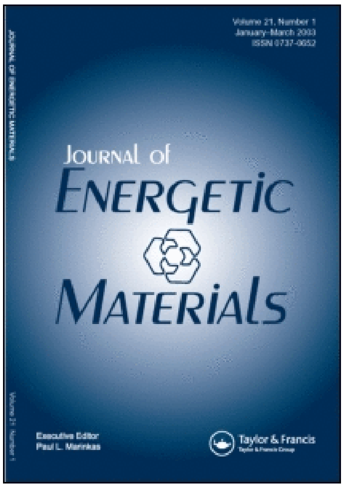


Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Safety aspect of a non-azide propellant for automotive airbag inflators

Takashi Kazumi[a]; Kazuo Hara[b]; Yuhua Yu[b]; Yo Yamato[c]; Takeshi Takahori[d]; Yasuo Shimizu[c]; Tadao Yoshida[b]
[a] Nippon Koki Co. Ltd., Fukushima, Japan [b] Department of Materials Chemisitry, Hosei University, Tokyo 184, Japan [c] Ohtsuka Chemical Co. Ltd., Tokushima, Japan [d] Daicel Chemical Industries, Ltd, Hyogo, Japan

To cite this Article Kazumi, Takashi , Hara, Kazuo , Yu, Yuhua , Yamato, Yo , Takahori, Takeshi , Shimizu, Yasuo and Yoshida, Tadao(1996) 'Safety aspect of a non-azide propellant for automotive airbag inflators', Journal of Energetic Materials, 14: 2, 81 — 95

To link to this Article: DOI: 10.1080/07370659608216059

URL: http://dx.doi.org/10.1080/07370659608216059

SAFETY ASPECT OF A NON-AZIDE PROPELLANT FOR AUTOMOTIVE AIRBAG INFLATORS

Takashi KAZUMI *, Kazuo HARA **, Yuhua YU **, Yo YAMATO ****,
Takeshi TAKAHORI ***, Yasuo SHIMIZU **** and Tadao YOSHIDA **

* Nippon Koki Co. Ltd.,
Nishigo-mura, Nishishirakawa-gun, Fukushima 961, Japan

** Department of Materials Chemisitry, Hosei University,
3-7-2 Kajinocho, Koganei-shi, Tokyo 184,Japan

*** Daicel Chemical Iudustries, Ltd.,
1239 Shinzaike, Aboshi-ku, Himeji-shi, Hyogo 671-12, Japan

**** Ohtsuka Chemical Co. Ltd.,
463 Kagasuno Kawauchi-machi, Tokushima-shi, Tokushima 771-01, Japan

ABSTRACT

Safety hazards of a non-azide propellant containing azodicarbonamide(ADCA), potassium perchlorate($KClO_4$) and other additives were evaluated using various test methods to determine impact and shock sensitivity, ignition sensitivity, heat sensitivity, propagation of explosion and burning, and violence of burning. With BAM 50/60 tube test, the new propellant, both in the form of dry powder and granule,was detonated, while when wetted with 10% water, it did not propagate detonation, and the addition of 15% water permitted no ignition. In the form of dry pellets BAM test resulted in no propagation of detonation but propagating deflagration. On the other hand, the pellets, when tested with 30 mm diameter PVC tube, neither detonated nor deflagrated by initiation with a no.6 detonator on the ground. From these test results a wet process is recommended espeially for blending raw materials and for granulating the mixed composition.

Journal of Energetic Materials Vol. 14, 81-95 (1996)
Published in 1996 by Dowden, Brodman & Devine, Inc.

1. INTRODUCTION

Sodium azide has been mainly used as a basic ingredient of propellants for automotive airbag inflators, because it releases pure nitrogen gas when decomposed. However, sodium azide and propellants containing it have caused several fires and explosions during manufacturing and handling [1] [2] [3] . We have developed a non−azide propellant for inflators of next generation automotive airbag. One of objectives of this study is to offer a safer propellant than conventional azide−based propellants used for airbag inflators.

Here we describe the safety aspect of the new propellant and test results. Some of the performances, and aspects of health and envirommont of this non−azide propellant will be published else where [16] [17] . A safety hazard evaluation of a propellant for automotive airbag inflators was made by F. Volk [4] with NaN_3/Fe_2O_3/$NaNO_3$/SiO_2/bentonite composition.

2. EXPERIMENTAL

2.1 Materials

Raw Materials for the basic composition are listed in Table 1.

Table 1. Raw Materials for Propellant Compositions

Name(Symbol)	Av. dia, μm	Supplier
Azodicarbonamide (A)	23	Otsuka Chemical
KC104 (K)	37	Nippon Carlit
CuO (C)	2.5	Nisshin Kagaku
Soluble Starch (S)	-	Wako Chemical
Si02 (Si)	0.06	Tokuyama Soda

Typical compositions tested and discussed in this paper are A/K/C/S/Si=45/55/10/0/0 and 45/55/10/0.55/1.1 in mass ratio. Raw materials are mixed without soluble starch, which is separately dissolved in water, followed by being boiled for five minutes and then added to the mixture. The mixture, which is wet with 5 percent of water is formed into granules, some of which are subjected to the tests under the wet conditions while some were dried for the tests under the dry condition. The granules are in part dried before formed into pellets by a pelletizing machine, and then the formed pellets are completely dried in an oven at 80 °C for 1 hr. and used for several tests.

2.2 Test Methods

2.2.1 Mechanical and Shock Sensitivity

a. Friction Sensitivity Test

For friction sensitivity, BAM friction sensitivity test [5] for secondary explosives is used.

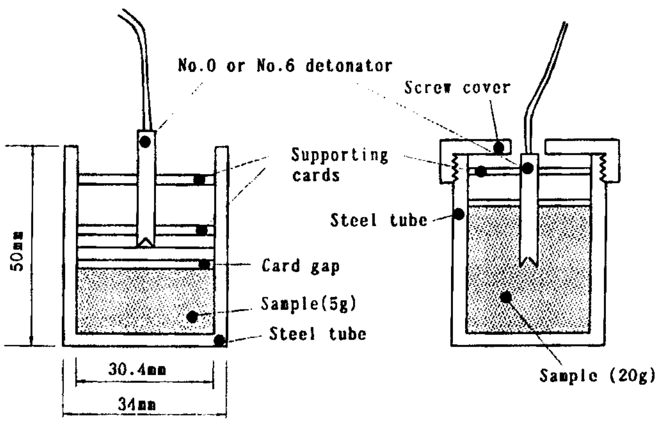
b. Drop Hammer Test

A drop hammer test is conducted according to Japanese Industrial Standards JIS−K4810−1979 using 5kg hammer. Bruceton's up−and−down method [6] was employed for estimating E_{50} or the energy at which a sample fires in 50% probability.

c. Shock Ignitability Test

The shock ignitability test [7] was designed to test low−and medium−sensitive energetic materials, especially pyrotechnic compositions. The test configurations, as shown in Fig.1, consist of a propellant sample, about 31mm ϕ i.d. steel tube with one end closed, 30mm ϕ circular polyethylene(PE) cards, and a no.0 detonator supported by two perforated cards. When a low−sensitive material is tested, 20g of propellant is used and the open end of the steel tube is covered by a screwed lid with a small hole at the center. The lid may give strong confinement to provide easy ignition and burn of the propellant. The test is conducted on the ground usually, but when the sample is expected to datonate, it is recommended that the test piece be buried in the sand in order to prevent fragments from scattering.

For testing of medium−sensitive materials, a 5g propellant is placed in the steel tube with the other end open.



gap (a) For medium-sensitive materials

insert with cover (b) For low-sensitive materials

Fig. 1 Sample assemblies for the shock ignitability test

d. VP−30 Tube Initiation Test

Previously,this test is called the shock sensitivity test for commercial explosives.[6)] [7)] But the name of VP−30 tube initiation test has been adopted because it was found that this test is applicable not only to commercial blasting explosives but also to pyrotechnic compositions.

A sample assembly of the VP−30 tube initiation test consists of a 100g sample in a VP−30 polyvinyl chloride(PVC) tube 38mm i.d., 38mm o.d. and 150mm long, a no.0,1,2,3 or 6 detonator, and PE cards 30mm in diameter and with various thickness. The bottom of the tube is covered by an adhesive paper. The VP−30 tube initiation test is similar to the shock ignitability test in principle except that former can detect the propagation of detonation, deflagration or slow combustion through the sample. The sample assemblies are shown in Fig. 2.

The sample assembly is buried in the sand 0.20m below the surface and the detonator is initiated. If a crater is formed and no unreacted sample remains, the result is judged as positive. The critical gap of a material in this test is the longest gap at which a sample is initiated.

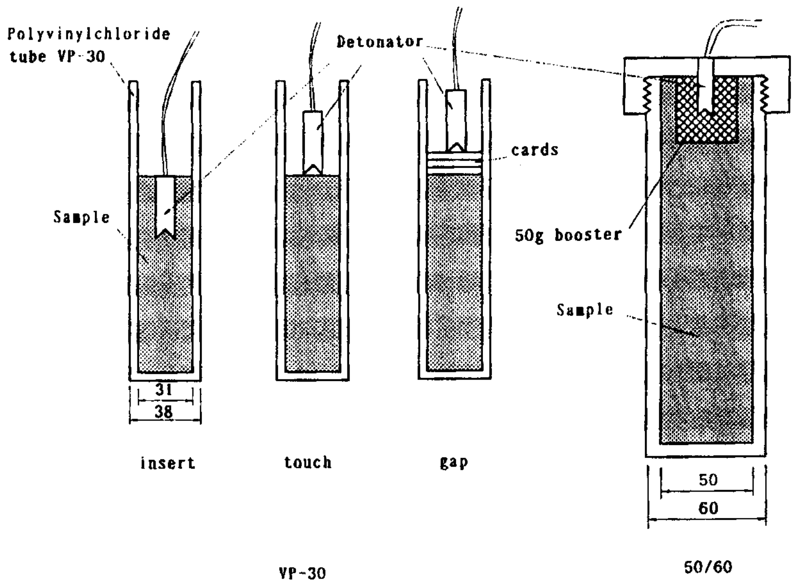


Fig.2 Sample assemblies of PV−30 tube initiation test and 50/60 steel tube test

2.2.2 Propagation of Detonation and Deflagration

a. Critical Diameter Test for Explosion Propagation(See Fig. 4 for reference)

This test is conducted for a composition which propagated detonation or deflagration by the VP−30 tube initiation test. A sample is filled up in a plastic tube

150mm long and less than 30mm in inner diameter, and initiated by a no.6 detonator. Result is judged as negative by observing the unreacted sample remained, and vice versa. The critical diameter in this paper is defined as the inner diameter of the tube which is between neighboring diameters giving positive and negative results.

b. VP−30 Tube Initiation Test

This test is also used for evaluating ability of a material to propagate detonation and deflagration or combustion in the 31mm i.d. PVC tube by a no.6 detonator initiation.

c. BAM 50/60 Steel Tube Test(Fig. 2)

The BAM 50/60 steel tube test is conducted according to UN Recommendations [10] .

d. PE Bag Initiation Test

This test simulates the explosion behaviors of the propellant when a strong shock is given to a bulk of propellant in the form of powder or pellets during transportation, storage, or mamufacture, although such case, is not likely to happen under ordinary circumstances. Several hundreds grams of propellant in a PE bag are placed on the sand and initiated by a no.6 detonator. When the sample exploded, a crater is formed in the sand, and its diameter and depth indicate the intensity of the explosion.

e. Sympathetic Explosion Test

A sympathetic explosion test is performed to confirm the safety of pellets which are filled up into small PE bottles. The nine PE bottles filled with the propellant are squarely arrayed on the ground with the neighboring bottles touched as shown in Fig. 3. The bottle at the center is fired by the iniation of a no.6 detonator to observe whether or not the explosion of the center bottle propagates to the neighboring bottles or not.

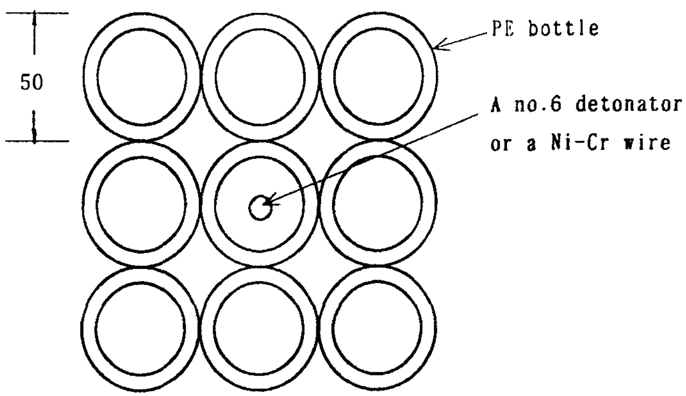


Fig. 3 Array of bottles in sympathetic explosion test and fire spread test. Each bottle contains 40g propellant pellets

2.2.3 Ignitability and Violence of Burning

a. UN Burning Rate Test [11] (Fig. 4)

The powder, granules or pellets of AKCSSi composition is formed into a train with the cross section of isosceles triangle about 250mm long, 20mm wide, 10mm high on an adiabatic plate. A hot Ni–Cr wire is applied to the one end of the train until the material ignites or for maximum 2 minutes. It is noted whether the burning sustains along the train during 2 minutes of test period, or the burn rate is determined by measuring time in which it took to propagate between two points marked 0.20m apart along the train.

b. Critical Diameter Test for Burning Propagation(Fig. 4)

This test is conducted in the same way as the critical diameter test for explosion propagation described before and only differs in that in this test a hot Ni–Cr wire is used to ignite the sample in stead of a no.6 detonator. It is noted whether the burning propagates along 150mm of the filled material within 10 minuts test period. If the burning propagates, the burning time is recorded.

c. VP–30 Tube Burning Test(Fig. 4)

The propellant which may take dry or wet form of powder, granule or pellet, is filled up in VP–30 PVC tube 150mm long and 31mm in inner diameter, and is ignited by a hot Ni–Cr wire. This test is to see whether it propagates burning and to determine burning rate under the test condition.

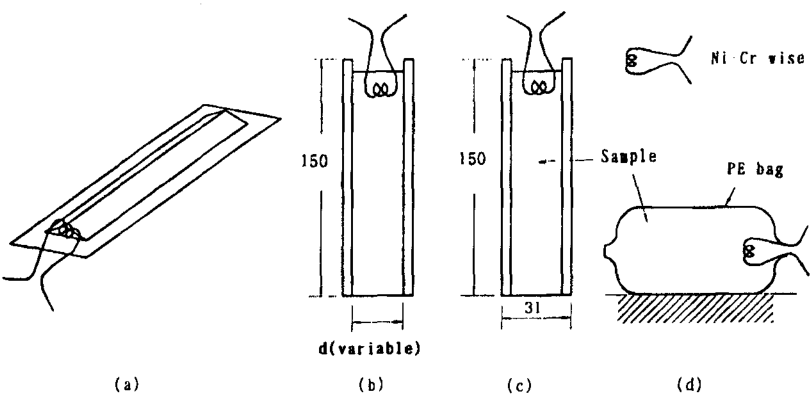


Fig. 4 Tests for ignitability and violence of combustion
(a) UN burning rate test (b) Critical diameter test
(c) VP–30 tube burning test (d) PE bag burning test

d. PE Bag Burning Test(Fig. 4)

The PE bag burning test is to see how the propellant in the form of powder, granule or pellet will burns in an open space. This test is similar to the VP−30 tube burning test but different, as shown in Fig. 4.−(d), in that a thin PE bag is used in stead of a PV−30 tube.

e. Fire Spread Test

Nine PE bottles containg 40g propellant pellets are squarely arrayed with the neighboring bottles touched with each other, and the bottle at the center is ignited by a hot Ni−Cr wire to see whethere the fire spreads to the other bottles or not. The arrangement of the bottles is the same to that of the sympathetic explosion test shown in Fig. 3.

2.2.4 Thermal Stability

a. Sealed Cell−Differential Scanning Calorimetry(SC−DSC) [12) 13)]

SC−DSC using Seiko Model DSC220 Instrument is run for determining DSC onset temperature(T_{DSC}) and DSC reaction heat(Q_{DSC}) of the propellant and constituting materials. The temperature is elevated at the rate of 10 °C /min with about 1 mg of the sample in the sealed cell.

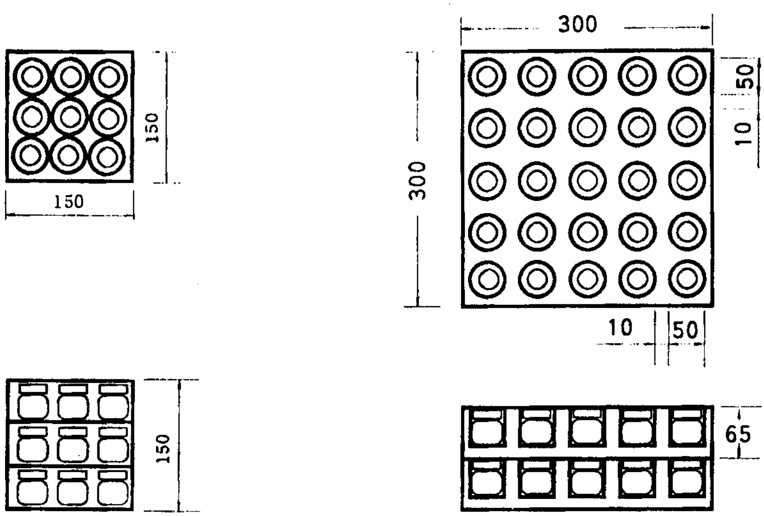
b. Accelerating Rate Calorimetry(ARC) [14)]

ARC using Columbia Scientific Industries(CSI) ARC System 851−0001 is run for estimating the thermal stability of AKCSSi. The run is ordinary one, that is, the combination of search−wait−heat and adiabatic runs.

2.2.5 Behavior of Propellant Package in External Fire

a. External Fire Test

Two types of external fire tests were carried out. The one test involves 27 PE−bottles containing 40g propellant pellets in each bottle and the bottles are bottle packaged in a carton box in 3 × 3 × 3 array. This package is staked on a steel frame by a kerosene fire below. The other test involves 50 PE−bottles, each of which is restrained by a circular recess made in two sheets of calcium silicate foam having 25 PE−bottles a sheet. Two sheets of calcillm silicate foam are piled up in a carton box, and heated on a steel frame by a wood fire below. The ways of packaging are shown in Fig. 5.



(a) (b)

Fig. 5 Packages of bottles containing propellant pellets for external fire test
(a) Non–separating package in carton board box
(b) Separating package in cavitated caleium silicate foam blocks

3. RESULTS AND DISCUSSION

3.1 Mechanical and Shock Sensitivities and Explosion Propagation

Test results of explosion properties of AKC compositions are listed in Table 2. AKC powder composition was found quite insensitive to BAM friction sensitivity test, and reactive in JIS drop hammer test using 5kg drop hammer, but the reaction may not propagate to the surrounding material. Shock ignitability test revealed that although the AKC composition either in the form of powder and granules exploded when it is confined on initiation by a inserted no.0 detonator it was less sensitive than conventional azide based propellant compositions.

AKC dry powder propagated detonation with the VP–30 tube initiation test performed under the sand,while the wet powder with 10% water did not propagate detonation nor deflagration. With VP–30 test the dry granules propagated deflagration but no detonation, while the wet granules wetted with 5% water did not propagate deflagration. The dry pellets did not explode with a large portion of the pellets remaining unreacted in the VP–30 test.

With the BAM 50/60 steel tube test, the dry power of AKC propagated detonation and 10% wet powder propagated deflagration. The 15% wet powder did not propagate deflagration and a part of the sample remained intact. AKC powder detonated in the PE bag by a no.6 detonator where the quantity of the propellant tested surpassed about 200 grams, but the dry pellets did not explode. No sympathetic explosion was observed with any test of AKCSSi dry pellets.

In conclusion, the dry powder and granules of the AKC composition propagate detonation under some conditions, but this hazard can be eliminated by wetting with more than 10% of water. So it is strongly recommended to adopt wet processes for blending and granulating the AKC or AKCSSi composition.

Table 2 Test results of explosion properties of AKC compositions

ADCA/KClO4/CuO=45/55/10

Property	Powder	Granule	Pellet
BAM Friction	> 36 kg	-	-
E_{50} JIS Impact	25J(dry) > 50J(10%H_2O)	> 50J(dry)	>50J(dry)
Critical diameter 6D	> 30mm(dry, detonation) 10mm(dry, combustion)	-	> 30mm(dry)
Shock ignitability 0D	Insert(dry)	Insert(dry)	Insert(dry)
VP-30 initiation 6D Under sand	No(dry, on ground) Detonation(dry) Detonation(5%H_2O) No(10%H_2O)	Deflagration(dry) No(5%H_2O)	No(dry)
BAM 50/60 initiation 50g boostor	Detonation(dry) Detonation(5%H_2O) Deflagration(10%H_2O) No(15%H_2O)	- - -	Deflagration (dry)
PE bag initiation	No(dry, 6D, ≦ 100g) Yes(dry, 6D, ≧ 200g) No(dry, 0D)	-	No(dry)
Sympathetic explosion 6D	-	-	No(dry)

0D: no.0 detonator, 6D: no.6 detonator

3.2 Ignitability, Burning Propagation and Violence of Burning

Test results of burning properties of AKCSSi composition are listed in Table 3. 50% ignition energy by an electric spark tester of dry AKCSSi powder is 32J and similar to that of TNT(E_{50} =23J). Powder, granules and pellets of AKCSSi do not propagate burning in UN burning rate test. This is principally because the amount of propllant tested was too small to do self-sustarning burning. But the burning becomes propagative and violent as the amount increases.

Dry and 10% water wet powders of AKCSSi composition propagated burning with the VP−30 tube burning test, though the 10% wet powder lose the ability to propagate combustion when tested in a day after the preparation of test sample. This result may suggest that 10% of water addition is a critical point for the propagation of burning.

Test results of the granules and pellets show that addition of 5% water reduces burning rate tremendously in this test. However, results of dry and 10% wet powder in the PE bag test show that 10% addition of water does not nescessarily reduce the violence of burning when the amount is large. But 15% wet compositions are not ignited by a hot Ni−Cr wire.

Table 3 Experimental results of burning properties of AKCSSi(45/55/10/0.55/1.1)

Properties	Powder	Granules	Pellets
E_{50} Electrostatic spark sensitivity	32J(dry) 36J(10%H_2O)	28J(dry)	-
UN burning rate	No propagation	No propagation	No propagation
Critical burning diameter	10mm(dry)	-	-
VP-30 burning	sec(dry) Yes(10%H_2O) No(15%H_2O)	30sec(dry) 206sec(5%H_2O)	25sec(dry) 42sec(5% H_2O)
PE burning time	36sec(100g,dry) 26sec(200g,dry) 103sec(400g,dry) 120sec(1600g,dry) 55sec(100g,10%H_2O) 135sec(200g,10%H_2O) 122sec(400g,10%H_2O) 105sec(800g,10%H_2O) No(15%H_2O)		20sec(100g, dry) 22sec(200g, dry) 15sec(400g, dry) 13sec(1600g,dry)
Fire spreading between bottles	-	-	Yes(dry)

With the PE bag burning test using both powder and pellets of AKCSSi, it is found that the burning rate becomes large as the amount of test sample increased. This is illustrated in Fig. 6.

It is also seen that the pellets burn faster than the powder in both of VP−30 tube and PE bag burning tests. In the fire spread test, a fire of central PE bottle containing 40g pellets of the AKCSSi composition spreads to surrounding PE bottles.

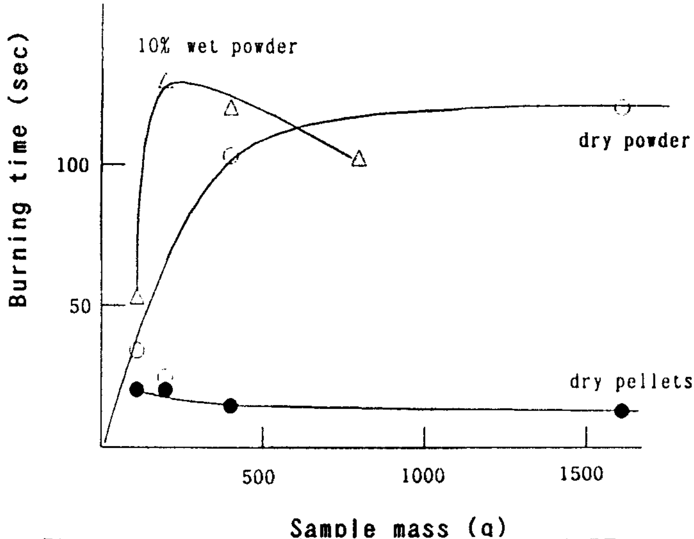


Fig. 6 Plot of burning time of AKCSSi against sample mass in PE bag burning test

3.3 Thermal Stability

The thermal stability of AKCSSi powder is estimated by SC−DSC and ARC. Results are outlined in Table 4, Fig.6 and Fig.7. The SC−DSC curve of AKCSSi composition has 4 ethothermic peaks showing that the reaction is complex. The DSC extraporating onset temperature(T_{DSC}) is 184 °C, DSC reaction heat(Q_{DSC}) being 3250J/g(0.78kcal/g) which is smaller than the theoretical heat(0.97kcal/g) pased on the following equation:

$$115C_2H_4N_4O_2 + 118KClO_4 + 37CuO + C_6H_{10}O_5 + 5.3SiO_2$$
$$= 230N_2 + 236CO_2 + 235H_2O + 118KCl + 37Cu + 18.5O_2 + 5.3SiO_2 + 32020kcal$$

The difference may be attributable to the incomplete reaction of the composition in the SC−DSC cell, because the sample is a physical mixture of oxididants and reductants, the amount is small and reaction temperature is much lower than the combustion temperature. Therefor, the DSC reaction heat of a mixture can not be used for estimating its combustion reaction heat.

In the ARC run, the ARC onset temperature of the AKCSSi composition is 112 °C, which is the temperature when the heat rate reaches 0.038 °C/min. If we use this onset temperature, the time to maximus heat rate is 140 min. The maximun temperature is 173 °C, These data were obtained under the condition for $\phi = 5.86$. Under this condition the reaction stops at the first statage of decomposition of ADCA corresponding to the first exothermic DSC peak of AKCSSi as shown in Fig. 6. Therefore the ARC data under this condition does not represent the thermal run−away reaction of AKCSSi.

Table 4. Results of SC-DSC and ARC of AKCSSi

Test	Condition		Result	
SC-DSC	Sample mass	2.59mg	$T_{DSC}(1)$	184°C
	Heat rate	10°C/min	$T_{Peak}(1)$	199°C
			$T_{Peak}(2)$	281°C
			$T_{Peak}(3)$	389°C
			$T_{Peak}(4)$	471°C
			Q_{DSC}	3250J/g
ARC	Sample mass	1.02g	T_{onset}	112.39°C
	Bomb mass	8.79g	Initial rate	0.038°C
	C_P of sample	0.213cal/g	$T_{max\ rate}$	161.63°C
	C_P of bomb		Time to max rate	140.28min
	Slope sensitivity	0.01°C/min		
	Heat step	5 °C	T_{max}	172.62°C
	Wait time	10 min		
	ϕ	5.86		

The ARC onset temperature of 112 °C can not be used for evaluating thermal stability of the AKCSSi composition, from same reason. We have done ARC run using less ϕ value and experienced bursting of the sample bomb. It is found difficult for only ARC to be used for estimating thermal stability or SADT (Self-Accerelating Decomposition temperature).

Therefore we are planning to use other tests such as the micro watt DSC and mass reduction determination on heating.

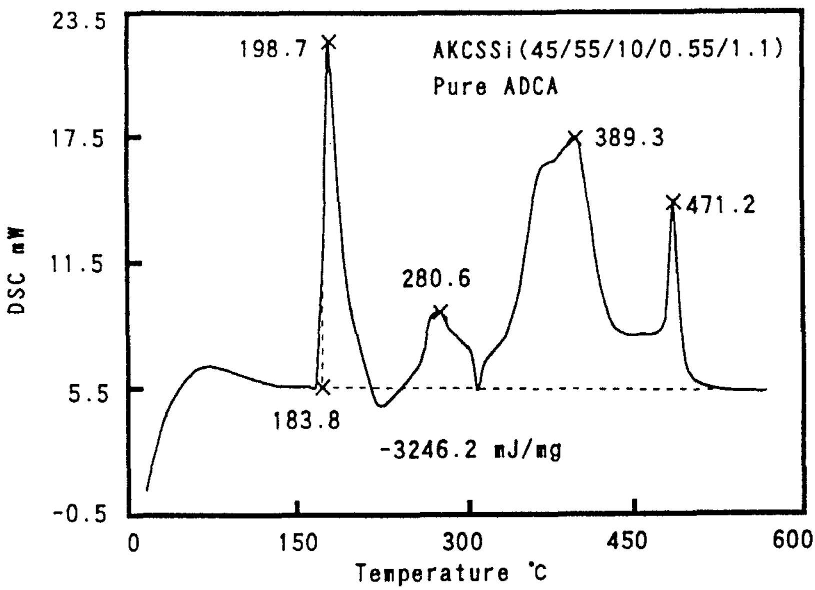


Fig. 6 SC−DSC curve of AKCSSi composition

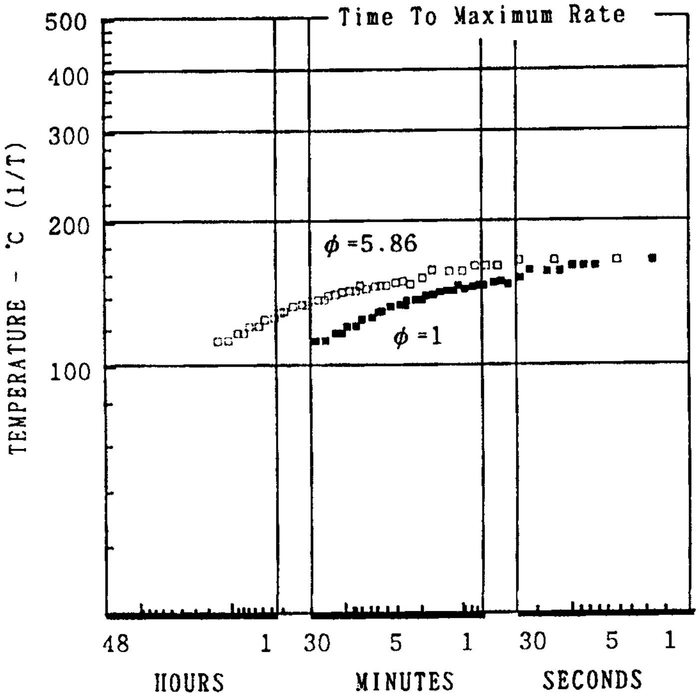


Fig. 7 Plot of temperature vs. time to maximum rate in ARC of AKCSSi

REFERENCES

1)US General Accounting Office, GAO/RCED-90-230(1990)

2)Newsday, Feb. 16, 1992

3)Four incidents are reported in a recent meeting of AORC(1993).

4)F.Vlok, Proc., 9th Symp. Chem. Probl. Connected Stabil. Explos., Margretetorp, Aug. 23-27, 1992

5)H.Koenen, K.I.Ide and K.H.Swart, "Sicherheitstechnische Kenndaten Explosionstahlgen Stoffe", Explosivestoffe, 9, 4, 30(1961).

6)W.J.Dixon and F. J. Masseg, "Introduction to Statistical Analysis", McGrawHill, 2nd Ed., 1957, p. 318

7)K.Aoki, et al., Proc. 18th International Pyrotechnics Seminar, Beckenridge, USA, 12-17 July, 1992

8)Y.Wada, et al., J.Energetic Materials, 9, 105(1991)

9)T.Okitsu, et al., Proc. 9th Symp. Chem. Prob. Connected Stabil. Explos., Margretetorp, Aug. 23-27, 1992

10)"Recommendationa on the Transport of Dangerous Gooda. Tests and Criteria", Second Edition, United Nations, New York, 1990, p. 11.

11)"Recommendations on the Transport of Dangerous Goods", Seventh revised edition,United Nations, New York, 1991, p. 371

12)T.Yoshida, "Safety of Reactive Chemicals", Elsevier, Amsterdam,1987, p. 230

13)T.Yoshida, "Safety of Reactive Chemicals and Pyrotechnics",Taisei Shippan, Tokyo, 1988, p. 97; English Translation is available from the auther.

14)Colunbia Scientific Industries Corporation, "Accerelating Rate Calorimeter(ARC) Instruction Manual", P/N 851-9001, REVE, 1990.

15)K.Hara, et al., "Concept and Performance of a Non-Azide Propellant for Automotive Airbag Inflators", Submitted to Propellants, Explosives and Pyrotechnics.

16)Y.Yamato, et al., "Health and Environment Aspects of a Non-Azide Propellant for Automotive Airbag Inflators", Submitted to J. Hazardous Materials.