

Q & A on Fire and Fire Prevention of Rigid Polyurethane Foam

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Preface

Rigid polyurethane foam has been widely used as an indispensable material for energy conservation and improving livability in buildings on account of numerous excellent characteristics such as processability, cost effectiveness, and insulation properties. On the other hand, polyurethane foam fires still occur despite various countermeasures being adopted such as flame retardation because after all the material is based on organic polymers that have in common the characteristic of combustible properties. Therefore, Japan Urethane Industries Institute (JUJI) has carried out further activities directed at a higher level of fire safety.

The technical safety committee of JUJI has collected literature regarding polyurethane foam fires and combustion from combustion toxicology and fire safety specialists and proceedings have been offered, while fire-prevention activities have also been promoted in cooperation with related industries. As part of this activity, the view was that an easier explanation of newer findings was necessary and here, a Q&A collection concerning a fire and fire prevention chiefly for rigid polyurethane foam has been compiled.

Rigid polyurethane foam insulation is usually foamed onsite onto plasterboard or with steel sheet as the surface material in composite materials. It is a problem when the fire relates to exposed foam.

This Q&A collection focuses on the combustibility of polyurethane foam as materials, and aims to arouse attention to risk management of flames coming into contact with polyurethane foam directly in when new buildings are built, or existing ones are repaired or demolished work, etc. and a fire occurs.

It would be greatly appreciated if this document is helpful and useful for various people concerned with polyurethane foam to further deepen the understanding of fire and fire prevention and contribute to industry development.

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I. Fire case studies

Q1. Please introduce cases of fires involving rigid polyurethane foam.

A: In fires involving rigid urethane form, rather than occurring while the polyurethane foam is being processed, most occur when the welding or cutting-touch work is carried out after foam installation. When use of flames is unavoidable, thorough measures must be implemented such as covering polyurethane foam with a nonflammable tarpaulin so that it does not come into contact with sparks or cutting away exposed foam. Fire, however, results when these measures are neglected.

Typical examples of recent fires are introduced below.

Table 1.1. Recent cases of fires

Date	Place	Burnt area	Ignition source	Operation
97.5	Yokohama	Wall, ceiling	Welding	Under new construction at amusement arcade. Insulation material on wall caught fire while welding. Burnt 500m ²
98.3	Tokyo	Wall	Welding	Under remodeling of elevator in cold ware-house. Welding spark ignited PU foam. Burnt 900m ²
98.4	Miyagi Pref.	Wall, ceiling	Welding	Under new construction of mushroom factory. Welding spark started fire when simultaneous works (welding, painting, PU foam spraying) were going on. One died, 15 injured, burnt 13,200m ²
99.2	Nara Pref.	Wall	Welding	Under repair work of door at mushroom factory/office. Welding spark ignited wall insulation material. Burnt 400m ²

Q2. What types of fires are common?

A: In new construction work, welding for ducts and air conditioners, etc. is carried out after processing of polyurethane foam, and there are numerous examples of polyurethane igniting due sparks from welding. In particular, if sprayed polyurethane foam in the ceiling is ignited by welding work for duct construction above the ceiling, combustion is rapid and can lead to major accidents.

On the other hand, in almost all case of fire in dismantling and renovation work are due to welding and cutting-torch work being carried out without verifying the existence of polyurethane foam. In particular, when warehouse doors are repaired, for example, welding work might carried out and the polyurethane foam on the back wall may be ignited out of sight of the worker, causing a fire.

Q3. What types of fires have occurred abroad?

A: Similar cases as those seen in Japan. A recent example was at a refrigerated warehouse under construction in Incheon in South Korea on January 7, 2008. Welders were welding in the machine room and sparks came into contact with oil vapors that saturated the basement floor, which had no ventilation or mobile ventilating fan. These vapors were ignited, and the polyurethane spray foam on the wall also ignited, causing a fire that killed 40 peoples.

II. Phenomena of compartment fire

Q4. What is flashover? Does it occur in fires with polyurethane foam?

A: Flashover is a phenomenon that spreads combustion rapidly as the heat generated by a fire is accumulated in a building, inflammables such as the ceiling, sidewalls, and furniture are heated and reach a condition where they easily combust, and the whole room begins to combust simultaneously at a time. (See Q8. Fig 1)

If combustibles such as indoor furniture are easily combusted, the fire spreads at the early stage and the flashover phenomenon readily occurs. For this reason, the combustibility of inflammable interior materials such as walls and ceilings also greatly influences flashover.

Flashover occurs when a fire spreads in the presence of polyurethane foam, as is the case with general combustible materials.

The photograph below is an example of a real large scale test.

Photo 4.1 Flashover at room corner test ISO 9705



Q5. What is “Deflagration Phenomenon”?

A: A combustible gas is generated from imperfect combustion due to air shortage in a building fire. Deflagration phenomenon is explosive combustion that occurs when air is rapidly supplied to such a combustible gas by opening of an opening due to the temperature rise brought about by indoor combustion. In particular, in a fire developed stage in a building fire, it is easy to have flashover when air flows in from the openings because indoor oxygen density lowers and an incomplete combustion state is reached.

Q6. Why do flames spread faster after they reach the ceiling?

A: When flames reach the ceiling, they spread along it in a crawling motion due to buoyancy. At this time, the fire spread speed quickens rapidly if there are combustibles on the exposed side of the ceiling. Even when the exposed ceiling is made from nonflammable materials, the radiation heat source expands and combustion is expanded easily as thermal radiation emitted toward the floor and combustible furniture increases. Thus, it is important to take refuge immediately because it is a very hazardous situation which results when a fire grows and reaches the ceiling.

Therefore, when polyurethane foam is applied to the ceiling, it is generally effective to cover it with a material that is at least semi-noncombustible or with a fire prevention coating in order to prevent combustion spread.

Q7. In what situation does polyurethane foam catch fire from welding/cutting-torch sparks?

A: The energy of welding sparks is significant and on this account, polyurethane foam ignites when sparks contact with it. Combustible gas is generated if a specific area comes into contact with welding sparks and is heated, and it is likely that this gas will be ignited. Moreover, falling molten material will pierce polyurethane foam and ignite it.

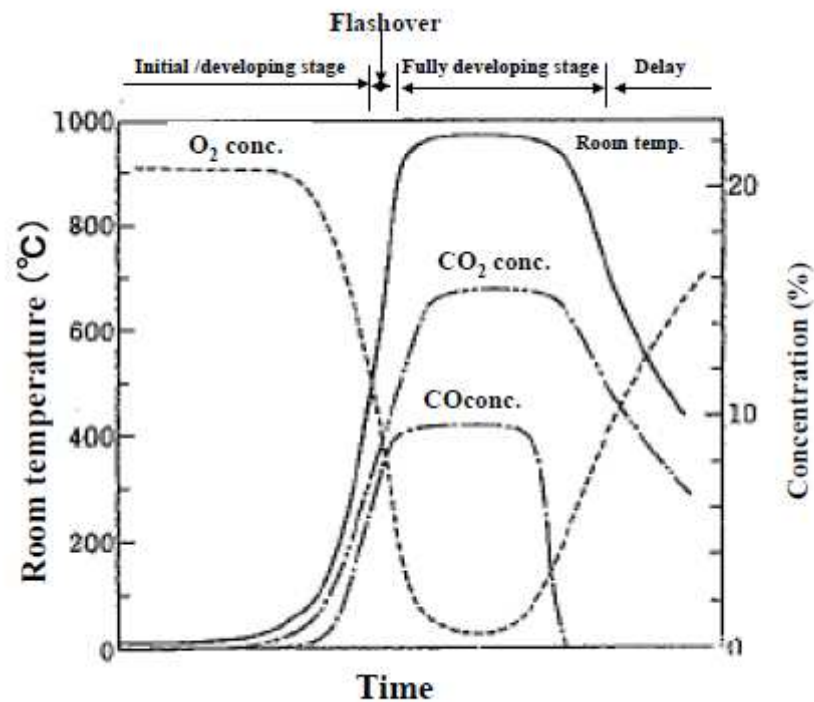
When use of flames is unavoidable, thorough measures must be implemented such as covering polyurethane foam with a nonflammable tarpaulin so that it does not come into contact with sparks or cutting away exposed foam.

Q8. To what level does the temperature rise in fires with polyurethane foam?

A: The processes in a building fire are generally breakout, early stage, fire growth stage, fully developed fire, and end stage fire as shown in Figure 8.1. The indoor temperature starts to rise rapidly during the growth stage, reaching a fully developed fire stage via flashover when the entire room burns. At this point the indoor temperature rises most, and reaches as much as 1000°C.

There are some cases where fire relates to the polyurethane foam.

Figure 8.1. Temperature and concentration profiles in room fire¹⁾



¹⁾ Fire Engineering Handbook, 3rd Ed. p.8 (1997)

III. Combustibility and smoke evolution

Q9. What are the flash point, ignition point and oxygen index of rigid polyurethane foam?

A: The combustion characteristic values of combustible materials are flash point, ignition point, and oxygen index.

The data of various materials are shown below.

Table 9.1. Ignitability of materials

	Flash point (°C) ¹⁾	Ignition point (°C) ¹⁾	Oxygen index (%) ²⁾
Red Oak	260	450	22~23 ^a
Polyethylene	340	350	17 ^b
Polystyrene	370	495	18 ^b
Polyurethane foam	310	415	20~21 ^a

According to these data, neither the flash point nor the ignition point of plastics material including rigid polyurethane foam is low compared with wood.

¹⁾ Fire Engineering Handbook, 3rd Ed. p.800, 802 (1997)

^{2-a)} E.K. Moss, Journal of Cellular Plastics, Nov./Dec. 332-336 (1976)

^{2-b)} M.M. Hirschler, Journal of Fire Sciences, 5, 289-307 (1987)

Q10. Does polyurethane foam ignite spontaneously?

A: Polyurethane foam products do not ignite spontaneously. Moreover, polyurethane never ignites spontaneously under a usual foam manufacturing conditions where it is made from mixing two components: the polyol component and the isocyanate component. However, the foaming process generates heat and it is possible that spontaneous ignition may occur due to foaming excessive amounts of foam. Therefore, making a larger block of foam than that required should be avoided, and the application manual should be followed in order to avoid heat accumulation in the polyurethane foam block.

Q11. Is the combustion rate of polyurethane foam faster than those of other materials?

A: As criteria for the combustibility of materials, the standard method for measuring the combustion rate had been based on mass decrease when that material is combusted. Judgment is now also possible based on the calorific value generated during combustion. Both groups of data are compared in the table below.

Table 11.1 Materials for combustion rate test ¹⁾

Name	Material	Thickness mm
PW3.0	Plywood	3.0
PW5.5	Plywood	5.5
G • B	Plasterboard	9.0
D • B	Pasteboard	0.7
A • B	Methyl methacrylate board	4.0
RF-A	Conventional rigid PU foam	25.0
RF-B	Fire retardant (additive type) PU foam	25.0
RF-C	Fire retardant (reactive type) PU foam	25.0
PIF-B	Fire retardant (additive type) PIR foam	25.0

Table 11.2. Combustion rate test results ¹⁾

Name	Furnace temp. (°C)	Mass burnt (g)	Combust. rate (g/s.cm ²)	Smoke conc. (m ⁻¹)	CO max (%)	CO ₂ max (%)	- O ₂ (%)	Heat release rate (W/cm ²)
PW3.0	600	12.3	1.39×10^{-3}	9.82	0.95	7.99	7.90	22.1
	800	12.3	1.89 "	5.78	1.32	8.44	9.76	27.8
PW5.0	600	25.2	1.66 "	11.00	0.37	6.23	6.07	11.8
	800	26.7	2.02 "	6.41	0.29	7.02	6.58	17.9
G • B	600	13.2	–	1.43	0.14	0.55	0.44	0.4
	800	17.2	–	0.99	0.18	0.53	0.54	0.6
D • B	600	5.3	–	1.44	0.73	6.14	5.62	13.6
	800	4.7	–	1.90	0.45	6.92	5.79	14.3
A • B	600	63.9	2.71 "	13.66	0.44	9.75	10.11	33.0
	800	64.5	4.34 "	16.05	0.57	10.00<	16.88	60.0
RF-A	600	8.4	1.11 "	20.39	0.82	7.50	6.50	19.9
	800	8.1	1.20 "	10.89	0.54	5.31	5.37	14.0
RF-B	600	8.0	–	21.63	0.88	6.50	5.30	11.5
	800	7.6	1.11 "	19.31	0.59	3.89	3.63	9.7
RF-C	600	6.8	–	23.92	0.95	6.21	5.10	10.9
	800	7.5	1.46 "	23.66	0.66	3.98	4.00	11.1
PIF-B	600	7.0	–	19.65	0.41	4.92	3.71	8.1
	800	8.1	1.06 "	22.71	0.47	4.56	4.33	11.1

The results show that the combustion rate of rigid polyurethane foam in terms of mass decrease and calorific value is not faster than other materials.

On the other hand, foam plastic has a large surface area, it exhibits good insulation efficiency and it does not diffuse heats and for these reasons, it possesses the general characterization that it combusts relatively easily. Because flames might spread rapidly if polyurethane foam ignites, sufficient measures for ignition and fire prevention are necessary for a exposed foam.

¹⁾ F. Saito, M. Yoshida, Annual Report, Construction Research Institute, 131-133 (1982)

²⁾ G.E. Hartzel, Toxicology, 115, 7-23 (1996)

Q12. Does polyurethane foam evolve much smoke in fires like other plastic materials ?

A: Though smoke evolution varies according to combustion conditions such as temperature and the amount of air supplied, polyurethane foam does not necessarily generated more smoke than other foams. The table shows data comparing smoke evolution from various materials.

Table12. 1. Emitting smoke factor¹⁾

Material	σ_m (m ² /kg)* ¹
Fire retardant expanded polystyrene foam (Density : 16kg/m ³)	1292
Extruded polystyrene foam (Density : 32kg/m ³)	1374
Rigid polyurethane foam (spray) (Density : 38.4kg/m ³)	1312
Rigid polyurethane panel foam (Density : 41.6kg/m ³)	403
Non-fire retardant rigid polyurethane foam (spray) (Density : 51.2kg/m ³)	683
Polyisocyanurate foam (board) (Density:25.6kg/m ³)	264
Phenolic foam (Density : 41.6kg/m ³)	72

*1. Specific extinction area:

*1. Smoke quantity emitted per mass of sample pyrolyzed.

Table 12. 2. Various smoke test results

Material	Smoke evolution $V/L(\ln I_0/I)^2 (m^2/min)$	Smoke density $OD/m^3 (l/m)$	NBS Smoke Test $Dm^{4)} (-)$
Polystyrene foam	340	Max.18.7	Max. 780
Rigid PU foam	200	" 15.7	" 45

¹⁾ T.G. Cleary, PB 92-123033, 85-88 (1991)

²⁾ T. Morikawa, E. Yanai, Journal of Fire Sciences, 7, 131-141 (1989)

³⁾ W.D. Woolley, Journal of Cellular Polymers, 4, 99 (1985)

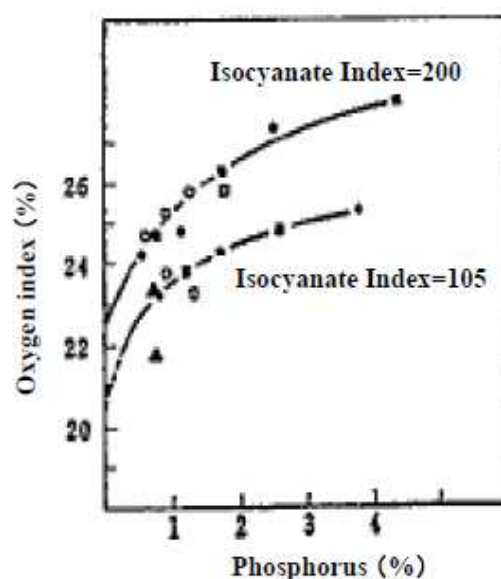
⁴⁾ C.J. Hilado, R.M. Murphy, Journal of Thermal Insulation 3, 276 (1980)

Q13. Is it possible to produce fire retardant polyurethane foam?

A: While rigid polyurethane foam can be made fire retardant (harder to combust) by increasing the amount of phosphoric acid ester flame retardant or increasing the isocyanate index, it will not become fully fire retardant as long as it is an organic material.

Flame retardance of polyurethane foam aims to increase the time available for persons to evacuate before a fire spreads by delaying spread at the early stage of a fire. The following data exists for flame retardation of polyurethane foam.

Figure 13.1. Oxygen index of flame retardant PU foams¹⁾



¹⁾ J.E. Kresta, Journal of Cellular Plastics 11 (2), 71 (1975)

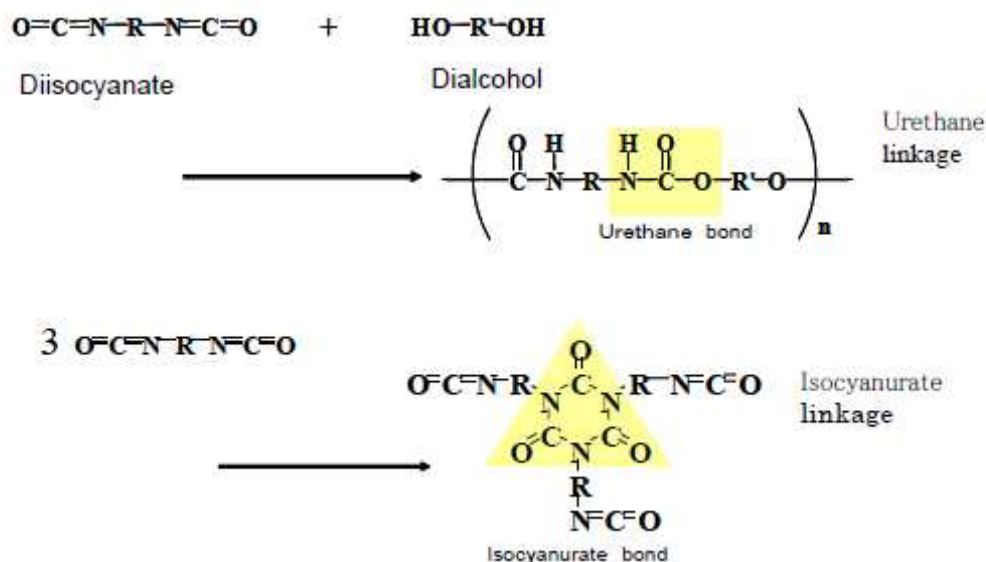
²⁾ G.E. Hartzell, Journal of Cellular Plastics, 28, 330-358 (1992)

The oxygen index of air is 21% and combustion becomes more difficult the higher the oxygen index becomes, as shown in the oxygen indices in the above figure. However, there are limitations to flame retardation and use of isocyanurate is necessary in order to further increase the difficulty of combustion for polyurethane foam. (see Q14)

Q14. What is the difference between polyurethane foam and polyisocyanurate foam ?

A: Polyisocyanurate foam features improved flame and thermal resistance by using an excessive amount of isocyanate and a special catalyst to introduce an isocyanurate ring structure.

Though it becomes difficult to combust if a lot of these ring structures are incorporated, it's fault is it also easily becomes brittle and thus cannot endure practical use. Then, urethane-modified polyisocyanurate foam that makes the best use of the advantages of polyurethane is actually used. In general, this is called polyisocyanurate polyurethane foam.



It is clear that there is the difference in the combustibilities of polyurethane foam and polyisocyanurate foam from test data below. Polyisocyanurate foam does not burn easily, and the calorific value and the combustion speed are low compared with polyurethane foam.

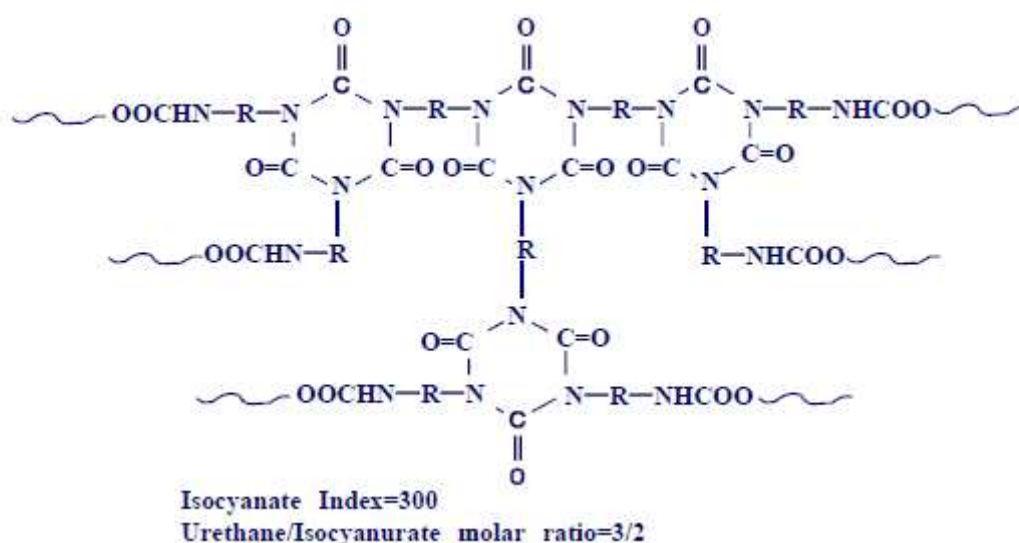


Table 14.1. Heat release and rate of heat release

Material	Total heat released ¹⁾ (MJ/m ²)	Heat release rate ²⁾ (J/cm ² .min)
Rigid PU panel foam (Density : 41.6kg/m ³)	13.9	738
Polyisocyanurate foam (board) (Density:25.6kg/m ³)	4.7	96

¹⁾ T.G. Cleary, J.G. Quintiere, PB Report 92-123033, p.88 (1991)

²⁾ A. Deleon, Journal of Thermal Insulation, 6, 169 (1983)

Q15. Is there any difference in combustion behavior between rigid polyurethane foam and other commercial plastic foams?

A: There are two kinds of plastics foam used as construction materials. One is thermoplastic resin such as polyethylene foam and polystyrene foam, which is melted by heat. Another is thermoset resin which is not melted by heat, such as polyurethane foam, polyisocyanurate foam or phenolic resin foam.

The combustibility of a material tends to be seen in its heat release rate and gross calorific value. Material comparison data is shown in Table 15.1. Because the characteristic of combustibility is different, these materials cannot indiscriminately be judged to be combustible.

Table 15.1 Cone calorimeter: Heat release and rate of heat release ¹⁾

Material (50mm thick)	Total heat released(MJ/m ²)	Heat release rate (kW/m ²)* ¹
Fire retardant expanded polystyrene foam* ² (Density : 16kg/m ³)	22.1	1280
Non-fire retardant expanded polystyrene foam* ² (Density : 32kg/m ³)	47.3	1590
Fire retardant extruded polystyrene foam* ² (Density : 32kg/m ³)	33.5	1350
Rigid polyurethane foam (spray) (Density : 38.4kg/m ³)	21.9	331
Rigid polyurethane panel foam (Density : 41.6kg/m ³)	13.9	147
Non-fire retardant rigid PU foam (spray) (Density : 51.2kg/m ³)	55.0	361
Polyisocyanurate foam (board) (Density : 25.6kg/m ³)	4.7	79
Phenolic foam (board) (Density : 41.6kg/m ³)	36	111

*¹. With external heat flux of 50kW/m², *². During melting, distance from regressing sample surface to cone heater is maintained to be same as initial.

¹⁾ T.G. Cleary, J.G. Quintiere, PB Report 92-123033, p.85-88 (1991)

IV. Combustion gas and its toxicity

Q16. What gases are generally evolved in building fires and what are their properties?

A: Fires and the situation regarding generation gas are classified from the standpoints of the gas composition and toxicity as shown in Table 16.1, although the composition and the toxicity of the gas generated vary according to the progress of the fire.

Table 16.1. Fire development and combustion gas evolution

Fire development	Temp. range	Evolution and toxic effects of fire gases
1. Nonflaming– thermal /smouldering fires	<500°C	Evolution of many decomposed products e.g. HCN, HCl, acrolein, depending composition of materials. CO ₂ and CO generate most and always. Main danger here is generally the toxicity of CO.
2. Early/developing flaming fires	400°C ~700°C	Once flaming occurs, high temperature oxidative flame converts most of decomposed gases into CO ₂ and H ₂ O. Generation of toxic gases increase due to development of fire, although irritant gases and CO are relatively low.
3. Fully developed or post-flashover fires	>800°C	O ₂ concentrations are low at high temperature. Pyrolyzed products break down into low molecule substances e.g. CO, HCN. High concentrations of these gases increase danger of gas toxicity.

HCN: Hydrogen cyanide, HCl: Hydrogen chloride, CO₂: carbon dioxide,
CO: Carbon monoxide, H₂O: Water, O₂: Oxygen

Table 16.2 shows the toxicity of the gas generated in a fire. The toxicities of the constituent gases combine as the overall gas generated.

Table 16.2. Toxicity of major fire gases**

Toxicity	Gas component	LC ₅₀ ^{*1} ppm (v/v, 30min.)	RD ₅₀ ^{*2} ppm
Narcotic gas	CO ¹⁾	5000 ~ 6600	–
	HCN ¹⁾	110 ~ 200	–
	CO ₂ ²⁾	(narcotic; CO ₂ 5%)	–
	Hypoxia ^{2),3)}	(effect on memory; O ₂ 14%)	–
Irritant gas	HCl ²⁾	1600 ~ 6000	309
	Acrolein ²⁾	140 ~ 170	1.7
	Ammonia ²⁾	1400 ~ 8000	303
	NO _x ²⁾	NO ₂ 60 ~ 250	349

^{*1}. LC₅₀: Concentration statistically calculated to cause the death of one half of the animals exposed to a toxic substance for a specified time (e.g. 10, 30 min.).

^{*2}. RD₅₀: Statistically calculated concentration of a sensory irritant required to reduce the breathing rate of laboratory rodents by 50%.

** Details in Table 16A (page-XX)

Harmful gas generated in a fire and an outline of its toxicity are displayed in Table 16A.

On the other hand, the hazards of a fire always include heat and smoke in addition to the gas toxicity generated from the combustion materials, and the toxicity of the generation gas is a part of the overall hazard of fire.

Smoke and heat negatively affect evacuation in the second stage (from early stage to growth stage) in Table 16.1, and humans find it extremely difficult to survive in a high temperature fire of the third stage (from fully developed stage to end stage) due to skin burns, and inhalation and heatstroke of high temperature gas, etc.

Literature references

- 1) ISO/TR 9122-5 (1993)
- 2) D.A. Purser, SFPE Handbook of Fire Protection Engineering Section 2/ Chapter 8 (1995)
- 3) G.E. Hartzell, Toxicology, 115, 7-23 (1996)
- 4) ISO/TR 9122-1(1989)

Q17. What gases are evolved in fires with rigid polyurethane foam?

A: A fire involving rigid polyurethane foam is in general the same as a normal fire. Carbon monoxide and carbon dioxide are the main components of the gas generated, as is the case with other organic materials. (See Q16)

Tables 17.1, 17.2 and 17.3 show the example of the combustion gas measurement findings of various materials obtained from a small-scale experiment device.

Table 17.3 compares generation of hydrogen cyanide (HCN) from nitrogen-containing organic materials but besides the concentration of hydrogen cyanide from flexible polyurethane foam being relatively low, a marked difference with other materials could not be recognized

Figure 17.1 shows an experiment example where the pyrolysis products of nitrogen-containing material convert to HCN under high temperature, and it is found that the HCN conversion rate (weight ratio (%) of generated HCN to original weight of the material) of a material with a high nitrogen content is high

Table 17.1. Combustion test products (mg/g) ¹⁾

Fire Product	CEL* ¹	PES* ²	Silk	Wool	Nylon	PAN* ³	PU foam	PE* ⁴	PP* ⁵	PMMA* ⁶	PVC* ⁷
CO ₂	202	290	170	69	35	73	88	120	21	99	< 8
CO	88	85	13	21	13	12	57	120	25	61	7.0
HCl	-	-	-	-	-	-	-	-	-	-	230
NH ₃	-	-	21	12	6	2.6	-	-	-	-	-
HCN	-	-	1.3	1.8	-	6.6	< 2	-	-	-	-
COS	-	-	-	1.8	-	-	-	-	-	-	-
CH ₄	2.4	1.7	1.7	1.9	0.84	3.4	4.6	2.5	1.5	0.56	1.7
C ₂ H ₄ , C ₂ H ₂	2.8	2.7	0.57	1.6	3.6	0.6	3.9	18	2.1	0.51	0.98
C ₂ H ₆	0.52	0.14	0.62	0.91	0.92	0.79	1.3	1.6	3.1	0.08	1.7
C ₃ H ₆	0.88	0.18	0.6	2.0	2.6	0.27	29	12	27	1.23	0.73
C ₃ H ₈	0.11	-	-	1.3	0.7	1.4	-	2.5	-	-	0.83
C ₄ H ₈	-	-	-	1.1	2.9	-	0.38	-	4.8	-	-
C ₆ H ₆	-	2.7	-	-	-	-	-	-	-	-	11
C ₆ H ₅ CH ₃	-	0.23	-	-	-	-	-	-	-	-	-
CH ₃ OH	-	-	-	-	0.68	2.0	-	6.2	5.6	-	-
CH ₃ CHO	2.5	14	-	-	0.81	-	32	10	7.9	-	0.3
CH ₂ =CHC	2.1	-	-	-	-	-	-	8.4	3.9	-	-
HO	-	-	-	-	-	-	-	-	-	-	-
CH ₃ COCH ₃	-	-	-	-	-	-	13	-	-	-	-
CH ₃ CN	-	-	5.7	1.6	1.2	3.0	-	-	-	-	-
CH ₂ =CHCN	-	-	-	0.83	-	5.6	-	-	-	-	-
MMA* ⁸	-	-	-	-	-	-	-	-	-	89	-
Residue	4.1	9.1	19.3	12.7	4.3	19.5	4.3	32.3	4.0	0	15.5

*¹ Cellulose, *² Polyester, *³ Polyacrylonitrile, *⁴ polyethylene, *⁵ Polypropylene,

*⁶ Polymethylmethacrylate, *⁷ Polyvinylchloride, *⁸ Methymethacrylate

Decomposition temperature: 500°C, O₂ concentration: 21%, Air flow: 0.22 ml/min.

Decomposition time: 4 min. Sample weight: 100 mg

Table 17.2. Combustion products of organic materials ²⁾

Material	(mg/sample 1g)					
	CO ₂	CO	HCN	NH ₃	HCl	Other hydro-carbons
PU foam* ¹	666	173	3.3			78
Polyethylene	738	210				291
Polystyrene	619	178				37.5
Polyvinylchloride	657	177			286	11
Nylone 66	590	205	31	9.8		149
Polyacrylamide	796	157	18	17		34.5
Polyacrylonitrile	556	108	56			13.3
Epoxy resin	1,138	153	2.2			25.7
Ceder	1,573	16				

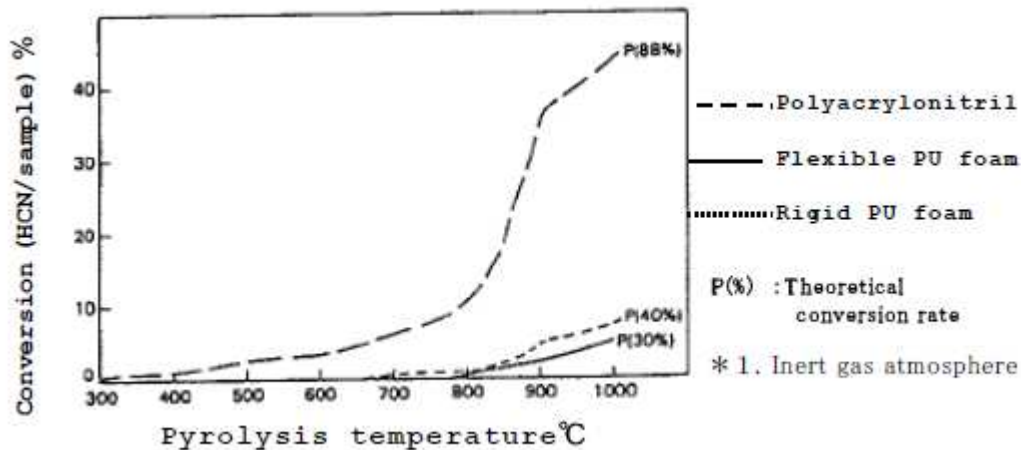
Combustion parameters: temperature 700°C, air flow 100l/hr

*¹ Polyurethane foam made from TDI and polyester polyol

Table 17.3. Generation of HCN through combustion of N-containing materials³⁾

Material	HCN peak conc. ppm	Peak temp. °C
Nylon	328 – 520	485 – 429
Wool	368	567
Polyacrylonitrile	445	381
Urea formaldehyde resin	458	321
Rigid PU foam	321 – 467	587 – 549
Flexible PU foam	181	388

Figure 17.1. Conversion rate to HCN for pyrolysis^{*1}



On one hand, it is said that the gas composition of a single, small-scale experiment will not represent the entire generation gas of a real fire because the composition of the generation gas is different according to the progress of a fire.

On the other hand, small-scale experiment results are used in methods for correcting concentrations to use as input data for combustion gas models. (See Q18)

¹⁾ T. Saito, E. Yanai, Technical Report, Fire Research Institute, No.10 5-60(1977)

²⁾ T. Morimoto, Highpolymers, Vol. 22, No.253, 190-195 (1973)

³⁾ F.M. Esposito et al., Journal of Fire Sciences, 6, 195-242 (1988)

⁴⁾ W.D. Woolley, et al., Fire Safety Journal, 5, 29-48 (1982)

Q18. What are the toxic effects of fire gases from rigid polyurethane foam ?

A: The combustion gas toxicity of various materials is evaluated by the LC₅₀ value. LC₅₀ means that when laboratory animals are exposed to gases for 30 minutes, this is a statistical calculation value of the concentration of the combustion gas whereby 50% of the laboratory animals die. Such values lie within the range of about 5-60 mg/L for many plastic materials and natural materials.

It can be seen from Table 18.1 that the combustion gas toxicity value of rigid polyurethane foam is on a par with those of other plastics materials.

Table 18.1. Toxicity of thermal decomposition products of various plastic materials ¹⁾

Plastic materials	Test methods and parameters					Toxicity LC ₅₀ (mg/l)
	Test method	Test animal	Mode* ¹	Time -I* ² (min.)	Time -II* ³	
ABS	NBS	Rats	NF	30	14 day	19.3-64.0
ABS	Pittsburgh	Mice	M	30	10 min	9.3-10.5
Polyester resin	Pittsburgh	Mice	M	30	10 min	58
Polyester batting	NASA	Mice	M	30	14 day	20
PE wire insulation	NBS	Rats	NF	30	14 day	>75
PE	NBS	Rats	F	30	14 day	46
Polystyrene	NBS	Rats	F	30	14 day	33.0-53.5
Polystyrene	Pittsburgh	Mice	M	30	10 min	9.7
PVC wall covering	NBS	Rats	NF	30	14 day	51.0
PVC	Pittsburgh	Mice	M	30	14 day	4.7
Rigid PU foam	NBS	Rats	NF	30	14 day	34.0->39.6
Rigid PU foam	DIN	Rats	NF	30	-	6.6

*1. F; Flaming, NF; Non-flaming, M; Mixed mode

*2. Exposure time *3. Post-exposure time

* Biological data are usually distributed widely and are not judged to be significantly different unless the differences exceed one order.

However, when the hazards of combustible gases is evaluated from the findings of combustion gas toxicity examinations, it is necessary to consider the difference with a real fire. (See Q17)

Table 18.2 shows a comparison between a simulation of a real fire scale and small-scale experiments. The data of two small-scale experiments are corrected to the level of a high concentration of carbon monoxide of a real fire after - flashover. As for these data that simulate a real fire, it is understood that rigid polyurethane foam exhibits no special combustion gas toxicity compared with the other two materials.

Table 18.2. Fire gas toxicity test of various materials²⁾

Test method	LC ₅₀ (mg/l)		
	Douglas fir	Rigid PU foam	PVC sheet
NBS Cup Furnace ^{*1}	21-24	9-12	16-19
SwRI/NIST Method ^{*1}	21-23	14-19	13-17
Real-scale Test ^{*2}	>70	30-40	35-45

^{*1} CO values are adjusted to reflect CO evolution at real scale fire.

^{*2} Combustion room (2.4 x 3.7 m), Corridor (2.4 x 4.6 m), Test room (2.4 x 3.7 m)

¹⁾ B.C. Levin, Fire & Materials, 11, 143-157 (1987).

²⁾ V. Babrauskas et al., Journal of Fire Sciences, 9, 125-148 (1991).

V. Fire test methods

Q19. What are the fire test methods of rigid polyurethane foam?

A: Combustibility parameters such as ignitability, flame spread, heat release, and smoking, and harmfulness parameters such as the smoke and gases generated are elements of fire resistance performance for building materials and interior materials that relate to rigid polyurethane foam used for building insulation. The main combustibility tests used in Japan are based on JIS standards, the Ministry of Construction notification, and ISO standards.

When speaking of combustibility testing, the test method applied is different depending on the combustion phenomenon to be evaluated. Moreover, test methods themselves are classified as ones to understand the basic performance of material and ones to understand the performance of a material in a real fire. The main test methods used to evaluate polyurethane foam are shown below.

Further, various test methods, test items, and outlines of test devices are summarized in reference at the end of this document. (See Q19-A,B)

Table 19.1. Rigid polyurethane insulation foam fire tests* *

Standard/ code	Name	Category	Note
JIS A9511	Foamed plastic insulation materials		Regulated by the combustion length (6cm or less) and the afterflame time (within 120 seconds).
JIS A9526	Rigid PU spray foam insulation materials		
JIS A1321	Test method of flame retardancy for building interior materials and construction	Heat release, smoke evolution	To specify flame retardant class 1 to 3
MOC Notice No. 1231 No.1372 New (2000.6)	Surface combustibility test, Annexed test	Heat release, smoke evolution	To specify flame retardant to semi non-flammable materials
	Combustion gas toxicity test method	Gas toxicity	
	Box model fire test	Heat release, semi full-scale heat release rate, combustion gas toxicity	
	Cone calorimeter test		
ISO 5660	Rate of heat release from building products	Heat release	to be applied for MOC Notice
ISO 5658	Surface spread of flame on building products – Vertical specimen	Flame spread	
ISO 9705	Full scale room test for surface products	Full scale fire	

MOC; Ministry of Construction, current Ministry of Land, Infrastructure, Transport & Tourism (MLIT)

** Details of main test methods, test items, and apparatus in Table 19A, (page 34-35)

Q20. Are there some simplified test methods for evaluating the combustibility of polyurethane foam?

A: While in some cases JIS A9511 can be used to determine the extent of low combustibility by using a flame from a lighter or match to heat a sample, it is though that comparison of flame retardant products under JIS A 1321 and suitability to each standard cannot necessarily be understood. This is because when comparing using flame from a lighter, the same combustion tendency is not necessarily shown with the JIS A 1321 test that uses a high calorie heat source (heating wire.)

Moreover, when speaking of combustibility, there are several evaluation

characteristics such as ignitability, smoking, calorific value, and combustion rate, and the current situation is that there is no technique to adequately evaluate each of these by a simple and easy method.

Q21. Have grades such as “JIS A 1321 flame retardant class 3” or “MOC Notice 1231 flame retardant material” acquired certification?

A: Certification is not necessarily acquired. For instance, certification is not awarded in the case of onsite foaming. This is because the manufacturing conditions are not managed easily at a construction site. In a word, in the case of onsite foaming, strictly speaking, “Grade 3 incombustibility” and “Flame resistant materials in the notification of Ministry of Construction” are those that met relevant standards and regulations when samples were tested by independent testing organizations, and it does not mean that certification has been acquired. However, in the case of onsite foaming, the combustion performance of foams is classified by a decision of “the Building Contractors Society” as “Grade 3 flame retardant products with pink coloring”. Certification can be acquired from JIS standards and the Ministry of Land, Infrastructure, Transport & Tourism (MLIT, old Ministry of Construction MOC) for so-called factory production products such as laminate boards and insulated panels if the flame retardant and fireproof properties of the products satisfy management items prescribed in manufacturing.

Q22. What is meant by flame retardant or semi-noncombustible materials prescribed under tests in the Building Standard Law Notification?

A: Generally, materials that can be used for exterior structures and interior finishing materials for rooms and passages are restricted by ordinances based on the usage and structure of the building. The objective is to suppress the danger at a fire as much as possible by prescribing the use of materials with high fire preventions properties for exterior and interior materials.

For example the fire preventions properties required of materials differ depending on the usage, structure, and floor area of the building. There are interior finishing

restrictions mandated as “Flame resistant material”, more than “Semi-noncombustible material”, and “Noncombustible material” based on notification tests. Construction is carried out using materials certified by MLIT.

Q23. What is the difference between JIS A1321 and ISO 5660 in the fire prevention material combustion test method?

A: The evaluation method for fire protection materials was changed along with the revision of the Building Standard Law of Japan in 1998, and the heat release test method (ISO 5660) was adopted in place of the conventional surface combustion test method (JIS A1321). Then the evaluation method changed to the performance evaluation method in June 2000.

This is because in characterizing the combustibility of materials for building construction, heat release property is the key factor and heat release from interior materials is an important fire property which influences propagation and expansion of room fires. Both test methods differ greatly in the heating method and evaluation method.

The surface combustion test method is a method of evaluating heat release, smoke generation, and residual flame. The surface combustion test method does not sufficiently evaluate characteristics as a fire protection material and incombustibility.

On the other hand, the heat release cone calorimeter method is a global standard method for evaluation of the combustibility of a material. The heat generation rate and gross calorific value are calculated by the oxygen consumption method. The test utilizes the fact that regardless of the type of substance, an almost constant numerical value is obtained for the calorific value from combustion (13.1MJ per oxygen kg).

Various, engineering data related to combustion such as heat release rate, smoke density, change with passage of time of the amount of the CO and CO₂ generation, and gross calorific value, etc., are obtained upon ignition.

Table 23.1 Japan regulation and test methods for building construction

Test method / class	Non-combustible materials	Quasi-noncombustible materials	Fire retardant materials
Cone calorimeter test ISO 6550-1 at 510KW/m ²	≤ 8MJ/m ² and ≤ 200kw/m ² during 20 min	≤ 8MJ/m ² and ≤ 200kw/m ² during 10 min	≤ 8MJ/m ² and ≤ 200kw/m ² during 5 min
Non-combustibility test ISO 1182	Δ T ≤ 20k and Δ m ≤ 30%	—	—
Model box test ISO CD17431	—	≤ 50MJ and ≤ 140kw During 10 min	≤ 50MJ and ≤ 140kw During 5 min
Gas Toxicity test on 8 mice Notification No1231	Movable time > 6.8 min		

The non-combustibility test and the model box test are alternatives for the cone calorimeter test.

VI. Fire prevention activities

Q24. What are the necessary precautions and practices to prevent fire accidents with polyurethane foam?

A: The main cause of polyurethane foam fires is welding or gas-torch work after onsite spraying of rigid polyurethane foam. In the case of construction of new buildings, this is because process control by site managers is insufficient and the understanding of the combustibility of polyurethane foam on the part of welding workers is insufficient. Moreover, in repair and demolition work, welding work is carried out without understanding the locations of polyurethane foam in the building

The Ministry of Health Labor & Welfare (MHLW), which manages welding qualification lectures, is urging that qualifying examinations and safety course texts for welding-cutting torch workers should include instruction on polyurethane fire prevention measures but it seems as though these measures have not yet been thoroughly implemented. On the other hand, the Building Contractors Society has issued the booklet “Prevention of Polyurethane Foam Fires” for site supervisor and workers at construction sites, and attention has been aroused by a hazard

assessment sheet that refers to past examples of incidents. Therefore, in order to prevent fires, the site supervisor should first direct safety confirmation. Next, if the presence of polyurethane foam is confirmed, it should be covered with a nonflammable tarpaulin or removed from all sides for a distance of one meter. Then, welding-cutting torch work should be carried out in the presence of the supervisor

Q25. What activities are you performing in order to prevent fires involving polyurethane foam?

A: The Rigid Polyurethane Safety Advisory Council was established by the Japan Urethane Industries Institute (JUII), Japan Urethane Foam Association (JUFA) and the Japan Urethane Insulation Association in order to promote various activities regarding safety for onsite construction by member companies. The following activities are carried out by the council.

1. Advice to make full use of authorized safety manuals for welding. A leaflet was published under the supervision by Tokyo Metropolitan Fire Defense Agency
2. Safety campaigns at Japan Welding Association through trade (industry) newspapers and journals
3. Periodical meeting with Construction Industries Association (Zenken)
4. Campaign on polyurethane fire prevention at onsite construction bodies through three trade newspapers.
5. Cooperation with MHLW and MLIT: advice at meeting organized by MLIT, and at seminar for licenses by MITL.

VII Supplement Q&A Dust explosion

Q What is “Dust explosion”

A; Dust explosion is the phenomena that flammable dust floated in atmosphere with enough oxygen (dust cloud) is ignited by a source like spark and oxidized suddenly resulted in a explosion. Because dust size is very fine, dust have a very large surface area compared to their mass which is resulted in contact with enough oxygen, dust is

very sensitive for oxidization and ignition. Coal mining explosion is very famous due to coal dust, but many otherwise mundane materials can also lead to a dust explosion such as metal powder like aluminum, iron, and magnesium, and such as sugar and flour. Minimum ignition energy means the minimum energy for source of ignition. Electrostatic discharge can also become a source of ignition energy.

Q. Can polyurethane foam generate a dust explosion?

A: Because plastics are organic compounds and combustible, plastics may generate a dust explosion if plastic dust is floating in atmosphere. Polyurethane foam itself never generate a dust explosion, but if polyurethane is powdered into fine dust, it can generate a dust explosion same as other plastic dust. Because minimum ignition energy or explosion limit of polyurethane dust is not larger than that of other plastic dust, the risk of dust explosion of polyurethane is not so large.

Polyurethane dust can arise from cutting, crashing and grinding polyurethane products. Furthermore dust can arise during compounding of thermoplastic polyurethane (TPU). In order to avoid dust explosion, following countermeasures are required; enough ventilation not to generate dust cloud, keeping ignition source away. Nitrogen purge or high humidity is also effective as a countermeasure.

Figures and tables

APPENDIX

Table 16-A. Major combustion gases and their toxic effects

Fire gas	Toxic effects	Toxicity *
<u>Narcotic gas</u>		
1) Carbon monoxide (CO)	Combining with hemoglobin in blood to form carboxy -hemoglobin, CO reduces oxygen supply to brain tissue, resulting in loss of consciousness and incapacitation.	LC ₅₀ = 5000~6600 ppm(v/v) ¹⁾
2) Hydrogen cyanide (HCN)	Traces of HCN can generate in fires of nitrogen containing materials. It is carried rapidly to body (brain) and inhibits the utilization of O ₂ at cells. HCN, like CO, finally depresses cerebral function, and its intoxication takes effects rapidly.	LC ₅₀ = 110~200 ppm(v/v) ¹⁾
3) Carbon dioxide (CO ₂)	CO ₂ is present always in fires. It is not toxic up to 5%, but it stimulates breathing and increases uptake of other toxicant gases. It is a narcotic at about 5% and subjects become intolerable within 20 min. at approximately 6%.	
4) Hypoxia (low O ₂)	O ₂ concentration decreases in a compartment fire. Low concentration below 18% is dangerous for humans. Their motor coordination is impaired at about 14% and they may exercise faulty judgement at about 10%. ²⁾³⁾	
<u>Irritant gas</u>		
1) Hydrogen chloride (HCl)	HCl generates at fires of chlorine containing materials. Irritating extremely eyes and upper respiratory tracts (as low as 100ppm), it impairs activities such as escape from fires.	LC ₅₀ = 1600~6000 ppm ²⁾ RD ₅₀ = 309 ppm ²⁾
2) Acrolein and other organics	Many organic irritant materials are formed in pyrolysis and/or incomplete combustion of organic materials. Acrolein, which irritates eyes and upper respiratory tracts strongly at a few ppm, is found to be present in many fire atmospheres.	LC ₅₀ = 140~170 ppm ²⁾ RD ₅₀ = 1.7 ppm ²⁾
3) Ammonia (NH ₃)	NH ₃ irritates eyes and upper respiratory tracts. It may cause pulmonary edema.	LC ₅₀ = 1400~8000 ppm ²⁾ RD ₅₀ = 303 ppm ²⁾
4) Nitrogen oxides (NO _x)	NO _x is primarily a pulmonary irritant.	NO ₂ : LC ₅₀ = 60~250 ppm ²⁾ RD ₅₀ = 349 ppm ²⁾

*1. LC₅₀: Concentration statistically calculated to cause the death of one half of the animals exposed to a toxic substance for a specified time (e.g. 10, 30 min.).

*2. RD₅₀: Statistically calculated concentration of a sensory irritant required to reduce the breathing rate of laboratory rodents by 50%.

¹⁾ ISO/TR 9122-5 (1993)

²⁾ D.A. Purser, SFPE Handbook of Fire Protection Engineering Section 2/ Chapter 8 (1995)

³⁾ G.E. Hartzell, Toxicology, 115, 7-23 (1996)

Table Q19-A Fire Test Methods

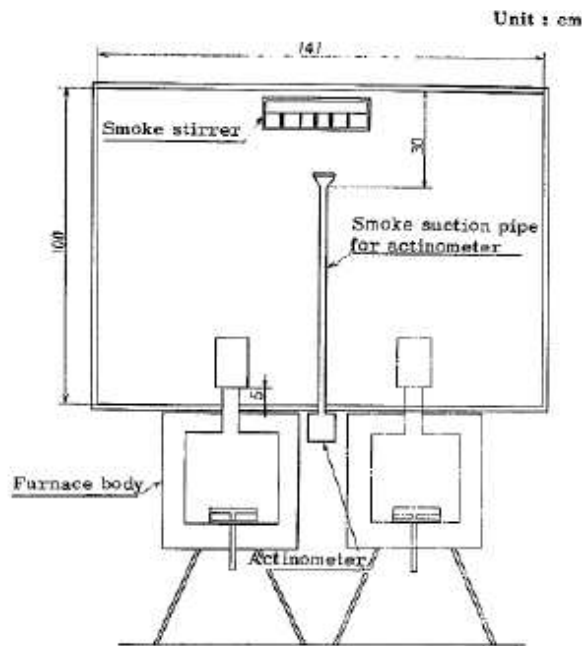
Building products/related to interior materials : Burning and combustion gas test method

compiled by moriya 2008.12.25						
	Ignition/Combustion duration	Flame spread	Heat release(burning)rate	asorific (mass combustion) value	Smoke generation	Toxicity
Japan law and JIS	•JIS K7201-95 Combustion test method (Oxygen index test) of polymer materials		•Notification No 1231 S51 quasi-noncombustible and flame resistance material	•Notification No 1231 S51 quasi-noncombustible and flame resistance material •JIS A1321-94 Incombustibility of Internal finished materials and proceeding of buildings	•Notification No 1231 S51 quasi-noncombustible and flame resistance material •JIS A1321-94 Incombustibility of Internal finished materials and proceeding of buildings •JIS A1326-83 smoke concentration (light depreciation method) •JIS A7228-87 plastics smoke concentration combustion gas	•Notification No 1231 S51 quasi-noncombustible and flame resistance material
ISO	•ISO 5657-97 Ignitability of building products using a radiant heat source •ISO 5658-2:96 building material ignition (plate radiation furnace) •ISO 11925-2:02 Ignitability of building products Part 2-02: Single flame source test Part 3-07: Multi-source test	•ISO 5658-2:06 Lateral spread on building and transport products in vertical configuration (plate radiation furnace) •ISO 9238-1:02 Reaction to fire tests for floorings •ISO 12392:95 Plastics --- Vertical flame spread determination for film and sheet	•ISO 5650-1:2002 Heat release, smoke production and mass loss rate --- (corn radiation furnace)	•ISO 5650-3:08 building material Heat release, smoke production and mass loss rate (corn radiation furnace)	•ISO 5958-2:08 Lateral spread on building and transport products in vertical configuration (plate radiation furnace) •TR 5924:89 Smoke generated by building products (dual-chamber test) •ISO 5659-2:2006 Plastics Smoke generation (single-chamber test)	•ISO 13344:04 Estimation of the initial toxic potency of fire effluents •TR 91221-5:89-93 toxic test of combustion products
ASTM	•D1929-96 Self and flash ignition temperatures •E 1321-08 Ignition (radiant-heat pane)	•E84-06 building material horizontal combustion characteristic for underlayment (Steiner Tunnel) •E182-8a Surface Flammability of Materials Using a Radiant Heat Energy Source (downward vertical test) (radiant-heat pane) •E1321-08 Determining Material Ignition and Flame Spread Properties lateral flame spread (radiant-heat pane)	•D935-06 plastics Rate of Burning and/or Extent (Horizontal Position) •E806-07 Heat and Visible smoke release rates •E1354-08 Heat and Visible Smoke Release rates (Oxygen Consumption Calorimeter)		•E662-06el Specific Optical Density of Smoke Generated by Solid Material •E806-07 Heat and Visible Smoke Release Rates •E1354-08 Heat and Visible Smoke Release Rates (Oxygen Consumption Calorimeter) •D2843-04 density of smoke from burning or decomposition of plastics	•E1678-8a Standard Test Method for Measuring smoke Toxicity for Use in fire Hazard Analysis
DIN	DIN 4102: fire behaviour in building materials and products : concept object-test method					•DIN 53436:Part1~5 toxicological testing for thermal decomposition products from materials in an air stream •KSF 2271 part16
KSF			•KSF-ISO 6560-1	•KSF-ISO 660-3	•KSF 2271	
GB	•GB/T14523 Ignitability of building products •GB/T2406 Oxygen Index Test for Plastics		•GB/T16172-2007 Heat release	•GB/T16172-2007 Heat release, mass loss rate	•GB/T8627- Building Products smoke concentration	GB/T20285-2006 Toxic Test for Building products

Table 19-B. Fire test apparatuses ¹⁾

Surface Combustion Test

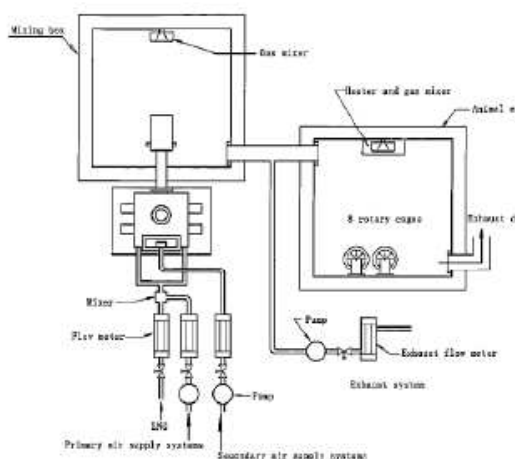
Category	Heat release , smoke
Code No.	Notification No 1828
Name	Surface combustion test
Related Code/standard	Notification No 1231, JIS A 1321



When the testing specimen is heated with electricity and the LP gas , an exhaust temperature, a smoking coefficient ,the melt, presence of the crack, and a harmful transformation and the afterflame are measured.

Gas Hazard Toxic test

Category	Gas Hazard, Toxicity
Code No.	Notification No 1231
Name	Gas Toxic test
Related Code/standard	



The gas generated from the test material is introduced into a test box, where the time is observed for 8 mice breathing the gas to incapacitation from the time starting of the heating.

X: Average time to the incapacitation for 8 mice

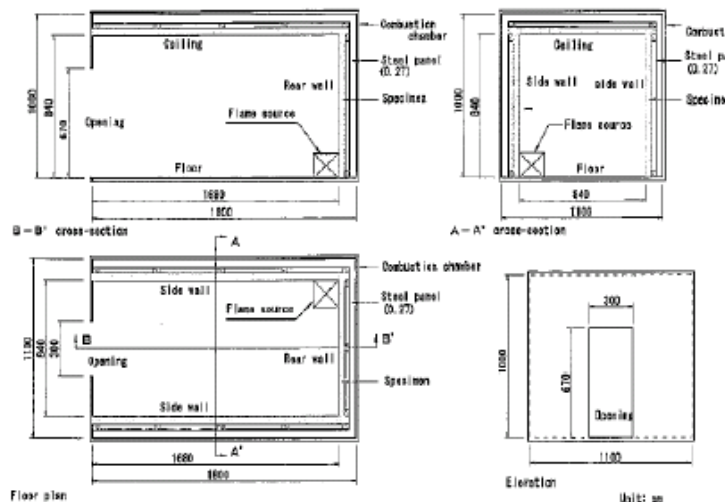
σ : Standard deviation

Xs: Time to the incapacitation

In case that Xs is longer than 6.8 min. (time to the incapacitation for red lauan, standard wood) the test material is considered to fulfill the requirement.

Model Box Test

Category	Heat release
Code No.	Notification No 1231
Name	Model Box test
Related Code/standard	

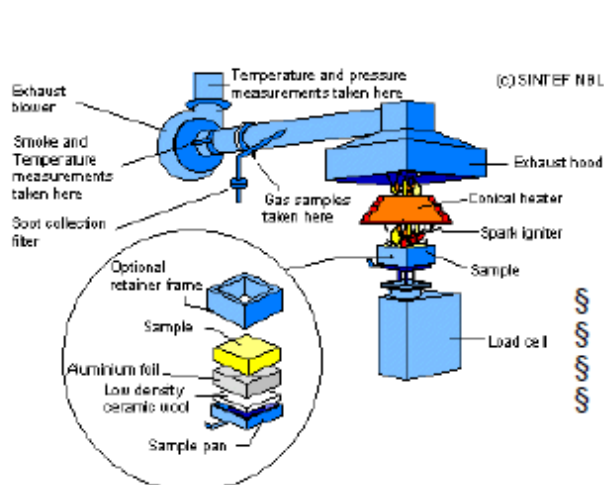


Outline of test method

It is burnt to put the specimens on all aspects except the opening and the floor of the device of figure by wood the crib as an origin of fire, and measures the maximum heat release rate, the gross calorific value, and flashover.

Cone Colorimeter Test

Category	Heat release
Code No.	ISO 5660
Name	Rate of heat release from building products
Related Code/standard	ASTM-E 1354-90, NFPA 264A



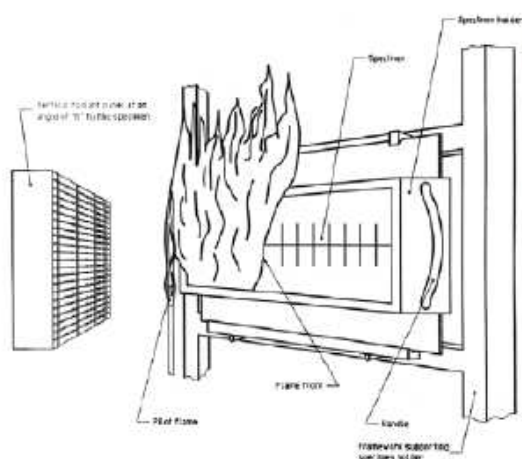
The surface of the test specimen is exposed to a constant level of heat irradiance, within the range 0-100 kW/m², from a conical heater. Volatile gases from the heated specimen are ignited by an electrical spark igniter. Combustion gases are collected by an exhaust hood for further analysis

The test gives a possibility to evaluate:

- Ignitability
- Combustibility
- Smoke production
- Production of toxic gases

Fire Spread Test

Category	Flame spread
Code No.	ISO 5658
Name	Surface spread of flame on building products (vertical)



Specimen : 3 specimens 800mm × 155mm

Specimen : Vertical in specimen holder

Position

Heat source : Gas fired radiator panel

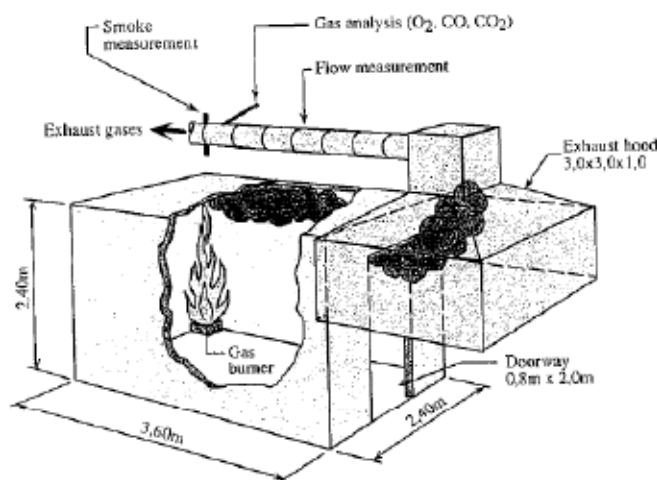
Test duration: 30 min or earlier if flame front stops or if the flames spreads to the end of the specimen

Conclusions : Average heat sustained burning

Critical heat flux at extinguishments

Full Scale Room Test

Category	Full scale fire test
Code No.	ISO 9705
Name	Full scale room test for surface products



- Room test with heat release rate (HRR) and smoke production rate (SPR) in duct
- Used for wall and ceiling linings
- 2.4m (W) x 3.6m (L) x 2.4m (H)

Y. Hasemi, Seminar text on revision of Building Standard Law, July 1998

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