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Highly Flame retardant Polyol for Rigid Polyurethane Foam

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Polyurethane foam is a plastic foam obtained by mixing the main components of polyol (PPG) and polyisocyanate with foaming agents (e.g., water, hydrofluorocarbon [HFC]), foam stabilizers (e.g., silicone oil), catalysts (e.g., amine compounds), and other components to simultaneously generate resin and gas formation reactions **[Fig. 1]**.

Of the different types of polyurethane foam available, the demand for rigid polyurethane foam is increasing mainly in China, Southeast Asia, and Central and South America where thermal insulation is required, including buildings, heat-insulation equipment, vehicles, and ships **[Table 1, Photo]**. This foam is most often used as thermal insulation material for residential and non-residential (e.g., office buildings, warehouses) buildings, and the demand for its use is growing as an alternative to glass wool, for example, in detached houses (Table1, Photo). Glass wool has a number of disadvantages such as sagging and heat leakage, As such, the adoption of rigid polyurethane foam as thermal insulation material in houses has been growing, as it has good airtightness and thermal insulation properties. However, the Building Standards Act in Japan stipulates that this foam cannot be used as an insulating material in houses unless it passes an incombustible authorization test and is certified as an incombustible material by the Ministry of Land Infrastructure and Transport and Tourism. Aromatic ester polyol has higher flame retardancy than polypropylene glycol, which is the most commonly used raw material in polyurethane foam.

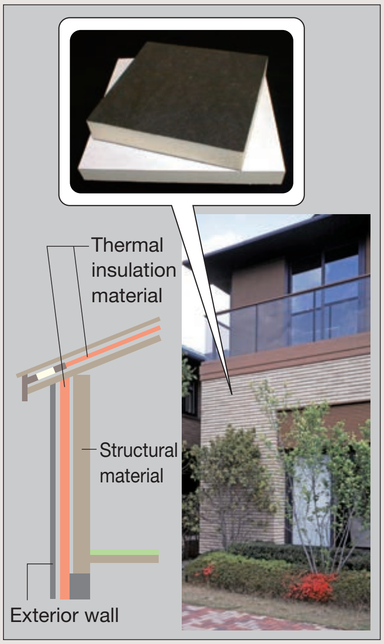
Urethane formation reaction (resin formation reaction)

$$\underset{\text{Polyol}}{HO-R'-OH} + \underset{\text{Polyisocyanate}}{OCN-R-NCO} \longrightarrow \underset{\text{Urethane bond in polyurethane foam}}{\left[OCONH-R-NHCOO-R'\right]}$$

Urea formation reaction (gas formation reaction and resin formation reaction)

$$\underset{\text{Polyisocyanate}}{2\ OCN-R-NCO} + \underset{\text{Water}}{2\ H_2O} \longrightarrow \underset{\text{Urea bond in polyurethane foam}}{\left[R-NHCONH-R-NHCONH\right]} + \underset{\text{Carbon dioxide (generated gas)}}{2\ CO_2}$$

Fig. 1 • Chemical reaction formula for polyurethane foam



As a thermal insulation material for buildings and houses

Table 1 • Major fields in which rigid polyurethane foam is used and its applications

Field	Application
Architecture	Thermal insulation in houses and office buildings (walls, under the floor, ceiling, below the roof, etc.), thermal insulation building materials (laminate boards, siding materials, etc.), thermal insulation in bathtubs, thermal insulation in freezing storage warehouses, refrigerated warehouses, barns, etc.
Heat-insulation equipment	Refrigerators, freezers, thermal insulation components of air conditioners, show cases, vending machines, water heaters
Ships	Fishing boards, large ships, reefers, thermal insulation of containers, LNG carriers, LPG carriers, large vessels
Vehicles	Thermal insulation of railroad containers and tank lorries, vehicles (bullet trains, etc.), thermal insulation of ceilings in trucks
Plants, etc.	Thermal insulation of facility tanks and pipes for chemical industry, heat retention of piping and other equipment, tank lids

Therefore, it is used as the main raw material polyol in the manufacture of rigid polyurethane foam. However, the addition of a large amount of flame retardant is necessary to satisfy the flame retardancy standard. As this flame retardant does not become incorporated into the urethane skeleton structure, it can cause deterioration in the strength, heat-insulation, and other physical properties of the polyurethane foam. Furthermore, phosphorus-based flame-retardants, which enjoy mainstream use today, have also raised concerns about their burden on the environment, as they are gradually released into the soil after the disposal of thermal insulation material.

To resolve these problems, our company has successfully developed a PPG combined with an aromatic ester polyol that realizes flame retardancy without causing deterioration of the physical properties of the foam. This dramatically reduces the amount of phosphorus-based flame retardant needed. This article describes 'NONFLAPOL,' the high flame retardancy polyol we developed for use in rigid polyurethane foam.

◇Performance of various thermal insulation materials used in the architectural applications

As described above, some materials excel as flame-retardants but exhibit inferior thermal insulation performance, such as glass wool and rock wool. Other materials excel as thermal insulators but have low flame retardancy performance, such as rigid polyurethane foam. Materials such as phenol foam excel as both thermal insulators and flame-retardants, but are high in cost **[Table 2]**.

◇Combustion cycle of rigid polyurethane foam and the current flame retardant additive technology

As described above, rigid polyurethane foam, which is used as thermal insulation material in residential and other buildings, has the disadvantage of low flame retardancy performance as it is an organic material. Flame retardancy is currently achieved by changing the flame retardant components added.

In general, combustion processes follow a successive cycle [1] that involves the combustion of flammable gas (supply of flammable gas and oxygen), [2] the generation of radiated heat from the combustion (temperature increase on the organic material surface), [3] thermal conduction to the organic material (temperature increase in organic material), [4] thermal decomposition of the organic material (generation of flammable gas), [5] diffusion of flammable gas to the material surface (diffusion in the solid phase), and [6] diffusion of the flammable gas into the combustion field (diffusion to gaseous phase part) **[Fig. 2]**.

To stop the combustion process, one of these processes must be inhibited.

The types of flame retardants currently used to inhibit combustion include the following. First, to dilute the amount of oxygen and flammable gas generated and achieve an oxygen blocking effect in the gaseous phase, auxiliaries are used, such as halogen compounds, which not only trap the active OH and H radicals but also generate incombustible hydrogen halide and a combination of halogen compounds and antimony trioxide. Alternatively, to dilute the oxygen and flammable gas generated, hydrated metals are also used, including aluminum hydroxide and magnesium hydroxide, which absorb heat and generate steam by dehydration reaction during combustion. To block the

Table 2 • Various thermal insulation materials and their performances

	Density (kg/m³)	Thermal insulation (W/mK)	Flame retardancy performance
Rigid polyurethane foam	25 to 35	0.019 to 0.040	Flame retardant
Polystyrene foam	20 to 25	0.028 to 0.040	Flame retardant
Phenol foam	13 to 45	0.020 to 0.036	Incombustible
Glass wool	10 to 35	0.036 to 0.052	Incombustible
Rock wool	25 to 100	0.038 to 0.051	Incombustible

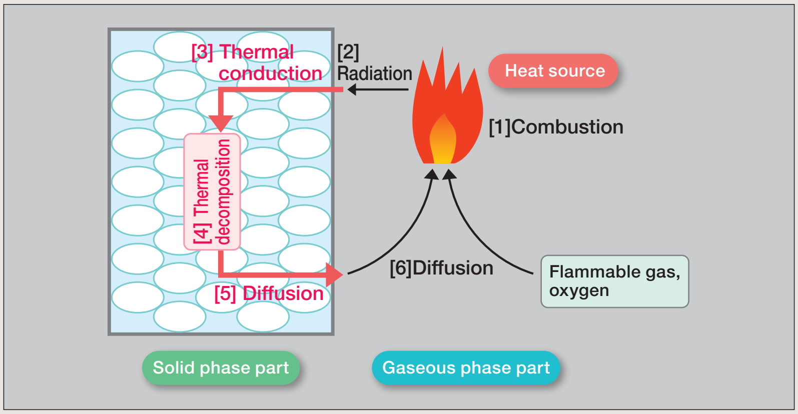


Fig. 2 • Combustion cycle of rigid polyurethane foam

Table 3 • Flame retardant additive techniques used for 'NONFLAPOL' and other major flame retardants

● : Effective

	Combustion inhibition effect	Dilution of flammable gas	Blocking of flammable gas	Stopping of the combustion reaction	Promotion of carbonization	Heat absorption by dehydration reaction
Developed product	NONFLAPOL		● By char formation	● Radical trap	● Char formation reaction (by radical polymerization)	
Flame retardants	Halogen compounds	● Generation of HBr, HCl		● Radical trap		
Flame retardants	Antimony oxide		● Synergistic effects with halogen compounds (Sb_2O_3 => $SbBr_3$)	● Radical trap		
Flame retardants	Hydrated metal compounds	● Dilution effect with steam				● Dehydration and heat absorption reaction
Flame retardants	Phosphorus compounds	● Dilution effect with steam	● By char formation		● Char formation reaction (generation of polyphosphoric acid)	

Table 4 • Comparison between 'NONFLAPOL' and conventional polyol

	NONFLAPOL (an example)	Conventional polyol (SANNIX HD-402)*
Presence of double bond group	Present	Not present
Hydroxyl value (mgKOH/g)	165	400
Viscosity mPa·s (25°C)	2,400	1,800

*Product of our company

oxygen and diffuse and block the flammable gas generated by thermal decomposition, phosphorus compounds are used, which promote the formation of char (carbide film) through dehydration during thermal decomposition.
As shown here, the mechanisms of the flame retardant additives vary with respect to the combustion process **[Table 3]**.

◇Features of 'NONFLAPOL,' a product developed at our company

'NONFLAPOL,' which we introduce in this article, incorporates components that trap radicals within the molecules **[Table 4]**. Specifically, it can trap the radicals (flammable gas) generated by thermal decomposition during the combustion of rigid polyurethane foam. This causes a radical polymerization reaction on the foam surface that generates the formation of char on the surface. This char suppresses the temperature increase in the internal areas of the foam where radicals are generated. Furthermore, the char serves as a gas barrier that prevents oxygen and flammable gas from entering into the internal areas of the foam **[Table 3]**. By the above effects of 'NONFLAPOL,' the flame retardancy of rigid polyurethane foam is improved.

◇Reduction in flame retardant usage and improved intrinsic flame retardancy

Figure 3 shows an example of the data obtained with the use of 'NONFLAPOL' in a panel of rigid polyurethane foam, whereby the amount of phosphorus-based flame retardant is reduced when the flame retardancy of the foam is improved.
At present, aromatic ester polyol is used in panel applications to improve the flame retardancy of polyurethane foam. It is evident that by combining 20% to 30% 'NONFLAPOL' with this aromatic ester polyol, the amount of phosphorus-based flame retardant (tris(β-chloropropyl) phosphate [TCPP]) can be reduced to approximately 1/5 to 1/10 of the amount used in foam manufactured with aromatic ester polyol alone.
In addition, the results of the flame retardancy test (ISO-5660-1 cone calorimeter method **[Fig. 4]**) show that the

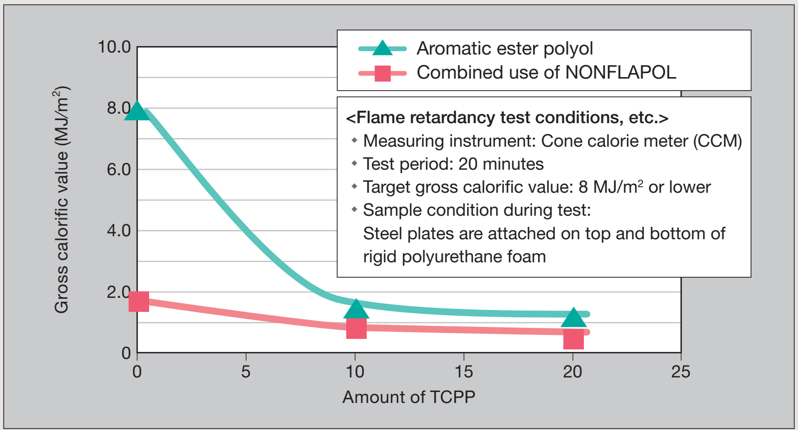


Fig. 3 • Reduction in the amount of phosphorus-based flame retardant used

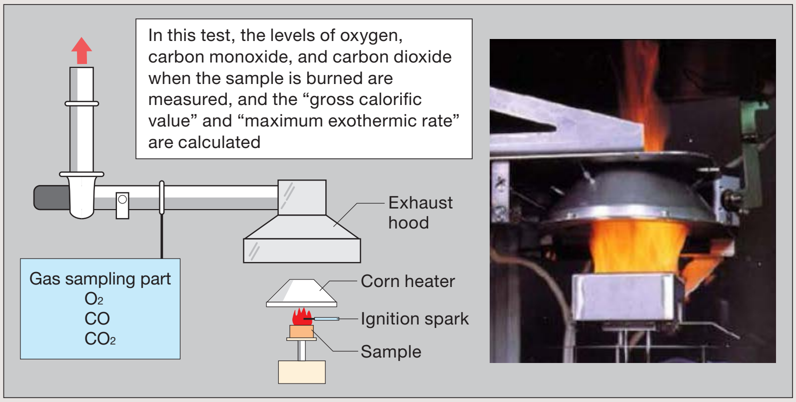
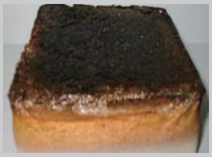


Fig. 4 • ISO-5660-1 Cone calorimeter method (flame retardancy test)

Amount of TCPP used	Combined use of NONFLAPOL (PE-2005)	Aromatic ester polyol
20 parts		
10 parts		
0 parts		

Note) The photographs were taken after CCM testing with the top steel plate removed

Fig. 5 • Samples after flame retardancy test (corn calorie meter method)

shape of the foam was maintained and no thermal decomposition occurred as no heat was transmitted into the internal areas of the foam sample, even when using only a small amount of phosphorus-based flame retardant (tris(β-chloropropyl) phosphate [TCPP]) **[Fig. 5]**. These results confirm that the flame retardancy was improved by the use of 'NONFLAPOL.' In general, a large amount of flame retardant must be used to realize adequate flame retardancy in polyurethane foam, which causes deterioration of its physical properties, such as strength and degree of thermal insulation. However, 'NONFLAPOL' does not degrade the physical properties of foam, because it contains a hydroxyl group that reacts with the isocyanate group to become incorporated into the urethane resin skeleton.

As such, the strength and thermal insulation properties of the polyurethane foam are equivalent to those of the foam made only from aromatic ester polyol, while ensuring a high level of flame retardancy.

◇Future prospects

Hydrofluoroolefin (HFO) as a substitute for the current mainstream chemical hydrofluorocarbon (HFC) is associated with a lower global warming potential and its use in foaming agents is advancing in the manufacture of rigid polyurethane foam.

Cyclopentane is another foaming agent with a low global warming potential in some cases.

However, its degree of flame retardancy tends to be lower than that of HFO, as cyclopentane is flammable. In this study, we confirmed that 'NONFLAPOL' improves flame retardancy even for these foaming agents. In fact, 'NONFLAPOL' enables the manufacture of rigid polyurethane foam with high flame retardancy when any of the foaming agents is used.

In the future, we plan to expand the sales of this product mainly for thermal insulation materials for houses that must be certified as incombustible. We will also promote its application in fields other than residential thermal insulation, including heat-insulation equipment such as refrigerators and vending machines, ships, and vehicles.

NONFLAPOL can thus contribute to the general improvement of flame retardancy in thermal insulation materials and reduce environmental loads.

[Contact (about the product)]
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