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Durability of Polyethylene-Coated Steel Pipe at Elevated Temperatures

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Abstract:

A new polyethylene-coated steel pipe of superior characteristics was developed for use in pipelines operating at 80°C. Various tests including corrosion resistance and underground piping tests were conducted, and the following results were obtained: (1) The newly developed polyethylene coating exhibited excellent mechanical, physical, chemical, and adhesion properties at the elevated temperature of 80°C. (2) Blended with a special antioxidant stabilizer, the polyethylene coating demonstrated high durability at 80°C in various accelerated degradation tests. (3) The coating, being reinforced with an adhesive of high elevated-temperature adhesive strength and an epoxy primer high in the glass transition temperature, displayed tight adhesion to the steel pipe at the elevated temperature, as well as long-lasting adhesion in water. (4) The polyethylene-coated steel pipe exhibited excellent corrosion resistance in underground piping tests lasting for about 3 years at an accelerated test temperature of 100°C.

1. Introduction

In recent years, the pipeline operating temperature has been rising with increasing oil well depth and temperature, oil specific gravity and transportation efficiency, among other factors. Protection of the global environment has been prompting the installation of district air-conditioning systems, mainly in Europe, and has been raising the piping operating temperature[1]. Polyethylene coatings have been traditionally used as heavy-duty protective coatings on general pipelines in Europe and Japan, and have been credited with very high reliability. Nippon Steel developed polyethylene-coated steel pipe[2], which is made and marketed under the trade name "HI-PL" and is highly rated by its users. Polyethylene coatings are now highlighted in North America where fusion-bonded epoxy coatings have been mainstream in the past[3]. The rise in the operating temperature of pipelines and district air-conditioning system piping has called for the development of heavy-duty protective coatings that are durable at elevated temperatures.

The authors set the coating service temperature at 80°C considering the operating temperature of main parts of elevated-temperature pipelines and district air-conditioning system piping. Then, they improved the 80°C durability of polyethylene coatings that were field proven, reliable and capable of being continuously applied to steel pipe by existing extrusion coating equipment[4,5]. This development work was carried out to meet the basic requirements for coating property described below.

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First, there are mechanical properties that are required of coatings during piping installation, including indentation resistance and impact resistance. Then, there are physical properties that are important for the corrosion resistance of coatings, such as water absorption resistance, water vapor transmission resistance and electric resistance. There also are equally important chemical properties, including resistance of the coating to oxidative degradation during operation at elevated temperatures. Various accelerated test methods are proposed to evaluate the oxidative degradation resistance of coatings. Given its importance, the oxidative degradation resistance of coating specimens was evaluated by several accelerated test methods. A new polyethylene coating material blended with a special antioxidant stabilizer was devel oped to meet these mechanical, physical, and chemical property requirements. Bond strength is another important property for the new polyethylene coating material to adhere to the outside surface of steel pipe tightly and stably over a long period of time. To meet this requirement, an adhesive with an excellent adhesive strength at elevated temperatures and a primer with sufficient adhesive strength in water at elevated temperatures were developed. The authors had tested the newly developed polyethylene-coated steel pipe installed underground for about 3 years to investigate its elevated-temperature durability.

2. Experimental

2.1 Materials

Medium-density polyethylene (MDPE) featuring a melt index of 0.13 and density of 0.943 and is blended with a special antioxidant stabilizer was used as the polyethylene resin. Two types of specimens were used in various tests. One type was a free film (0.5 mm in thickness), press formed from MDPE. The other was steel pipe (216 mm in outside diameter, 5.8 mm in wall thickness, 5.5 m in length), first coated with the primer and adhesive and then extrusion coated with MDPE to a thickness of 3 mm. **Fig.1** shows the coating composition of the polyethylene-coated steel pipe.

2.2 Methods

2.2.1 Mechanical properties

The mechanical properties of the polyethylene coating was investigated by indentation and impact tests. The test specimens and methods are summarized in **Table 1**. The indentation and impact tests were conducted at temperatures of 40 to 80°C and −45 to +80°C, respectively.

2.2.2 Physical properties

The physical properties of the polyethylene coating were investigated by water absorption, water vapor transmission, and

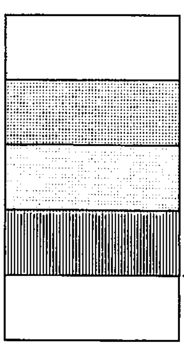

Fig. 1 Coating composition of polyethylene-coated steel pipe

Table 1 Mechanical property test methods and specimens

Properties	Standard	Specimen
Indentation	DIN 30670	Cut specimen from coated pipe Size: 50mm × 50mm × 5.8mm Coating thickness: Polyethylene: 3mm
Impact strength	ASTM G14	Cut specimen from coated pipe Size: 100mm × 300mm × 5.8mm Coating thickness: Polyethylene: 3mm

Table 2 Physical property test methods and specimens

Properties	Method and device
Water absorption	Measurement of weight differences before and after hot water immersion at 80°C
Water vapor transmission rate	Measurement of H_2O vapor transmitted from an atmosphere of 100% relative humidity to one of 10% relative humidity through the film at 40°C and 80°C Device: Vapor transmission tester (Type L-80) manufactured by Lyssy Co., Ltd.
Electric resistance	Measurement according to DIN 30670 after 100 days storage in 0.1M NaCl

Specimen: Free film size: 100mm × 100mm
Thickness: Polyethylene: 0.5mm
Fusion-bonded epoxy: 0.4mm (as reference)

Table 3 Chemical property test methods and specimens

Methods	Measurement	Temperature
(1) OIT test	Oxydation induction time	200-240°C
(2) Oven test I	Half - value period of elongation of polyethylene after test	120-160°C
(3) Oven test II	Time when free film had crack by bending it with fingers after test	100-120°C

Specimen:
(1) Free film size of polyethylene : 100mm × 50mm × 2mm
(2) Antioxidant stabilizers contents : 0.1-1.0 times (standard contents)
(3) Melting point of polyethylene : 120°C

electric resistance tests. The test specimens and methods are summarized in **Table 2**. A free film (0.4 mm in thickness) of a fusion-bonded epoxy and steel sheet coated with the fusion-bonded epoxy coating were used as reference materials.

2.2.3 Chemical properties

Oxidative degradation resistance was investigated as a representative chemical property of the polyethylene coating. The test specimens and methods are summarized in **Table 3**. According to the amount of the antioxidant stabilizer added, the specimens are classified as follows: The specimen to which the antioxidant stabilizer is added in a standard amount is the 1.0 blend specimen; One to which the antioxidant stabilizer is added in the standard amount less 70% is the 0.3 blend specimen; One to which the antioxidant stabilizer is added in the standard amount less 90% is the 0.1 blend specimen. One to which the antioxidant stabilizer is not added is the 0 blend specimen. The oxidative degradation resistance of the polyethylene coating was comparatively evaluated by three accelerated test methods: Oxidation induction time (OIT) test; oven test I; and oven test II. In each accelerated oxidative degradation test, the oxidative degradation time was measured at three different test temperatures, Arrhenius plotted, and extrapolated to estimate the life of the polyethylene coating.

2.2.4 Bond strength

The adhesive strength of the polyethylene coating was inves-

Table 4 Adhesive strength test method and specimen

Property	Method
Adhesion strength	Measurement of peel strength of coating before and after hot water immersion at 95°C

Specimen : Cut specimen from coated pipe
Size : 75mm × 150mm × 5.8mm
Coating thickness of polyethylene: 3mm

tigated by peel test and hot-water immersion test. The test specimens and methods are as summarized in **Table 4**. The primary adhesive strength was measured by the peel test (90° peel, temperature: room temperature to 80°C, peel speed: 10 mm/min). In the hot-water immersion test, the specimen was immersed in 95°C hot water for 8,000 h and peel tested.

2.2.5 Underground piping test

The polyethylene-coated steel pipe was underground piping tested. The test conditions are shown in **Fig. 2**. The underground piping depth was 1.5 m, and 100°C heat transfer oil was circulated through the polyethylene-coated steel pipe. After 3 years of underground piping, some of the polyethylene-coated steel pipe was removed and examined for the mechanical and physical properties of the coating. These properties were compared with those registered prior to the underground piping test.

3. Results and Discussion

3.1 Mechanical properties

The indentation ratio was calculated by Eq. (1) from the depth of indentation into the polyethylene coating measured at the test temperatures.

$$\text{Indentation ratio} = \frac{\text{Depth of indentation}}{\text{Coating film thickness}} \times 100 \quad .....\ (1)$$

The polyethylene coating thickness was 3 mm. **Fig. 3** shows the indentation ratio calculated by Eq. (1). The indentation ratio increases with increasing temperature. Even 80°C, however, the ratio is no higher than about 6%, which is too low to have any effect on the corrosion-protective performance of the polyethylene coating. The impact test results of the coating are shown in **Fig. 4**. The impact strength decreases with increasing temperature, but is still about 10 J at 80°C, which is a practically high value. The polyethylene coating did not crack at any test temperature. These test results mean that the polyethylene coating of the polyethylene-coated steel pipe is scarcely damaged by sand and gravel in an elevated-temperature underground piping environment, is strong against impact during handling, and has excellent mechanical properties.

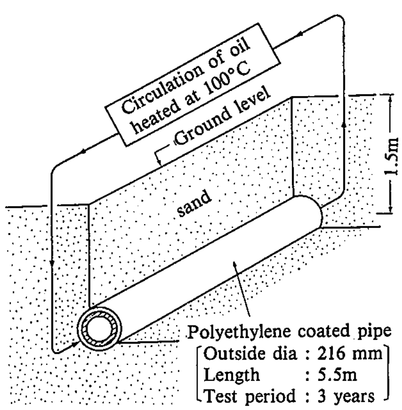

Fig. 2 General view of polyethylene-coated steel pipe in 100°C underground piping test

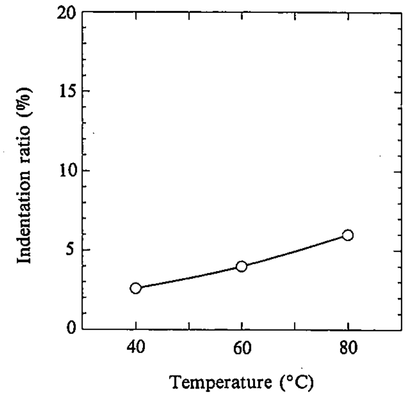

Fig. 3 Relationship between temperature and indentation ratio of polyethylene coating

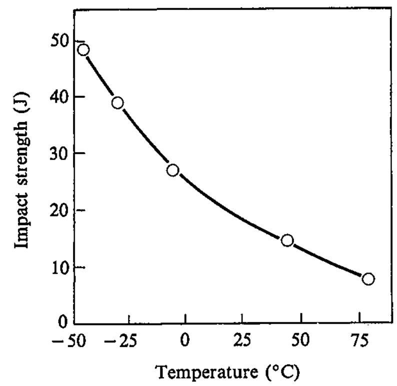

Fig. 4 Relationship between temperature and impact strength of polyethylene coating

3.2 Physical properties

In **Table 5**, the water absorption and water vapor transmission test results of the polyethylene coating are compared with those of the fusion-bonded epoxy coating. As indicated, the water absorption and water vapor transmission rate of the polyethylene coating are very low and stable compared with those of the fusion-bonded epoxy coating. **Table 6** compares the polyethylene coating and fusion-bonded epoxy coating in electric resistance. It shows that the electric resistance of the polyethylene coating

Table 5 Water absorption and water vapor transmission rate of polyethylene coating and fusion-bonded epoxy coating

Properties		Polyethylene	Fusion bonded epoxy*
Water absorption (%) after hot water immersion at 80°C		0.003	0.83
Water vapor transmission rate (g/m^2-24h)	40°C	0.04	1.8
	80°C	0.16	4.4

*As reference

Table 6 Electric resistance of polyethylene coating and fusion-bonded epoxy coating

Coating	Electric resistance ($\Omega \cdot m^2$)
Polyethylene	1.0×10^{11}
Fusion bonded epoxy	7.2×10^{8}*

*As reference

is much higher than that of the fusion-bonded epoxy coating. These results indicate that the polyethylene coating has better corrosion protection and physical properties than the fusion-bonded epoxy coating at high temperature and humidity[6].

3.3 Chemical properties

The oxidative degradation resistance data of the polyethylene coating as measured in three accelerated degradation tests are summarized in **Fig. 5**. The estimated life of the polyethylene coating at 80°C widely varies among the three tests. The 80°C life of polyethylene estimated by extrapolation of the oven test result II conducted below the melting point (120°C) of polyethylene is by far shorter than that estimated by extrapolation of the results of the OIT test and oven test I conducted above the melting point of polyethylene. The new polyethylene coating has an estimated service life of over 40 years at 80°C, which translates into high oxidative degradation resistance[3].

The reason why the three accelerated degradation tests produced different estimated life values at 80°C is discussed here. As shown in **Table 6**, the OIT test and oven test I accelerate the degradation of polyethylene at 200 to 240°C and 120 to 160°C, respectively, or above the melting point of polyethylene. Since the polyethylene coating is molten or semi-molten in this condition, the antioxidant stabilizer is readily mobile in the polyethylene coating, rapidly moves to oxidation initiation sites (radicals) at the surface of the polyethylene coating, and traps the radicals. The oxidative degradation of the polyethylene coating surface can be early prevented in the process. This is considered to increase the activation energy for oxidative degradation and decrease the slope of the Arrhenius plot. The oven test II accelerates the degradation of polyethylene at 100 to 120°C or below the melting point of polyethylene. Since the polyethylene coating is solid in this condition, the antioxidant stabilizer cannot be mobile in it and diminishes in its effectiveness of inhibiting the oxidative degradation of the polyethylene coating surface. This is considered to decrease the activation energy for oxidative degradation and increase the slope of the Arrhenius plot. As the polyethylene coating is solid at 80°C where the polyethylene-coated steel pipe is installed, underground, the oven test II is regarded as a desirable accelerated test method for predicting the coating life.

3.4 Bond strength

Fig.7 shows the relationship between the test temperature and the peel strength of the polyethylene coating. With the newly developed adhesive, the peel strength decreases with increasing temperature, but is still high at about 50 N/cm at 80°C. The relationship of the hot-water immersion time with the peel strength of the polyethylene coating is shown in **Fig. 8**. The peel strength is about 250 N/cm even after 8,000 h of immersion, thanks to the adoption of an epoxy primer with a high glass transition temperature. A peel strength decline with time is hardly recognizable, indicating that it is stable[7].

When the glass transition temperature of the primer is near

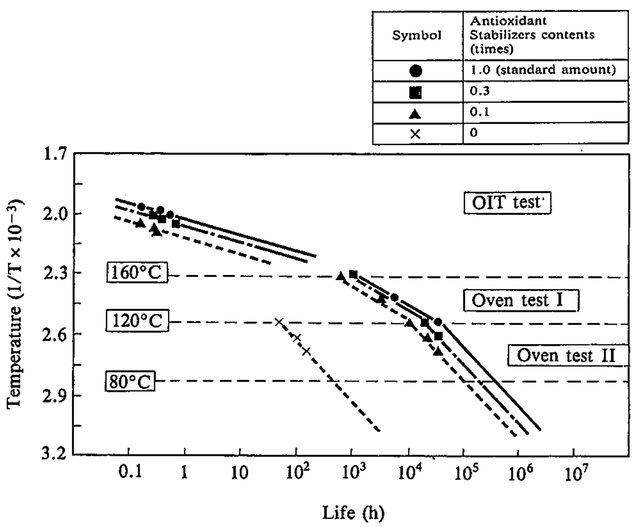

Fig. 5 Arrhenius plots of results of accelerated degradation tests for life prediction of polyethylene coating

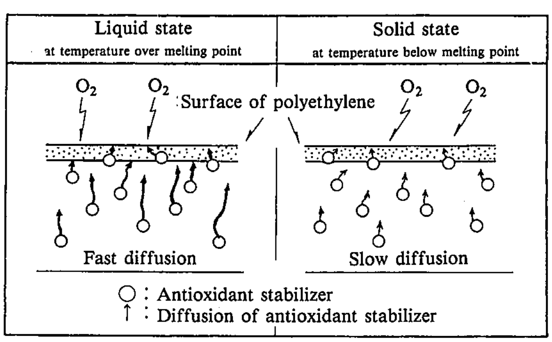

Fig. 6 Hypothesis for behavior of antioxidant stabilizer in polyethylene coating

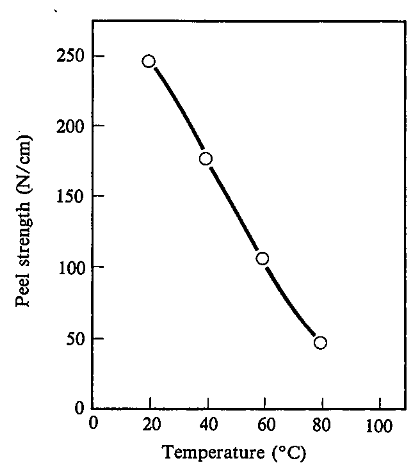

Fig. 7 Relationship between temperature and peel strength of polyethylene coating

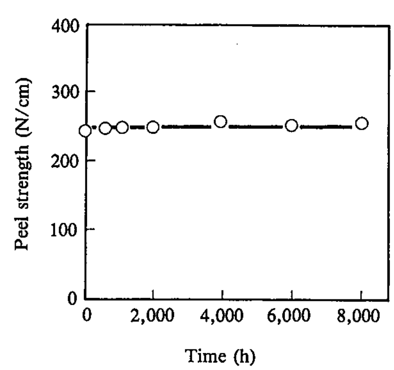

Fig. 8 Peel strength of polyethylene coating after 95°C hot-water immersion

80°C that is the operating temperature of the polyethylene-coated steel pipe, its crosslinked structure turns glassy during the hot-water immersion test, accelerating the degradation of the primer and lowering the adhesive strength of the polyethylene coating in the water. The authors added a polyfunctional epoxy resin and a special hardener (hardener B) to the conventional epoxy primer to raise its glass transition temperature to such a level that its adhesive strength does not suffer. When applied to steel pipe using the new epoxy primer, the polyethylene coating develops a stable and high peel strength even after hot-water immersion, as shown in **Figs. 9** and **10**. The new epoxy primer not only has a high glass transition temperature, but also readily forms a three-dimensionally tight crosslinked structure in terms of molecular structure and has greater adhesion to the steel pipe.

3.5 Underground piping test

The polyethylene-coated steel pipe had been subjected to accelerated degradation in underground piping test at 100°C for 3 years. Some of the mechanical and physical properties measured in the test are given in **Table 7**. The elongation, melt index, and density of the polyethylene coating after the 3-year test are slightly different from the initial values. The indentation and electric resistance of the polyethylene coating after the 3-year test are practically the same as the initial values. These results indicate that the polyethylene coating can maintain its excellent corrosion protection performance over a long period of operation at elevated temperatures.

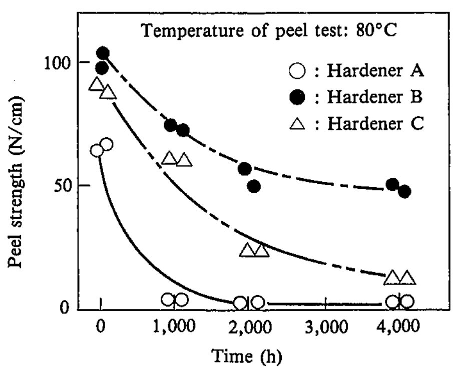

Fig. 9 Peel strength of polyethylene coating after 95°C hot-water immersion

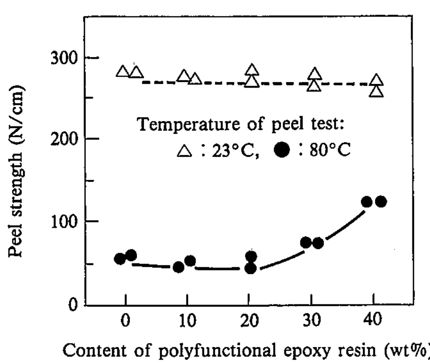

Fig. 10 Effect of polyfunctional epoxy resin on peel strength of polyethylene coating after hot-water immersion at 95°C for 2,000 h

Table 7 Results of underground piping test at accelerated degradation temperature of 100°C

Item	Test method	Unit	Initial	After 3 years
Elongation	ASTM D638	%	800	550
Melt index	ASTM D1238	g/10min	0.18	0.23
Dentsity	ASTM D1505	g/cm^3	0.9443	0.9480
Penetration (80°C)	DIN 30670	mm	0.18	0.17
Electric resistance	DIN 30670	Ω·m^2	9.0×10^{11}	5.1×10^{11}

4. Conclusions

The newly developed polyethylene-coated steel pipe has excellent mechanical, physical, chemical, and adhesive properties at elevated temperatures. It can perform well when used as heavy-duty corrosion-protective coated steel pipe in pipelines operating at the high temperature of 80°C and piping for district air-conditioning systems.

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