Development of Polypropylene Coated Steel Pipe for High Temperature Service

by

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Synopsis

Recently, the demand for coated pipe applicable in high temperature service has increased because the temperature of material transported in linepipes has risen. A polypropylene coated seel pipe used at more than 80°C *was developed and its mechanical properties, thermal oxidation resistance, and corrosion resistance were discussed.*

Of the mechanical properties, low temperature embrittlement was improved with the use of a block-copolymer PP.

Thermal oxidation resistance was improved by the addition of antioxidant.

A one-liquid type thermosetting epoxy primer which is both easily applied and rapid curing improves corrosion resistance at high temperature without adversely affecting performance. The developed PP coating is expected to protect steel pipe from corrosion under severe conditions of more than 80°C*, and to be useful for* 30 *years at* 110°C *but less so at* 120°C*. This developed PP coating has been already used practically and is beginning to be used as linepipes for high temperature service all the world.*

1. Introduction

Recently, polyethylene coated steel pipes and fusion bonded epoxy coated steel pipes are being used in pipelines which transport crude oil and natural gas[1),2)]. However, pipeline temperature seems to be increasing as a result of higher transport pressure. As a result, the demand for external corrosion-protection-coated steel pipe applicable with temperatures over 80°C is increasing.

Polyethylene (PE) coated steel pipes have shown excellent corrosion protection properties, but in high temperature service, the coating becomes fairly soft and is susceptible to damage[3)].

On the other hand, fusion bonded epoxy (FBE) coated steel pipes have been thought to be much more suitable for high temperature service. However, this coating is susceptible to damage by mechanical impact, and has a high water absorption ratio[2)].

Polypropylene (PP) resin is a semicrystalline polyolefin resin like PE resin. A new coated steel pipe for high temperature service was developed by using the PP resin block-copolymerized with PE[4)].

The PP resin undergoes easily thermal oxidation deterioration with heat and oxygen though it has excellent strength at high temperature in comparison with PE resin. Improvement to thermal oxidation resistance using on antioxidant (AO) was investigated .

Moreover, it tend to disbond from steel material, especially in wet condition, but superior in water-proof barrier because of a no polarity polymer same as the PE resin.

Improvement to bonding properties by chromate treatment and primer coating has been studied[5)~7)]. In this report, improvement to corrosion protection properties at high temperature with application of a one-component liquid-type thermosetting epoxy primer was investigated.

2. Coating Composition and Problem of PP Coated Steel Pipe

Figure 1 shows the coating composition of a PP coated steel pipe.

It is important for PP coating to have excellent impact resistance at both high and low temperature because it is used in cold areas, as well as excellent corrosion protection. Moreover, indentation by gravel under soil pressure is a big problem for the PP coating when it is used underground at high temperature. These phenomena were investigated in section 3.

In general, it is easy for PP resin to deteriorate with heat oxidation because it has a lot of the third class carbons (carbon combined with three carbon atoms and a hydrogen atom) in the structure though it has high strength at high temperature. Therefore, it was important to analyse heat deterioration in the PP resin and give the long lasting durability to the PP coating, investigated in section 4.

On the other hand, bonding durability of the coating was an important factor and bonding durability under cathodic protection was mainly investigated in section 5. The modified PP in each the internal layer, the primer, and the chromate film plays a bonding role and improves bonding durability. This study aimed at imporoving the primer in consideration of higher productivity.

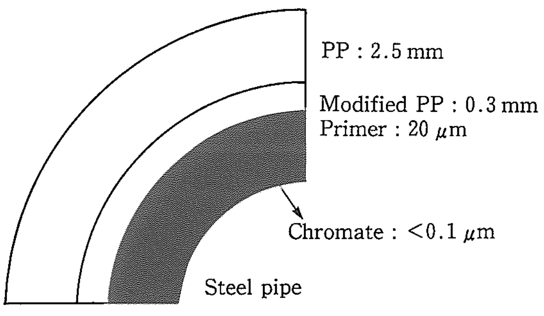

Fig. 1 Composition of polypropylene coated steel pipe

3. Mechanical Properties of PP Coating

3.1 Mechanical Properties of PP Coating at Low Temperature

Homo-PP resin, which is made solely from the propylene, can not be used as on external coating in linepipes because it has a high brittleness point (approx. 0°C).

In order to solve this problem, modification of PP resins with PE resins which have excellent low temperature embrittlement is investigated.

Figure 2 shows the impact resistance of four coatings, applied Homo-PP resin and three kinds of modified PP resins, across a wide temperature range. The impact tests were done by the ASTM G 14 method. The impact resistance was estimated based on the minimum impact energy needed to damage the coating down to steel substrata.

The test results show that the modified PP resin coating have higher impact strength at low temperature than the Homo-PP resin coating and that the Block-copolymer PP resin coating has a much high impact strength even at -30°C. The fracture mode of the Block-copolymer PP resin coating wasn't ductile. The Block-copolymer PP resin has an Ethylene Propylene Rubber (EPR) intermediate layer between the PP matrix layer and PE dispersion layer (**Photo 1**), and so, the impact force is transmitted from the PP matrix layer to the PE dispersion layer, which absorbs the impact force. On the other hand, PE-blend PP isn't ductile at low temperature because it has no EPR intermediate layer between the PP matrix layer and PE dispersion layer.

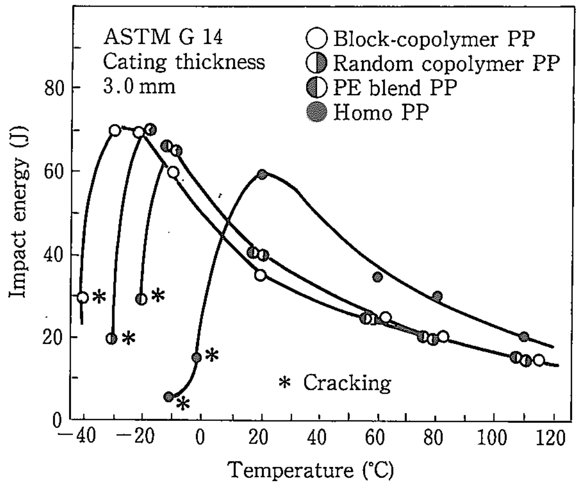

Fig. 2 Effect of temperature on impact strength of various PP coating
(Adhesive : PP modified with maleic anhydride
Embrittlement temperature : −53°C
Coating thickness : 0.3 mm)

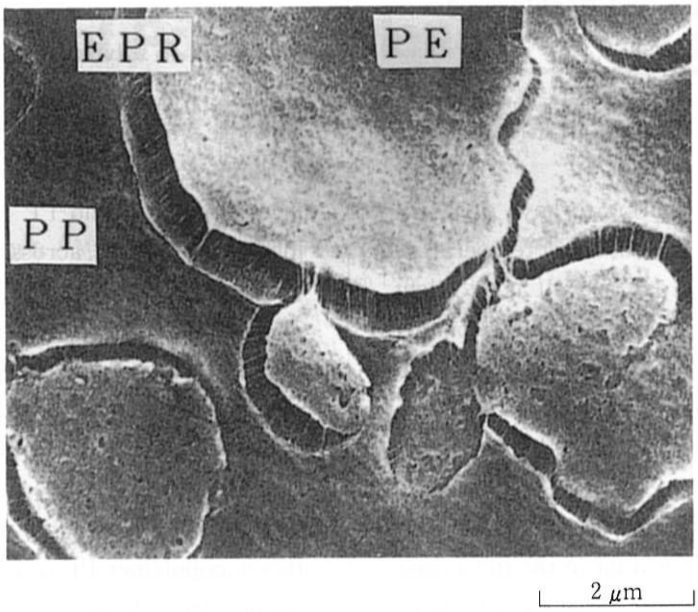

Photo 1 Domain structure of block copolymer PP

3.2 Mechanical Properties of PP Coating at High Temperature

PP resin softens with a rise in temperature and does remarkably in the melting point neighborhood because it is a semicrystalline thermoplastic resin. Modification by PE influences in the direction where high temperature strength is decreased because the melting point of PE is about 40°C lower than that of PP.

Gravel indentation under soil pressure might decrease corrosion protection performance when the external coating in a buried steel pipe softens. So, high temperature strength was evaluated in accordance with the indentation test specified by DIN 30670 (Push for 24 hours under 9.8 N/mm^2 of pressure with a needle of 2.5 mm^2 in cross-section area).

Figure 3 shows the indentation resistance of various PP coatings and the PE coating at high temperature. The test results show that the indentation resistance of the modified PP coatings is lower than that of the Homo-PP coating but higher than that of the PE coating, and that the decreasing degree of indentation resistance is not related to the kind of the modified PP resin. Thus, it was found that the Block-copolymer PP resin coating did not soften even at 120°C.

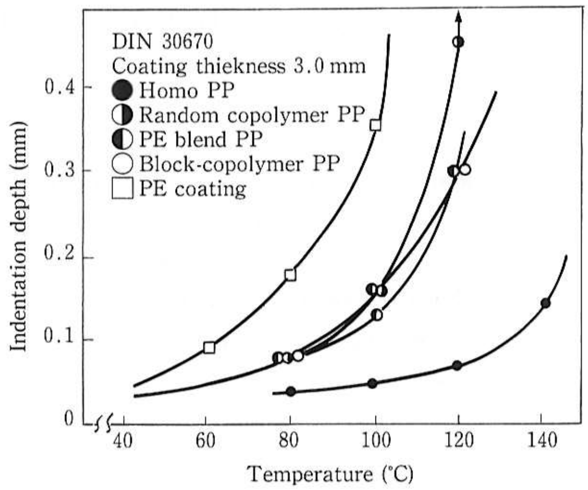

Fig. 3 Indentation resistance of various PP coating at high temperature

3.3 Summaries

The Block-copolymer PP resin was selected for PP coating from the above-mentioned test results. Characteristics of this Block-copolymer PP resin and adhesive PP resin modified with maleic acid anhydride are given in **Table 1**, and mechanical characteristics on the coated steel pipe in **Table 2**. It is found that high temperature characteristics are improved in comparison with conventional PE coating.

Table 1 Characteristics of block-copolymer PP and modified PP adhesive

Items	Test method	Block copolymer PP	Modified PP adhesive
Density (g/cm³)	JIS K 6760	0.89	0.89
Tensile strength (N/cm²)	JIS K 6760	3 700	2 450
Yield strength (N/cm²)	JIS K 6760	2 150	1 400
Elongatipn (%)	JIS K 6760	630	730
Melt index (g/10 min)	ASTM D 1238	0.9	0.6
Embrittlement temperature (°C)	ASTM D 746	−45	−53

Table 2 Comparison of mechanical properties in PE and PP coatings

Items	Test method		PE coating	PP coating
Coating thickness (mm)			3.0	3.0
Adhesion strength (N/cm)	DIN 30670		200	>200
Impact strength (J)	ASTM G 14	−30°C	55	70
		23°C	25	40
		100°C	<5	20
Lime stone drop resistance (times)	ASTM G 13		>20	>20
Hardness	ASTM D 2240		60	67
Indentation resistance (mm)	DIN 30670	23°C	0.02	0.01
		60°C	0.10	0.05
		100°C	0.36	0.16

4. Long Term Durability at High Temperature

4.1 Heat Deterioration Test

In this study, deterioration was promoted by aging the PP resin in an oven at a high temperature below the melting point of PP, and thermal oxidation resistance was evaluated by measuring the change in various physical properties over time.

The specimen used was the above-mentioned Block-copolymer PP with AO (hindered phenol + sulfide) and rutile type titanium dioxide. The amount of the additives was changed .

Moreover, the oven temperature was gauged in four steps, 110, 120, 150, 160°C, and service life of this PP coating on thermal oxidation resistance was predicted using on Arrhenius equation.

4.2 The form of Heat Deterioration

In **Figure 4**, an example of the results obtained by oven aging tests are shown. In this oven aging test, the density, the melt index, and tensile elongation were measured initially and after aging at certain times, and the retention rates from the initial value was estimated. In this example, temperature was 150°C, and the tested coating layer contained 0.3% AO and 0.7% TiO_2. In all the samples, the pattern of change in properties was the same as in **Fig. 4**. That is; at the initial stage, there was a slight increase in density due to an increase in crystallines, a decrease in melt index and tensile elongation due to

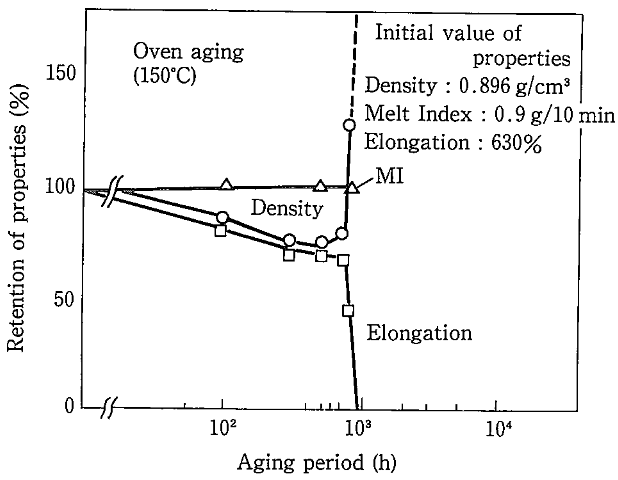

Fig. 4 Heat deterioration behavior of PP in oven aging

cross-linking reaction. At the next stage, there was an abrupt increase in melt index , and an abrupt decrease in tensile elongation followed as essential deterioration. Just after that, there were many cracks in the PP coating.

4.3 Service Life Prediction

In general, it is known that the addition of AO is very effective towards improving oxidation resistance in PP resin. AO controls the radical chain reaction which progresses the oxidation reaction of PP resin explosively. That is; a radical chain reaction cannot be controlled when the AO in the PP resin is consumed. As a result, a rapid oxidation takes place and rapid changes in physical properties occur. Therefore, service life is influenced by the consumption of AO.

Moreover, because this reaction is a chemical reaction, there is the possibility of it becoming on Arrhenius type reaction as shown in following equation.

$k = Ae^{(-E/RT)}$ ·················(1)

k : Reaction rate coefficient E: Activation energy

R : Gas constant T : Absolute temperature

If it is an Arrhenius type reaction like that shown in equation (1), a logarithm of service life and an reciprocal of the absolute temperature show a linear relationship.

Figure 5 shows the relation of the PP coatings which contain various addition ratio of AO. It is found that this reaction is Arrhenius type because plotting is linear, and that the reaction phase doesn't change because inclination is constant even in various AO ratios. Service life of a PP coating with 1.2 % AO was predicted based on this result.

The straight line is drawn from a measured point at 160°C to run side by side with other lines. It is predicted that service life at 110°C is 30 years, according to this line.

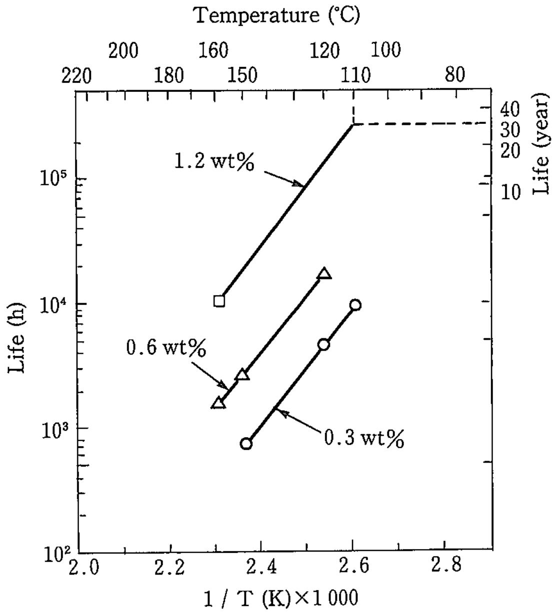

Fig. 5 Effect of antioxidant quantity on service life at high temperature

5. Corrosion Protection Properties

5.1 Idea of Adhesion

PP has an excellent water-proof barrier like PE because of the extremely small polarity. **Figure 6** shows the changing behavior of electrical resistance in the coating with immersion time in 80°C tap water. It is found that the PP coating has a high electrical resistance even after long term immersion in hot water. On the other hand, there is problem, of poor adhesion to steel material. Adhesion deteriorates easily because of the extremely small polarity, as with PE resin.

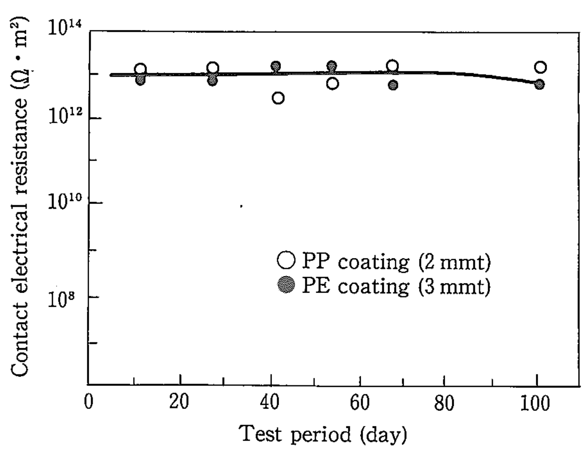

Fig. 6 Electrical resistance after 80°C water immersion test

In order to solve this problem, the PP coating system is applied for the multilayer coating system shown in **Fig. 1**.

5.2 About Cathodic Disbonding

In general, the external coating in linepipes is used together with cathodic protection. Cathodic disbonding resistance is required for the external coating. The cathodic disbonding of the coating is said to occur by OH^-, formed by the electrolysis of water at any damaged area of coating. It is known that chromate treatment and primer coating shown in **Fig. 1** are very effective towards improving cathodic disbonding resistance.

5.3 Outline of Developed Primer

A primer coating is usually applied online, and a high-speed curing primer is strongly demanded as a small and medium diameter pipe coating because of the high productivion line speed.

In order to solve this problem, an ultraviolet ray (UV) curable primer was developed and used practically. However, the performance of this UV curable primer was insufficient at high temperature because it was developed for the PE coating[6].

Performance improvement of the UV curable primer at high temperature has been investigated for the PP coating, but it is limited to an improvement in cathodic disbonding resistance at high temperature because there is a lot of ester linking in the molecular structure[7].

On the other hand, a two-component type thermosetting epoxy primer, which had been used before, had the problem of being hard to coat online, though it offers excellent corrosion protection performance at high temperature. Because its curing rate was slow and because its coating function decreased if its curing rate was risen.

A one-liquid type thermosetting epoxy primer was investigated to solve this problem in this report. That is; this primer doesn't cure at ambient temperature but cures rapidly when the microcapsule wall melts at high temperature because it contains a mycrocapsuled imidazole hardener which improves the reactiveness very much.

It is believed that this epoxy primer which is both easily applied and rapid curing improves the cathodic disbonding resistance at high temperature because its molecular structure does not contain the ester linking.

5.4 Cathodic Disbonding Resistance

Figure 7 shows the results of cathodic disbonding tests at 20°C and 65°C. It was found that the newly developed primer greatly improved the cathodic disbonding resistance at high temperature in comparison with an UV curable primer.

On the other hand, there are cases where the linepipe is laid not only underground but also on the bottom of the sea.

For this case, coated linepipes will be used under a thermal gradient between internal and external.

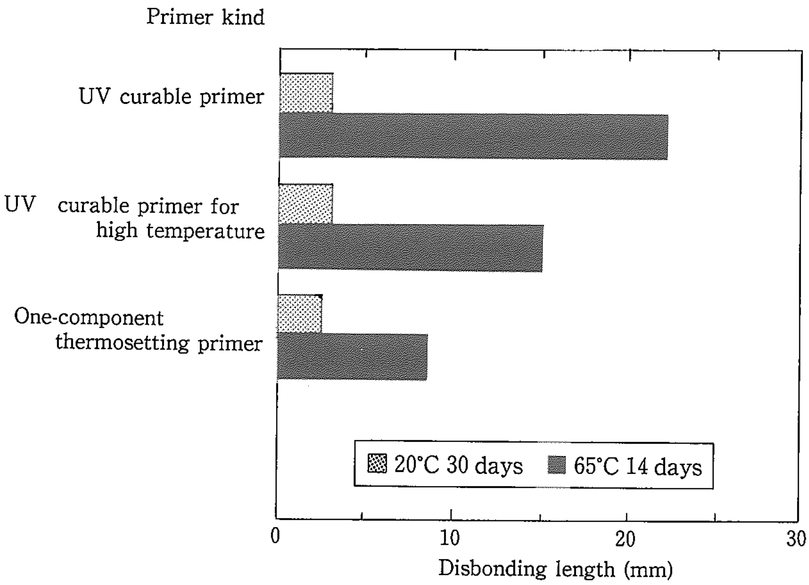

Fig. 7 Results from cathodic disbonding test

In order to simulate such states, the cathodic disbonding test was done under the thermal gradient shown in **Fig.** 8.

Figure 9 shows the change in cathodic disbonding by test cycle under a thermal gradient condition of an internal fluid at 120°C and external 3 % brine solution at 30°C.

Cathodic disbonding tends to saturate in 60 days. In general, it is known that the disbonding rate decreases gradually when disbonding length gets large, because cathodic current gets smaller through the narrow crevice at the disbonding edge. But, an other effect is suggested because disbonding stops rapidly in this test.

The interface temperature between the steel substrata and PP coating gets near the internal fluid temperature if the coating is enough thick, for example this coating. This is because the heat conduction coefficient of the PP resin is 1/100 or less the that of steel materials, and most of the thermal gradient is generated in the PP coating.

That is; it is sure that there is an interfacial temperature near 120°C in this test.

It is thought that the disbonding edge becomes high temperature because the flow of the liquid through the narrow crevice at the disbonding edge departs from the initial coating. defects do not occur easily and because the PP resin over the crevice plays a role of insulation even if coating defects are cooled by brine water.

It is thought that the temperature at the disbonding edge rises gradually as disbonding progresses and finally passes 100°C and dries there. It is thought that the disbonding doesn't progress in such situations any longer and stops as a result. This appearance is shown in **Fig. 10** in the schematic diagram.

That is; long term cathodic disbonding does not have reason to be alarmed in the situation of an internal fluid over 100°C, though the cathodic disbonding progresses somewhat at the initial stage near the coating defect, because it is controlled by the drying effect afterwards.

5.5 Heat Cycle Resistance and Salt Water Resis Tance

The heat cycle resistance of the PP coating was investigated. 20 cycles were examined at 120°C for 16 hours and -30°C for 8 hours. This was a very severely accelerated condition because it was thought that this coating was applicable in temperatures from -30

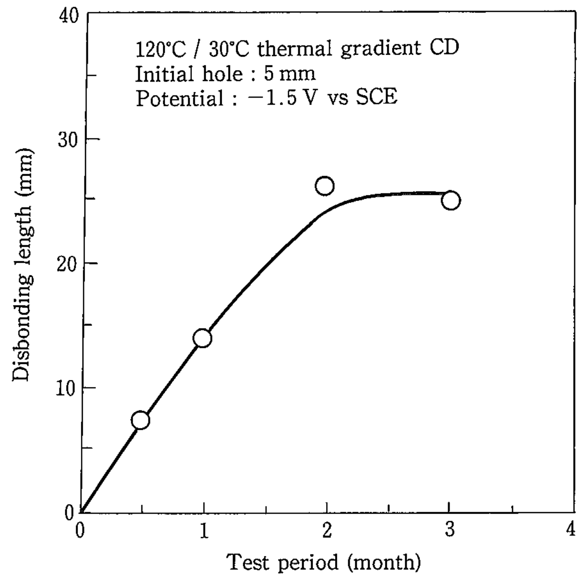

Fig. 9 Results of cathodic disbonding test under thermal gradient

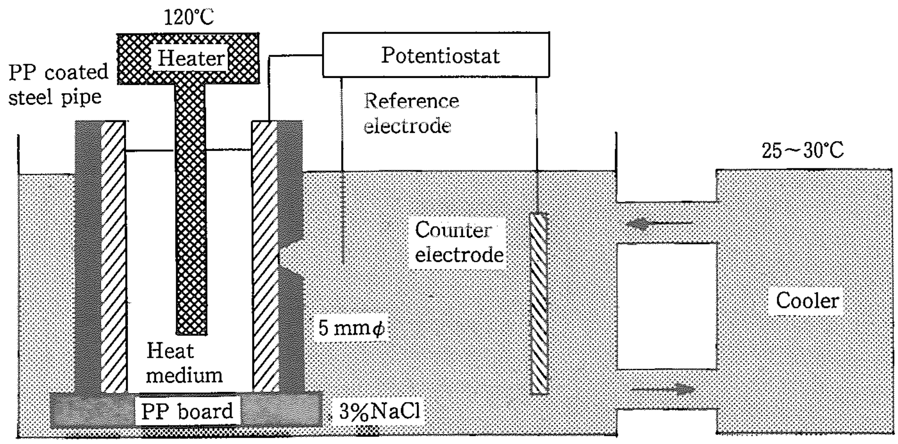

Fig. 8 Equipment of cathodic disbonding test under thermal gradient

to 120°C, as above mentioned.

Moreover, edge creeping was investigated in the salt water immersion test at high temperature.

The results of these corrosion protection tests are given in **Table 3**.

It was found that this developed PP coated steel pipe has excellent corrosion protection and the adhesion durability.

6. Conclusion

The mechanical properties, thermal oxidation resistance, and corrosion resistance were discussed herein in regards to the developed PP coated steel pipe.

Of the mechanical properties, low temperature embrittlement was improved with the use of Block-copolymer PP. Thermal oxidation resistance was improved by the addition of AO.

A one-liquid type thermosetting epoxy primer which is both easily applied and rapid curing improves corrosion resistance at high temperature without adversely affecting performance. The developed PP coating is expected to protect steel pipe from corrosion under severe conditions of more than 80°C, and to be useful for 30 years at 110°C but less so at 120°C.

This developed PP coating has been already used practically and is beginning to be used as linepipes for high temperature service all the world.

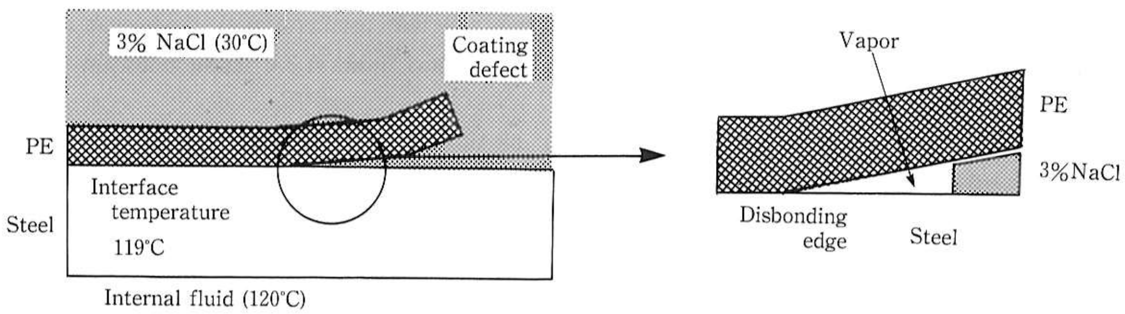

Fig. 10 Schematic diagram of disbonding edge on thermal gradient CD

Table 3 Corrosion resistance of PP coating

Test items		Results
Coating thickness (mm)		3.0
Electrical resistance ($\Omega \cdot m^2$)	Initial	$\geqq 10^{13}$
	20°C water immersion 100 days	$\geqq 10^{13}$
	80°C water immersion 100 days	$\geqq 10^{13}$
Cathodic disbonding length (mm) 3%NaCl−1.5 V vs. SCE	20°C 30 days	2.5
	65°C 14 days	8.5
	120/30°C 30 days	14
Heat cycle resistance (disbonding length : mm) −30°C 8 hours ⇄ 120°C 16 hours 20 cycles		0 (No disbonding)
90°C 3%NaCl immersion (disbonding length : mm)		0 (No disbonding)

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