Development of Lightweight Fire-resistant Putty

Hidenobu Mochigase[*1], *Yutaka Suzuki*[*1], *Eiji Miki*[*2],
Shota Mitsumune[*2], *Yoshihiko Ohba*[*2], *Yukihiko Inoue*[*2]

ABSTRACT For the fire protection measure method of cables and through-holes of wall and floor (closing the openings), it is necessary to use the fire-resistant materials from the viewpoint of fire regulations. However, because the fire-resistant putty which is commonly used has large specific gravity and is heavy, the need of lightweight putty is very high from the viewpoint of carrying and workability during the construction. Therefore, the fire-resistant putty "DANSEAL-KP" which achieved a significant weight reduction and has half the weight in comparison to the conventional one has been developed. As a fire protection measure method at the various penetrations of wall and floor, the Minister of Land, Infrastructure, Transport and Tourism certificate of the fire-resistant property defined in the Building Standards Act has been obtained.

1. INTRODUCTION

In the buildings, when the various types of cables and pipes are installed, the through-holes (openings) will be created at the wall or floor which divides the rooms or the machines. If these openings are not sealed properly for the fire protection, the material such as a cable jacket gets burned like fuse and the fire will spread to the next room. Therefore, the opening filling material requires the fire-resistant property as per the Building Standards Act and it is mandatory to take fire protection measures using the material and construction method which obtained a public certification[1)].

A typical construction method is to fill the openings with putty which has a fire-resistant property (Figure 1). This fire-resistant putty consists of resins such as a liquid rubber or oil, inorganic filler and a flame retardant material. There are curable and non-curable putties after construction. Curable putty can hold the openings firmly after construction, but because the dismantling is difficult, there is a drawback that it cannot cope with the re-construction associated with renovation of building or expansion of the equipment (cable re-installation). On the other hand, the contractor prefers non-curable putty because the dismantling and the re-construction for the cable re-installation are easy. Because of the large amount of flame retardant material which has large specific gravity to maintain enough fire-resistant property, many non-curable putty products have large specific gravity and are heavy in comparison to curable putty. In the fire-resistant measures at the high elevation place such as the ceiling or the narrow space, the heavy putty has the disadvantage for carrying and construction so there is a need to develop the lightweight putty.

In addition, several requirements listed below were considered.

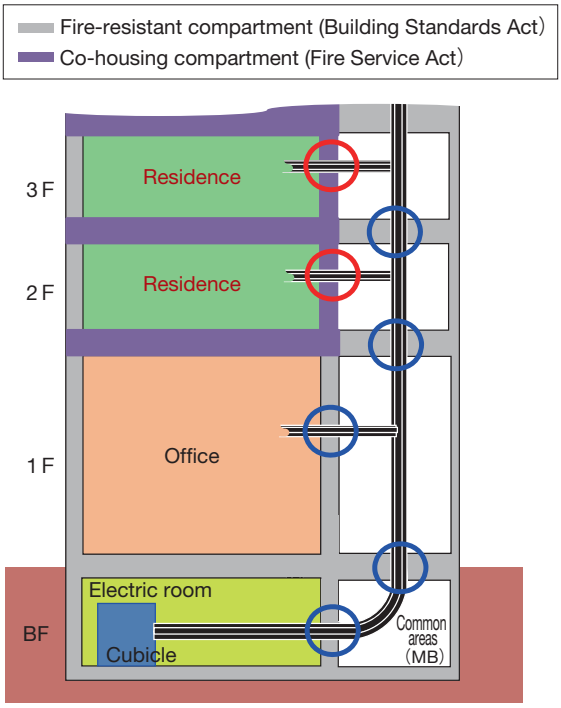


Figure1 Usage example of fire-resistant putty.

*1 Furukawa Electric Co., Ltd. Research & Development Div. Polymer Materials R&D Laboratories
*2 Furukawa Techno Material Co., Ltd. Fire Prevention Div.

1. To work comfortably even at the construction site at the low temperature.
2. The putty is hard to come off with good adhesion between cables and building materials.
3. To have long term stability such as insulating properties and waterproof properties.

As for the fire-resistant property, the performance which is capable to seal the openings effectively without burning out and without losing the shape in the fire-resistant test of one hour was targeted and the examination of the composition was conducted repeatedly. As a result, we have succeeded in the development of a putty which has a specific gravity of lower than 1.0. The product is lighter than before and has an excellent fire-resistant property.

2. INVESTIGATION OF COMPETITOR'S PRODUCTS

In recent years, new fire-resistant putty manufacturers entered the market and dealt with similar products. Our main product is non-curable fire-resistant putty, but it becomes difficult to differentiate the putty only by its fire-resistant property. Therefore, we investigated the distribution of the specific gravity and the price per usage for the competitor's fire-resistant putty in order to find an area that can differentiate us from other companies (Figure 2). As a result, it was found that there is no rival product in the area where the specific gravity is less than 1.0 and the price is inexpensive. So we targeted the area to develop the putty which performance falls in this area.

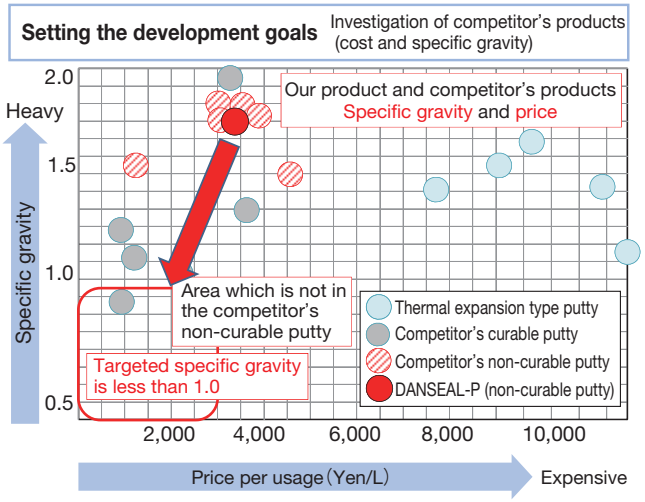


Figure 2 Investigation result of competitor's products (Relationship between price per usage and specific gravity)

3. EXAMINATION OF WEIGHT-SAVING MATERIALS

For weight-saving, the survey results of weight-saving materials are summarized in Table 1. From the view point of weight-saving effect (specific gravity) and share resistance (collapse resistance), the artificial inorganic hollow filler L3 and the organic hollow filler L4 were selected as candidate materials.

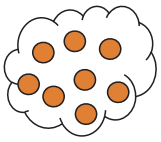
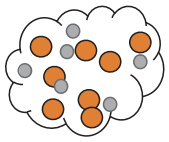
Table 1 List of weight-saving materials.

Weight-saving material	Material	Particle size (um)	Specific gravity	Share resistance	Shape
L1 (Artificial inorganic hollow filler)	Inorganic	15-135	0.1-0.5	×	Spherical form
L2 (Natural inorganic hollow filler)	Inorganic	150 (ave.)	0.5-1.0	×	Indeterminate form
L3 (Artificial inorganic hollow filler)	Inorganic	5-300	0.5-1.0	△	Spherical form
L4 (Organic hollow filler)	Organic	50-70	0.1-0.2	◎	Spherical form

◎ : No collapsing △ : Partial collapsing × : Collapsing

To investigate the effect of the weight-saving and the fire-resistant properties, oil, inorganic filler and weight-saving material are mixed and processed into a putty-like and then it was evaluated. As the inorganic filler, the material which there was a good effect on the shape stability after burning of putty in the past examination is used (M2 in Table 3 of next chapter). When only artificial inorganic hollow filler L3 which has high fire-resistant property is used as a weight-saving material, the specific gravity of the putty is calculated as 0.99, but the actual one was 1.16. From this fact, L3 is easily collapsed and it is expected that it cannot withstand the kneading process. On the other hand, in the case that only organic hollow filler L4 is used as weight-saving material, the actual specific gravity after kneading was exactly same as the calculated value. From this fact, it was confirmed that the L4 is hard to collapse, even after kneading process. However, since L4 is organic, it is burnt out in a fire so its fire-resistant property was insufficient. In order to take an advantage of those 2 hollow fillers and compensate for the disadvantage, the mixing composition of 2 hollow fillers is examined. As a result, the fire-resistant putty which has a specific gravity exactly same as the calculated value and holds the shape after a fire has been developed. It was found from above results that the putty which has simultaneously a lightweight and a fire-resistant property can be obtained by mixing the 2 types of weight-saving materials.

Table 2 List of experiment for weight-saving material examination.

Artificial inorganic hollow filler L3	Organic hollow filler L4	L3+L4 Mixed Composition
		
Wt.% (Oil, L3 ,M2) 30.2%, 32.1%, 37.7% Gravity Cal culated : 0.99 Actual : 1.16	Wt.% (Oil, L4,M2) 42.4%, 4.5%, 53.1% Gravity Calculated : 0.99 Actual : 0.99	Wt.% (Oil, L3, L4, M2) 41.0%, 3.8%, 3.8%, 51.3% Gravity Calculated : 0.99 Actual : 0.99
× Hollow filler collapsed →Little effect for weight-saving ◎Not burn out	◎Hollow filler not collapsed × Burn out	◎Hollow filler not collapsed ○There is residue

4. OPTIMIZATION EXPERIMENTS OF FIRE-RESISTANT PUTTY COMPOSITION

The inorganic filler other than the oil and the weight-saving material described above is used for the constituent materials of the fire-resistant putty. Optimum amount of the inorganic filler was examined. The inorganic fillers which were investigated this time are listed in Table 3. M1 (aluminum hydroxide) and M3 (magnesium hydroxide) which are metal hydroxide among inorganic fillers are useful because they exhibit a flame retardant effect by a dehydration endothermic reaction[2)-4)]. This time, M1 which has a material cost lower than M3 is selected as one of the inorganic filler. Also, by mixing M2 into the putty, the effect that the residue of putty during the combustion becomes hard to collapse was confirmed. Therefore, it was decided to adopt the combination of M1 and M2. Then the basic composition of oil, weight-saving material, inorganic filler M1 and M2 are selected and the optimization experiment of inorganic filler mixing ratio was conducted.

Table 3 List of inorganic fillers.

Inorganic filler	Specific gravity	Flame retardant property	Hardness of collapsing after combustion
M1 (Metal hydroxide)	2.0-3.0	◎	△
M2 (Natural mineral)	2.0-3.0	○	◎
M3 (Metal hydroxide)	2.0-3.0	◎	△
M4 (Natural mineral)	2.0-3.0	△	×

◎ : Excellent ○ : Good △ : Slightly poor × : Poor

A simplified fire-resistant test was conducted by using an electric furnace. The evaluation method is described below.

①The obtained composition is formed into a cube.
②The cube is put into the preheated furnace and left for a certain time.
③The cube is removed from the furnace after the predetermined time and observed.

The evaluation was done by checking the shape of the residue after heating visually and by rating the easiness of collapse when touching it.

As illustrated in the pictures of before and after test, a large difference of the residues after heating test was observed (Figure 3). In this evaluation, the composition which is already broken when removed from the electric furnace or collapses easily when the residue is touched, has a poor fire-resistant property also in the case that it is subjected to a combustion test simulating the actual construction conditions. On the other hand, in the case when the residue keeps the shape without collapsing and does not shrink even after this test, the tendency that the fire-resistant property is improved in the combustion test of actual construction conditions was confirmed. The results were summarized in Figure 4. It was found that if the ratio of the inorganic materials (total volume of artificial inorganic hollow filler L3, inorganic filler M1 and M2) is more than 25 volume % and the ratio of M2 within the inorganic fillers is more than 0.4 (to be 1 by adding M1 and M2), the fire-resistant putty can be obtained.

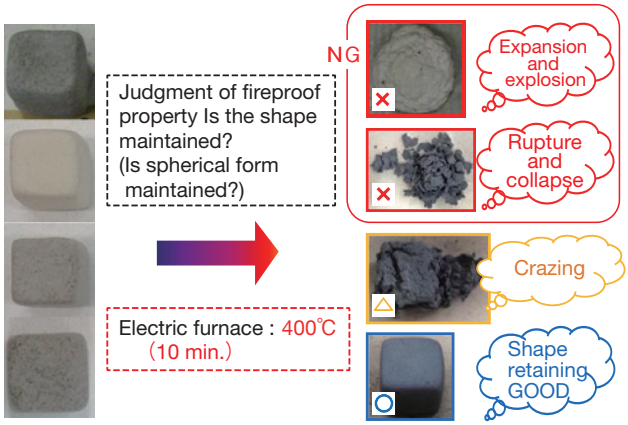


Figure 3 Judgment criteria of the electric furnace test.

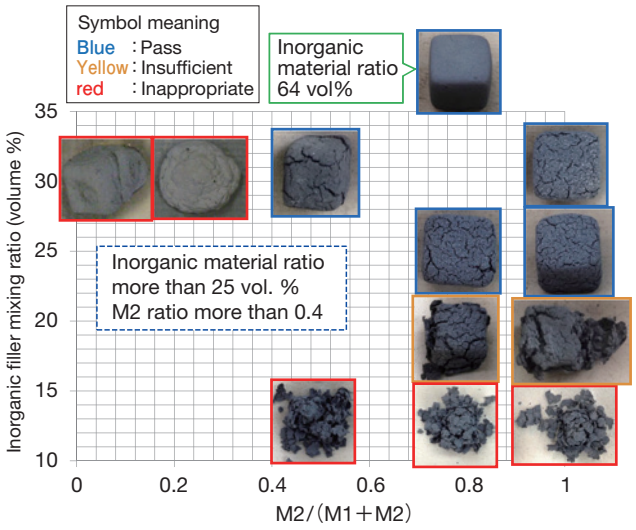


Figure 4 Optimization experiment for inorganic filler mixing ratio.

5. WORKABILITY EVALUATION AT THE LOW TEMPERATURE (TEMPERATURE DEPENDENCE OF PUTTY HARDNESS)

In addition to the fire-resistant property, the fire-resistant putty requires the easy workability without hardening even at the construction site at the low temperature of the winter season. Because many conventional types of putty become hard at the low temperature, they are usually used after warming. Therefore, it is necessary to examine the hardness at the low temperature for this development. Thus, by conducting the test to investigate the easiness of compression (easiness of collapse) of putty, the comparison with competitor's product was carried out. The testing method is shown below (Figure 5).

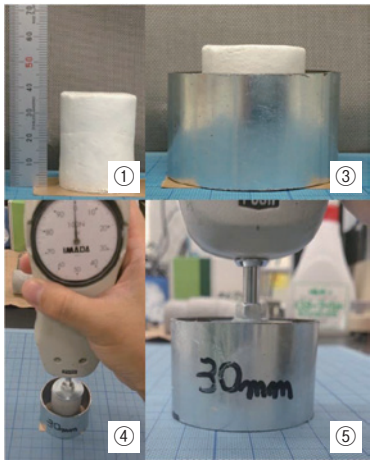


Figure 5 Testing method of compression.

①The putty is formed into cylindrical shape.
②Leave it at measuring temperature for a certain period of time.
③The sample is placed into the center of a steel pipe which is shorter than sample as shown in the picture and has a margin space in a diameter.
④Press the push-pull gauge just above the sample and crush the sample at a constant rate.
⑤Crush the sample till the height of putty reaches the same height of the steel pipe and measure the maximum force. (The force N which requires collapsing putty.)

In case of the competitor's product of A and B, the force became more than 100 N (Figure 6), which is difficult for hand mixing. On the other hand, it was confirmed that the newly developed "DANSEAL-KP" is difficult to become hard (about 70 N) and has an excellent workability at the low temperature by optimizing the combination of the resin components.

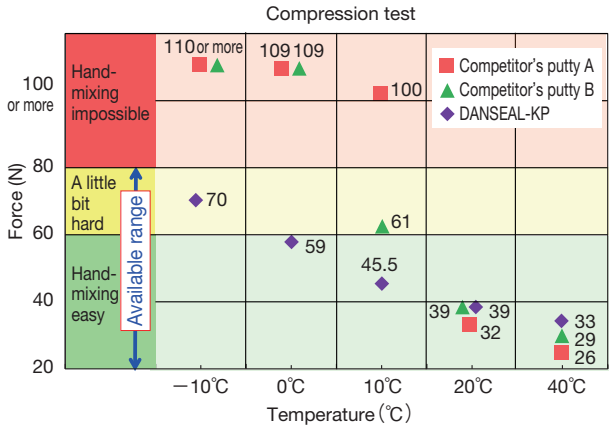


Figure 6 Relationship between workability of putty and working temperature.

6. EXAMINATION FOR FLAME RETARDANCY IMPROVEMENT OF THE FIRE-RESISTANT PUTTY COMPOSITION

V-0 of UL 94 vertical flame test is mentioned as one of the most severe flame retardant level. The study was conducted to meet this flame retardant level. The testing method is to broil the putty formed in a strip as shown in Figure 7 in the flame for a certain period of time from below, to measure the combustion time and to make the determination whether the fire disappears within a prescribed time in seconds.

Figure 7 Vertical flame test (UL-94).

The samples, for which the types of flame retardant materials and quantity were modified, were prepared and the combustion test was conducted. The flame retardant materials which can achieve V-0 were F2 and F4 which are phosphorous-based. F2 is treated as a dangerous material in some areas and needs attention in handling. Therefore, F4 is used as the flame retardant material by mixing it to the resin at a weight ratio of more than 5% by weight this time.

Table 4 Physical property list of flame retardant materials.

Flame retardant materiala	Specific gravity	Flame retardant property
F1 (Phosphorous based)	1.0-2.0	×
F2 (Phosphorous based)	2.0-3.0	○
F3 (Inorganic)	2.0-3.0	×
F4 (Phosphorous based)	1.0-2.0	○

○ : Acceptable × : Failure

7. FIREPROOF TEST

Assuming the setup of the actual situation where the round hole of 160 mm in diameter is set through the autoclaved lightweight concrete of 75 mm thickness, the fire-resistant putty is applied to the testing specimen through which the cable and pipe are penetrating as shown in Figure 8. The 60 minutes fire-resistant test based on the testing method certified by the Minister of Land, Infrastructure, Transport and Tourism was conducted. The heating was performed according to the standard heating curve based on ISO 834 in Figure 9 and heated to 945℃. As a backup material to prevent putty fall, a block of a ceramic blanket wrapped by nonwoven fabric is built in the openings and the developed putty was filled in it with a thickness of 10 mm, 20 mm and 50 mm. As per the result of the fire-resistant test (Figure 10), it was confirmed that even the putty of 10 mm thickness has a sufficient fire-resistant property (Table 5). This is one third filling thickness in comparison to the conventional construction method. As per these testing results, it is confirmed that this newly developed product, consisting of a weight-saving material, an inorganic material and a flame retardant material mixed into the base oil at optimum ratio, has an excellent fire-resistant property and also has a specific gravity of less than 1.0. This means the fire-resistant and lightweight properties are both satisfied.

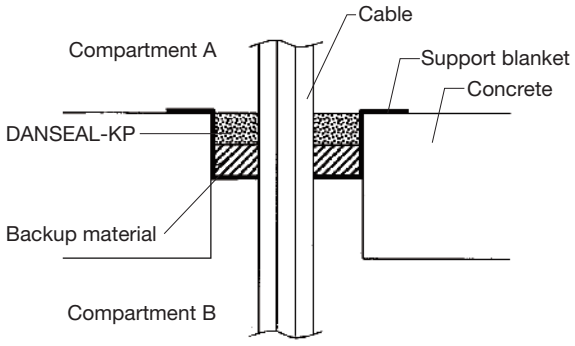


Figure 8 Example of construction method.

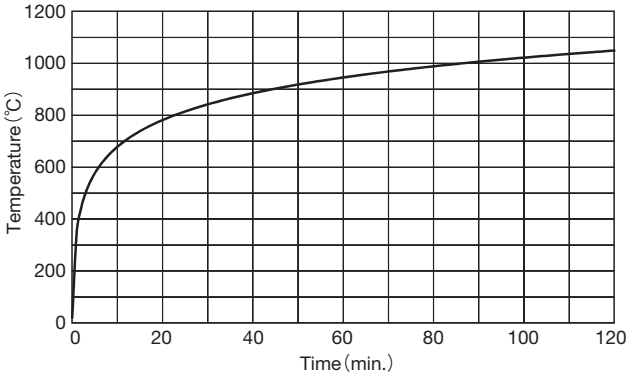
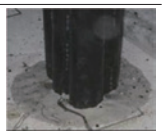


Figure 9 Standard heating curve based on ISO834.

Figure 10 Pictures of fire-resistant test.
Above Upper view
Below Entire view

Table 5 Optimization of putty thickness.

Used Putty	DANSEAL-KP		
Filling thickness (mm)	10	20	50
Before test Picture			
After test Picture			

8. CONCLUSION

By this development, the non-curable putty which is not available in the current market and has a specific gravity of less than 1.0 has been developed. This newly developed product has an advantage that there is a property which is difficult to harden even at the low temperature. This product can be used in the construction method of round hole in wall and in floor, and has obtained the Minister of Land, Infrastructure, Transport and Tourism certificate. This product has been already commercialized as a part of the materials for the kit of "ICHIJIKAN PAT" and "ICHIJIKAN MARUYUKA". In the future, we will try to get certification of other construction methods in order to use it in various other applications.

REFERENCES

1) Building Standard Low Enforcement Ordinances, Article 129-2-5, Section 1, Paragraph 7
2) Hitoshi Nishizawa: "Flame Retardant, Flame Retardant Materials Utilizing Technology" CMC Publishing Co., Ltd., (2004), 119 (in Japanese)
3) Hitoshi Nishizawa: "Development of New Polymer Materials Flame Retardant Technology –State of the Art Technology, Materials, Recycling, Evaluation, Patent and Regulatory", GIJYUTUKYOUIKU SYUPPANNSHA, (2006), 125 (in Japanese)
4) Hitoshi Nishizawa: "Flame Retardant Polymer =Its Chemistry and Actual Technology=", TAISEISYA LTD. (1989), 71 (in Japanese)