Letter

Thermal stability of flavianic acid disodium salt

Zhi-Min Fu*, Yusaku Iwata**, and Hiroshi Koseki**†

*Department of Fire Protection Engineering, Chinese People's Armed Police Force Academy, P. O. Box 424, Langfang 065000, Hebei, China

**National Research Institute of Fire and Disaster, 4-35-3 Jindaiji-higashimachi, chofu, Tokyo, 182-8508 JAPAN
†Corresponding address : koseki@fri.go.jp

Received : December 7, 2008 Accepted : March 25, 2009

Abstract

The thermal stability of flavianic acid disodium salt was studied theoretically and experimentally. The prediction results with the Computer Program for Chemical Thermodynamic and Energy Release Evaluation (CHETAH version 7.3) show flavianic acid hydrate and flavianic acid disodium salt have high rank of maximum heat of decomposition and fuel value-heat of decomposition. The experimental results by the Accelerating Rate Calorimeter (ARC) and C 80 demonstrate particle size difference has no significant effect on the thermal stability of flavianic acid disodium salt and flavianic acid hydrate has the low thermal stability than that of flavianic acid disodium salt.

Keywords : Flavianic acid disodium salt, Flavianic acid hydrate, CHETAH, Accelerating rate calorimeter, C 80

1. Introduction

Flavianic acid disodium salt (CAS No.846-70-8) is yellow colorant, which is used as cosmetic for dyeing hair. This is regarded as thermal stable and is not easier to decompose and combust. It is difficult to acquire the thermal stability information of flavianic acid disodium salt from the published literatures[1-3] and MSDS. In August 2003, however, a spontaneous combustion accident of flavianic acid disodium salt occurred in Yokohama, Japan, which arose from the grinding process of flavianic acid disodium salt from 3 mm to 50-100 μm. Smoke and fire emerged, and one workman was dead and another one was injured. Flavianic acid disodium salt is called 2,4-dinitro-1-naphthol-7-sulfonic acid disodium salt or naphthol yellow S[4]. The brief producing process of flavianic acid disodium salt is as follows ;

To elucidate the thermal stability of flavianic acid disodium salt, prediction method by the Computer Program for Chemical Thermodynamic and Energy Release Evaluation (CHEATH) was used. Then the screening tests for thermal stability by the Differential Scanning Calorimetry (DSC), Accelerating Rate Calorimeter (ARC) and Calvet heat flow calorimeter C 80 were carried out.

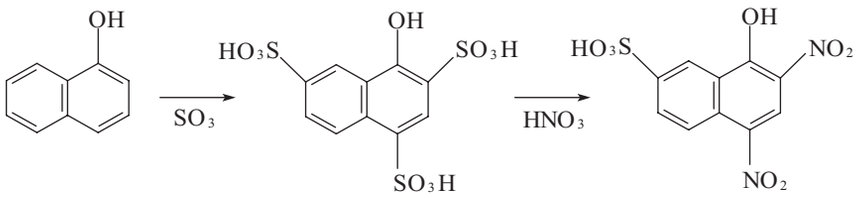
2. Thermal stability prediction for flavianic acid disodium salt by CHETAH

2.1 Thermal stability prediction for flavianic acid hydrate

The CHETAH program is useful for classifying materials for their abilitiesto decompose with violence and for estimating heats of reaction or combustion[5-7]. Due to the limitation of Benson Groups data bank, it is difficult to predict calculation for flavianic acid disodium salt is impossible while it is possible for flavianic acid hydrate. According to the prediction results by CHETAH (version 7.3), the heat of formation for flavianic acid hydratewas -617.39 kJ·mol^{-1} (-1.97kJ·g^{-1}) at 25°C, and the averaged heat capacity was 1.19J·g^{-1}·K^{-1} in the temperature range between 150 and 300°C. Table 1 shows the main prediction results for flavianic acid hydrate by CHETAH. It suggests flavianic acid hydrate is of high rank of maximum heat of decomposition, over-all energy release potential and fuel value-heat of decomposition.

2.2 Determination of neutralization heat and thermal stability prediction

To predict the thermal stability of flavianic acid disodium salt by CHETAH, the neutralization heat between flavianic acid hydrate with 97% purity (wt) made by Sigma-Aldrich, Inc., USA and sodium hydroxide with 97% (wt)



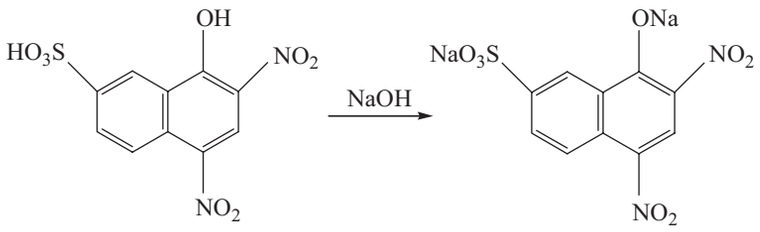


Table 1 The prediction results for flavianic acid hydrate and flavianic acid disodium salt by CHETAH

Name	Criterion	Maximum heat of decomposition / kJ·g^{-1}	Fuel Value−Heat of Decomposition / kJ·mol^{-1}	Oxygen Balance / gO$_2$·100g^{-1}	CHETAH ERE Criterion4 / kcal^2·gmole^{-1}·g^{-1}	Over−all Energy Release Potential	Net Plosive Density
Flavianic acid	Value	−3.47	−10.33	−86.56	80.18	−0.485	0.308
Hydrate	Hazard Classification	High	High	High	Medium	High	Plosive
Flavianic acid	Value	−2.87	−9.67	−75.93	64.46	—	—
disodium salt	Hazard Classification	High	High	High	Medium	—	—

made by Kanto Chemical, Co., Inc., Japan was measured with C 80 using membrane mixing cell. In the tests, 1.20 g sodium hydroxide water solution with molecular ratio of 0.05 mol NaOH to 1mol H_2O and 1.21 g flavianic acid hydrate water solution with molecular ratio of 0.0125mol flavianic acid hydrate to 1mol H_2O were used. The results suggest that neutralization heat between flavianic acid hydrate and sodium hydroxide was −17.88kJ·mol^{-1}. Based on estimating the heat of formation of flavianic acid disodium salt, the thermal stability for flavianic acid disodium salt was predicted (Table 1),and the averaged heat capacity was 1.15J·g^{-1}·K^{-1} in the temperature range between 150 and 410°C. It can be seen that flavianic acid disodium salt was of high rank of maximum heat of decomposition and fuel value−heat of decomposition.

3. Experiments

The DSC (Thermo plus2 DSC 8230), ARC (Columbia Scientific Industries) and C 80 (Setaram Scientific & Industrial Equipment, France) were used to investigate the thermal stability of flavianic acid disodium salt.

3.1 Sample

Flavianic acid disodium salt sample was supplied by Kishi Kasei Co. Ltd, Yokohama, Japan. The manufacturer provided MSDS, but did not show its dangerous property. Four samples with different particle size of flavianic acid disodium salt (Samples1−4) and the mixture sample of the four different particle sizes (Sample5) were used in the experimental study (Table 2). In order to compare the thermal stability between flavianic acid hydrate and flavianic acid disodium salt from ARC and C 80, flavianic acid hydrate with 97% purity (wt) made by Sigma−Aldrich, Inc., USA was used.

Table 2 Sample particle sizes of flavianic acid disodium salt

Sample No.	Particle size of sample d / μm
1	≤ 105
2	$105 < d \leq 149$
3	$149 < d \leq 210$
4	> 210

3.2 DSC Experiments

The DSC tests were conducted with sample5. In order to compare the results of flavianic acid disodium salt with benzoyl peroxide (BPO, with 97% mass purity, made by Sigma−Aldrich, Inc., USA) and 2,4−dinitrotoluene (DNT, with 98% mass purity, made by Wako Pure Chemical Industries, Ltd., Japan), the DSC tests for BPO and DNT were carried out following the method of the Japanese Fire Service Law. The scanning rate of the DSC tests was 10.0°C·min^{-1} with nitrogen atmosphere, using SUS closed cell.

3.3 ARC Experiments

In order to acquire the thermodynamic and kinetic information under adiabatic condition, the ARC tests were carried out under both the Heat−Wait−Search (H−W−S) mode and the Isothermal (ISO) mode. The four kind sam-

Table 3 Results of flavianic acid disodium salt, BPO and DNT of DSC

Sample	Sample mass / mg	Onset exothermic temperature /°C	Heat generation / J·g^{-1}
Flavianic acid disodium salt	1.97	371.9	1795
BPO	1.97	110.9	1267
DNT	1.04	315.4	3857

Table 4 The thermal decomposition characteristic data of ARC

Sample No.	Sample mass / g	Bomb mass / g	Thermal initial factor	Mode	Onset exothermic temperature of the sample system/°C	Onset self-Heating rate of the sample system/°C·min^{-1}	Maximum self-heating rate of the sample system/°C·min^{-1}	Maximum temperature of sample system/°C
1	1.09	9.71	4.69	H-W-S	284.63	0.023	293.38	404.04
2	1.03	9.75	4.92	H-W-S	294.66	0.027	278.00	400.25
3	1.02	9.81	4.99	H-W-S	299.80	0.036	299.14	409.63
4	1.04	9.70	4.87	H-W-S	299.70	0.030	284.23	409.54
Average					$294.70^{+5.10}_{-10.07}$	—	$288.69^{+10.45}_{-10.69}$	$405.87^{+3.76}_{-5.62}$
1	1.03	9.71	4.91	ISO	272.14	0.017	331.23	395.17
3	1.05	9.82	4.88	ISO	273.51	0.021	255.43	383.08
Average					$272.83^{+0.68}_{-0.69}$	—	$293.33^{+37.90}_{-37.90}$	$389.13^{+6.04}_{-6.05}$
Flavianic acid hydrate	1.00	9.74	5.11	H-W-S	159.88	0.027	473.25	299.18

ples with different particle size of samples1–4 in Table 2 were used to examine the effect of different particle size on the thermal hazard of flavianic acid disodium salt. Moreover, the experiments by ARC for flavianic acid hydrate were conducted also in order to compare the thermal stability with it. In the H-W-S mode, the slope sensitivity and heat step were set as 0.02°C·min^{-1} and 3.0°C, respectively. In the ISO mode, the initial isothermal temperature and the slope sensitivity were set as 270°C and 0.01°C·min^{-1}, respectively.

3.4 C 80 Experiments

The experiments by C 80 with sensitivity of 0.10 μW were carried out for confirming the results of ARC. For both flavianic acid hydrate and flavianic acid disodium salt, the tests started at 60°C with heating rate of 0.10°C·min^{-1} using 0.1 g sample, then the temperature increased according to the heating rate of 0.02°C·min^{-1} after the testing system temperature reached 100°C. Finally, the testing system temperature was maintained at 290°C (The maximum temperature limitation is 300°C for C 80) until reaction process ended.

4. Results and discussion

4.1 Results of DSC

The results of flavianic acid disodium salt with BPO and DNT by DSC are shown in Table 3. They suggest that the onset exothermic temperature and heat generation of flavianic acid disodium salt were 371.9°C and 1.79kJ·g^{-1}, respectively. Compared with BPO and DNT, both the onset exothermic temperature and heat generation of flavianic acid disodium salt were higher.

4.2 Results of ARC

The experimental results for flavianic acid disodium salt by ARC with both the H-W-S mode and ISO mode are shown in Figs. 1–4 and Table 4.

Based on the data in Figs. 1–2 of ARC with the H-W-S mode, it can be seen that there was a first endothermic decomposition process in the temperature range of 169–190°C for the four different particle sizes of flavianic acid disodium salt. Then an exothermic process occurred when the temperature went up to more than 280°C. The average onset exothermic temperature of the sample system was 294.7°C and the average maximum self-heating rate of 288.7°C·min^{-1} for the four different particle sizes of flavianic acid disodium salt from ARC with the H-W-S mode.

The results of Figs. 1–2 and Table 4 suggest that for the four samples with different particle size, there were small difference among the measured thermal decomposition characteristic data of flavianic acid disodium salt, including onset exothermic temperature, onset self-heating rate, maximum self-heating rate and maximum temperature, and the very small difference may results from the effect of the different thermal inertia factor on the thermal de-

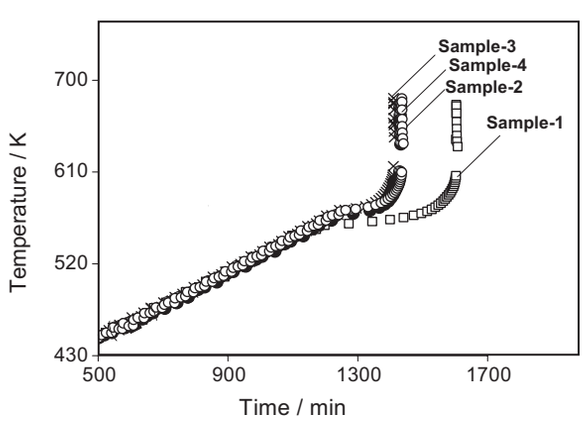


Fig. 1 Curves of temperature vs. time for flavianic acid disodium salt under the H-W-S mode by ARC

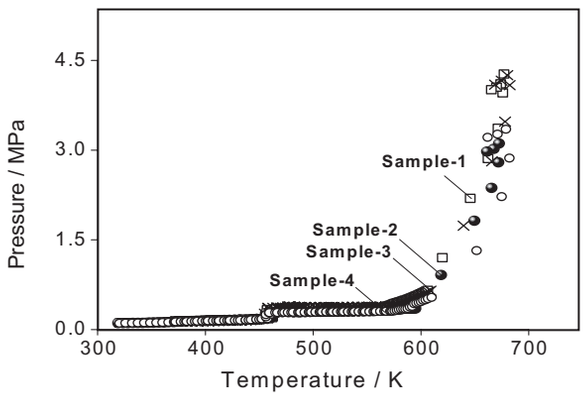


Fig. 2 Curves of pressure vs. temperature for flavianic acid disodium salt under the H−W−S mode by ARC

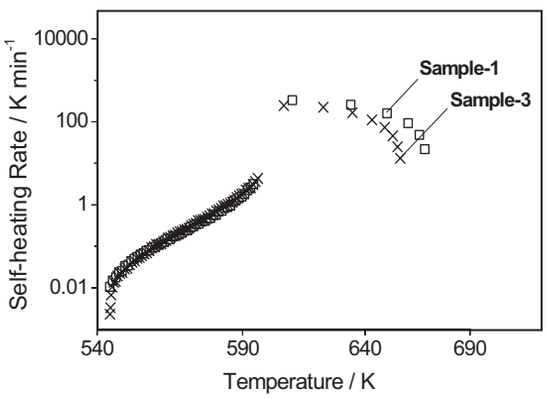


Fig. 3 Curves of self−heating rate vs. temperature for flavianic acid disodium salt under the ISO mode by ARC

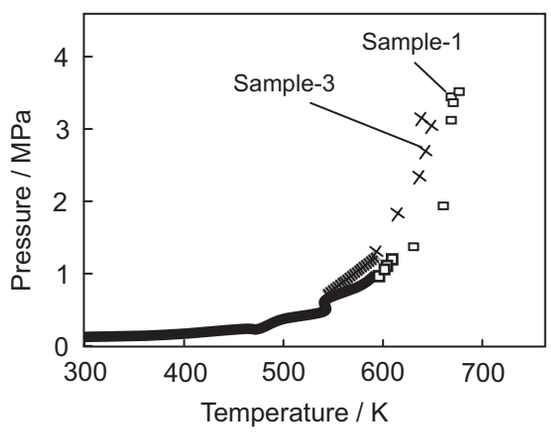


Fig. 4 Curves of pressure vs. temperature for flavianic acid disodium salt under the ISO mode by ARC

composition characteristics.

The results for flavianic acid disodium salt of ARC with the ISO mode (Figs. 3−4) suggest the average onset temperature of the sample system was 272.8°C, which was 22°C lower than that under the H−W−S mode, and the average self−heating rate was 299.3°C·min^{-1}.

Compared with flavianic acid disodium salt, the onset thermal decomposition temperature of flavianic acid hydrate was 1ow as 160°C of ARC with the H−W−S mode (Figs. 5−6 and Table 4), and the self−heating rate was high as 473.25°C·min^{-1}. And there was an unapparent endothermic process before the exothermic process for flavianic acid hydrate, which occurred at 148°C and was lower 42°C than that of flavianic acid disodium salt of ARC.

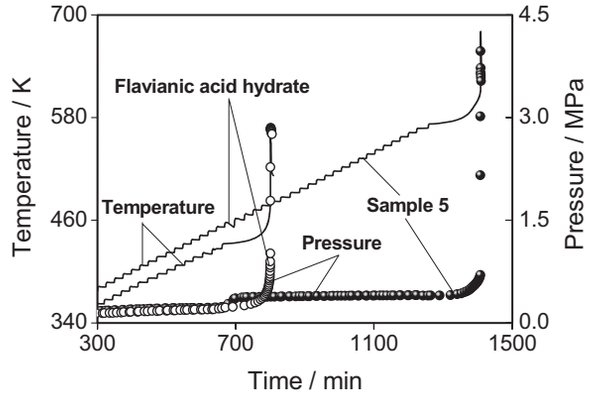


Fig. 5 Comparison of temperature/pressure vs. time under the H−W−S mode by ARC

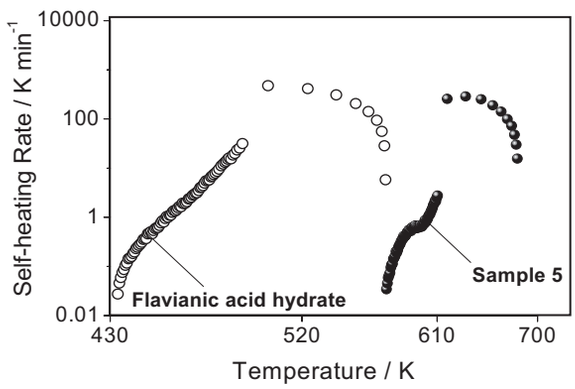


Fig. 6 Comparison of self−heating rate vs. temperature under the H−W−S mode by ARC

4.3 Results of C 80

The experimental results for flavianic acid hydrate and flavianic acid disodium salt with C 80 are shown in Fig. 7 and Table 5.

Based on the data of Fig. 7, it can be seen that there was a significant endothermic process for both flavianic acid hydrate and flavianic acid disodium salt before exothermic reaction occurred. The endothermic decomposition of flavianic acid hydrate occurred at 130°C, which was lower than that of 176°C for flavianic acid disodium salt. The minimum heat flows of flavianic acid hydrate and flavianic acid disodium salt were −7.46 μ W·g^{-1} and −10.78 μW·g^{-1}, respectively.

For flavianic acid hydrate, a rapid exothermic process followed the endothermic process immediately, and the onset exothermic decomposition temperature was approximately 149°C. For flavianic acid disodium salt, there was the first slow exothermic process from 211°C after the endothermic process finished at 184°C, and a subsequent rapid exothermic reaction occurred at 280°C. The maximum heat flows of flavianic acid hydrate and flavianic acid disodium salt were 26.90 μ W·g^{-1} and 34.79 μW·g^{-1}, respectively. And the maximum heat generation was 2.46 kJ·g^{-1} for flavianic acid hydrate and 2.09kJ·g^{-1} for flavianic acid disodium salt.

4.4 Discussion

Based on the data with the ARC and C 80, it can be seen that it shows lower onset exothermic temperature of flavi-

Table 5 The thermal decomposition characteristic data of C 80

Sample	Sample mass (mg)	Onset endothermic temperature of the sample system/°C	Minimum heat flow of the sample system / $\mu W \cdot g^{-1}$	Onset exothermic temperature of the sample system/°C	Maximum heat flow of the sample system / $\mu W \cdot g^{-1}$	Maximum heat generation / $kJ \cdot g^{-1}$
Flavianic acid Hydrate	100	129.96	−7.46	148.67	26.90	2.46
Flavianic acid disodium salt	100	176.0	−10.78	210.89 (280.38)*	34.79	2.09

* The datum in the parenthesis is the onset temperature of rapid exothermic reaction after the slow exothermic process for flavianic acid disodium salt by C 80.

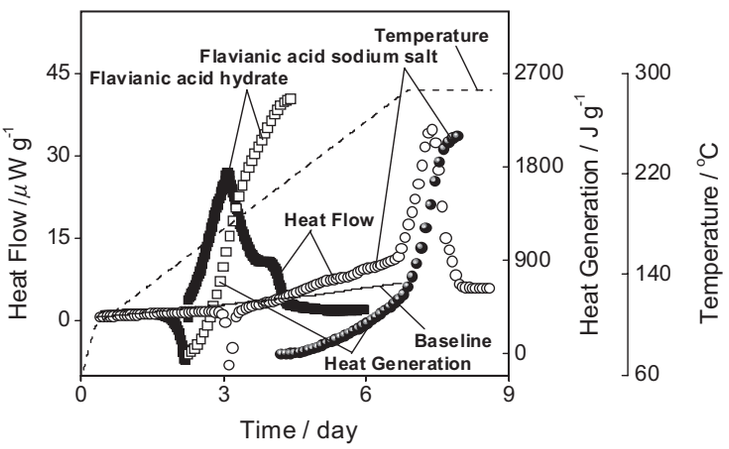


Fig. 7 Comparison of heat flow/heat generation vs. time using with C 80

anic acid disodium salt compared with the results from DSC. And the difference was approximately 100°C for between DSC and ARC, and 160°C for between DSC and C 80.

The experimental results of ARC suggest the difference of particle size has no significant effect on the thermal stability of flavianic acid disodium salt. The exothermic decomposition occurred with the average onset exothermic temperature of 273°C under the ISO mode of ARC for flavianic acid disodium salt. Compared with flavianic acid disodium salt, flavianic acid hydrate had low thermal stability with the onset thermal decomposition temperature of 160°C under the H−W−S mode of ARC.

The results of C 80 show an immediately exothermic process occurred after an endothermic process for flavianic acid hydrate, and the onset exothermic decomposition temperature was approximately 149°C. For flavianic acid disodium salt, a first slow exothermic process occurred from 211°C followed with a subsequent rapid exothermic reaction at 280°C after the endothermic process finished at 184°C. This result was consistent with that of ARC because the first slow exothermic process detected by C 80 can not be measured by ARC due to its relative low sensitivity and the onset temperature of the second rapid exothermic reaction was similar between results of the C 80 and ARC.

Compare with the theoretical prediction value by CHETAH, the heat generation of C 80 was slightly lower. The maximum heat generation was 2.46kJ·g^{-1} for flavianic acid hydrate and 2.09kJ·g^{-1} for flavianic acid disodium salt, respectively. Nevertheless, the results of both CHETAH and C 80 was very similar that the decomposition heat generation of flavianic acid hydrate was higher than that of flavianic acid disodium salt.

5. Conclusions

Both flavianic acid hydrate and flavianic acid disodium salt have high rank of maximum heat of decomposition and fuel value−heat of decomposition. The difference of particle size has no significant effect on the thermal stability of flavianic acid disodium salt. Compared with flavianic acid disodium salt, the onset thermal decomposition temperature of flavianic acid hydrate was about 100°C lower than that of flavianic acid disodium salt.

The results of C 80 show the onset exothermic decomposition temperature was approximately 149°C for flavianic acid hydrate, and the first slow exothermic process starting from 211°C followed with a subsequent rapid exothermic reaction at 280°C for flavianic acid disodium salt. And the maximum heat generation was 2.46kJ·g^{-1} for flavianic acid hydrate and 2.09kJ·g^{-1} for flavianic acid disodium salt. Therefore, the thermal stability of flavianic acid hydrate was lower than that of flavianic acid disodium salt due to the lower onset decomposition temperature and the higher heat generation. The thermal decomposition would occur if flavianic acid hydrate was involved in the final product of flavianic acid disodium salt and the temperature can reach to 150°C when the excess heat occurred in the grinding process.

References

1) S. Budavari, M.J. O'Neil, A. Smith, P.E. Heckelman, J.F. Kinneary, The Merck Index, an encyclopedia of chemicals, drugs, and biologicals, twelfth ed., Merck Research Laboratories, division of Merck & Co., Inc., 1996.
2) Compilation Committee for Encyclopaedia Chimica, Encyclopaedia Chimica6, Kyoritsu Shuppan, Tokyo, 1997.
3) R.E. Lenga, The Sigma−Aldrich Library of Chemical Safety Data. second ed., Sigma−Aldrich Corporation, 1988.
4) Compilation Committee for Encyclopaedia Chimica, Encyclopaedia Chimica7. Kyoritsu Shuppan, Tokyo, 1997.
5) W.H. Seaton, E. Freedman, D.N. Treweek, CHETAH: The ASTM Chemical Thermodynamic and Energy Release Potential Evaluation Program, ASTM Data Series Publication DS 51, Philadelphia, 1974.
6) P. Cardillo, M. Nebuloni, Reactivity limits of aluminum and halohydrocarbon mixtures: determination by the ASTM CHETAH program. J. Loss Prev. Process Ind. 5 (1992) 81−88.
7) ASTM, The ASTM computer program for chemical thermodynamic and energy release evaluation, CHETAH version 7.3, ASTM International, Pennsylvania, 2002.

フラビアン酸二ナトリウム塩の熱安定性の研究

Fu Zhi-Min*, 岩田雄策, 古積　博**†**

横浜市内での火災の原因調査に関連してフラビアン酸二ナトリウム塩の熱的安定性について調べた。CHETAHを使って，その分解熱，燃焼熱を調べたところ，高い危険性を有していることが判った。また，DSCによる試験でも消防法第５類としての危険性を有していることが判った。次いで，ARC及び高感度熱量計C80によって，熱安定性を調べた。その粒度の差は，熱安定性に影響がないこと，水和物の方がより不安定であることを示した。

*Department of Fire Protection Engineering, Chinese People's Armed Police Force Academy, P. O. Box 424, Langfang 065000, Hebei, China

**消防大学校消防研究センター　〒182−8508　東京都調布市深大寺東町4−35−3

†Corresponding address ; koseki@fri.go.jp