Service Life Prediction of Polyethylene Coated Steel Pipe for Elevated Temperature

by

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Synopsis

The indentation and thermal oxidation resistances of polyethylene coated steel pipe at elevated temperature were investigated. A polyethylene coating with 3 700 *ppm phenolic antioxidant which improved thermal oxidation resistance was developed. It is predicted that this developed coating is indented by only less than a quarter of initial coating thickness under* 9.8 N/mm^2 *compression stress at* 80 °*C after* 40 *years. This is no problem on the practical use.*

The service life of this polyethylene coating at 80 °*C is predicted over* 40 *years under both dry and wet conditions from results of oven aging and autoclave tests. This polyethylene coated steel pipe has been applied to local air conditioning service, and showed excellent durability at elevated temperature.*

1. Introduction

Recently, polyethylene resin (PE) coating and fusion bonded epoxy (FBE) coating have been used instead of bitumen (asphalt and coal tar enamel, etc.) coating as the external corrosion protection coating of buried steel pipe because of their superior corrosion protection properties[1),2)].

However, high temperature operation of the pipelines which transport crude oil and natural gas seems to be increasingly as a result of higher transport pressures for greater flow efficiency. Moreover, steam and high temperature water piping is increasing used for local air conditioning piping. As a result, external corrosion protection coating now requires high temperature properties.

FBE coating softens very little at high temperature because of the thermosetting resin. However this coating is susceptible to being damaged by mechanical impact and has a high water absorption ratio[2)].

On the other hand, PE resin provides excellent corrosion protection because it does not have polarity in individual molecules, but in high temperature service, softening and long-term heat oxidation deterioration with heat and oxygen becomes a problem.

Thereupon, the improvement of heat oxidation resistance with antioxidant (AO) was investigated. Moreover, service life of PE coating with AO was predicted with respect to mechanical strength and heat oxidation deterioration.

2. Development of PE Coating for Elevated Temperatures

Figure 1 is schematic diagram showing the PE coated steel pipe applied to steam composite pipe.

PE coated steel pipe is applied to the outside tube of an insulated double tube, and the temperature of an external coating reaches about 80°C or less when the fluid inside is steam at 200°C.

To operate at such temperatures, softening and oxidation of the PE resin are problems. PE resin of a range of densities is manufactured by various methods, and resin of 0.915-0.965 g/cm³ in density is used in general.

The reason why the density of the PE resin changes

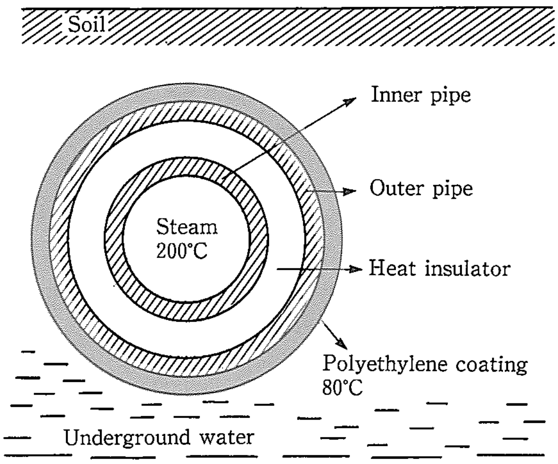

Fig. 1 Schematic diagram of steam composite pipe

is that crystalinity changes depending on the number and the length of the branch chains which derives from the PE main chain. The change in the crystalinity influences the other physical properties as well as resin density very much[3].

In general, the PE resin is improved in strength at ambient temperature and high temperature by increase in density.

On the other hand, environmental stress crack resistance (ESCR) tends to decrease with increase in density[4].

Medium density PE (MDPE) of 0.938 g/cm^3 in the density was selected as the coating resin in considera-tion of these points. **Table 1** shows properties of this MDPE.

The addition of AO was examined with the aim of improvement of the heat oxidation resistance of this PE resin. In the evaluation of heat oxidation resis-tance, the OIT correlating with effective remaining AO in the PE resin was measured with a differential scanning calorimeter (DSC). The OIT measurement sample is cut from 1 mm depth from the surface of the test specimen and has temperature rising by 20°C/min during the N_2 flow (50 cm^3/min). Then, it maintained fixed temperature after reaching that temperature, and N_2 flow was substituted for O_2 flow (50 cm^3/min). Time from substitution to exothermal beginning based on the oxidation reaction of PE was assumed to be OIT[5].

Table 1 Properties of polyethylene

Items	Unit	Typical test results
Density	g/cm^3	0.94
Melt index	g/10 min	0.21
Vicat softening point	°C	≧115
Tensile strength	kgf/cm^2	≧250
Elongation	%	>500
Hardness (Shore D)	—	≧55
Water absorption	%	0.02

Moreover, OIT of the PE resin with addition of hindered phenol AO or sulfide AO was measured at various temperatures, and the effect on the improve-ment of heat oxidation resistance was investigated.

Figure 2 shows the result. Plotting the logarithm of OIT to reciprocal of the absolute temperature (Arrhenius plot) became linear and the consumption reaction of the AO progressed by the reaction of the Arrhenius type[4),6),7]. It is clear that the reaction is Arrhenius type because the inclination of the straight line of Arrhenius plot does not change even if the amount of the addition of hindered phenol AO addi-tion is increased.

Moreover, sulfide AO performance at the high temperature is excellent. However, service life at 80°C predicted with Arrhenius plot becomes shorter compared with hindered phenol AO. It is certain that the difference of the activation energy in the con-sumption reaction of AO caused this.

When the target of the service life at 80°C is assumed to be 40 years, neither of these three kinds of AO addition PE clear the target.

Hindered phenol AO 3 700 ppm addition PE was selected as a development material from the view-point of offering more excellent product in durability in consideration of the error of the service life predic-tion.

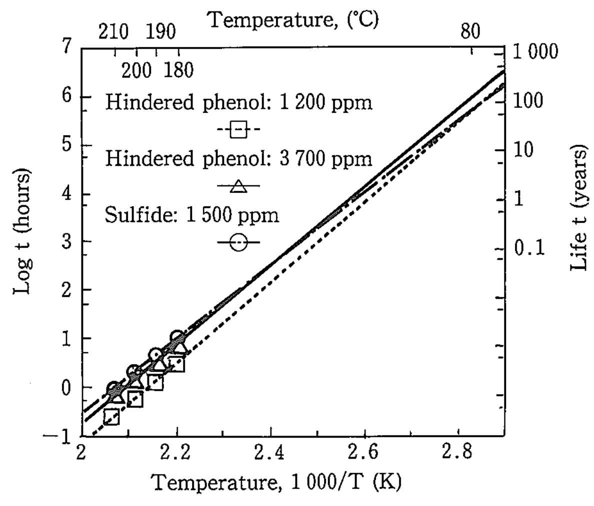

Fig. 2 Improvement in durability with antioxidant

3. Mechanical Properties of Heatproof PE Coating

In general, the PE coated steel pipes are applied to lays underground.

At this time, the problems are creep indentation with the gravel in use for laying underground and impact generated when the gravel is returned to bury the pipe.

Impact resistance was excluded from the examination item because the impact strength is enough at ambient temperature and the temperature when the impact is generated is ambient.

On the other hand, creep deformation generated by gravel indentation with the resin softening at high temperature (ex. 80°C) is a serious problem.

Then, a change of the compression indentation depth at 80°C with the lapse of time was examined in accordance with the indentation test specified by DIN 30670 (Push for 24 hours by pressure 9.8 N/mm^2 with the needle of 2.5 mm^2 in the area). The indentation test was done in the 3 % brine solution to consider resin softening by water absorption.

Figure 3 shows the result. The change of indentation depth becomes linear on Log-Log plot after 100 hours or more passed. In general, the resin is viscoelastic and has both elasticity the viscosity. It is sure to be mainly deformed by the viscosity a long time later, that is, after 100 hours or more, but the elastic deformation happens in a short time.

In general, this viscositic deformation is called creep deformation and it is known that the creep deformation of polymer resin follows the Nutting equation below[8),9)].

ε (t)=Kσtn

Where ε (t): Strain at time t K, n : Constant which depends on temperature σ : Loading stress

When you take the logarithm of both sides of this equation

Logε (t)=nLogt+LogKσ

That is, it is found that the Log-Log plot becomes linear. The indentation depth after 40 years at 80°C was therefore predicted with extension of the straight line. Its value is 0.596 mm and 1/4 or less of the PE coating of 2.5 mm in the initial film thickness. Therefore, it is certain not to have a big influence on the performance.

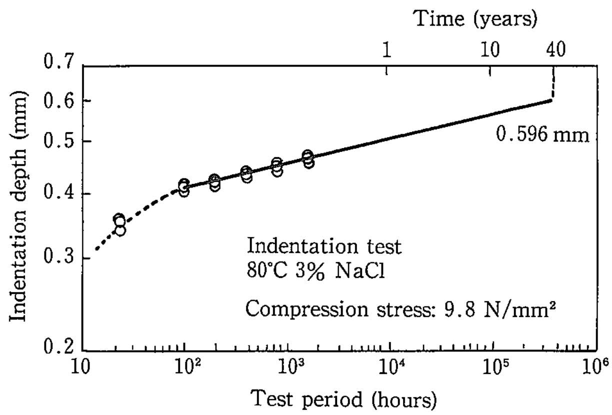

Fig. 3 Change in indentation depth at 80°C

4. Service Life Prediction of PE Coating

4.1 Heat Deterioration Test of PE Coating

In Chapter 2, it was stated that PE coating was expected to have service life of 40 years or more, which is predicted by Arrhenius plot of OIT.

However, the error of the prediction with this method becomes large because extension of the straight line is based on the measurement value at a very high temperature. Moreover, it is pointed out that prediction based on the OIT measurement value at such high temperatures does not agree with the measurements from the oven aging test at a lower temperature[7),10)].

Moreover, the underground environment is not limited to being a dry one like oven aging test and can be assumed to be a wet environment with underground water as shown in **Fig. 1.**

The heat deterioration resistance was evaluated with the oven aging test as a simulation test of a dry environment and with the autoclave test as a simulation test of the wet environment. Disk PE sheet was applied as the specimen for the heat oxidation test at a fixed time. The tensile test specimen was cut out as a dumbbell shape from the sheet and the OIT measurement test specimen was cut from 1 mm depth from the surface of the sheet. Both were evaluated.

The heat deterioration test conditions are shown in **Table 2** and the evaluation test method of the PE resin after heat deterioration test is shown in **Table 3.**

Table 2 Test conditions

Test	Temperature (°C)	Test period (months)	Atmosphere	Specimen shape and size	Evaluation method
Oven aging test	80 120 140 160	0.25 0.5 1,2,3,4 6,12,18	Air	Disk shape 100 mm dia. 2.5 mm thickness	Yield strength Elongation OIT
Autoclave test	80 120 140 160	0.25 0.5 1,2,3,4 6,12,18	Deionized water	Disk shape 100 mm dia. 2.5 mm thickness	Yield strength Elongation OIT

Table 3 Evaluation test method

Test	Condition	Specimen
Tensile test	JIS K 6760 Tensile rate 50 mm/min	JIS K 6760 half dumbbell
OIT measurement	DSC method Temperature 200°C N_2, O_2 flow 50 cm^3/min	Cutting sample surface layer 1 mm about 10 mg

4.2 Heat Deterioration Test Result

Figures 4-7 show the result of the tensile test. The yield strength of the PE resin increases gradually in both dry and wet conditions over time, but the change is comparatively small. On the other hand, the elongation of PE resin tends to decrease rapidly after a certain time passes but not linearly.

It decreases earlier at high temperatures, and in dry conditions than in wet conditions. It is certain that PE resin deteriorates earlier in dry conditions with high concentrations of oxygen because the heat deterioration happens as heat oxidation deterioration.

A change in OIT with the passing of time is shown in **Figs.** 8 and **9.**

It is found that OIT decreases gradually with the passing of time, and that the decrease speed of OIT becomes larger at the higher test temperature. A reason why 5 minute OIT is assumed to be the starting point for deterioration in **Figs.** 8 and **9** is described in the next paragraph.

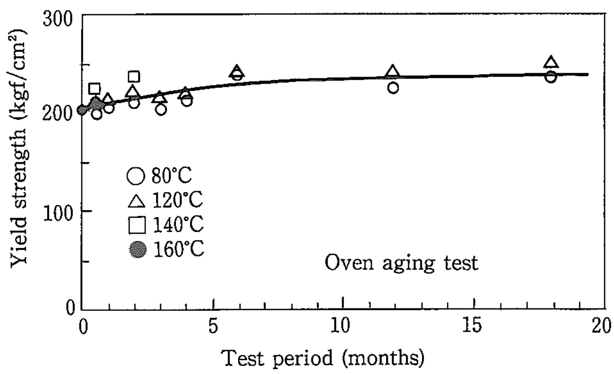

Fig. 4 Change in PE yield strength at various temperatures

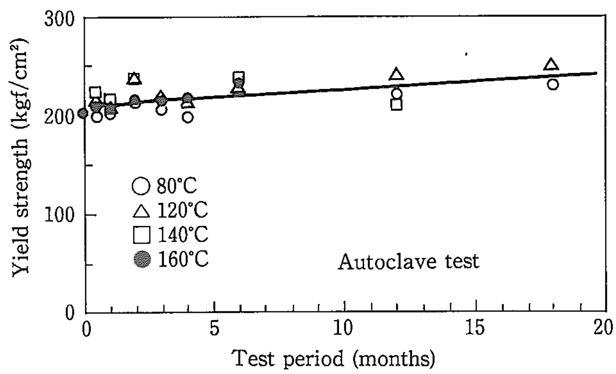

Fig. 5 Change in PE yield strength at various temperatures

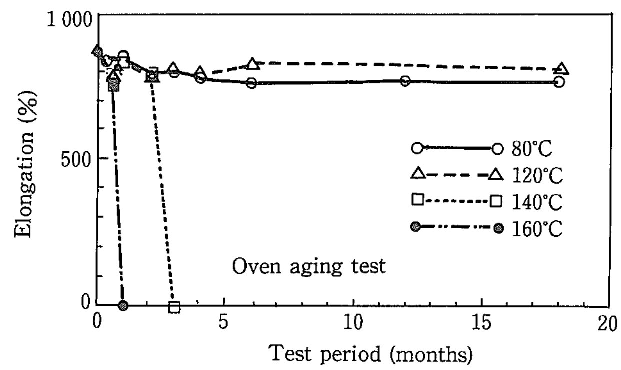

Fig. 6 Change in PE elongation at various temperature

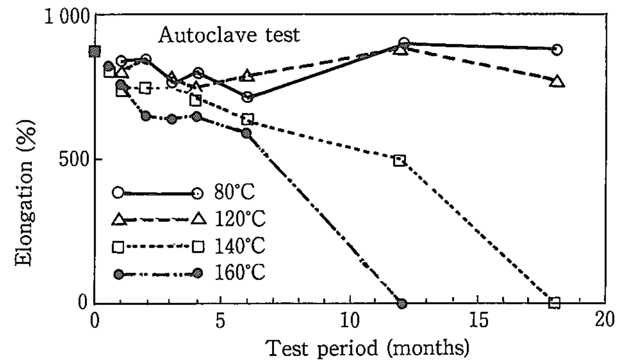

Fig. 7 Change in PE elongation at various temperature

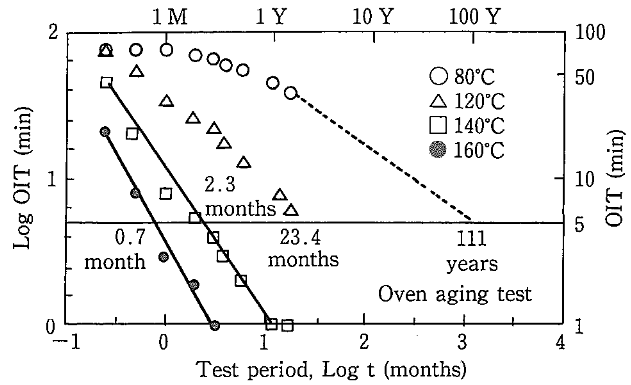

Fig. 8 Change in OIT at various temperature (5 minutes OIT means starting point of deterioration)

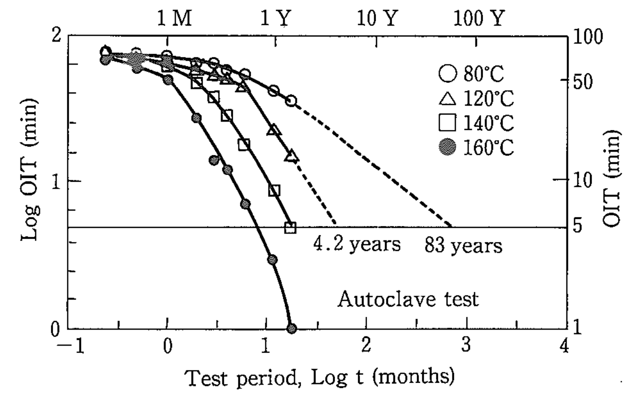

Fig. 9 Change in OIT at various temperature (5 minutes OIT means starting point of deterioration)

4.3 Service Life Prediction

It is important for the service life prediction to be evaluated method. However, there is no clear definition in service life, and the time when the demand property is lost is called the service life in general.

The evaluation is very difficult, though the time when corrosion resistance of the coating is lost is sure to represent the service life for the corrosion protection coated steel pipe.

In general, the service life of polymer resin on heat resistance is evaluated as the period when the elongation reduces to half of initial value. In this paper, a specimen for which elongation retention ratio is more than 50 % (430 % in the elongation) is considered sound according to this idea.

On the other hand, it is difficult to specify the time of reducing by half because the decrease in the elongation is not linear as mentioned above.

Figures 10 and **11** show an Arrhenius plot between a sound state (○) and a deteriorated one (●) for elongation.

It is known that the service life of the polymer resin (time when a certain performance becomes below a certain threshold) is expressed by Arrhenius type equations and that the plot becomes linear when the logarithm of service life is plotted for the reciprocal of the absolute temperature[7)11)].

At this time, the highest and lowest inclinations of the service life prediction line which meets the condition of being over ○ and below ● will show the range of the service life prediction. In dry conditions, a service life of 96-181 years was predicted at 80°C. On the other hand, the result has a big difference of about 40 times between maximum and minimum for 2.5-85 years in wet conditions. The accuracy improves if the interval of the tensile test is made shorter and time of reducing by half in the elongation is specified, but to test a large amount of specimens needs excessive labor.

Next, a change in OIT was given attention. The OIT changes comparatively linearly in the neighborhood of 5 minutes OIT, which is shown in **Figs.** 8 and **9.**

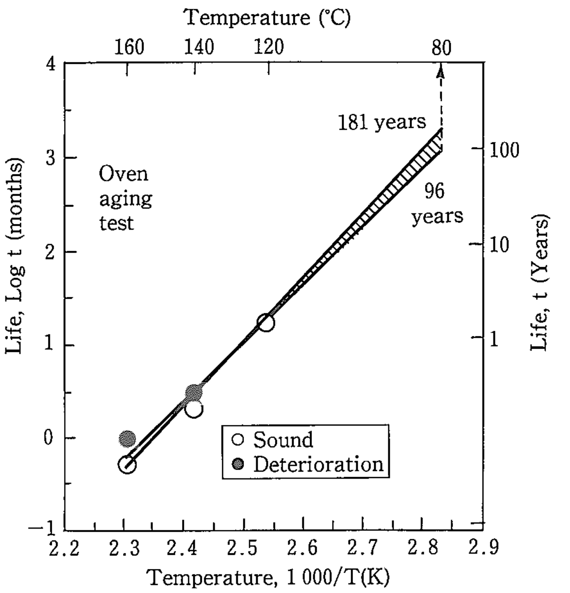

Fig. 10 Service life prediction of PE coating with Arrehenius plot on PE elongation
Sound: Elongation > 430%
Deterioration: Elongation < 430%

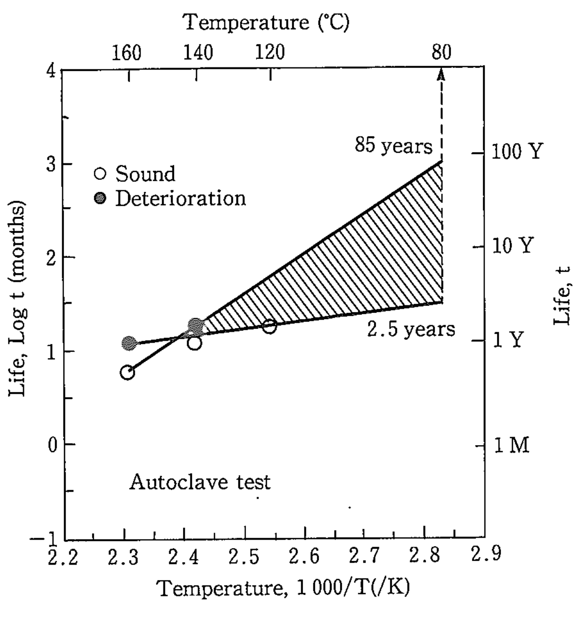

Fig. 11 Service life prediction of PE coating with Arrehenius plot on PE elongation
Sound: Elongation > 430%
Deterioration: Elongation < 430%

Theoretically, it is thought that the time when OIT becomes 0 is the service life. However, there is the possibility that OIT indicates a certain value other than 0 in the deteriorated state because remaining AO which related to OIT has a concentration gradient between the surface and interior of the PE resin.

It is found that the elongation is lost when OIT became five minutes or less, which is shown in **Fig. 12.** Then, the time when OIT becomes five minutes was considered to be service life. It is feared that the error of prediction becomes larger if the measurement value at 80°C is applied to prediction, though OIT changes comparatively linearly.

The OIT measurement value used and the test data at 120°C or more which approached for 5 minutes or less or 5 minutes was used.

The test periods which OIT became 5 minutes was obtained with extension of straight line about test data at 120°C or more except for 80°C, which shown in **Figs.** 8 and **9.**

A reciprocal of the absolute temperature and the logarithm of service life based on that value is plotted (Arrhenius plot), which is shown in **Figs. 13** and **14.** The service life of 47 years is predicted in the wet state and 126 years in the dry state. The predicted service life in the wet state is shorter than in the dry one though the deterioration at high temperatures is slower in the wet state than in the dry one because of the difference in the deterioration mechanism.

That is, the radical generated by heat oxidation of PE consumes AO in dry state[12], though bleeding or the lapse of AO by water becomes predominant because there is less oxygen in the wet state.

40 years or more is expected as the service life at 80°C for this coating in both dry and wet conditions.

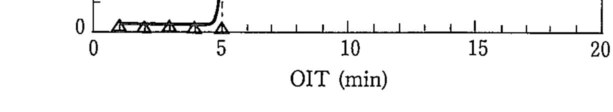

Fig. 12 Relationship between OIT and elongation

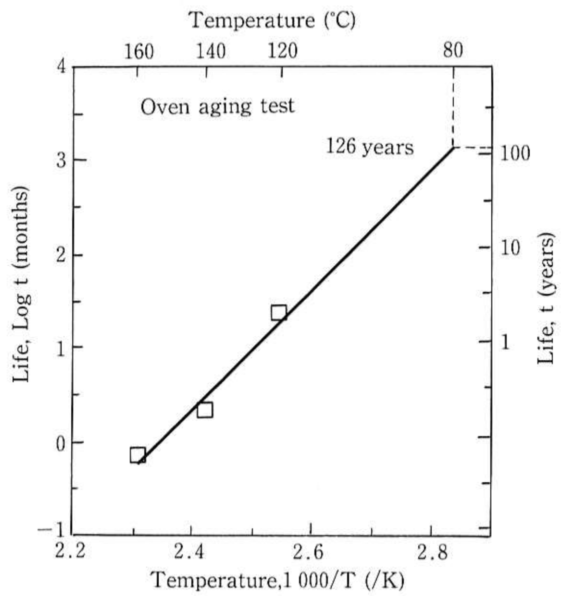

Fig. 13 Service life prediction of PE coating with Arrehenius plot (Life is time when OIT becomes 5 minutes)

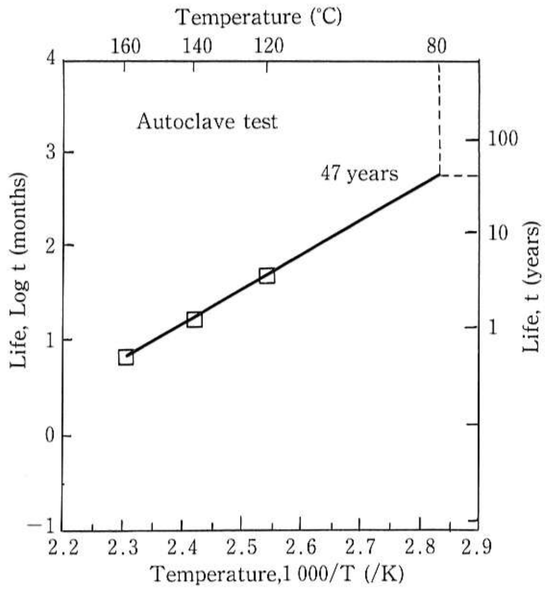

Fig. 14 Service life prediction of PE coating with Arrehenius plot (Life is time when OIT becomes 5 minutes)

5. Conclusion

The mechanical properties and thermal oxidation resistance were discussed from the viewpoint of service life prediction for PE coated steel pipe for elevated temperatures .

As for mechanical properties, indentation with gravel in the state of the resin softening at high temperature becomes a problem. However, the indentation depth under 9.8 N/mm^2 compression stress after 40 years at 80°C was predicted to be 0.596 mm and 1/4 or less of the PE coating of 2.5 mm in the initial film thickness. Therefore, it is certain not to become a problem on practical use.

Moreover, thermal oxidation resistance was investigated under both dry and wet conditions. Service life of this PE coating is predicted to be 47 years in the wet state and 126 years in the dry state and is expected to be more than 40 years in both cases.

This PE coated steel pipe has already been applied to local air conditioning and showed excellent durability at elevated temperatures.

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