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High-durability Corrosion Protection of Marine Steel Structures Using Titanium Covers

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Abstract

Petrolatum lining is used increasingly for corrosion protection of substructures of piers and quays composed of steel pipe piles, sheet piles and pipe sheet piles. Conventionally, FRP covers were used to protect such petrolatum lining, but FRP degrades through exposure to ultraviolet light, and its impact resistance is insufficient. As an improvement, Nippon Steel & Sumitomo Metal Corporation, jointly with Nippon Steel & Sumikin Anti-Corrosion Co., Ltd., has developed a petrolatum covering method using titanium, excellent in resistance to corrosion and impact, and confirmed the durability of the covers through application to piers and quays in the premises of its steelworks. This paper presents the developed method for protection of marine steel structures, and evaluation of its durability through impact tests and measurement of the oil content in the lining.

1. Introduction

Steel pipe piles, sheet piles and pipe sheet piles are used for the substructures of many piers, quays and other port structures, and they are constantly exposed to the severely corrosive environment of saltwater and salt grains. Steel structures in such marine environment are protected from corrosion, in most cases, by a lining from the tidal zone to the splash zone and the atmospheric zone above the water. Of the various lining methods using organic or metal materials, petrolatum lining is widely used due to easy pretreatment and good durability. Fiber-reinforced plastics (FRP) have been used as the protective covers for petrolatum lining, but there is concern about their durability because they are prone to degradation through exposure to ultraviolet light and cracking due to the impact of floating objects such as logs. [1)]

As a countermeasure against the above, we devised a method for protecting petrolatum lining using titanium covers, which are excellent in the resistance to impact and corrosion in marine environments, and applied the method (hereinafter called the TP method) to many steel structures of port facilities in and outside the premises of the steelworks of Nippon Steel & Sumitomo Metal Corporation. [2)]

The present paper reports the effectiveness of the titanium covers for high-durability petrolatum corrosion protection lining confirmed through durability evaluation by an impact test and measurement of the oil content in the petrolatum lining as well as an exposure test in a real environment.

2. Petrolatum Anticorrosive Lining

The petrolatum corrosion protection method consists of shielding steel surfaces from corrosive factors using an anticorrosion material mainly composed of petrolatum, a mixture of petroleum wax extracted from petroleum distillation residue and corrosion suppression agents, excellent in water repellency and electrical insulation, and fitting protective covers onto the lining layer. It is applied mainly to steel pipe piles, sheet piles and pipe sheet piles forming the substructures of port facilities, due to the advantages of simple pretreatment work and applicability to old structures as well as new ones. [3)]

For steel pipe piles, there are two types of protective covers: a flange type and a flangeless type. When the covers are made of FRP, the flange type is more common. In the case of quay walls of sheet piles or pipe sheet piles, on the other hand, stud-bolt type covers are used, which are fixed to the object piles using fixing belts with stud bolts. The protective lining layer is composed of a base coat of petrolatum paste or petrolatum paste tape, which is nonwoven fabric

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cloth impregnated with petrolatum, and a top coat of petrolatum anticorrosion tape, which contains filler material and anticorrosive agents in addition to petrolatum to increase protective effects.[4, 5)]

The protective covers are formed beforehand according to the shape of the piles to be protected, and in consideration of the cost and the ease of forming, plastics such as FRP are widely used as the cover material (see **Photo 1**). They are, however, prone to degradation due to ultraviolet light and cracking due to collision with floating objects such as driftwood, and not considered sufficiently durable. To this end, aiming at improving the durability of petrolatum corrosion protection, we developed the TP method using titanium, which exhibits an excellent corrosion resistance (corrosion rate less than 0.001 mm/y[6)]) even under severe marine conditions, for the protective covers.

3. TP Corrosion Protection Method

3.1 Structure and work flow by TP method

Figure 1 shows the variations of the TP method. In TP-1, the pipe pile coated with the petrolatum protective layer is wrapped with a titanium cover sheet, and the titanium sheet is tightly fixed to the pile surface by fitting a sheath pipe of titanium to its two vertical ends, which are turned outwards beforehand to engage with the pipe. In TP-W, in contrast, the titanium sheet is fixed by lapping and welding the two vertical ends together using a resistance welder.

Figure 2 illustrates the configurations of TP-1 for pipe piles, TP-SP for sheet piles and TP-SPP for pipe sheet piles. The petrolatum protective layer is wrapped with a shielding sheet to prevent the oil component of the petrolatum from flowing out and keep it watertight, and the inner surface of the titanium cover is coated with a cushioning material of foamed polyethylene (PE). By the tightening pressure of the titanium cover, it is possible to press the petrolatum lining layer onto the pipe pile evenly and have it protect the steel without gaps. The titanium covers for pipe piles are easier to set, and their thickness is 0.6 mm. Those for sheet piles and pipe sheet piles, in contrast, are required to have a higher rigidity for edge forming for fitting, and their thickness is 1.0 mm.

Figure 3 shows the flow of the cover fitting work of TP-1. The work is performed by two or more divers. Scaffolds are erected around the pile to be protected, and then marine life, rust layers and protrusions on the steel surface are removed using three types of scrapers. The sheath pipe is placed while the titanium cover is tightly pressed by straps to the petrolatum protective layer so that there are no gaps between them. After the cover is fixed, the circumferences at its upper and lower ends are sealed with water-hardening epoxy putty. The work flow is basically similar for TP-SP and TP-SPP, but there are more work steps because, unlike TP-1 or TP-W, the titanium covers are fixed with bolts to the sheet pile or pipe sheet pile, where required, and it is necessary to weld steel belts with stud bolts to the steel after the scraping work.

3.2 Evaluation of impact resistance by drop weight test

In the development of the titanium cover, a drop weight test was conducted to confirm the impact resistance of titanium sheets.[7)] **Figure 4** shows the test piece configuration, and **Table 1** the thicknesses of the FRP/titanium cover. To simulate real environmental conditions, the test pieces were composed of the following from the bottom to the top: a steel plate, 400×900×16 mm in size, with two stud bolts, petrolatum tape covering the upper surface of the plate, a sheet of foamed PE as a cushioning material and a specimen of the

Photo 1 Steel pipe piles with petrolatum lining and FRP covers

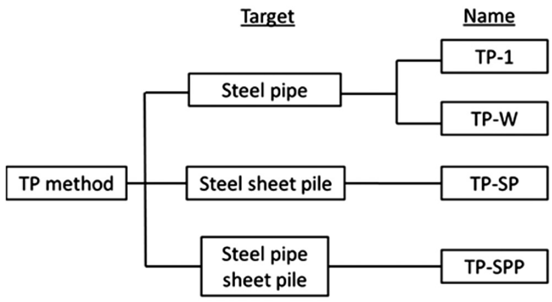

Fig. 1 Type of TP method

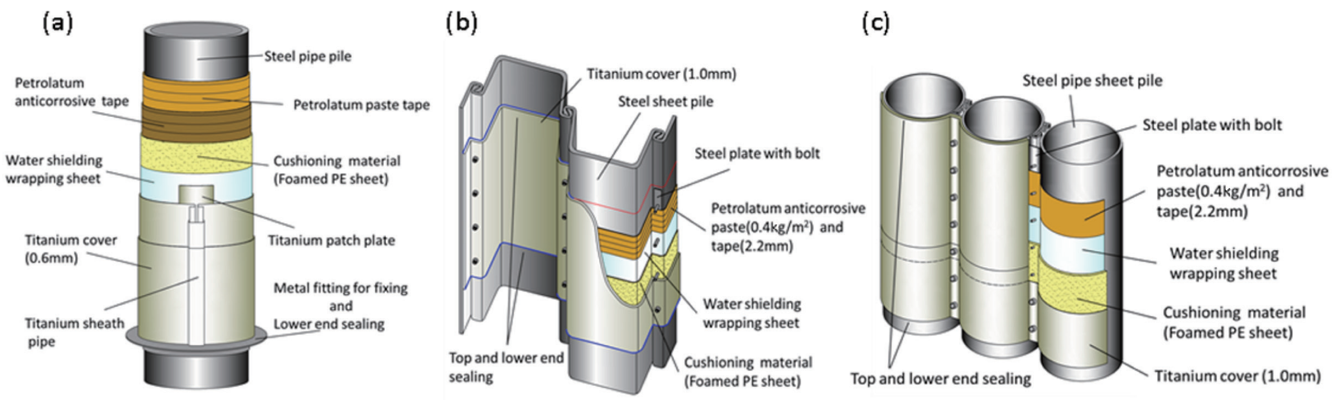

Fig. 2 Configurations of different types of TP method
(a) TP-1, (b) TP-SP, (c) TP-SPP

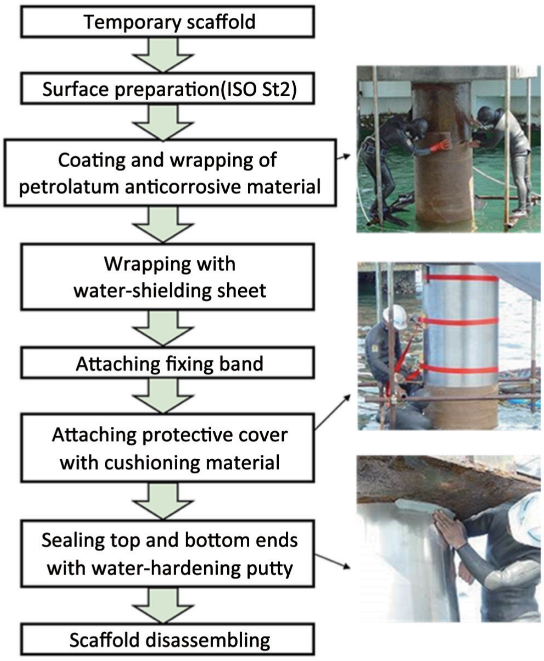

Fig. 3 Work flow of TP-1 (sheath pipe type)

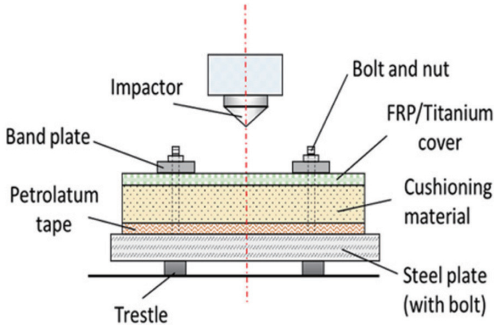

Fig. 4 Test piece for impact test

Table 1 Test-piece thickness

Cover material	Thickness (mm)		
	Protect cover	Cushioning material	Petrolatum tape
Titanium	0.6	15.0	2.2
	1.0		
FRP	2.5		
FRP (exposure sample)			

Table 2 Impact test results (×: Cracked, ○: No cracking)

Test cover level	Impact energy (N･m)														
	5.0	10.0	15.0	20.0	30.0	50.0	70.0	100.0	120.0	140.0	150.0	200.0	300.0	400.0	500.0
Titanium cover (0.6mmt)	–	–	–	–	○	○	○	○	○	○	×	×	×	×	–
Titanium cover (1.0mmt)	–	–	–	–	○	○	○	○	○	○	○	○	○	×	×
FRP cover (2.5mmt)	○	○	×	×	×	×	×	×	–	–	–	–	–	–	–
FRP cover (exposure sample)	○	×	×	–	×	×	×	×	–	–	–	–	–	–	–

protective cover. Titanium plates 0.6 mm thick for steel pipe piles and those 1.0 mm thick for steel sheet piles and pipe sheet piles were used as the protective cover. New FRP plates and old ones exposed to a real environment for 25 years, each 25 mm thick, were used as comparative specimens. The impact was applied using a steel impactor 60 mm in diameter, 50 mm in height and 0.6 kg in weight with an additional weight of 30 kg. The protective function of the cover is maintained as long as it is not cracked, and therefore, the impact resistance was judged by the cracking or otherwise of the specimen; the existence of a through hole and water penetration was checked visually and by a pinhole test.

Table 2 shows the cracking or otherwise of the specimens, and **Fig. 5** the appearances of the upper and lower surfaces of the specimens after the test. As the table shows, the new FRP covers cracked under an impact energy of 15 N·m. In contrast, the 0.6-mm-thick titanium sheets cracked under an impact energy of 150 N·m, and those 1.0 mm thick did so under the same of 400 N·m, which means that a 0.6-mm-thick titanium sheet has an impact resistance 10 times that of an FRP cover, and a 1.0-mm-thick sheet 27 times. Comparing titanium sheets with different thicknesses, the impact resistance of a 1.0-mm-thick sheet is 2.5 times or more that of a 0.6-mm-thick one.

The impact energy required for cracking an FRP plate exposed for 25 years (10 N·m) is only 2/3 that for cracking a new one (15 N·m), which indicates that the mechanical properties of FRP are expected to deteriorate by aging during exposure.

As seen in Fig. 5, under an impact of 150 N·m, the titanium sheet specimen 0.6 mm in thickness deformed by elongation and partially cracked in the area of impact. On the other hand, under an impact of 30 N·m, the FRP specimens cracked radially from the point of impact. This difference in the mode of failure is presumably because, whereas plastics fail by brittleness, metals do so by ductility.

The above test result shows that titanium covers are more resistant to impact than FRP covers and thus are more adequate for maintaining the protective effects for a long period.

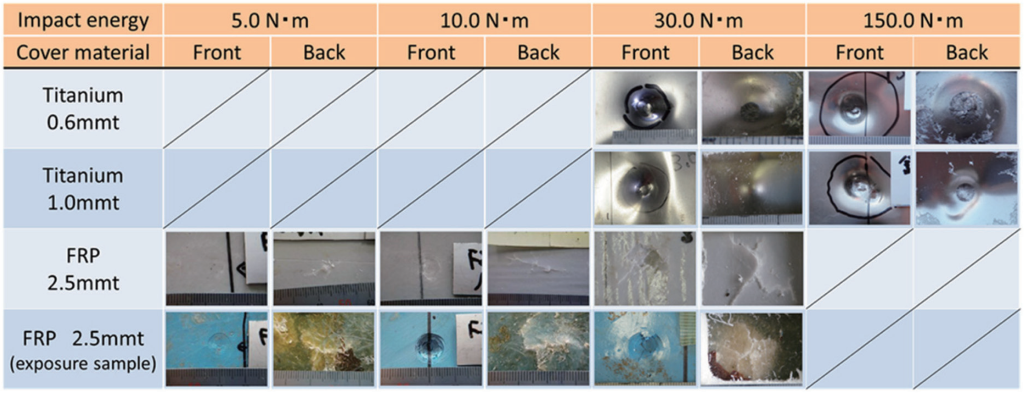

Fig. 5 Appearances of test pieces after impact test

Table 3 Application references of TP method inside company's steel-works

Time of construction	Works	Object piles	Number of piles	Diameter/ Size (m)	Coating area (m^2)	Ti weight (kg)
September 2001	Oita	Steel pipe pile (TP-1)	2	1016, 1500	20	100
September 2003	Yawata	Steel pipe pile (TP-1)	45	355 ~ 650	150	500
March 2006	Kimitsu	Steel pipe pile (TP-W)	8	508	30	112
September 2006	Kamaishi	Steel sheet pile	5	FSP-Ⅳ type	9	27
February 2007	Nagoya	Steel sheet pile	12	FSP-VL type	18	55
November 2007	Muroran	Steel sheet pile	6	FSP-Ⅲ type	6	17
January 2010	Hirohata	Steel pipe pile	4	406	18	55
November 2012	Muroran	Steel pipe sheet pile	4	900	11	41
April 2013	Kashima	Steel pipe pile (TP-1)	8	800, 1000	63	187

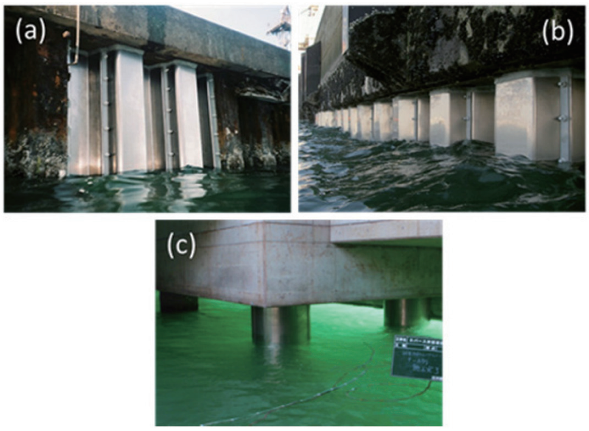

Photo 2 Application examples of TP method inside company's steelworks (a) Kamaishi, (b) Nagoya, (c) Kashima

3.3 Application references of TP method in steelworks premises

Table 3 lists the application references of the TP method at the steelworks of Nippon Steel & Sumitomo Metal, and **Photo 2** the examples at Kamaishi, Nagoya and Kashima Works (TP-S, TP-S and TP-1, respectively).

Up to 2006, the TP method was applied mainly to steel pipe piles in the forms of TP-1 and TP-W, but from 2007, TP-SP for sheet piles was applied for trial purposes at Kamaishi and Nagoya Works, then in 2012, TP-SPP was applied to pipe sheet piles also for trial purposes at Muroran. Thereafter, the TP method began to be used widely for steel structures of port facilities.

Table 4 Items and manners of inspection and test [8]

Object		Content of inspection/Test
Covers	Visual inspection	Loosening or otherwise of fixing bolts Cracking of protective cover
	Tensile and bending tests	According to applicable criteria under JIS
Anticorrosive lining	Testing	Measurement of residual oil content (80% or more being acceptable)
Steel	Wall thickness measurement	Ultrasonic thickness measurement after removing cover and anticorrosive lining

4. Evaluation of Durability of Petrolatum Lining

4.1 Degradation evaluation of petrolatum lining

The petrolatum corrosion protection layer deteriorates owing to external causes and chemical reactions, and it is necessary to take adequate maintenance measures in consideration of the site condition. The external causes include waves and the impacts of floating objects, and the chemical reactions include the degradation of protective covers by ultraviolet light and metal corrosion.

Table 4 lists the items and methods of inspection of petrolatum corrosion protection according to the Corrosion Protection and Maintenance Manual for Port Facilities in Steel Structure.[8] The interval of periodical inspections is set generally at one to two years, and the main items of inspection are visual inspection of the appearance of the protective covers regarding loosening of the fixing bolts, cracking of the cover, etc. Besides the visual inspection of the appearance, the manual specifies performance evaluation of the petrolatum-based anticorrosion material and corrosion inspection of the steel piles proper. Since the steel protecting effect of petrolatum depends on whether its water- and air-shielding properties are maintained, it is essential to maintain it in good condition.

As a method for evaluating the properties of anticorrosion material containing petrolatum, the manual stipulates degradation judgement based on the amount of residual petrolatum after a prescribed period of use; more specifically, the content of petrolatum in the protective layer must be 80% or more.

4.2 Effects of temperature over petrolatum-base anticorrosive material

One factor that defines the effective life of the anticorrosive material is the content of petrolatum (hereinafter called the residual oil

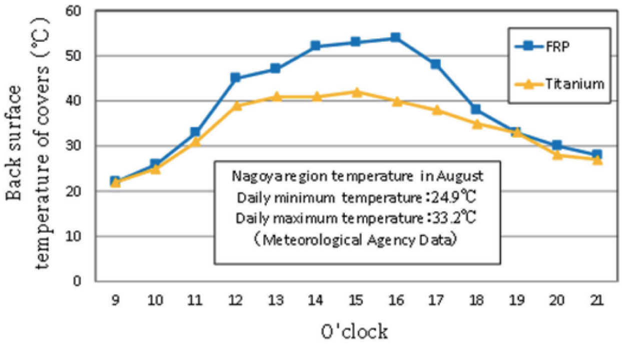

Fig. 6 Lining temperature beneath protective covers (August, Nagoya)

content). The decrease in the oil content results from the fluidization and outflow of petrolatum paste due to the temperature rise of the anticorrosive paste above the melting point (40°C)[4] and that of the anticorrosive tape above the softening temperature (60°C).[5] Based on the above, considering that the fluidization and outflow of petrolatum may occur when its temperature is 40°C or higher, we measured the temperature of the protective lining behind a titanium cover and an FRP cover in real use conditions.

Figure 6 shows the change in the lining temperature behind titanium and FRP covers measured in the Nagoya region in August; the mean minimum temperature was 24.9°C, and the mean maximum temperature was 33.2°C. The graph shows that while the temperature behind a titanium cover remained near 40°C from 1300 to 1600 hours, it exceeded 50°C behind an FRP cover from 1400 to 1600 hours. This seems to indicate that the decrease in the residual oil content is greater with FRP covers.

4.3 Measurement of residual oil content at laboratory and exposure tests

4.3.1 Laboratory test

We devised a method for a rotation immersion test of the petrolatum anticorrosive material in laboratories. The method consists of accelerating the degradation of petrolatum tape due to water permeation by applying it to the surfaces of cylinders (no additional lining), rotating the cylinders in artificial seawater kept within prescribed temperature ranges and evaluating the petrolatum quality before and after the test. In addition, the effectiveness of wrapping sheets was evaluated by estimating the durability of petrolatum tape shielded with them.

Figure 7 schematically shows the configuration of the rotation immersion tester and a photograph of the specimens set in the tester. The test was conducted by applying petrolatum tape to the outer surfaces of PVC pipes, immersing them in artificial seawater kept at 40, 50 and 60°C and rotating them at a constant speed (0.5 m/s). The test period was set at 30 days and 90 days, and at the end of the period, the residual oil content of the specimens was measured according to the Maintenance Handbook for Marine Steel Structures.[9]

4.3.2 Examination of specimens exposed to real environment

Specimens of petrolatum tape were taken from real marine structures of steel pipe piles at the following locations and the residual oil content was measured in the same manner as the laboratory test: Mikawa, Aichi Prefecture (with FRP covers, 21 years of use)[10]; Hazaki, Ibaraki Prefecture (with FRP covers, 18 years)[11]; Naruto, Tokushima Prefecture (with titanium covers, 10 years); and Akita, Akita Prefecture (with titanium covers, 5 years). Note here that none of the above had been protected with water-shielding wrapping sheets beneath the covers.

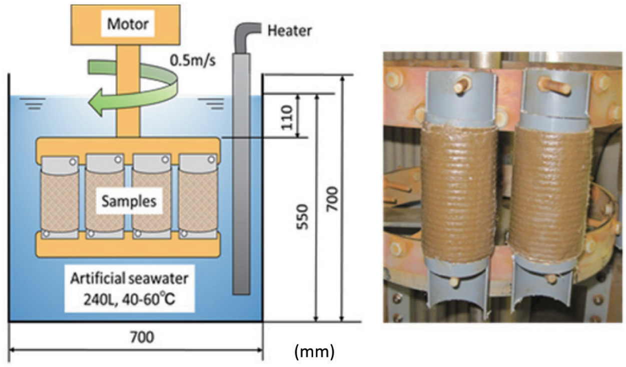

Fig. 7 Rotation immersion tester

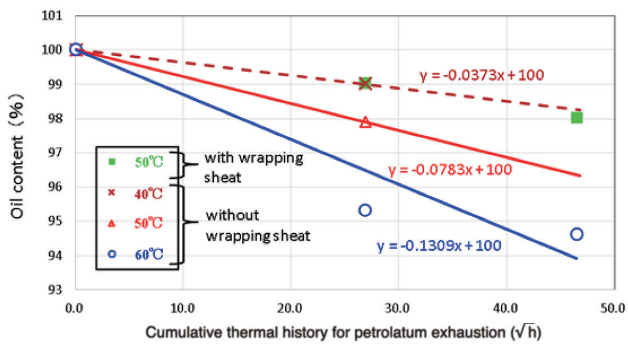

Fig. 8 Change in residual oil content over time at laboratory test

4.4 Estimation of durability of protection by TP method

Figure 8 shows the time-dependent change of the residual oil content in petrolatum tape measured in the laboratory test. The horizontal axis represents the square root of the thermal history. Here, the thermal history t means the total time period (in h) during which the temperature inside the protection cover is 40°C or higher, the range where the properties of petrolatum are presumed to degrade. Since the temperature of the artificial seawater was kept constant at the laboratory test, the thermal history in the graph is equal to the test period. The change in the residual oil content at the test temperatures can be expressed in the form of the formulae given in the graph. The fall of the residual oil content was fastest in the case of the environmental temperature of 60°C. The residual oil content with wrapping sheets at 50°C is also plotted in the graph, which indicates that the deterioration behavior of the petrolatum tape under this condition was substantially equal to that at 40°C without a wrapping sheet. Then, regarding this graph as a model for evaluating the durability of petrolatum tape, the measurement results of the residual oil content of the specimens taken from the real structures mentioned in 4.3.2 above were plotted along the extensions of the curves of the graph.

Figure 9 shows the graph of the residual oil content relative to the thermal history of the specimens, combining the results of the laboratory test and the measurements of the specimens taken from the real structures. The thermal histories of the specimens taken from the real structures were defined as the total of the time during which the weather condition was such that the temperature behind the cover was presumed to be 40°C or higher, i.e. clear weather and 25°C or higher according to the records of the Japan Meteorological Agency. The readings of the specimens of Mikawa and Hazaki, with

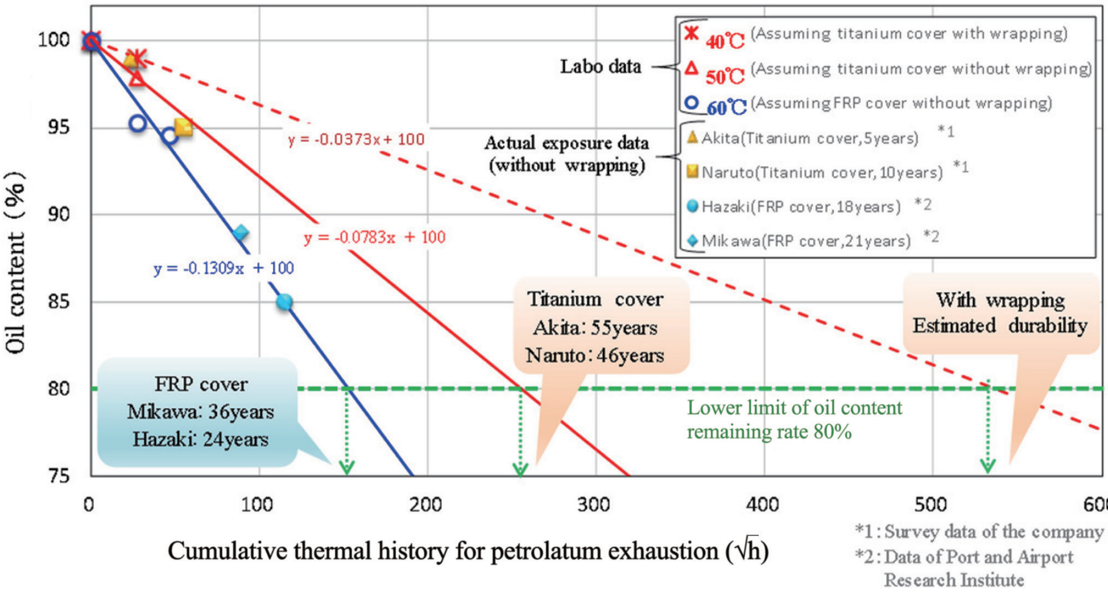

Fig. 9 Estimated durability of anticorrosive lining

FRP covers, are on the extension of the curve approximating the laboratory test results at 60°C. On the other hand, those of Naruto and Akita, with titanium covers, are on that approximating the laboratory test results at 50°C.

From the above and in consideration of the temperature difference between titanium and FRP covers, the change in the residual oil content in the laboratory test at 60°C is regarded as equal to that of real structures with FRP covers, and the same in the laboratory test at 50°C to that of real structures with titanium covers.

From the point of the thermal history defined by the intersection of the change in the residual oil content over time with the lowest permissible residual oil content (80%),[9] we calculated the expected durability of the petrolatum protective layer with either titanium or FRP covers. As a result, the expected durability with FRP covers was 30 years, and the same with titanium covers was 50 years, approximately, which means that petrolatum protection with titanium covers is expected to remain effective 1.5 times longer or more than that with FRP covers.

Since no wrapping sheets were used for any of the real structures from which the specimens were taken, the figures of the expected durability at 50 and 60°C described above are assumed to be those without wrapping sheets. In addition, with wrapping sheets, the air-tightness of the petrolatum layer is improved, and presumably it is less affected by the temperature rise behind protective covers. From this and from the fact that the change in the oil content of the protective layer with wrapping sheets at 50°C is equal to the same without wrapping sheets at 40°C, the laboratory test result at 40°C (dotted line) is considered to represent the case with wrapping sheets at 50°C; therefore, the durability is expected to be longer with wrapping sheets than without. However, the number of specimens of real structures where the oil content of the petrolatum layer with wrapping sheets has been measured is still very small, and the credibility of the results of the present study will increase as the number of such measurements increases in the future.

5. Examination Result of Specimens Exposed for 29 Years

To confirm the credibility of the durability evaluation based on the laboratory test and the examination of the specimens taken from real structures, we inspected the surfaces of the petrolatum pastes and the steels of other pipe piles with the protective lining. **Photo 3** is a photograph of the Hazaki Oceanographical Research Station of the Port and Airport Research Institute.[12] The station has a pier for structural tests for port facilities, the largest of its kind in Japan. It is exposed to very severe corrosive conditions when the weather is rough, and to take advantage of the conditions, many structural specimens are installed there for different types of exposure tests. Steel pipe piles coated with petrolatum protective layers and exposed for 29 years as part of the substructure of the pier, some with FRP covers and others with titanium covers, were observed in the tidal zones.

Figure 10 shows photographs of the surface appearances of the petrolatum pastes and the steel pipe piles.[13] The petrolatum paste of the pile with a titanium cover was generally in black, judged to be in a good condition based on past findings[14], and there was no corrosion of the steel pipe proper. On the other hand, the surface of the petrolatum paste with an FRP cover had a rusty hue locally, and the

Photo 3 Hazaki Oceanographical Research Station [12]

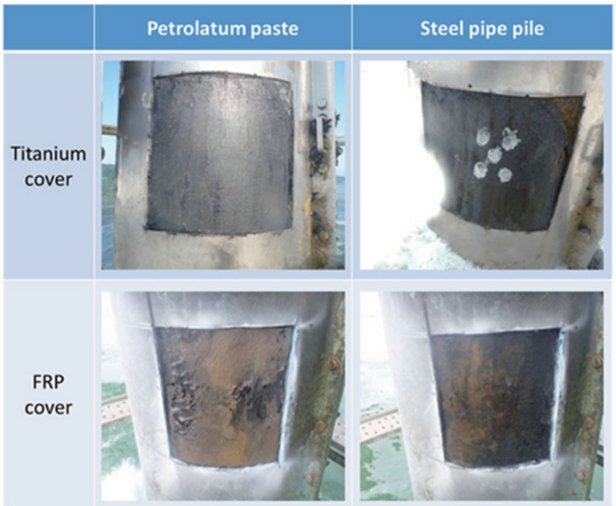

Fig. 10 Result of exposure test at Hazaki Oceanographical Research Station [13]

pipe pile was found to have rusted.

Thus the anticorrosive lining with titanium covers is more durable than that with FRP covers, and the durability evaluation shown in Fig. 9 is largely reliable.

6. Closing

For the petrolatum anticorrosive lining applied to marine steel structures, a protection method using covers of titanium excellent in resistance to impact and corrosion has been developed, and applied for trial purposes to the substructures of piers and berths of the steelworks of the company. The following findings were obtained through tests and examination of samples:

(1) A titanium cover 0.6 mm thick is 10 times more resistant to impact than an FRP cover, and a cover 1.0 mm thick, 27 times.

(2) At temperature measurement in real use conditions, the temperature of the petrolatum lining behind FRP covers was higher than the same behind titanium covers, which indicates that the anticorrosive layer is affected less adversely with titanium covers than with FRP covers.

(3) The result of evaluation of the durability of the petrolatum lining based on the residual oil content in it indicates that the effective life of the lining is 1.5 times or more longer with titanium covers than with FRP covers.

(4) Through the exposure test for 29 years at the Hazaki Oceanographical Research Station, whereas the petrolatum paste covered with a titanium cover was sound, and no rusting was seen on the steel pipe pile beneath it, the petrolatum paste with an FRP cover was degraded and the pipe pile rusted.

The results verify the superiority of the TP corrosion protection method using titanium covers, and the application of the method is expected to expand.

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