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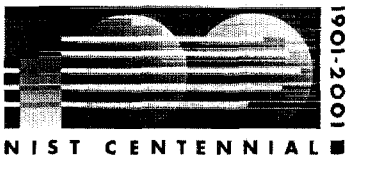
VOLUME 1

Sheilda L. Bryner, Editor



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FLAMMABILITY TEST FOR FLAME RETARDANT PLASTIC PALLET

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ABSTRACT

Fire risk of plastic pallet was recognized by a big rack storage fire occurred in Japan on Nov.1995. Thereafter NRIFD started research and development of fire-retardant (FR) plastic pallets in collaboration with Japan Pallet Association and a fire retardant chemical company. Flammability and mechanical properties of some FR synthetic resins are examined to select appropriate synthetic resins for plastic pallets. The flammability of the resins is tested by the cone calorimeter, UL94 and the Oxygen Index Test prescribed in Japan Industrial Standards (JIS) K7201, and comparisons are made between each of test results. Finally the prototype of FR plastic pallet is produced of the FR plastic combined by $Mg(OH)_2$ and red-Phosphorus. The fire tests of full-scale pallets are conducted with furniture calorimeter and the effect of the fire retardant is examined.

INTRODUCTION

A fire occurred in a warehouse in Japan on Nov.1995. This warehouse had automatic high-palletized rack system and many plastic pallets were stored for stacking noncombustible products. Automatic sprinklers were installed and activated, however the fire spread very rapidly and fire suppression failed. The fire continued for more than 18 hours and three fire fighters were killed. After investigation of the warehouse fire [1], Fire and Disaster Management Agency addressed some fundamental countermeasures, i.e., 1) enhancement of fire safety equipments such as sprinkler installation, 2) mitigation of fire risk caused by plastic pallets including adoption of inflammable or fire retardant (FR) treated plastics.

In July 1998, the Fire Service Law Enforcement was revised to enhance fire safety countermeasures in warehouses and a new guideline [2] of the sprinkler installation is proposed depending on the total amount of heat source in warehouses. In this guideline, a new class of combustible material is introduced as "high calorie melting material", in which the threshold of heat release is set to be 34 MJ/kg. In addition to the conventional "designated combustibles" prescribed by Fire Service Law Enforcement, the total amount of such material including plastic pallets should be taken into account for installation of sprinklers.

As far as the FR plastic pallets are concerned, there are many research and development of FR plastic material [3][4][5], however very few FR pallets have been developed in Japan. The major material of the

plastic pallets prevailed in the market is olefin hydrocarbons such as polypropylene (PP). And as the FR chemicals for such plastic, halogen containing (mainly bromine compound) and non-halogen containing (magnesium hydroxide ($Mg(OH)_2$) with diantimony trioxide (Sb_2O_3)) are commonly used. As for the flammability classification of these FR plastics, UL94 [6] and the Oxygen Index test in JIS K7201 [7] are very popular in Japan. Especially special attention is paid for the Oxygen Index, because Fire Service Law Enforcement designated the plastic material of less than 26 in oxygen index as "flammable". A plastic pallet test has been proposed by UL2335 [8], however this is not well known in Japan currently.

Under these circumstances, development of FR pallets is one of our key issues for improving warehouse fire safety, and rational test methods to evaluate the flammability of plastic pallets are needed. National Research Institute of Fire and Disaster conducted research and development in collaboration with the Japan Pallet Association and a fire retardant chemicals company. The following describes the development process in three stages and related flammability test results by using cone and furniture calorimeter, UL94 and the Oxygen Index tests.

BLOCK FLOW OF THE R&D PROJECT

One of our immediate goals is to develop and introduce less flammable prototype plastic pallets which can be used practically in the near future. In this collaboration of R&D project, FR plastic pallets made of polypropylene basis were developed in three stages as shown in Figure 1. In each stage, flammability and mechanical properties are examined.

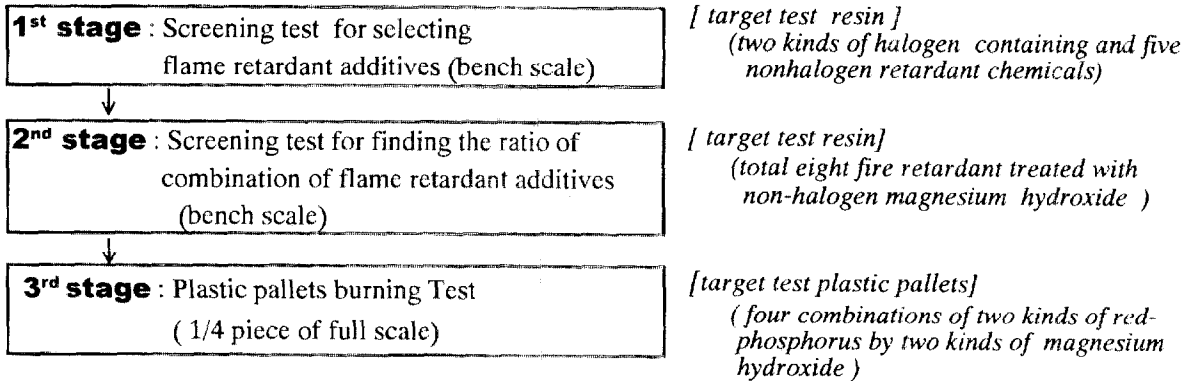


Figure 1. Outline of development process

RESULTS & CONSIDERATIONS

The 1st stage development

At the beginning of this R&D project, popular FR chemicals for basic resin PP are examined in bench scale by the cone calorimeter, UL94 and the Oxygen Index Test.

Test resins and flammable test : FR chemicals are classified roughly into two types, i.e., halogen and non-halogen containing additives. Recently adoption of the halogen additives tends to be avoided due to envi-

Table 1. Properties of test resins for plastic pallets

(the 1st stage screening test for selecting valid flame retardant chemicals)

Test Plastics			Properties				
	No.	fire retardant chemicals*1) [weight %]	Color	Density	Burning Test	Heat of Combustion	Oxgen Index
			observation	JIS-K7112	UL94*2)	calorimeter*3	JIS K7201
			—	(kg/m3)	rating	(kJ/g)	—
refference	J−750HP	base Poly-ropyren	Natural	0.90	HB	46.6	17.9
Red-Phosphorous flame retardant	EX696	r-P[8.3]+polyphosphate-melamine	Brown	0.99	V-2 out	41.7	22.7
	EX697	r-P[4.3]+Mg(OH)2[8.7]	Brown	1.14	V-2 out	31.0	22.2
	EX698	r-P.(4.5)+melamine-cyanulate[5.4]	Brown	0.95	V-2	43.7	19.6
	EX699	r-P[9.1]	Brown	0.95	V-2	44.5	20.3
Halogen and Non-halogen flan retardant	EX168S	$Mg(OH)_2$[10]	Gray	1.37	V-2	20.6	24.3
	EX187	Br + Sb_2O_3[20]	Gray	1.01	V-1	40.7	26.4
	8200R	Br+Sb_2O_3[not disclosed]	Gray	0.99	V-0	41.1	30.3

*cf . *1) r-P is red-phosphorous flame retardant additive*

**2) The rating on this table is corresponding to the UL 94 test rating, however those are not certificated by the UL.*

**3) Oxgen Bomb calorimeter.*

ronmental issues. In this development, two specimens of popular bromine halogen (non DBDPO type) FR treated resins are examined as reference. As non-halogen FR additives, popular $Mg(OH)_2$ is selected and r-P is also added to the resin. Table 1 shows the test resins examined in the 1st stage including base resin PP as reference.

Cone calorimeter test : Figure 2 shows the time curve of heat release rate of different FR treated resins and non-FR base resin PP. "8200R" and "EX187" containing bromine additive show similar time curve. These FR additives have an effect on suppressing ignition and burning rate. However, once the specimen burns, the FR effect becomes smaller and the heat release rate decreased only 20% less than that of the base PP. Regarding the plastic "EX-168S" to which $Mg(OH)_2$ is added, the total amount of heat release is 44% of the base PP. So the heat release rate becomes relatively lower and the peak heat release rate becomes about 20% compared with that of the base PP. And moreover dehydrated residue of the $Mg(OH)_2$ remains in layers on the surface and it gives thermal insulation effect which causes less burning rate.

In the case of only r-P is added, the peak heat release rate(PHR) is reduced by only 20% or 30%. However, being combined with melamine containing FR chemicals increases the FR effect. The test result shows that especially when r-P chemicals combined with polyphosphate melamine, the PHR is half the PHR of base PP. The above qualitative combustion phenomena can be observed under other radiant heat flux condition. The effect of the radiant heat flux will be mentioned later.

FR treatment on resins reduces heat release rate and retards ignition time, however generally it enhances to generate the large amount of hazardous combustion products. Figure 3 shows the time curve of CO yield. The figure indicates the CO yield generated from halogen-containing FR resin ranges from twice to three times in the peak compared with that of base PP. In contrast, in the case of $Mg(OH)_2$ additives, the smoke production is very small and the CO is hardly measured. When r-P is added, the amount of smoke is getting higher than that from the basic PP.

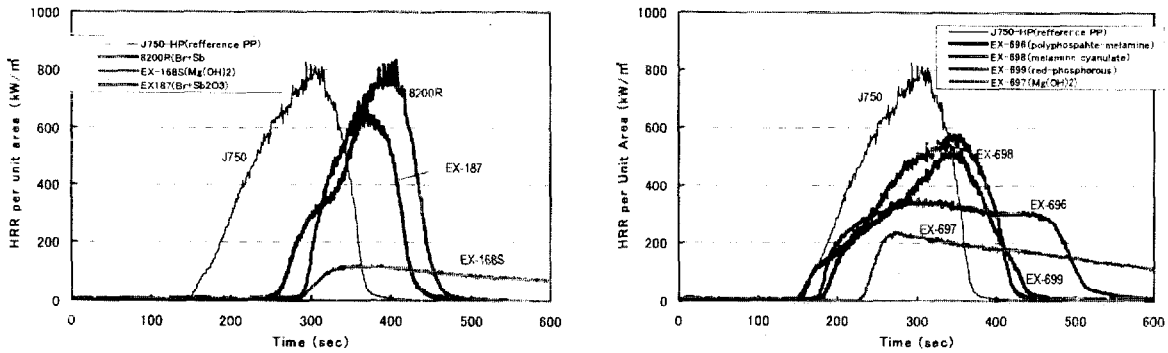


Figure 2. Heat release rate of FR treated plastics
(mixture of r-P and $Mg(OH)_2$; under 20 kW/m² radiative heat flux)

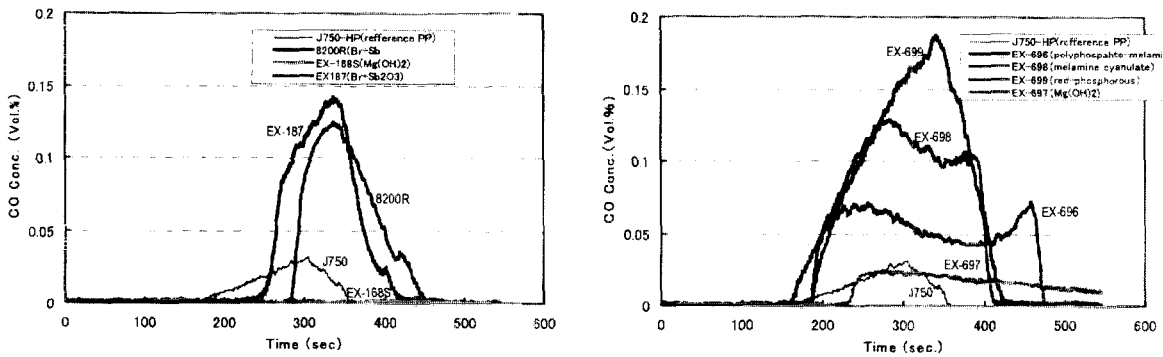


Figure 3. CO yield of FR treated plastics
(mixture of r-P and $Mg(OH)_2$; under 20 kW/m² radiant heat flux)

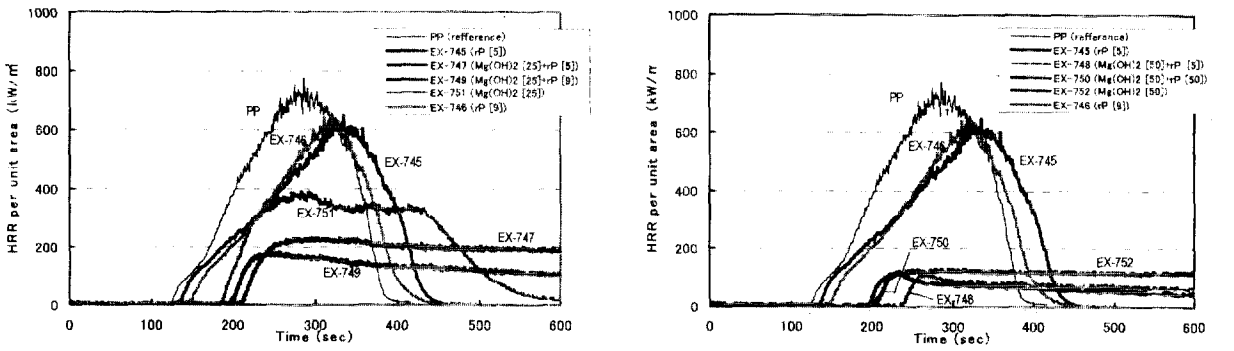
The 2nd stage development

Test resin and flammable test : From the flammability screening test results in the 1st stage, it is observed that FR additive of $Mg(OH)_2$ has relatively high FR effect. Then further details of weight ration of $Mg(OH)_2$ and the combination of $Mg(OH)_2$ and r-P are examined in the 2nd stage. As the basic FR

Table 2 Properties of test plastics for pallets : (the 2nd stage screening test for finding appropriate combination of flame retardant chemicals, i.e. r-P and $Mg(OH)_2$)

Test Plastics			Properties				
	No.	fire retardant chemicals*1) [weight %]	Color	Density	Burning Test	Heat of Combustion	Oxgen Index
			observation	JIS-K7112	UL94*2)	calorimeter*3	JIS K7201
			—	(kg/m3)	rating	(kJ/g)	—
refference	PP	base Polypropyren	Natural	0.89	V-2 out	46.6	17.7
Red-Phospho-rous added FR	EX745	r-P[4.8]	Brown	0.92	V-2 out	45.5	19.5
	EX746	r-P[9.1] (=EX699)	Brown	0.95	V-2	44.5	20.2
	EX747	r-P.[4.6]+Mg(OH)2 [25]	Brown	1.09	V-2 out	33.7	22.3
	EX748	r-P.[4.6]+Mg(OH)2 [50]	Brown	1.31	V-0	22.9	26.5
	EX749	r-P.[9.1]+Mg(OH)2 [25]	Brown	1.22	V-2 out	33.1	23.4
	EX750	r-P.[9.1]+Mg(OH)2 [50]	Brown	1.35	V-0	22.0	28.8
$Mg(OH)_2$ base FR	EX751	$Mg(OH)_2$[25]	Gray	1.05	V-2 out	35.0	19.8
	EX752	$Mg(OH)_2$[50]	Gray	1.28	V-2 out	23.7	22.9

*(cf) *1) r-P is red-phosphorous flame retardant additives*
**2) Ratings on this table correspond to the UL 94 test rating, however those are not certificated by the UL..*
**3) Oxgen bomb calorimeter.*
**4) The value derives from the property of popular pallete made of PP.*



(a) FR additives of 25 wt% of $Mg(OH)_2$ and /or r-P. (b) FR additives of 50 wt% of $Mg(OH)_2$ and /or r-P.

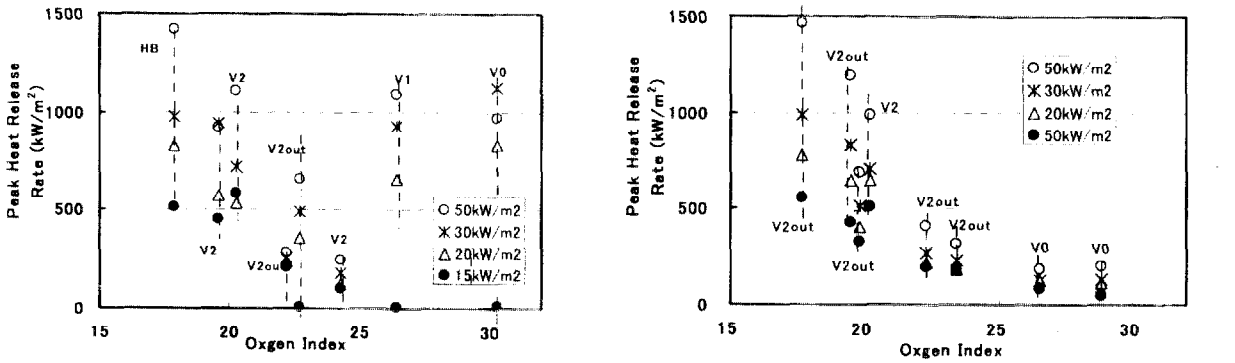
Figure 4. Heat release rate of FR treated plastics in the 2nd stage (mixture of rP and $Mg(OH)_2$, 20 kW/m² radiative heat flux)

chemicals, $Mg(OH)_2$ 50wt% and 25wt% are prepared and r-P is added with 4.6wt%,9.1wt% and none respectively. Table 2 shows the test resins examined and some of the test results.

Cone calorimeter test : Figure 4 shows the heat release rate in the cases where $Mg(OH)_2$ is of 25wt% in the left side (a) and 50 wt% in the right side (b) with test result of base PP as reference. The figures indicate that adding only r-P suppresses heat release rate after ignition, however the PHR is reduced only by 20%. When only $Mg(OH)_2$ is added, the PHR rate is highly reduced and slower combustion continues. When $Mg(OH)_2$ is of 25wt%, the FR effect of red phosphorous additives is larger than that in the case of 50wt% of $Mg(OH)_2$. In the case of $Mg(OH)_2$ FR treatment, combustion product is suppressed because heat release rate is small as observed in the 1st stage.

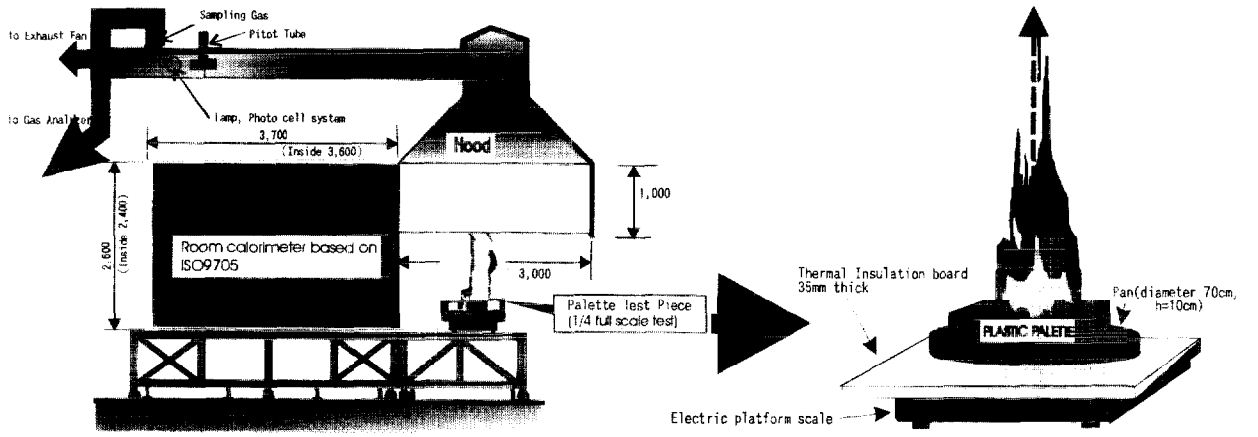
Relation between PHR by cone calorimeter & other flammability test classification

The PHR obtained by the cone calorimeter seems to be one of the important indices for fire safety. Figure 5 shows the relation between the PHR and flammability classifications obtained in other tests (oxygen index and UL94 test) in the 1st and 2nd stage. As shown in this Figure, the PHR decreases as the oxygen index increases. This tendency can be clearly observed in the 2nd stage test for non-halogen FR treated resins (Figure 5 (b)). When oxygen index is more then 26, heat release rate is very low and the UL94 classification corresponds to "V0" consistently. The Oxygen Index 26 is the criterion value to determine "flammable/inflammable synthetic resin" in Japan as mentioned above. However in the 1st stage test, even though the bromine containing FR treated resins give more than 26 oxygen index value and V0 or V1 UL94 classification, the PHR under radiant heat flux becomes higher than that of other FR resins. It indicates that the halogen containing flame retardant material retards ignition time, however once it burns, halogen chemicals burns as additional heat source. The "V2" classification resins tested by the UL94 test are in the range between 19 and 24 of oxygen index, however clear relation between oxygen index and "V2" and "V2 out" classifications are not found.



(a) 1st stage test result (b) 2nd stage test result

Figure 5. Relation between PHR by cone calorimeter & other flammability test classification



(a) Installation (b) Detail of 1/4 piece of plastic pallet burning test

Figure 6. Experimental Setting for 1/4 piece of plastic pallet burning test

The 3rd stage development

Test resin and flammable test : In the 2nd stage, three flame retardant plastics, Ex-752 ($Mg(OH)_2$(50wt%), EX-748 ($Mg(OH)_2$[50wt%]+r-P[4.6%]) and EX-750 ($Mg(OH)_2$ [50wt%]+r-P[9.1wt%]) are finally selected from the view point of both mechanical and combustion properties for plastic pallets. The two of them added with r-P correspond to "V0" classification by the UL94 test. Plastic pallets in full scale size are produced of the material and the combustion tests are conducted with furniture colorimeter as shown in Figure 6 and Table.3.

The size of the plastic pallet is about 1,110 x 1,110 x h.150 mm. 1/4 piece of the pallet is used for the burning test. The test piece is located on the stainless steel pan of 70cm diameter and 10cm depth as shown in Figure 6. Three sizes of methanol pan are adopted as ignition heat source, i.e., 5cm diameter pan with 20 cm^3, 10cm with 40cm^3 and 20cm with 80 cm^3 methanol. The ignition heat source is located at the center of the 70 cm diameter pan. In addition, solid fuel of 3cm diameter x h.1cm tablet made of Hexamethylenetetramine is used and put on the top surface of the plastic pallet. This supposes the case when burning firebrands of dripped plastic cause fire to spread downward.

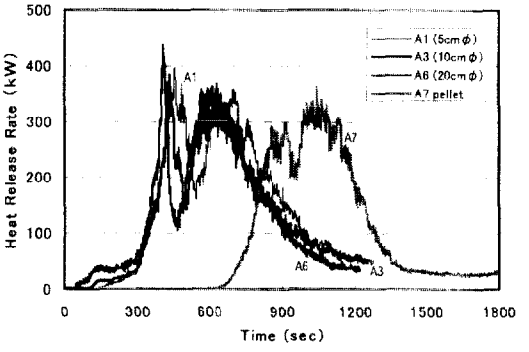
Table 3. Burning test list of 1/4 piece of full scale pallet by furniture caloriemeter

No.	Test Pallet [weight %]	Ignition Heat Source	PHR (kW)	time (sec)
A1	Pallet-PP (non-FR treated PP)	5cm ϕ [1)]	398	458
A2		5cm ϕ	484	502
A3		10cm ϕ	385	436
A4		10cm ϕ	432	378
A5		20cm ϕ	401	492
A6		20cm ϕ	439	410
A7		tablet	363	775
A8		tablet	526	526
A9		tablet	752	651
B1	Pallet 752 ($Mg(OH)_2$ [50])	5cm ϕ	83	1118
B2		10cm ϕ	88	1144
B3		10cm ϕ	82	510
B4		20cm ϕ	108	661
B5		tablet	N/A.	N/A.
C1	Pallet 748 (r-P[4.6] +$Mg(OH)_2$[50])	5cm ϕ	4	456
C2		10cm ϕ	5	218
C3		20cm ϕ	25	1206
D1	Pallet 750 (r-P[9.1] +$Mg(OH)_2$[50])	5cm ϕ	2	338
D2		10cm ϕ	5	266
D3		20cm ϕ	31	448

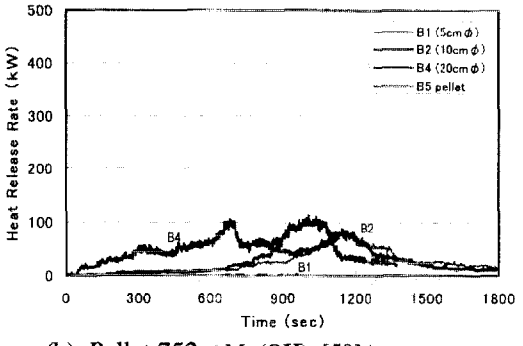
cf. 1) Value of ignition heat source is diameter of methenol pan

Furniture calorimeter test result : Figure 7 and Table 3 show the heat release rate of the 1/4 piece of full scale pallet. In the case of the pallet made of base PP, the differences of ignition heat source do not affect the heat release rate. Heat release rate reaches to almost 450kw at first. Afterwards the heat release rate decreases while the plastic pallet is melting, then heat release rate increases again as a pool fire. When the solid tablet fuel is used as an ignition heat source, ignition time gets longer, however once it starts to burn, the combustion behavior appears to be nearly the same as in the cases of other ignition heat sources. The heat release rate of plastic pallets made of PP added with only $Mg(OH)_2$ is relatively low, however once it burns, the burning continues in spite of the size of ignition heat source. In contrast when r-P is added, the heat release rate becomes lower and the burning of the pallets can not be sustained without ignition heat source.

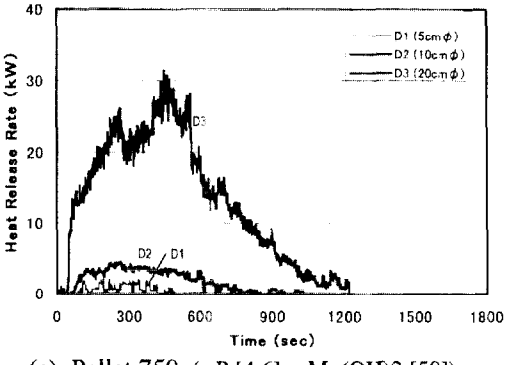
Mechanical properties : In this projects, mechanical properties of plastics have been examined by standard tests. The result indicates that "the flexural rigidity" of test pallets are about twice as strong as that of original non-FR treated pallets. "The sliding friction" of test plastic pallet does not change. However "the dropping impact test" results indicate that plastic of "EX-748" and "Ex-750" added with r-P are lower than that of standard ones. Also density of the developed plastic pallets is about 1.4 to 1.6 times heavier. These are remained for future tasks to be solved.



(a) Pallet -PP (non-FR treated poly-propyrene)



(b) Pallet 752 ($Mg(OH)_2$ [50])



(c) Pallet 750 (r-P.[4.6] + Mg(OH)2 [50])

Figure 7. Heat release rate of 1/4 piece of full-scale pallet by furniture calorimeter

CONCLUDING REMARKS

Development of fire-retardant plastic pallets has been conducted in collaboration with NRIFD and Association of plastic pallets and a fire retardant chemical company. Flammability and mechanical properties of some synthetic resins are examined in the two test stages to screen the material. The flammability of the resins are tested by cone calorimeter, UL94 and Oxygen Index Test. Finally appropriate combinations of $Mg(OH)_2$ and red-Phosphorus are selected as FR retardant additives. Major results obtained in the tests are as follows.

1) FR resins added with halogen containing retard the ignition time. However, once it burns, the FR effect decreases and more combustion products are generated.
2) In the case of FR resins added with magnesium hydroxide, the heat release rate and peak heat release rate become relatively low. Also combustion products are suppressed and mechanical properties satisfy practical requirements.
3) Red-Phosphorous additive has an effect on mitigation of the heat release rate, when it is used in combination with other FR chemicals. Single use of the r-P does not have a big FR effect and produces more combustion products.
4) In general the peak heat release rate decreases as the oxygen index increases as for non-halogen FR treated resin. When oxygen index is over 26, heat release rate becomes very low and the UL94 classification corresponds to "V0".
5) The prototype of FR plastic pallets is produced of the combination compound of $Mg(OH)_2$ and red-Phosphorus, and the fire test is conducted with furniture calorimeter. The FR effects of those plastic pallets are examined in full scale and sufficient FR effects are obtained with satisfaction. Along with the flammability tests, some of the mechanical properties are examined and a few mechanical properties are needed to be improved such as the dropping impact durability etc.

REFERENCES

1. Hiki Fire Department ; "Toyo Seikan Corp. Saitama Factory, Investigation report of warehouse fire having automatic high palletized rack storage *(in Japanese)*", (1996)
2. Oohashi, M., "Present Situation of Fire Detection and Extinguishment in Storage Facilities *(in Japanese)* ", Forum Text, Japan Assoc. for fire Science and Engineering, (1998)
3. Naba, H., Morikawa, T., and Kobayasi,T. "Evaluation of Combustion Characteristics of Red Phosphorus Fire Retardant Materials by means of Cone Calorimeter *(in Japanese)* " , Rep. of NRIFD No.81 (1996)
4. Scudamore, M.J.,Briggs,P.J. and Praager, "Cone Calorimetry : A review of Tests Carried Out on Plastics for the Association of Plastic Manufactures in Europe", Fire and Materials, Vol.15, No.2 April/June (1991)
5. Nishizawa, H.. "Fire Retardant treatment for Polymer *(in Japanese)*", Taiseisya, pp.120-135 (1993)
6. UL94, "Testing for flammability of plastic materials for parts in devices and applications"
7. JIS K7201, "Combustion Test method for high molecular polymer by oxygen index method *(in Japanese)*"
8. UL 2335 "Plastic Pallet Classification"