KAWASAKI STEEL TECHNICAL REPORT No. 6 September 1982

Performance of External Polyethylene Coating on Large Diameter Pipes in High Temperature Environments*

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In order to determine the maximum operating temperature of pipelines with external polyethylene(PE) coating, the durability of mechanical properties and water resistance of the coating were investigated over a temperature range from 20° to 100°C. The results are summarized as follows:

(1) High-density PE coating shows remarkably high penetration resistance up to 80°C.

(2) The lifetime of the high density PE coating is estimated to be more than 40 years at 100°C under dry conditions on the basis of Arrhenius plots of oxidative induction time and elongation at break.

(3) When heat is transmitted from the steel pipe to PE coating during operation of pipelines, the high-density PE coating has sufficient anticorrosive properties for prolonged periods in hot water environment due to the low water permeability of the coating layer.

1 Introduction

Large-diameter steel pipes with external polyethylene (PE) coating are used for large-diameter pipelines for long distance transport of natural gas, petroleum, fresh water, etc. Since 1979 Kawasaki Steel Corporation has been operating a complete line of facilities capable of coating large-diameter pipes within the range of 20″ (508 mm) to maximum 64″ (1 626 mm)[1], and has supplied such steel pipes for the Transmediterranean Pipeline, fresh water pipelines in Saudi Arabia and natural gas pipelines in the Soviet Union.

Owing to the tight energy supply situation in recent years, energy source development found its way far into the arctic region and greater ocean depths at an increasing pace but, coupled with the quality deterioration of energy sources, has also caused problems of remoter locations of energy sources and a longer distance hauling. Developed to cope with these situations and enhance pipeline transportation efficiency are the heating of heavy oil and the use of high pressure for natural gas, and this has generated a growing trend of the rising temperatures of coated pipelines. Such a trend of rising temperatures of the fluid during pipeline operation naturally intimidates the performance of coated steel pipes with their possible significant effect. There have been many reports about the quality performance of PE-coated pipes[2-4], but most of them gave the results of quality performance tests at room temperature or low temperature, and investigation reports on the anticorrosive property of PE-coated pipes taking into consideration environmental factors at elevated temperatures are lacking[5].

Against the above-mentioned background, this report describes the results of investigation aimed at clarifying the following points to grasp the high-temperature properties of PE-coated steel pipes:

(1) Heat effects on the mechanical properties of PE
(2) Relation between thermal degradation and the life-time of PE
(3) Effects of hot water on coating performance of PE-coated pipes
(4) Anticorrosive properties of PE-coated pipes under gradient temperature conditions.

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* Originally published in *Kawasaki Steel Giho*, **14** (1982) 2, pp. 32–39

** Research Laboratories

Table 1 Properties of PE for pipe coating

Item	Test method	Units	Properties of coating material
Density	ASTM D 1505-67	g/cm^3	0.950 - 0.955*
Melt flow index	ASTM D 1238-65T	g/10min	0.18 - 0.22
Softening point	ASTM D 1525-65T	°C	120 - 125
Melting point	ASTM D 2117-64	°C	125 - 130
Brittleness temp.	ASTM D 746-55T	°C	< -80
Disruptive voltage	ASTM D 149-64	kV/mm	>35
Hardness	ASTM D 2240-68	Shore D scale	60 - 65
ESCR**	ASTM D 1693	F_{50}, hour	>1 000

* Final carbon content : 2.5% weight
** ESCR : Environmental Stress Cracking Resistance

2 External Coating Process of Large Diameter Pipe with PE

The external surface of a steel pipe is subjected to shot blasting to remove rust and, after being coated with adhesives, is heated. Then the high-density polyethylene and adhesive polyethylene layers are co-extruded by the T-die and wound around the pipe by means of a pressure roll$^{1)}$.

Table 1 shows the properties of high-density PE which is used for the external coating of large diameter pipes made by Kawasaki Steel's T-die method.

3 Heat Effects on Mechanical Properties of PE

3.1 Penetration and Softening Temperature

Owing to its thermoplasticity, PE resin becomes softer and easier to push in as the temperature is raised, until it begins to melt. The point at which the resin begins to become soft is called the softening point, while the point at which the resin begins to melt is called the melting point. Since a large weight of the steel pipe is applied to PE on the PE-coated steel pipe, the softening point, that is, the temperature at which PE begins to deform, is considered a practical standard for measuring the thermal resistance of PE. The softening point of high-density PE used by Kawasaki Steel is 121°C, which is much higher than the softening point of low-density PE, 92°C, which was used for comparative studies. From this comparison, it is judged that high-density PE has definitely better thermal resistance than low-density PE. For measuring mechanical properties of the coated layer to see how good it can endure the weight of gravel or other sharp-edged substances, penetration is used and is explained below.

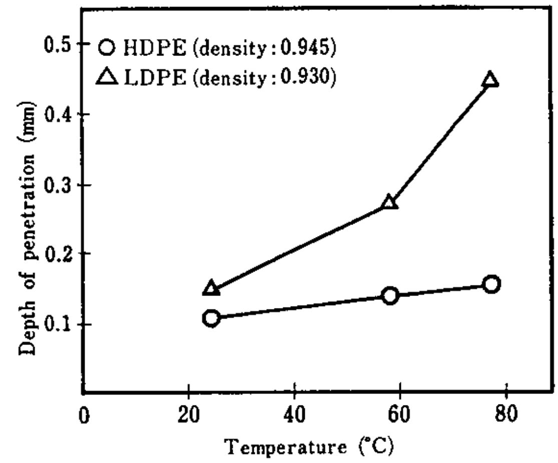


Fig. 1 Effect of temperature on depth of penetration for PE sheets

Penetration is measured by the depth of penetration of a 1.8 mm diameter needle made to penetrate into the coated film at a pressure of 100 kg/cm^2 over a 24 hour period. **Fig. 1** shows the temperature dependence of penetration of PE resin under DIN 30670. This penetration is highly dependent on density and is smaller in high-density PE than in low-density PE. This difference becomes more noticeable as the temperature rises. Penetration for low-density PE increases sharply as the temperature rises, whereas penetration for high-density PE shows a value as small as less than 0.2 mm even at a high temperature of 80°C, while deformation of the coated layer is markedly small. Since high-density PE has hardness at a high temperature of 80°C similar to that at room temperature, no problem is considered to occur in practical use of high-density PE.

3.2 Impact Resistance

The impact resistance of macromolecular materials is generally related to glass transition temperature, T_g, and the lower the T_g value of resin, the higher the resin's impact resistance. For instance, T_g of PE is −120°C and is much lower than those of polypropylene resin, epoxy resin and polyvinyl chloride resin. It is said, therefore, that the thermal resistance of PE-coated steel pipes is excellent in the normal operating temperature range of −45°C to 80°C[6].

Impact resistance was evaluated in the present report by causing a tup nose conforming to ASTM G14 which had a diameter of 5/8″ and weighed 2 kg, to fall from a height of 1 m and counting the number of such falls until the 3 mm thick PE film broke. **Fig. 2** shows the temperature dependence of the impact resistance of PE. There is little difference in impact resistance between low-density PE and high-density PE in the temperature range of −45°C to 0°C, but at a temperature higher than 20°C, the impact resistance of high-density PE is higher than that of low-density PE.

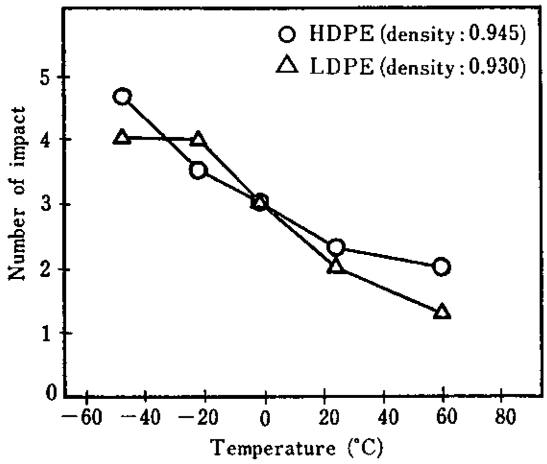


Fig. 2 Effect of temperature on impact resistance of PE sheets

4 Relation between Thermal Degradation and Lifetime of PE

4.1 Thermal Degradation

PE is a chemically stable macromolecular material, but when subjected to energies of ultraviolet rays and heat it generates a radical, which combines with oxygen in the air and causes an oxidative reaction, resulting in gradual degradation of PE[7]. As a result, mechanical properties such as elongation at break, tensile strength and impact resistance drop significantly.

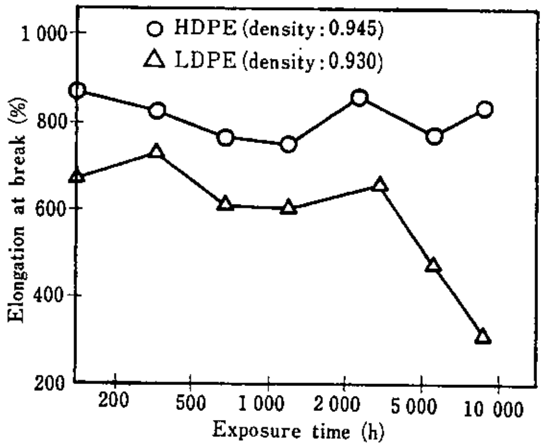


Fig. 3 Elongation at break vs. exposure time for PE sheets in air at 80°C

Fig. 3 shows the changes with passage of time in elongation at break of PE which has been kept in the air oven at 80°C for a maximum of one year. As can be seen in the figure, high-density PE is less liable to be affected by thermal degradation than low-density PE. The reason for this may be that high-density PE has more crystalline portions and consequently smaller amorphous portions, which are susceptible to thermal degradation, than low-density PE. Thermal stability of PE is dependent upon the kinds and amounts of addition of the antioxidant, which has been blended into PE, and is also affected by the residence of the antioxidant[8]. When the infrared spectrum of a low-density PE sample was measured which had been degraded for 9 000 hours and whose elongation had been greatly deteriorated, an absorption peak due to a carbonyl group was found in the vicinity of 1 720 cm^{-1}, thereby proving that the sample was affected by oxidative degradation.

4.2 Lifetime of PE Coating

PE-coated pipes must retain sufficient corrosion resistance for several ten years including transport and storage and eliminate leakage accidents due to pipe corrosion. Moreover, the recent trends of increased operation temperatures of coated pipelines have focused users' attention on the thermal stability of coated layers of pipelines. For this reason, PE for external coating of large-diameter pipes contains additives such as carbon black for preventing ultraviolet ray degradation which significantly affects the weather resistance and an antioxidant which suppresses oxidative degradation[9].

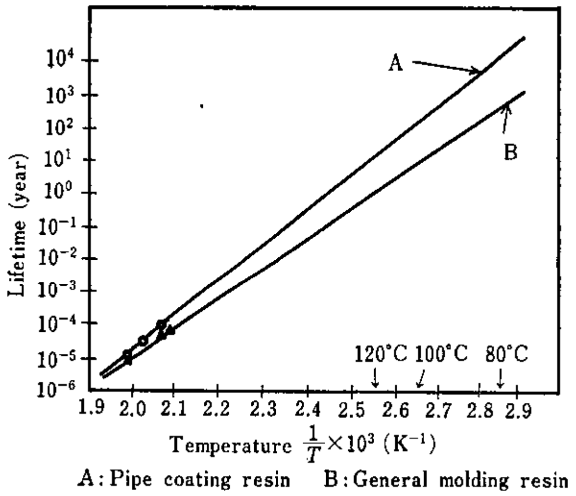


Fig. 4 Relation between temperature and life time of high density PE sheets in air

To estimate the lifetime of PE[10-12], a method was used which combined the measurement of oxidative induction time (O.I.T.) of PE employing differential scanning calorimetry (D.S.C.) and the ISO thermal degradation test (oven ageing method). Namely, when O.I.T. was measured at each temperature in respect of externally coating PE and the logarithm of O.I.T. and the reciprocal of measured temperature are plotted, a good linear relation was obtained between them and it was confirmed that eq. **(1)** becomes valid in respect of temperature dependence of O.I.T.

$$\log(\text{O.I.T.}) = \log A - \frac{\Delta H}{2.303\,RT} \quad \cdots\cdots\cdots\cdots(1)$$

R: Gas constant
T: Test temperature
A: Constant
ΔH: Activation energy

Then the time (lifetime) was measured at which elongation at break on the higher temperature side sharply dropped, and the lifetime on the lower temperature side was estimated, assuming that ΔH which had been calculated by the O.I.T. method was the same as that calculated by the oven ageing method. **Fig. 4** shows the results of estimation of the lifetime of PE. As can be seen from the figure, high-density PE ("A" in the figure) which has been specially developed for coating large diameter pipes has better thermal stability than ordinary high-density PE for forming ("B" in the figure) and is estimated to have a life of more than 40 years at 100°C. Thus the former is considered to endure satisfactorily long-term use at 80°C as stipulated in some fields of application.

5 Heat Effects on Performance of PE-coated Pipes

PE-coated steel pipes must satisfy the following quality requirement in coping with the growing trend toward higher operating temperatures of pipelines.

1. Adhesive strength between the coated layer of the coated pipe and the pipe surface will not deteriorate through ageing in the air at elevated temperatures.
2. Satisfactory adhesive strength between the coated layer and the pipe surface is retained and intermediate electroresistance will not deteriorate after the pipe is immersed in hot water.
3. Resistance of cathodic disbonding at elevated temperatures is excellent.

5.1 Relation between Adhesive Strength and Thermal Degradation of Coating

A test piece measuring 150×150 mm cut out of a 60 in. pipe coated with high-density PE was aged in the air at 100°C for 100 days. The 90° peeling strength of the coated film after ageing was 22 to 25 kg/cm which was only a slight drop from the 90° peeling strength of the coated film before ageing, 25 to 27 kg/cm. The coated film after ageing showed no peeling starting from the edge of coating and retains satisfactory adhesive strength.

5.2 Hot Water Effects on Adhesive Strength and Intermediate Electroresistance

Conceivable environments for laying pipelines are broadly divided into "under the ground," "in water" and "in the atmosphere." Under the ground and in water where the environment is more rigorous than in the atmosphere, water and oxygen, which are corroding factors for pipes, play an important role in performance degradation of coated piping. The amounts of permeation by the water and oxygen that pass through the coated film increase, as the temperature rises. Thus the coated film quickly deteriorates and its adhesive strength drops in a short period at elevated temperatures, resulting in a lowering of anticorrosive performance. Further, if the coated pipe is electrochemically protected, water permeation in the coated film is accelerated. This point also requires consideration[13].

A test piece measuring 150×150 mm cut out of a PE-coated large diameter pipe, and after being immersed in 3% NaCl solution at 60°C for 30 days, was measured for its 90° peeling strength and intermediate electroresistance at room temperature. The results are shown in **Table 2**.

The peeling strength after immersion in saline solution for the pipe coated with high-density PE was

Table 2 Effect of the density of PE on peel strength and intermediate electroresistance of PE coated on pipes after immersion in 3% NaCl solution for 30 days at 60°C

No.	Density of PE	Peel strength at room temp. (kgf/cm)	Intermediate electroresistance* in 3% NaCl solution at room temp. (Ωm^2)
1	High density PE (density : 0.945)	28.7 (29.8)**	4.6×10^{11} (5.4×10^{11})***
2	Low density PE (density : 0.930)	24.7 (28.3)**	3.7×10^{11} (5.6×10^{11})***

* According to DIN 30670

** Peel strength at room temperature before immersion

*** Intermediate electroresistance at room temperature before immersion

Table 3 Effect of temperature and the density of PE on cathodic disbonding of PE coated on pipes with an artificial damage of 5 mm diameter in 3% NaCl solution

No.	Density of PE	Length of delamination* at room temp. for 60 days (mm)	Length of delamination* at 60°C for 21 days (mm)
1	High density PE (density : 0.945)	4.2	12.3
2	Low density PE (density : 0.930)	4.5	17.7

* Length of delamination is the distance between the edge of artificial damage and detachable point of coating layer

Voltage between electrodes : 3.3 V

somewhat higher than for the pipe coated with low-density PE and the drop in peeling strength compared with peeling strength before immersion was little. The intermediate electroresistance of the PE coating after immersion in saline water at 60°C shows a large value almost equal to the value before immersion, thereby indicating retention of anticorrosive property.

5.3 Relation between High temperature Resistance of Cathodic Disbonding and Coating Materials

A 5 mm diameter hole was formed at the center of the coated film on each test piece measuring 150×150 mm cut out of a PE-coated large diameter pipe, until the hole reached the steel surface. The test pieces were immersed in the 3% NaCl solution at room temperature and 60°C, respectively. A cathodic disbonding test was then conducted by applying a voltage of 3.3 V (the initial electric potential of the pipe was about −1.5 V with respect to the saturated calomel electrode) across the anode (platinum) and the cathode (coated pipe). The results are shown in **Table 3**. There was almost no difference in resistance of cathodic disbonding among the types of PE layers at room temperature, but at 60°C, high-density PE showed better results than low-density PE. This may be attributable to the fact that water permeability which promotes peeling of the coated film is generally less in high-density PE than in low-density PE[14]. Studies are now under way on this temperature dependence of the resistance of cathodic disbonding, taking into consideration the water permeability of the coated film.

6 Coating Performance of PE-coated Pipe under Gradient Temperature Conditions

It is considered that in most cases of pipelines in commercial operation, the temperature of the internal surface of coated pipes rises owing to the heat and pressure given to the fluid in transport and that this will put the pipeline under a gradient temperature condition in which the heat passes through the pipe and flows to the external PE coating. If the PE-coated film is not in contact with water at this time, degradation of coating performance may not occur as long as the temperature remains below 80°C, as was studied earlier in this report. Whereas, if the external surface of the coated pipe is in contact with water, the water may permeate through the PE coating and lower its

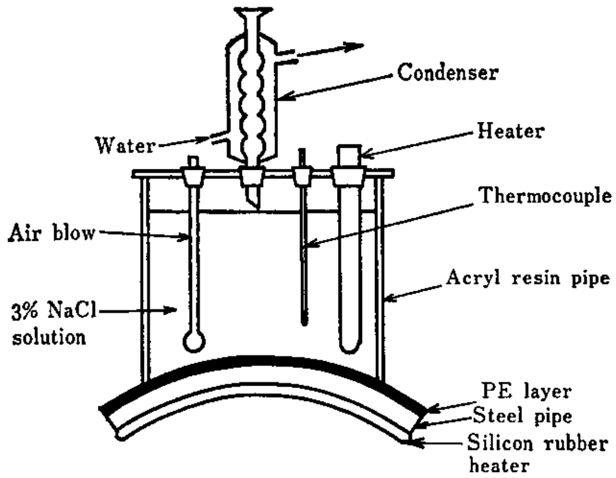


Fig. 5 Testing apparatus of temperature gradiant for PE coated on pipe

adhesive strength. In the conventional hot water resistance test for coated pipes, a method was adopted whereby the entire body of the test piece was immersed. In such method, the entire body of the coated-pipe test piece is maintained at an identical temperature, thereby making it difficult to accurately evaluate performance of the coated pipe under the gradient temperature conditions mentioned above.

For this reason, a plastic cell was fitted to the coated film side of the test piece cut out of a PE-coated large-diameter pipe as shown in **Fig. 5**. Then the cell was filled with a 3% NaCl solution, which was heated by an internal heater. Further, a silicon rubber heater was fitted to the internal surface of the pipe to heat it. Through maintaining the saline water and the pipe at different temperatures by this method, an immersion test was performed by providing a temperature gradient between the saline water and the steel pipe. Hereafter, this method is called the thermal gradient test[15-20)].

6.1 Performance of Non-defect Coated Film under Gradient Temperature Conditions

After the thermal gradient test of the PE-coated pipe, a 90° peeling strength was measured to evaluate the adhesive strength of the coated film.

To this end, the temperature of 3% NaCl was set at 80°C, with that of steel pipe varied in 4 stages, and after 30 days the measurement was taken of the peeling strength of PE-coated pipes. As shown in **Fig. 6**, the adhesive strength of the coated film sharply drops when the temperature of the saline water is higher than that of the pipe, but if the temperature of the saline water is lower than that of the pipe, the 90° peeling strength increases as the temperature of the pipe rises, that is, the temperature difference between the saline water and the pipe increases.

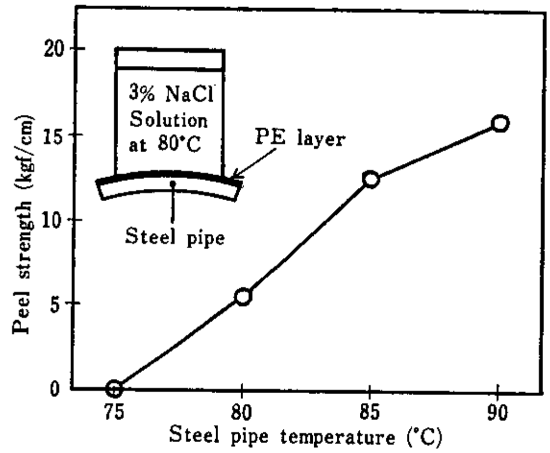


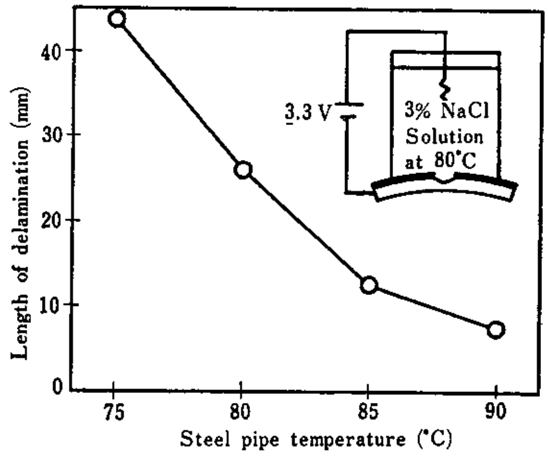
Fig. 6 Effect of gradient temperature on peel strength of PE coated on pipes after immersion in 3% NaCl Solution for 30 days

From this finding, it is observed that since the temperature of the pipe interior is considered higher than that of the PE coating under the commercial operation of the PE-coated pipeline, the pipeline can sufficiently retain its anticorrosive properties at a temperature as high as 80°C, even if the PE coated film is in contact with water.

6.2 Performance of Defectively Coated Film under Gradient Temperature Conditions

6.2.1 Cathodic disbonding

On a PE-coated test piece measuring 150×150 mm which was cut out of a PE-coated large-diameter pipe, a 5 mmϕ hole reaching the steel surface was made and a test was conducted according to the method described in Paragraph 5.3 by using the testing apparatus shown in **Fig. 5**. **Fig. 7** shows the peeling length



Test period: 30 days

Fig, 7 Effect of gradient temperature on length of delamination for PE coated on pipes after cathodic disbonding test of coated film from the initial hole on the PE-coated pipe after 30 days in the 3% NaCl solution at 80°C, with the temperature of the pipe varied. As indicated in this figure, the resistance of cathodic disbonding improves the better when heat flows from the pipe side to the saline water side as in commercial operations and the more the temperature difference between the pipe and saline water increases. This is the trend closely resembling that of adhesive strength of the coated film after the thermal gradient test given to the non-defective test piece as shown in **Fig. 6**.

6.2.2 Saline water resistance

In order to compare the effect exercised by the temperature difference between the pipe and saline water with the effect by cathodic disbonding on the peeling length from the defect on the PE film of the PE-coated pipe, test pieces with a 5 mmϕ hole on their PE-coated film were immersed in a 3% NaCl solution at 60°C for 30 days. The results are shown in **Table 4**. From the comparison between samples Nos. 1 and 2, it is found that samples which were given only saline water immersion developed significant peeling of coated film under the conditions in which heat flows from the saline water to the pipe. If the direction of the thermal flow is reversed, however, peeling of the coated film is suppressed. When the saline water immersion is combined with electrochemical protection as in sample No. 3, the peeling of the coated film is less than that in No. 1, even if the pipe temperature is raised to 90°C and the saline water temperature to 60°C. As a result, it has been clarified that the effect of the temperature difference between the saline water and the pipe, rather than the effect of the cathodic disbonding, is noticeably large on the peeling of PE-coated film by saline water immersion.

The water permeation through organic film is greatly affected by the temperature difference between the top surface and the bottom surface of the film; and when the direction of water diffusion coincides with that of the heat flow, a coefficient of permeability is measured which is far larger than the value calculated by concentration diffusion[20]. This phenomenon can be better understood, if mass transfer due to a thermal gradient, that is, the so-called thermal diffusion term shown in eq. **(2)**, is taken into consideration as a diffusion mechanism other than concentration diffusion[20].

$$\frac{\partial c}{\partial t}=\frac{\partial}{\partial y}\left(D_1\frac{\partial c}{\partial y}+D_2c\frac{\partial T}{\partial y}\right) \quad \cdots\cdots\cdots\cdots\cdots\cdots(2)$$

c: Concentration
t: Time
y: Depth
T: Temperature
D_1: Diffusion coefficient
D_2: Thermal diffusion coefficient

It is considered, therefore, that water permeation through the resin is accelerated by concentration diffusion and thermal diffusion, and water is accumulated between the resin and the base metal until fluid pressure is increased more than adhesive strength between the coated film and the base metal, thereby causing peeling of the coated film.

As can be seen from the results so far obtained, the thermal diffusion term in eq. **(2)** exercises a significant effect on the coating performance even in the case of a PE-coated pipe whose coated film is hydrophobic and of the thick (3 to 4 mm) film type, so that if PE-coated pipes are to be used in such an environment as will cause the PE film to come into contact with water in the pipeline operation, it is necessary to maintain and control the conditions under which the temperature of the pipe will become higher than that of water.

Table 4 Effect of gradient temperature on hot salt resistance and cathodic protection of PE coated on pipes with an artificial damage of 5 mm diameter after 30 days tests

No.	Test methods	Temperature* of PE coated side	Temperature of steel pipe side	Length** of delamination (mm)
1	Hot salt resistance	60°C	43°C	43.1
2	〃	60°C	90°C	4.5
3	Cathodic disbonding***	60°C	90°C	10.5

* Immersed in 3% NaCl solution
** Length of delamination is the distance between the edge of artificial damage and the detachable point of coating layer
*** Voltage between electrodes: 3.3 V

7 Conclusion

In order to obtain the maximum value of the operating temperature of pipelines externally PE-coated, an investigation was made mainly on hot water resistance which is most important for the mechanical properties, such as durability and an anticorrosive property, of the coating material at elevated temperatures. Major results of the investigation are shown below, and it was found that high-density PE-coated pipes manufactured by Kawasaki Steel can satisfactorily withstand long-term operation at an elevated temperature of 80°C:

(1) High-density PE is superior to low-density PE in mechanical properties such as the softening temperature as well as penetration and impact resistance at elevated temperatures.

(2) It is estimated that the high-density PE which has been developed for use in the coating material for large-diameter pipes will withstand use at 100°C for more than 40 years.

(3) The amount of water vapor that permeates the coated film is smaller for high-density PE than for low-density PE, and particularly, the pipe coated with high-density PE has excellent anticorrosive properties at an elevated temperature.

(4) Under the conditions where heat flows from the steel surface side to the coated film side during pipeline operation, it is considered that a satisfactory anticorrosive property can be maintained for a long period even in an environment where water exists outside the coated pipelines.

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