heating rates. In contrast to the AgI additive, the SIT of AgNO₃ additives decreased significantly when the heating rate was changed from 4.0 to 0.5°C/min.

Fig. 2 shows the temperature change curves of the ASP + NaNO₃ + Ni(NO₃)₂ + AgNO₃ sample under three different heating rates. The ignition of the sample can be detected by the jump in temperature. As the heating rate increases, the ignition temperature increases. At the heating rate of 4.0°C/min, ignition occurs at 300°C, followed by a very rapid temperature increase of 300°C, up to 600°C.

Table 2
Ignition temperature difference of AgNO₃ and AgI at different heating rates

Additive salts ^a	Heating rate [°C min ⁻¹]	SIT ^b [°C]
AgNO ₃ (1.0 g)	4.0	307
AgNO ₃ (1.0 g)	1.8	221
AgNO ₃ (1.0 g)	0.5	208
AgI (5.0 g)	2.0	319
AgI (5.0 g)	0.5	312

^aSample = PNC-ASP(25 g) + NaNO₃ (10 g) + Ni(NO₃)₂(5 g) + additive salt.

^bSIT = Self-ignition temperature.

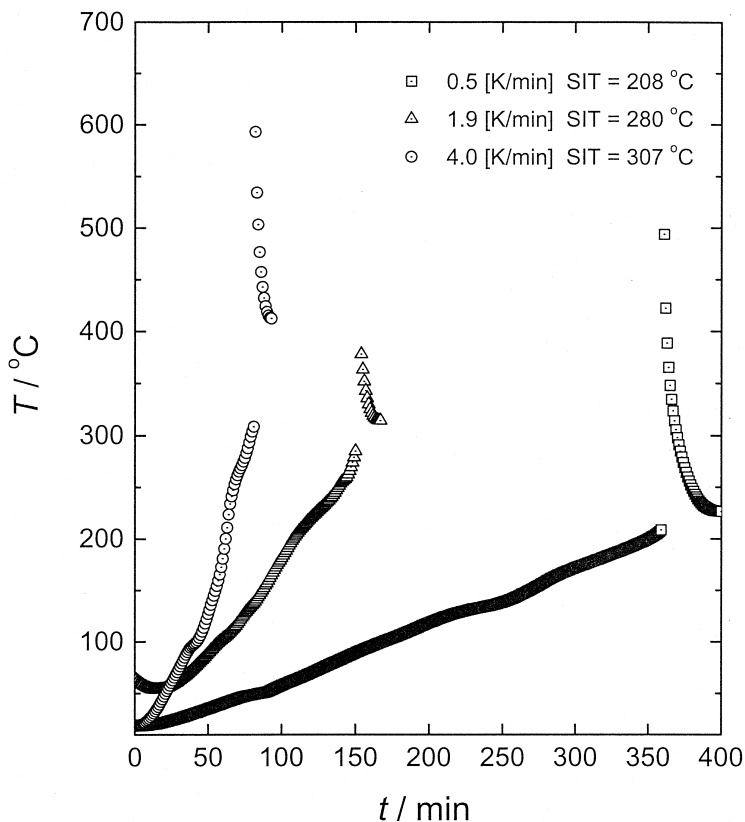


Fig. 2. Self-ignition curves for different heating rates for a bitumen sample (ASP(25 g)+NaNO₃(10 g)+Ni(NO₃)₂(5 g)+AgNO₃(1 g)).

Fig. 3 shows the relationship between the ignition temperature and the heating rate. At heating rates below 2.0°C/min, the SIT is approximately 210°C, whereas at heating rates higher than 2.0°C/min, the SIT is approximately 300°C.

3.2. Formation of explosive nitrated organic compounds in bitumen / nitrate mixture

Clerc and O'neal [9] reported that asphalt consists of three types of agents, namely asphaltenes, resins and oils. The molecular weight (ebullioscopic) of the asphalt they examined, which consists of C-84.1, H-8.9, S-4.6, N-0.7 and O-1.8 (mol%), is 1260. The *m/e* value measured by mass spectrometry ranges from 24 to 1900. Thus, this asphalt is assumed to contain a lot of >C=C< double bonds and aromatic compounds. Although the specifications of the asphalt used in the present work are different from those of the asphalt examined by Clerc et al., both types of asphalt are considered to have similar chemical compositions.

In the following discussion on chemical reactions involved in the present firing process, ignition is assumed to occur through two primary steps, i.e. the generation of

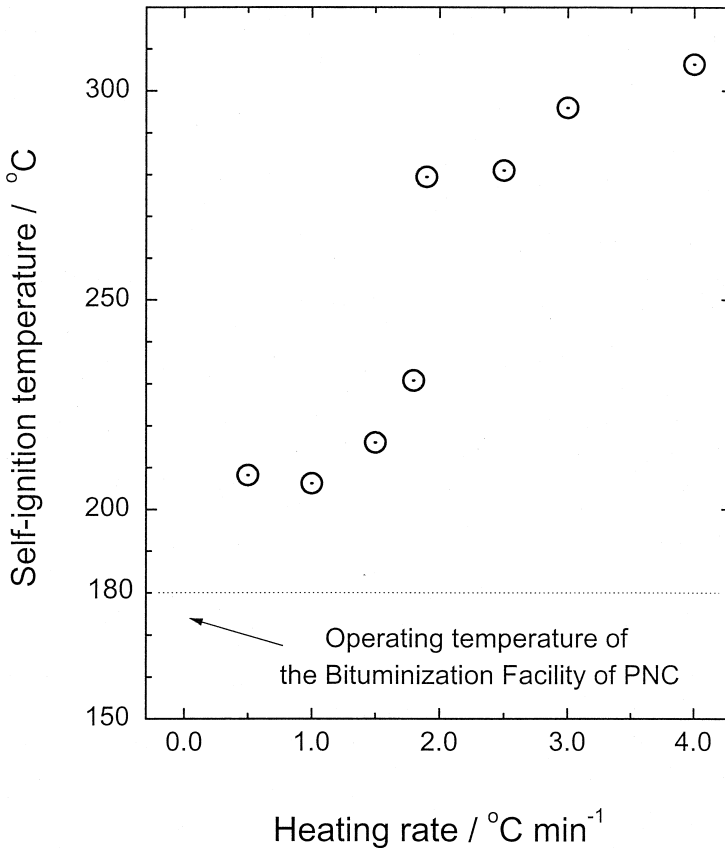
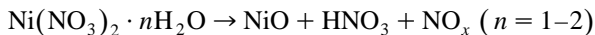


Fig. 3. Relationship between self-ignition temperature and heating rate for a bitumen sample (ASP(25 g) + NaNO₃(10 g) + Ni(NO₃)₂(5 g) + AgNO₃(1 g)).

HNO₃ or NO_x gases from Ni(NO₃)₂ and the formation of explosive or initiator materials. Concerning the former process, since Ni(NO₃)₂ · 6H₂O is very hygroscopic, crystal water is released in the range 100–200°C and hydrated Ni(NO₃)₂ is decomposed to NiO + HNO₃ + NO_x at temperatures above 200°C as [6,7]



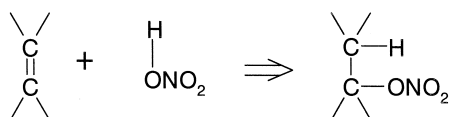
With respect to the latter step or the formation of explosives, Urbanski [10] reported that eight definite structural groupings exist in general explosive materials, as listed below.

- (1) –NO₂ and –ONO₂ in both organic and inorganic materials;
- (2) –N=N– and –N=N=N– in organic and inorganic azides;
- (3) –NX₂, where X is a halogen, as in NCl₃;

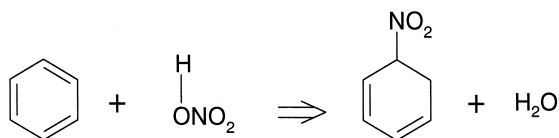
- (4) $-\text{C}\equiv\text{N}-\text{O}$ in fulminates;
 (5) $-\text{OCIO}_2$ and $-\text{OCIO}_3$ in organic and inorganic chlorates and perchlorates;
 (6) $-\text{O}-\text{O}-$ and $-\text{O}-\text{O}-\text{O}-$ in organic and inorganic peroxides and ozonides, respectively;
 (7) $-\text{C}\equiv\text{C}-$ in acetylene and metal acetylides;
 (8) $\text{M}-\text{C}$, metal bonded with carbon in some organometallic compounds.

The original bitumen asphalt and nitrate salts do not contain $-\text{N}=\text{N}-$ bonds and halogens. Since peroxide compounds are not formed in the presence of HNO_3 , the chemical species of (6) may be excluded. Thus the reactive groups (2), (3), (5), (6), (7) and (8) can be eliminated as possible initiating chemicals. The remaining, reactive groups, (1) and (4), may be generated in the oxidation process in hydrocarbon- HNO_3 mixtures.

In the case of the compound (1), asphalt has many double bonds ($>\text{C}=\text{C}<$) that react with inorganic acids such as HNO_3 and form $\text{C}=\text{O}$ groups. The nitric acid produced from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is assumed to react with the olefin hydrocarbons and benzene. Michael and Carlson [11] reported the following nitration process, in which nitric acid, as $\text{H} + \text{ONO}_2$, is considered to react with double bonds.

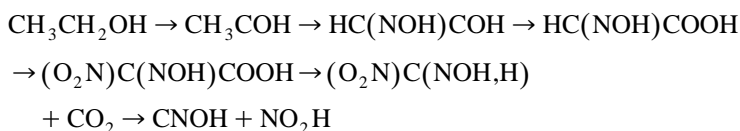


Generally, the nitration process proceeds easily in the presence of aromatic compounds. The reaction process is as follows:



These compounds are generally expected to be generated in bitumen. However, as mentioned in Section 1, the combination of $\text{Ni}(\text{NO}_3)_2$ and AgNO_3 has been found to greatly reduce SITs, and the above-mentioned nitro compounds would not explain the effect of silver nitrate.

In the case of compound (4), AgCNO is expected to form. The mechanism of formation of fulminate ions from alcohol and nitric acid has been discussed by Wieland [12], who described the formation process as follows.

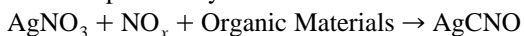


Wentrup [13] reported that fulminate can form from cyclic compounds. A new synthesis of fulminic acid from 4-substituted isoxazol-5(4*H*)-ones was confirmed. Although the reaction described in the present study has not yet been clarified, this reaction appears to be similar to that described by Wentrup.

Singh [14] has studied ultra violet spectra of fulminates and has suggested, based on quantum calculations, that the most probable structure of fulminates may be $\text{O-N}\equiv\text{C}$. However, his conclusions were not entirely correct. Britton and Duniz [15] reported that crystal structures of AgCNO occur in two polymorphic forms: one is orthorhombic and trigonal with a rhombohedral lattice (Fig. 4).

Collins and Holloway [16] reported that the temperature of ignition for silver fulminate is in the range between 200 and 204°C. These results are very similar to the lowest result of the present work. Generally, fulminate forms compounds with the following cations [17]: Na^+ , K^+ , NH_4^+ , Rb^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Cu^{2+} , Ag^+ , Au^+ , Tl^+ , Zn^{2+} , Cd^{2+} and Pb^{2+} . If a certain amount of these cation reagents is present, the bitumen/nitrate mixture can ignite at low temperatures.

In the present work AgI additive bitumen/nitrate mixture has shown the higher SIT of 300°C while AgNO_3 additive mixtures have shown low SIT depending on the heating rate. If we assume that fulminate is initiator of the firing, formation reaction of silver fulminate is expressed by



AgNO_3 is a very soluble salt in aqueous solution. This means AgNO_3 is fully dissociated in the forms of NO_3^- and Ag^+ ions hydrated with water molecules. When

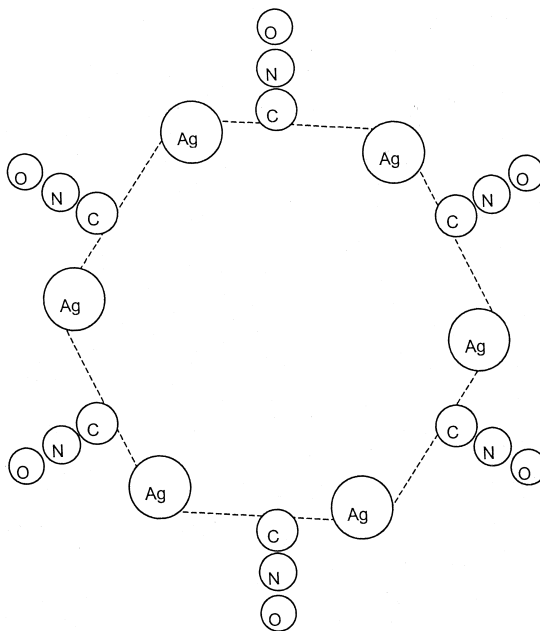


Fig. 4. Rhombohedral silver fulminate. View: down hexagonal *c*-axis.

NO_x gas is generated in the system, Ag^+ easily makes complex with NO_x . On the other hand AgI is known with its small solubility and is considered to exist in the forms of solid on critical state. Therefore it is conceived that AgI does not form easily complex with NO_x species released at around 200°C . At higher temperatures of about 300°C , probably dissociation of AgI is enhanced and disassociated Ag^+ or Ag is conceived to become the initiation materials of the firing.

3.3. Decomposition model of explosives

Although establishing what stages is the rate-determining step, doing so is essential for describing the kinetics of the decomposition of complex chemical systems that occur through several stages. Therefore, in practice, the behavior of such systems are described according to their heating, which is known as the formal kinetic approach. Such an approach does not consider each stage of the process separately, but rather the average process is considered without describing the mechanisms of the interim stages. Thus, a formal kinetic equation is used to describe the rate of this average process.

If the amount of the explosive compound is assumed to be the same at different temperatures, the following equations are generally used [18,19]. These equations were basically introduced by Ozawa [20]. The decomposition of explosives is a first-order reaction.

$$-\frac{dx}{dt} = kx \quad (1)$$

where t is the time, x is the fractional weight of the reacting materials, and k is the kinetic constant. The relationship between the kinetic constant (k) and the absolute temperature (T) of the reaction is expressed using an Arrhenius equation

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where A is the pre-exponential constant, E_a is the activation energy, and R is the gas constant (J/mol K). The temperature change is represented by

$$T = T_0 + at \quad (3)$$

where T is the absolute temperature, T_0 is the starting temperature (K), and a is the heating rate in K/min .

Even when the amount of x is unknown, the activation energy of the thermal behavior of the property can be estimated using the following equations:

$$-\int_{x_0}^x \frac{dx}{x} = \frac{A}{a} \int_{T_0}^T \exp\left(-\frac{E_a}{RT}\right) dT \cong \frac{A}{a} \int_0^T \exp\left(-\frac{E_a}{RT}\right) dT \quad (4)$$

where T_0 and x_0 are T and x at $t = t_0$, respectively. Ordinarily, the rate of reaction is very low at low temperatures. Therefore, this approximation is valid. The values of the right side of Eq. (4) have been calculated and tabulated by Doyle [21]. If E_a/RT is larger than 20, the following approximation is applicable [22].

$$\log\left(\frac{R}{E} \int_0^T \exp\left(-\frac{E_a}{RT}\right) dT\right) \cong -2.315 - 0.4567 \frac{E}{RT} \quad (5)$$

The left side of Eq. (4) is a constant which does not depend on the heating rate. From Eqs. (4) and (5), the following equation is obtained:

$$\log a = -0.4567 \times \frac{E_a}{RT} + \text{Const.} \quad (6)$$

Plotting $\log a$ with respect to $1/T$ yields a slope of $E_a \times 0.4567/R$. The experimental results of Fig. 3 are replotted in Fig. 5 in which $\log a$ is plotted with respect to $1/T$. The experimental data shows the linear relationship expressed by the Arrhenius equation in Fig. 5. Thus, the activation energy E_a is obtained from the slope as 30 kJ/mol using a least squares fitting of the plots in Fig. 5.

These results show that the decomposition of explosive compounds, or ignition, can be explained by general kinetic thermal analysis. Singh [23] reported the activation energy of 27.0 kJ/mol for the first-order reaction of the explosive compounds of silver fulminate. The activation energy obtained in the present work is well in accordance with the value obtained by Singh and supporting the previous discussion where silver fulminate is presumed as the initiator of the self-ignition.

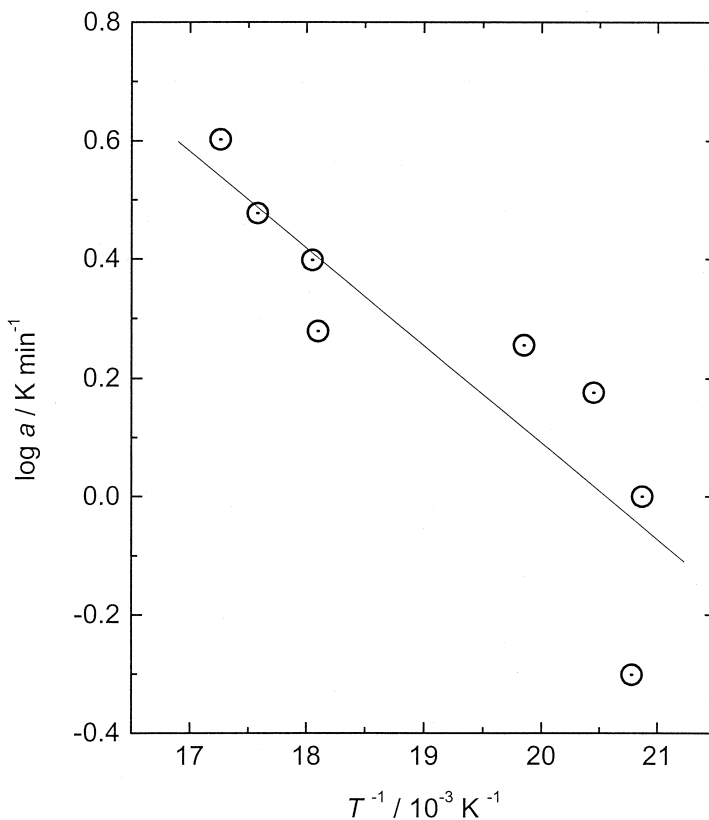


Fig. 5. Relationship between the logarithm heating rate and the inverse of self-ignition temperature.

4. Conclusion

The SITs of PNC type bitumen NaNO_3 mixtures were measured in the presence of $\text{Ni}(\text{NO}_3)_2$ and Ag compounds (AgNO_3 or AgI). The SIT of bitumen mixtures involving AgNO_3 is dependent on the heating rate (Fig. 3): The smaller the heating rate, the lower the temperature at which bitumen/nitrate mixture ignites. In contrast, the SIT of bitumen mixtures involving AgI does not depend on the heating rate. The activation energy E_a for the ignition of bitumen/nitrate mixtures have been calculated as 30 kJ/mol. This value is in close agreement with the currently accepted decomposition activation energy for the first-order reaction of silver fulminates. Furthermore, the SIT of bitumen mixture has been found to be similar to the ignition temperature of silver fulminate reported by Collins et al. Therefore, silver fulminate is presumed to be the initiator of the self-ignition of the bitumen/nitrate mixture involving AgNO_3 .

Acknowledgements

The authors wish to thank PNC for supplying the bitumen asphalt and Showa Shell for supplying the specifications for the bitumen asphalt.

References

- [1] M. Demonie, E. Detilleux, H. Eschrich, W. Hild, A. Osipenco, R. Reynders. The fire incident in the eurobitum plant on December 15, 1981: Description, Evaluation and Conclusions, ETR-314, Eurochemic, Belgium, December 1990.
- [2] N. Sasaki, T. Koyama, E. Omori, A. Maki, T. Yamanouchi, Study on the Cause of the Fire and Explosion Incident at Bituminization Demonstration Facility of PNC Tokai Works, SPECTRUM '98, Vol. III, Denver, CO, 1998, pp. 67–77.
- [3] Incident Investigation Committee, About the fire and explosion incident at the Bituminization Demonstration Facility of PNC Tokai Works (in Japanese), 1997.
- [4] B. Mishra, A.G. Rarez, D.L. Olson, W.A. Averil, Formation of explosive compounds in acid-contaminated leaded rubber gloves: Part I. theoretical analysis, J. Hazard. Mater. 56 (1997) 107–116.
- [5] B. Mishra, A.G. Rarez, D.L. Olson, W.A. Averil, Formation of explosive compounds in acid-contaminated leaded rubber gloves: Part II. Experimental verification, J. Hazard. Mater. 57 (1998) 13–28.
- [6] K. Okada, M. Nomura, Y. Fujii, Ignition Temperature of Bitumen Nitrate Mixture: Additive Salts Segregation Effects, SPECTRUM '98, Vol. II, Denver, CO, 1998, pp. 1129–1134.
- [7] K. Okada, M. Nomura, Y. Fujii, The self-ignition temperatures of bitumen mixtures containing transition metal nitrates, Nucl. Technol. (2000) in press.
- [8] Showa Shell, Specification of AD compound asphalt, Lot. No. 90514, 1997.
- [9] R.J. Clerc, M.J. O'neal Jr., The mass spectrometric analysis of asphalt, Anal. Chem. 33 (1961) 380–382.
- [10] T. Urbanski, Chemistry and Technology of Explosives, Vol. I, PWN-Polish Scientific Publishers, Warsaw, 1964.
- [11] A. Michael, G.H. Carlson, On the mechanism of the nitration process, J. Am. Chem. Soc. 57 (1935) 1268–1276.
- [12] H. Wieland, Eine neue Knallsäuresynthese. Über den Verlauf der Knallsäurebildung aus Alkohol und Salpetersäure, Chem. Ber. 40 (1907) 418–422.
- [13] K. Wentrup, B. Gercht, H. Briehl, A new synthesis of fulmic acid, Angew. Chem. Int. Ed. Engl. 18 (1979) 467–468.

- [14] K. Singh, Structure of fulminate ion, *J. Chem. Soc.* (1959) 459–461.
- [15] D. Britton, J.D. Dunitz, The crystal structure of silver fulminate, *Acta Crystallogr.* 19 (1965) 662–668.
- [16] P.H. Collins, K.J. Holloway, A reappraisal of silver fulminate as a detonant, *Propellants Explos.* 3 (1978) 159–162.
- [17] S. Nagakura et al. (Eds.), *Encyclopedia of Chemistry and Physics*, 5th edn., Iwanami, Tokyo, 1998.
- [18] H.E. Kissinger, Reaction kinetics in differential thermal analysis, *Anal. Chem.* 29 (1957) 1702–1706.
- [19] J. Li, X. Wang, R. Hu, B. Kang, Y. Ou, B. Chen, The thermal behavior of powder emulsion explosives, *J. Thermal Anal.* 45 (1995) 261–268.
- [20] T. Ozawa, A new method of analyzing thermogravimetric data, *Bull. Chem. Soc. Jpn.* 38 (1965) 1881–1886.
- [21] C.D. Doyle, Kinetic analysis of thermogravimetric data, *J. Appl. Polym. Sci.* 5 (1961) 285–292.
- [22] C.D. Doyle, Estimating isothermal life from thermogravimetric data, *J. Appl. Polym. Sci.* 24 (1962) 639–642.
- [23] K. Singh, G.D. Palkar, Solid-phase reactions in silver fulminates, *J. Chem. Soc.* (1965) 1474.