Evaluation of Fire and Explosion Hazards for a Non-Azide Gas Generant

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ABSTRACT

A hazard evaluation has been carried out for the safety assessment of a new non-azide gas generant for automotive airbag inflators. The gas generant (UN) is composed of urazole (U) and a metal nitrate (MNO_3;N) with other additives included to provide the required performance. The impact, shock, friction, electric spark, hot object and heat sensitivities were determined by the appropriate tests. Propagations of detonation, deflagration and combustion were examined using the United Nations gap test and VP 30 tube test. A mixture of urazole with $KClO_4$ in a stoichiometric ratio propagated detonation as measured by the gap test and self-sustaining combustion as measured by the tube test. The mixture of urazole with KNO_3 propagated combustion, but no detonation.

Keywords: airbag, gas generant, urazole, hazard evaluation, test methods

1. Introduction

A non-azide gas generant (AK) containing azodicarbonamide (ADCA;A) and potassium perchlorate ($KClO_4$;K) as basic ingredients was developed by our group.[1] Recently, a new composition (UN) containing urazole (1,2,4-triazolidine-3,5-dione;U) and a metal nitrate (MNO_3;N) as basic ingredients has been developed as a gas generant for airbag inflators. The new composition (UN) has higher thermal stability and lower combustion temperature than AK.

To assess the safety of manufacturing the UN gas generant, the Yoshida Hazard Analysis (YHA)[2] has been carried out for the two compositions typical of the UN gas generant. One composition is UKS, a mixture of urazole (U), $KClO_4$ (K) and soluble starch (S) in a mass ratio of 37:61:2, respectively. The second is UNSSi, a mixture of urazole (U), potassium nitrate (KNO_3;N), starch (S) and silicon dioxide (SiO_2;Si) in a mass ratio of 27:55:2:16, respectively. Both compositions are two extremes of our intended composition. The test methods used are sensitivity, burning and explosion propagation tests. The results of these tests are used in the YHA for the manufacturing process of the UN gas generant.

2. Experimental

2.1 Materials

Materials used are listed in Table 1.

Table 1. Materials Used.

Name	Symbol	Size (μm)	Supplier
Urazole	U	19	Otsuka Chemical Co., Ltd.
$KClO_4$	K	21.9	Japan Carlit Co., Ltd.
KNO_3	N	60	Otsuka Chemical Co., Ltd.
Starch	S	—	Wako Pure Chemical Industries Co., Ltd.
SiO_2	Si	7.5	Tokuyama Soda Co., Ltd.

Samples used in the experiments are listed in Table 2. KNO_3 and $KClO_4$ are practical oxidizers because they are not hygroscopic and have low toxicity. $KClO_4$ is more reactive than KNO_3 in this case.

Table 2. Composition of Sample.

	Symbol	Urazole	$KClO_4$	KNO_3	Starch	SiO_2
A	UKS	37	61	—	2	—
B	UNSSi	27	—	55	2	16
C	Urazole	100	—	—	—	—
D	KNO_3	—	—	100	—	—

2.2 Test Procedures

2.2.1 Drop Hammer Test

The drop hammer test is a method for determining the sensitivity of energetic materials to a mechanical impact. A drop hammer test in accordance with Japanese Standard JIS K4810–1979 was used in this work. The mass of the hammer is 5 kg. About 30 mg of sample in tin foil is sandwiched between two cylinders placed on the anvil as shown in Figure 1. The cover is then placed on the anvil. The iron hammer is dropped on the cylinder, and any explosion is noted.

If an explosion occurs (test positive), the height of the hammer is reduced. If none occurs, the height is increased. In either case, the height is varied in 0.1 log intervals in height. Twenty tests are carried out. The data are analyzed by the Bruceton up-and-down method.[3] If materials react with the tin foil, the test is carried out without the foil.

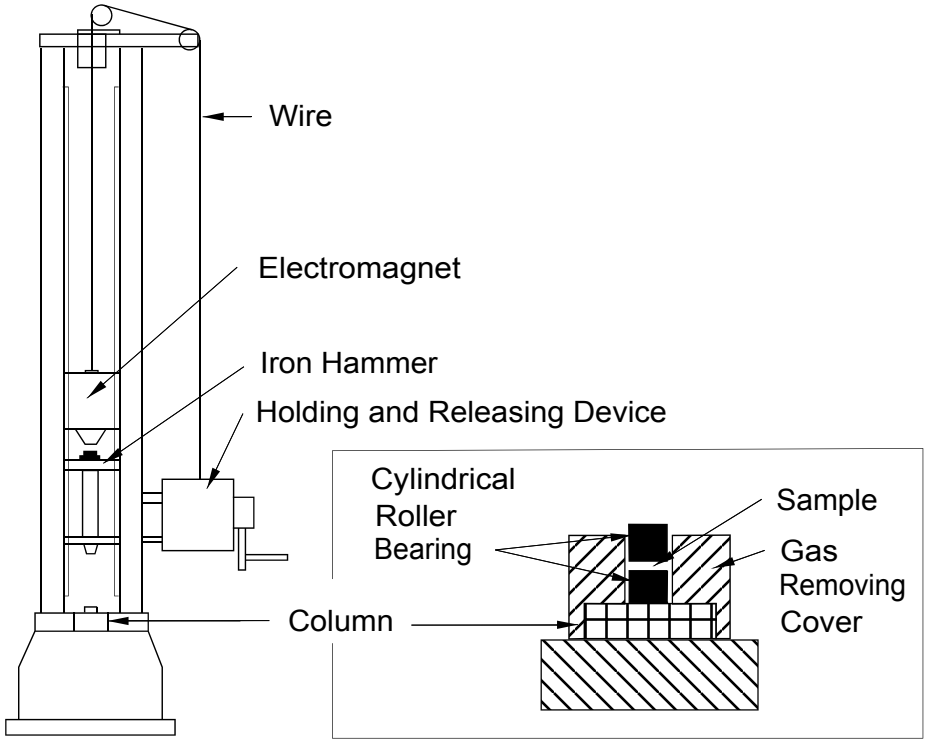

Figure 1. Assembly and the lower part of the JIS drop hammer test.

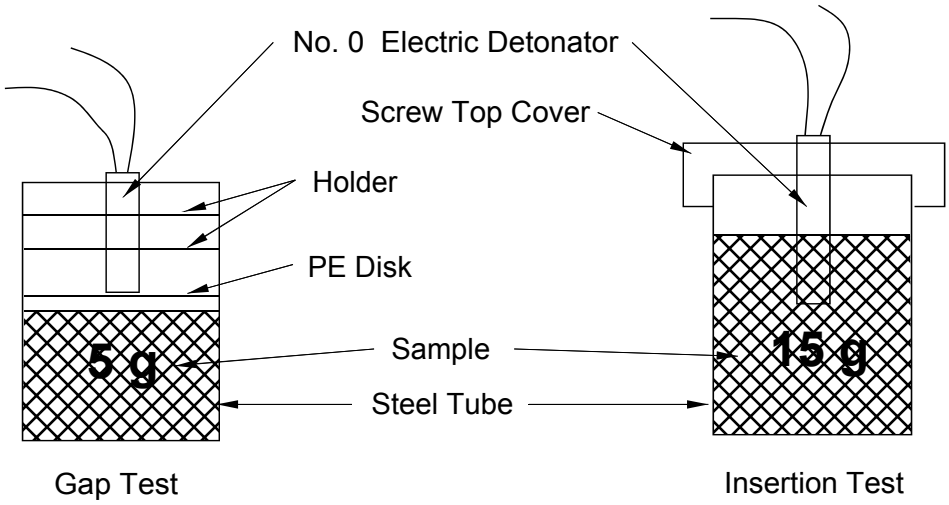

Figure 2. Sample assemblies for the shock ignitability test.

2.2.2 Shock Ignitability Test[4]

The shock ignitability test is a method for determining the shock sensitivity of medium-sensitive energetic materials, especially pyrotechnic compositions. The sample container has an inner diameter of 31 mm, an outer diameter of 34 mm, and a depth of 35 mm with the bottom cover in place. There are two types of containers: one with and one without the screw top cover as shown in Figure 2. Polyethylene (PE) gap disks with a diameter of 30 mm and a thickness of 1–4 mm are used for the gap test in the shock ignitability test. The sample in the container is initiated by a No. 0 detonator containing 18 mg of diazodinitrophenol (DDNP) inserted through the gap disks or directly into the sample.

2.2.3 VP 30 PVC Tube Initiation Test[5,6]

The VP 30 PVC tube initiation test is suitable for examining the ability of commercial explosives and pyrotechnic compositions to propagate explosions. A VP 30 polyvinyl chloride (PVC) tube with an inner diameter of 31 mm and a length of 150 mm (JIS K6742–1971) is filled with 100 g of sample. Both sides of the tube are covered with adhesive paper tape. A No. 6 detonator containing 18 mg DDNP and 40 mg pentaerythrytol tetranitrate (PETN) is inserted into the sample at one side of the tube. The sample assembly is placed horizontally 0.2 m deep in sand. The general arrangement is shown in Figure 3. Propagation of an explosion

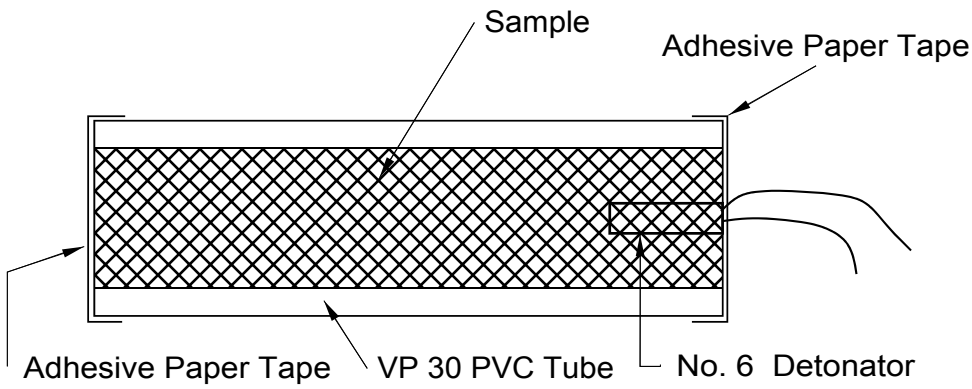

Figure 3. Setup for the VP30 PVC tube initiation test.

by the sample is judged from the size of the crater formed, the amount of unreacted sample remaining and/or the fragmentation of the PVC tube.

2.2.4 United Nations Gap Test[7]

The United Nations gap test is a method for examining the ability of low-sensitive energetic materials to propagate explosions and especially to propagate detonations. Figure 4 shows the setup of the United Nations gap test. Approximately 500 mL of sample is placed in a carbon steel tube with an outside diameter of 48 mm, a thickness of 4.0 mm, and a length of 0.4 m. A booster charge of 160 g cast pentrite (a 50:50 mixture of PETN/TNT) is used. The witness plate is a soft steel square plate 0.15 m × 0.15 m × 3.2 mm. A ring-shaped aluminum plate 50 mm (o.d.) × 40 mm (i.d.) × 1.6 mm is used as a spacer and sandwiched between the witness plate and sample. A No.6 electric detonator holder is fixed to the booster charge. The booster charge, the spacer and the witness plate are combined and fixed to the steel tube filled with the sample. The sample assembly is buried horizontally 0.5 m deep in sand to prevent scattering of any fragments.

2.2.5 Friction Sensitivity Test

The friction sensitivity test is used to examine the ease of ignition when an energetic material is subjected to mechanical friction. Bailey et al.[8] showed that incidents involving energetic materials caused by friction are the most frequent among those caused by external stimuli. The BAM friction tester[9] was used for evaluating the friction sensitivity of urazole, UKS and UNSSi. Figure 5 shows the BAM (Bundesanstalt für Mäterialforchung und prüfung) friction tester and the sample holder. A sample weighing several mg is placed on the rough surface of a porcelain plate and pressed by the rough surface of a porcelain peg with a known force. When the start button is pushed, the porcelain plate moves back and forth with a fixed speed through a distance of 10 mm. Ignition is judged by noise, a flash or smoke. The force exerted by the peg is selected by changing the weight and position of the hanging weight.

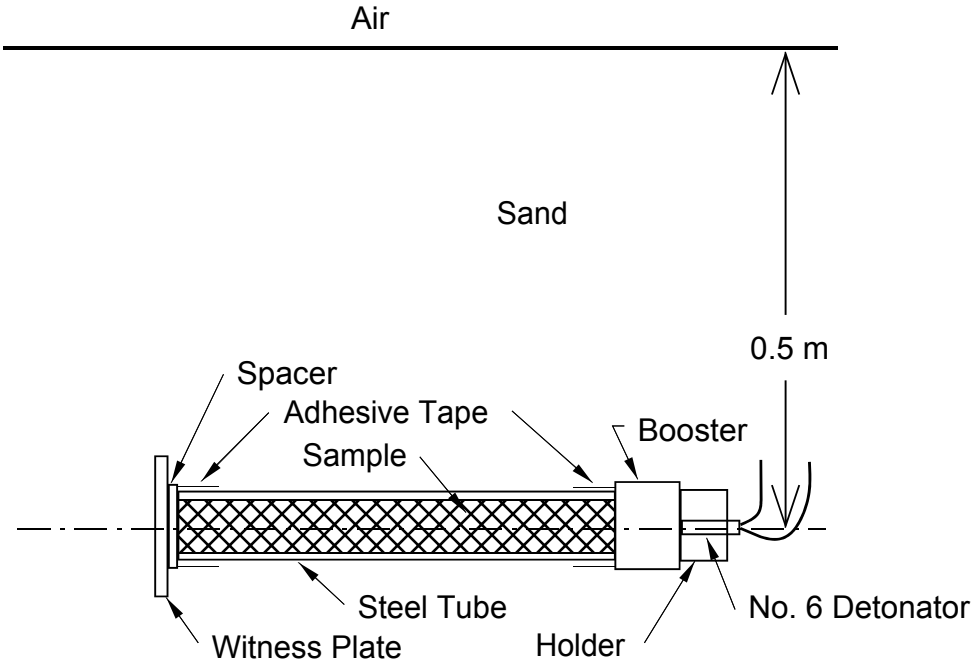

Figure 4. Setup for the United Nations gap test.

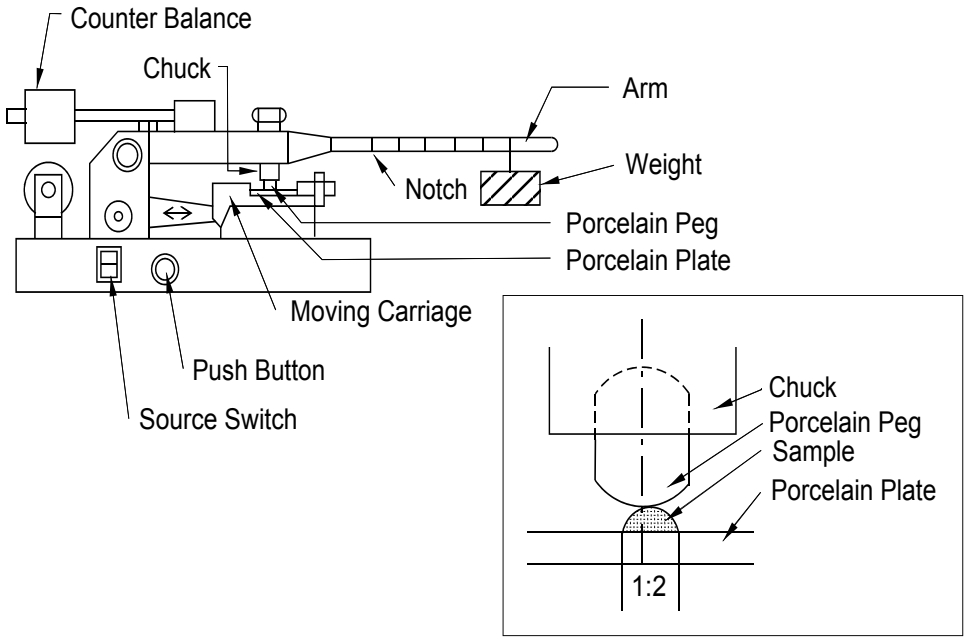

Figure 5. BAM friction sensitivity tester.

These experiments were carried out twenty times using the Bruceton up-and-down method and the results were analyzed. The increment of force in the experiment is 0.1 log unit. The 50% ignition mass (M_{50}) and the standard deviation of log M were calculated.

2.2.6 Electric Spark Sensitivity Test

The electric spark sensitivity test is a method for determining the ignition sensitivity of energetic materials to an electric spark. The tester used was developed by Dr. Mizushima for low- and medium-sensitive energetic materials.[10] Sample parts of the tester are shown in Figure 6. The structure of the electrode in the tester is a fixed pipette plate electrode according to Dahn et al.[11] This tester can give the sample from 10^{-1} to 80 J in capacitor energy depending upon the selection of capacitance and voltage. Experiments were carried out twenty times using the Bruceton up-and-down method with 0.1 log unit intervals of capacitor energy. Values of the 50% ignition energy (E_{50})

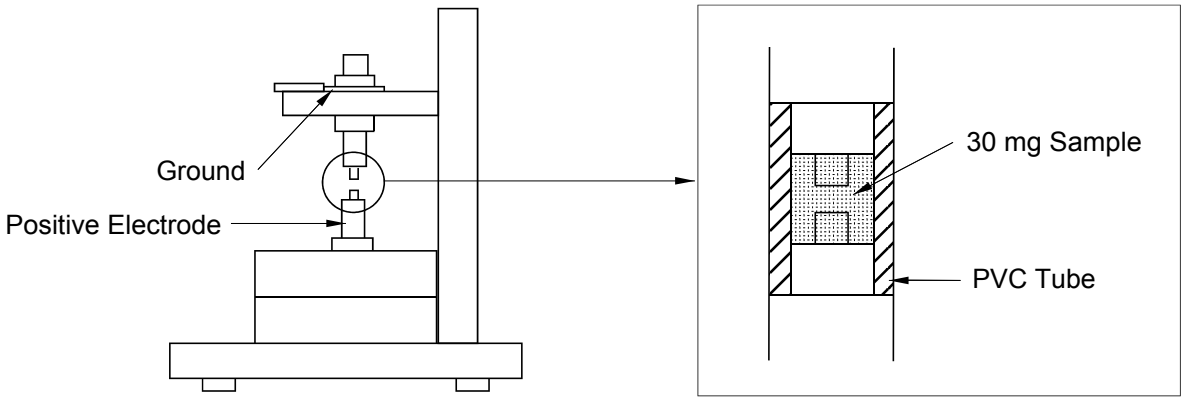

Figure 6. Electrodes of the electric spark sensitivity tester.

and standard deviation of log E were calculated.

2.2.7 VP 30 PVC Tube Burning Test

The VP 30 PVC tube burning test evaluates both the ability of energetic materials and pyrotechnic compositions to propagate combustion as well as the violence of that combustion. The sample is placed in the 0.1 m long VP 30 PVC tube and ignited by a 0.6 mm diameter Ni–Cr wire heated with an electric current of 10 A. Whether it is ignited or not is noted and, if ignition is observed, the burning time is measured. The sample assembly for the test is shown in Figure 7. When no ignition is noted, a 5 g mixture of 37:63 ratio of urazole and $KClO_4$ is used as an ignitor.

2.2.8 Conical Pile Burning Test

The conical pile burning test is a method for examining the effect of sample size on the violence of the combustion of pyrotechnic compositions. There is a suggestion that the combustion of pyrotechnic compositions becomes more violent as the mass of the composition is increased.[12] The test method is similar to that for oxidizing solids according to the Japanese Fire Services Law.[13] A sample of 25, 50, 100 or 200 g is piled conical on a heat resistant plate, a 0.6 mm diameter Ni–Cr wire is touched to the base of the cone and the sample is ignited. The duration of the combustion is observed. The setup of the experiment is shown in Figure 8. If the sample is not ignited by the Ni–Cr wire, the experiment is repeated using a 5 g mixture of ADCA–$KClO_4$–CuO as the ignitor.

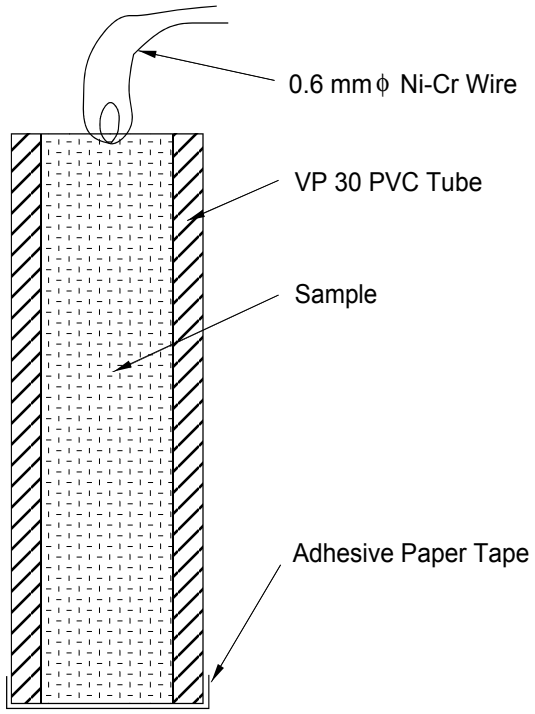

Figure 7. VP30 PVC tube burning test.

2.2.9 SC–DSC Test

The sealed cell-differential scanning calorimetry (SC–DSC) test is a screening method for examining the thermal stability of self-reactive materials including energetic materials. If a relationship between the SC–DSC data and the data from any practical test method is known, the practical test data can be estimated from the SC–DSC data.[14]

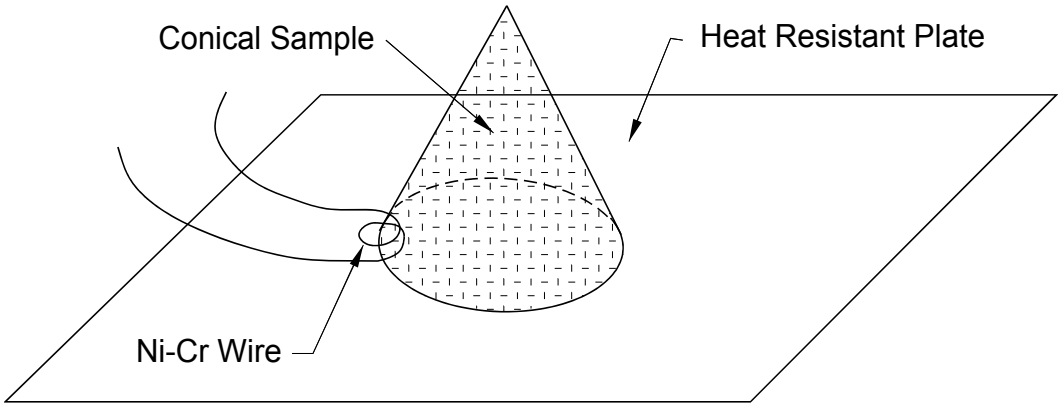

Figure 8. Conical pile burning test.

A sample of about 1 mg is weighed accurately in the sealed cell. The sealed cell containing the sample is placed in the DSC (Seiko Denshi) and heated at a rate of 10 ºC/min. The DSC extrapolated decomposition temperature (T_{DSC}) and DSC decomposition heat (Q_{DSC}) are recorded. Additional information is also obtained from the appearance of the DSC curve.

2.2.10 Pressure Vessel Test

The pressure vessel test evaluates the violence of the reaction of a self-reactive material when it is subjected to heating in an essentially closed container with a single small orifice of defined size. A pressure vessel in accordance with the Japanese Fire Service Law was used in this study.[15] A 5 g sample is placed in the pressure vessel which is equipped with either a 1.0 mm or 9 mm diameter orifice and is heated at a rate of 40 ºC/min. Less than ten trials are carried out for each size orifice. The bursting times of the rupture disk are noted as being either smaller or larger than five.

3. Results

3.1 Drop Hammer Test

Results of the JIS drop hammer test are listed in Table 3. Urazole reacted with the tin foil by the impact of the 5 kg drop hammer, and the apparent impact sensitivities of materials containing urazole were higher with the tin foil than without it.

Table 3. Results of the JIS Drop Hammer Test.

Material	With tin foil		Without tin foil	
	E_{50} (J)	$\sigma_{log}E_{50}$	E_{50}	$\sigma_{log}E_{50}$
Urazole	8.5	0.30	21.4	0.30
UNSSi	7.4	0.08	11.8	0.13
UKS	14.8	0.16	20.0	0.04

3.2 Shock Ignitability Test

Powdered UKS exploded in the shock ignitability test with a No. 0 detonator inserted and with the top covered. The bottom cover separated, but the explosion did not fragment the steel tube. This indicates that the explosion was not a detonation but a deflagration. The sample did not explode in the test with a No. 0 detonator in contact with the surface of the sample but without the cover. Powdered urazole, UNSSi and the 50:50 mixture of UKS/UNSSi did not explode in the test with a No. 6 detonator inserted in the top cover. Granules of UKS and UNSSi did not explode in the test.

3.3 VP 30 PVC Initiation Test

The VP 30 PVC initiation test with a No. 6 detonator inserted results in no propagation of explosion and unreacted material remaining in the tester for urazole, UKS, UNSSi and the mixture of both materials.

3.4 United Nations Gap Test

Powdered UKS propagated detonation in the United Nations gap test, whereas powders of UNSSi and urazole propagated neither detonation nor deflagration, and unreacted material remained in the tester.

3.5 Friction Sensitivity Test

Urazole and UNSSi reacted once in ten trials in the BAM friction tester under a load of 36 kgf (360 N). UKS reacted once under the a load of 32.4 kgf (324 N).

3.6 Electric Spark Sensitivity Test

Fifty percent ignition energy (E_{50}) of urazole, UNSSi and UKS by the tester for medium-sensitivity are listed in Table 4.

Table 4. Results of the Electric Spark Test.

Material	E_{50} (J)	$\sigma_{log}E_{50}$
Urazole	51 (3/10) *	—
UNSSi	38.1	0.04
UKS	25.2	0.20

* Urazole reacted three times in ten trials with 51 J capacitor energy.

3.7 VP 30 PVC Burning Test

In this test, urazole did not ignite, but the 100 mm strands of UNSSi and UKS burned for 198 s and 139 s, at the burning rates of 0.50 mm/s and 0.72 mm/s, respectively.

3.8 Conical Pile Burning

The conical pile burning test on 25 g each of powders and granules of urazole, UKS and UNSSi did not show sustained burning with either the hot Ni–Cr wire or the 5 g ignitor.

3.9 SC–DSC

The SC–DSC curves of urazole, UNSSi and UKS are shown in Figures 9 (a), (b), and (c), respectively. Each material showed an endothermic peak before the first exothermic peak which is assigned to the decomposition of urazole. For UNSSi and UKS, other exothermic peaks follow the decomposition peak of urazole.

The DSC onset temperature T_{DSC} of urazole, UNSSi and UKS were 284, 225 and 241 ºC, respectively.

3.10 Pressure Vessel Test

The pressure vessel test for urazole was carried out seven times, and the rupture disk burst five times. However, when the rupture disk burst, it was noted that the orifice had been plugged with sublimed material. When the disk did not burst, the orifice was open and smoke came out through the hole. When a 9 mm diameter orifice was used, it was not plugged with sublimed materials, and the decomposition products came out slowly through the orifice.

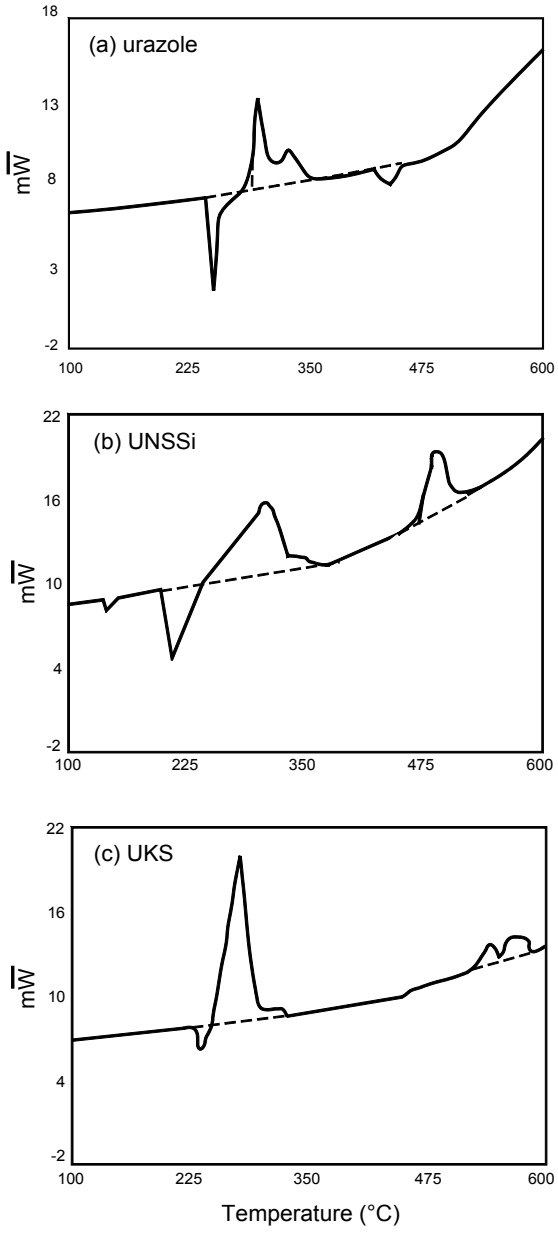

Figure 9. SC–DSC Curves of urazole (a), UNSSi (b) and UKS (c).

4. Discussion

4.1 Impact and Shock Sensitivity and Explosion Propagation by Urazole, UNSSi and UKS

All three samples were low-sensitive to the JIS drop hammer impact test. Only UKS among these three materials exploded in the shock ignitability test with the top cover in place and with a No. 0 detonator inserted. This explosion was classified as deflagration, not detonation, because the steel tube was not fragmented. Only the bottom cover separated.

Powders of all three materials were not initiated by the VP 30 PVC initiation test with a No. 6 detonator inserted, and unreacted sample remained in the tester. Only UKS powder propagated detonation in the United Nations gap test. In conclusion, UKS can propagate detonation under the severe conditions in the United Nations gap test, and urazole and UNSSi propagate neither detonation nor deflagration even under these severe conditions.

The impact and shock sensitivity of urazole and UNSSi are classified as negligible (D level). Urazole and UNSSi are also classified as combustible materials. The impact and shock sensitivity of UKS is low (C level), and UKS is classified as a deflagrating material.[2]

4.2 Friction Sensitivity of Urazole, UNSSi and UKS

Urazole, UNSSi and UKS reacted in the BAM friction tester. However, urazole did not propagate combustion by the burning test. Therefore, the reaction by the friction test will be not propagative and is not hazardous. In the burning tests urazole is classified as not hazardous. The friction sensitivity of urazole is negligible (D level), and the friction sensitivity of UNSSi and UKS are low (C level).

4.3 Electric Spark Sensitivity

All three samples are low-sensitive in the electric spark tester for low- and medium-sensitivity materials. The sensitivities of urazole, UKS and UNSSi are low (C level).

4.4 Ignitability, Propagation of Combustion and Violence of Combustion

Urazole is not ignitable by small heat sources. This material is only ignitable by an external fire and therefore is poorly combustible. The ignitability of urazole is negligible (D level), UNSSi and UKS can be ignited by a hot wire or ignitors in a tube but not in bulk. Self-reactive materials such as UNSSi and UKS were shown to burn more easily in a tube than in bulk. Ignitability depends on the ignition source. The 5 g ignitors were stronger ignition sources than the Ni–Cr wire.

The ignitability of UNSSi and UKS is low (C level). UNSSi is classified as a combustible material, but UKS as a deflagrating material, because it can be detonated by a strong initiator if in a closed container.

Granules of UKS burn more easily and more quickly than the corresponding powders.[12] All forms of UKS burn more quickly at high pressure than at atmospheric pressure. The powders, granules and pellets should not be handled in a tightly sealed vessel, because when ignited, the speed of combustion increases remarkably under those conditions.

4.5 Thermal Stability and Violence of Decomposition

The 107 ºC–400 hr test is used for evaluating the thermal stability of a gas generant for automotive airbag inflators. In this test, an inflator containing the gas generant is kept at 107 ºC for 400 hr. The 60 L tank test is applied to the inflators before and after heating. The test criterion is that no significant difference between the 60 L tank test results before and after the heating be observed. The 107 ºC heat and mass reduction test simulates the 107 ºC–400 hr test. A composition having a DSC onset thermal decomposition temperature (T_{DSC}) greater than 200 ºC is known to pass the 107 ºC heat and mass reduction test based on experience with the ADCA gas generant compositions.[16] The T_{DSC} of UNSSi and UKS are 225 and 241 ºC, respectively. These values are significantly higher than those for the ADCA gas generant compositions. The heat sensitivities of UNSSi and UKS are low (C level).

In the pressure vessel test for urazole, the rupture disk burst at an orifice size of 1 mm. In this case, however, the orifice was plugged with sublimed material. When the orifice was not blocked, the rupture disk did not burst and the decomposition gases did not blow out violently. Therefore, the thermal decomposition of urazole is not considered violent as long as sublimed material does not block the orifice, thereby sealing the container.

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