Durability of Color Polyethylene Coated Steel Pipe

by

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Synopsis

The corrosion resistance and weatherability of color polyethylene coated steel pipe was investigated. Polyethylene coated steel pipe shows excellent performance in terms of corrosion resistance because of its barrier effect to water, high electrical resistance, and it has superior mechanical properties as well. The weatherability of the color polyethylene coating depends upon not only antioxidant content but also ultraviolet screening properties with pigments and ultraviolet absorbers. A new model adopting the ultraviolet screening properties was constructed to analyze the antioxidant consumption and diffusion in polyethylene. The service life of color polyethylene coating is predicted quantitatively by model function computation. The newly developed color polyethylene coated steel pipe has high corrosion resistance in severe corrosion environments as well as weatherability of more than 20 years.

1. Introduction

Recently, the requirements for painted steel pipe have become highly sophisticated with regard to severe corrosive environments such as in the sea or near the seashore. On places where flying salt particles are present, paint coating is generally applied to protect the steel pipe from corrosion, but the paint doesn't have enough corrosion resistance. Moreover, it disbonds from the steel pipe not only because of corrosion but also due to its photo-degradation under sunlight. As a result, paint must be applied every several years.

On the other hand, heavy duty coating with polyethylene (PE) has been utilized for several decades of anti-corrosion protection of steel line pipe[1]. This heavy duty coating is composed of PE resin over 2mm in thickness, and it has proven corrosion resistance at a high level for a long time in the line pipe fields[2]~[4].

However, it is well known that PE without additives also degrades when PE is exposed to sunlight, and ultraviolet rays (especially $\lambda = 300$nm) are the most important factor for photo-degradation of PE[5],[6]. Therefore, the problem of PE photo-degradation should be solved to secure long term durability (service life). In order to prevent photo-degradation, PE coating has been restricted to a black color made with the addition of carbon black[4]. On the other hand, the demand for color PE coated steel pipe has been increasing in recent years. In the case of color PE, pigments as well as stabilizers such as antioxidants (AO) and ultraviolet absorbers (UVA), must be added to prevent PE photo-degradation. However, to evaluate the service life of such PE under natural exposure, a long term period of time would be required, since the requirement of service life for heavy duty PE is more than 20 years. Because of the above, an artificial accelerated exposure test (AAET) is generally carried out to evaluate length of service life, yet a quantitative prediction of the service life of PE is very complicated at the present conditions[7]~[10].

This report describes the fundamental properties and the corrosion resistance as well as the weatherability[11] and the new quantitative method for predicting the service life of color PE coated steel pipe[12].

2. Corrosion Resistance and Fundamental Properties of PE Coating

PE resin is a nonpolar and chemically stable polymer composed of carbon and hydrogen.
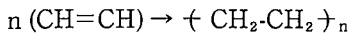
$$n\,(CH=CH) \rightarrow \left(CH_2\text{-}CH_2\right)_n$$

Table 1 shows the chemical resistance of PE[13]. Since it has good resistance to most acids, alkalis and solvents, PE coating is not damaged even if PE coated steel pipe is used in extremely polluted seas. Furthermore, in the result of immersion test at 20°C in 3 % NaCl shown in **Fig.1**, the high electrical resistance due to low water absorption, which is less than 0.1 %, showed no significant decrease. Therefore, PE steel pipe has a long term corrosion resistance because of its barrier effect to water. Furthermore, in comparison with painted steel pipe, it is undamageable during construction as well as during practical use, because of its superior mechanical properties shown in **Table 2.** This superior performance of PE coated steel pipe was supported by the results that no change was observed at atmospheric, splash or tidal, or submerged areas after 10-year exposure of PE coated steel pipe to natural sea[2),3)]. The representative fundamental properties used in this report are summarized in **Table 3.**

Table 1 Chemical resistance of polyethylene

Substance		Substance	
Hydrochloric acid	Y	Alcohol	Y
conc. Sulfuric acid	N	Glycerin	Y
dil. Sulfuric acid	Y	Gasoline	Y
conc. Nitric acid	N	Trichloroethylene	B
dil. Nitric acid	Y	Cresol	Y
Phosphoric acid	Y	Benzene	Y
Ammonia	Y	Toluene	N
Sodium hydroxide	Y	Asphalt	Y

Y : Usable, N : Unusable, B : Borderline cases

Table 2 Properties of PE coated steel pipe

Coating material	Coating properties
Polyethylene (PE)	1. Excellent chemical stability 2. High resistance to mechanical damage · Indentation resistance at 60°C (DIN30670) : 0.10mm · Impact resistance at 60°C (ASTM G14) : 1.5kgf·m

Table 3 Properties of polyethylene

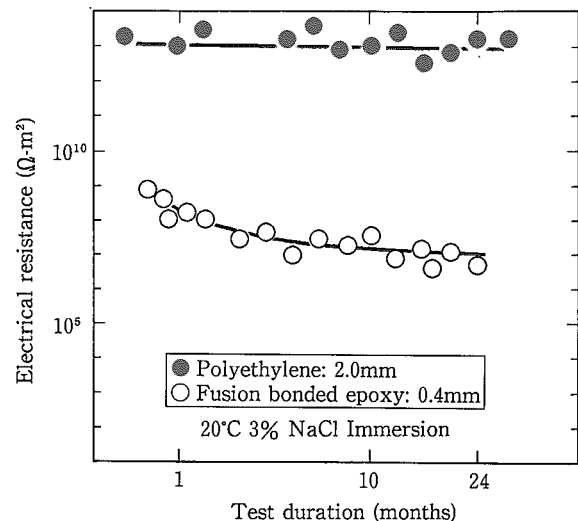| Items	Unit	Typical test results
Density	g/cm³	0.94
Melt index	g/10min	0.21
Vicat softening point	°C	$\geq$115
Tensile strength	kgf/cm²	$\geq$250
Elongation	%	>500
Hardness (Shore D)	—	$\geq$55
Water absorption	%	0.02

Fig. 1 The change in electrical resistance of polyethylene as a function of time of exposure to 3% NaCl solution

3. Weatherability and Life Prediction for Color PE Coating

To completely prevent the photo-degradation of PE surface directly exposed to ultraviolet rays is complicated because minute cracking (checking) grows even on the surface of black PE with carbon black[11]. Therefore, it is important to prevent the degradation of the mechanical properties of PE as anti-corrosive coating.

In this section, the weatherability as well as the method for service life prediction of color PE coating was investigated by analyzing the behavior of antioxidants which strongly affect the weatherability of PE coating.

3.1 Experimental

3.1.1 Materials and Sample Preparation

Middle density polyethylene (Density = 0.938g/cm³, MFR = 0.20g/min) was used. Three antioxidants (phenolic antioxidant, organic phosphite, hindered amine light stabilizer [HALS]), and UVA (benzotriazole ultraviolet absorber) were added to PE shown in **Table 1.** The proportions of the three added AO were constant. Samples were ivory PE, which have three different AO concentrations (in this report, high-, middle- and low-concentration are called Ivory (H), Ivory (M) and Ivory (L)). Green PE (Green), gray PE (Gray), blue PE (Blue), and brown PE (Brown) also have the same AO concentration as Ivory (M). The catalysis of pigments on photo-degradation was disregarded because the pigments used in this report were selected from pigments which have little effect on photo-degradation of PE.

Color PE and adhesive resin were pressed and laminated at 190°C, and the total thickness of PE sheet samples was 2.5mm (color PE : 2.2mm, adhesive : 0.3mm) after being formed.

Table 4   Additives content (mass%)

Sample	UVA	AO	Pigment	Color
Ivory (H)	0.20	0.60	2.51	Ivory
Ivory (M)	0.15	0.40	2.51	Ivory
Ivory (L)	0.10	0.23	2.51	Ivory
Gray	0.15	0.40	0.95	Gray
Green	0.15	0.40	0.94	Green
Blue	0.15	0.40	0.90	Blue
Brown	0.15	0.40	0.74	Brown

3.1.2 Testing

(1) Water Resistance Test

The immersion test in deionized water and 3% NaCl solution at 30°C was carried out, and oxidative induction time (OIT) at 210°C, which is correlated with the remaining AO concentration in PE, was measured using Mac Science DSC3200 differential scanning calorimetry (DSC). A sample (3.0mg) was taken from the PE surface after the immersion test and heated in nitrogen (50cm³/min) at a controlled heating rate (20°C/min) from ambient to 210°C. The purge gas was then switched to oxygen (50cm³/min) and the time from this change to the oxidative exotherm being recorded, was taken as the OIT[11] . Usually an average value from 2 to 3 measurements of OIT was adopted.

(2) Weathering Test

A "sunshine" type carbon arc weathering tester manufactured by Suga Test Instruments Co., Ltd. was used for the artificial accelerated exposure test (AAET). It was operated at 63°C black panel temperature, and samples were sprayed to simulate rain for 12 min out of every 60 min. After exposure to AAET, OIT measurement of the microtomed samples (180μm thick) from the PE surface was carried out, and AO concentration profiles were then obtained by the correlation between OIT value and AO concentration.

(3) Mechanical Test

The PE samples were removed at periodic intervals for elongation testing, and dumbbell shaped specimens for tensile testing were then cut from the PE sheets. The testing speed was maintained at the rate of 50mm/min in accordance with ASTM D638. When the retention of elongation is less than 50 %, PE durability is generally determined to be degraded and useless.

3.2 Results

3.2.1 Immersion Test Results

Figure 2 shows the change in OIT as a function of immersion test duration. The loss of OIT was minute and not influenced by the concentration of chloride ions in solution. Consequently, the added AO scarcely dissolves in water, regardless of whether it is sea,
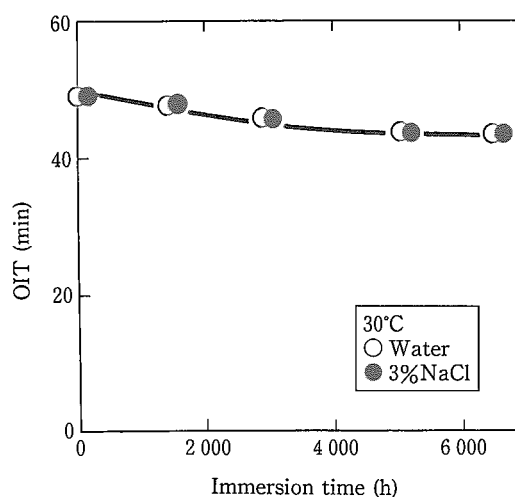

Fig. 2   The change in OIT as a function of time of exposure to deionized water and 3% NaCl solution

river and rain, since the water temperature of the natural environment does not exceed 30°C.

3.2.2 Elongation Test Result and the Effect of UV on Weatherability of PE

Figure 3 shows the change in the retention of elongation as a function of AAET time. In the case of Ivory, Gray, Green, and Blue PE samples, a significant decreased in elongation was not observed. On the other hand, the elongation of Brown PE decreased substantially in spite of having the same AO concentration as the others. Therefore, the weatherability of PE coating is not simply correlated with the AO concentration. In addition, the elongation of the black PE (BPE) with the addition of 2.5 mass % carbon black did not decrease, and natural PE (NPE) without additives decreased after 500 hours of exposure to AAET.

In order to clarify the cause of the Brown PE degradation, films of color PE were formed, and the UV absorbance spectrum of the films was then measured. The irradiated light energy decreases by absorption in the specimen, and is evaluated by the Lambert-Beer's law. It is expressed as:

$$log\ (I_0/I) = \varepsilon c d = A$$

where I_0 is the light intensity of incidence, I is the light intensity of transmission at the position d from specimen surface, ε is the absorption coefficient, c is the concentration, and A is the absorbance.

Figure 4 shows the relationship between the film thickness and the absorbance concerning the UV of 300nm which strongly affects PE photo-degradation. It fits a linear dependence in accordance with Lambert-Beer's law. In **Fig.4,** the slope angle is smaller than those of the others. Therefore, the Brown PE used in this report transmits the UV more deeply, and has lesser UV screening properties.

The minute cracking (checking) on the surface of every PE used in this report after 3500 hours exposure to AAET was observed using scanning electron microscopy. Although the depth of cracking initially increased with the increase of exposure time, the trend decreased as the time for AAET went on. The cracking of the Brown PE which has lesser UV screening properties grew more deeply than the others.

In addition, the cracking was also observed on the surface of BPE with greater UV screening prop-

erties, but its deepest depth was only 6μm after 16000 hours exposure to AAET. Therefore, to completely prevent the photo-degradation of PE surface is difficult to achieve. On the surface of NPE, the visible cracking (crazing) was observed after 1000 hours exposure to AAET, and its depth was over 350μm.
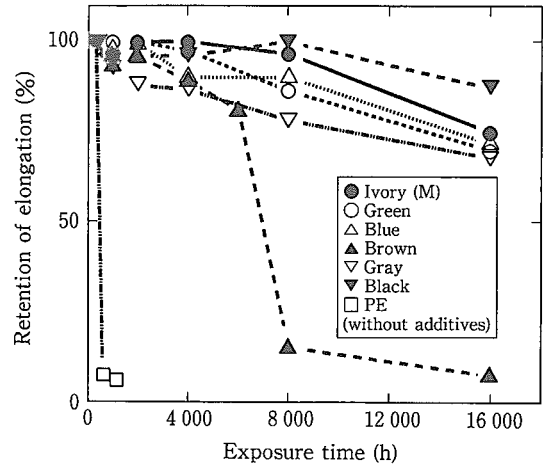

Fig. 3 Change in retention of elongation as a function of time of exposure in sunshine carbon arc weathering tester
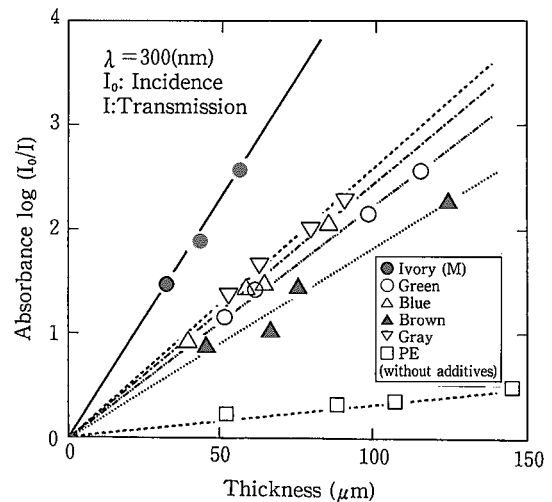

Fig. 4 Relationship between absorbance and sample thickness

3.2.3 Result of OIT Measurement

Figure 5 shows the result of AO concentration profile as a representative example. In **Fig.5**, the x axis shows the depth from the surface of only color PE without adhesive. At the back side of PE (the side of the adhesive), a gradient of AO concentration was observed, and at the position from the surface to the inside of PE, a gradient was also observed. At the back side, the gradient presumably arises by AO diffusing to adhesive because the adhesive contains no AO, and the back side of sample was sealed. From the above results, the gradient at the position from the surface to the inside of PE inevitably arises because the AO is consumed by the radicals produced by UV at the PE surface, and AO simultaneously diffuses from the inside to the surface of PE. Before exposure to AAET, the AO decrease at the back side of PE by AO diffusion to adhesive was also observed, but it was minute.
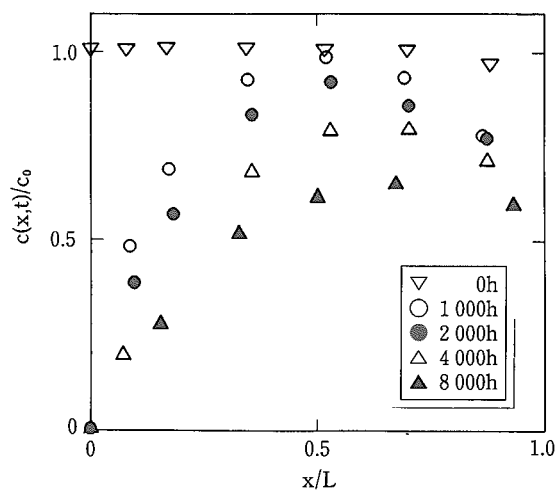

Fig. 5 Change in AO concentration profiles
x is the position from PE surface; L is the thickness of color PE without adhesive; c(x,t) is the concentration at position x and time t; c_0 is the initial AO concentration

3.3 Modeling AO Consumption and Diffusion, and Numerical Analysis

From the combined results of the above studies, an AO consumption and diffusion model adopting the UV screening properties with pigments and UVA was constructed in order to analyze the AO behavior in PE. The model is shown in **Fig.6.**

AO Consumption and Diffusion Model

(1) The AO diffusion in PE is one dimensional and in accordance with Fick's law.

(2) The AO is consumed from PE surface in proportion to the UV intensity of 300nm which strongly affects the PE photo-degradation.

(3) The AO diffuses to the adhesive.

In the numerical analysis, PE of 2.5mm in thickness is divided into 250 mesh cells (1 cell is 10μm in thickness in this report), and the AO is consumed in proportion to the UV intensity of transmission shown at the black part in **Fig.6 (b)** because the UV intensity decreases in accordance with Lambert-Beer's law shown in **Fig.6 (a).** The AO then diffuses from the inside to the surface as AO is consumed. At the back side, the AO also diffuses to the adhesive. After the AO concentration in the mesh cell is 0, only AO diffusion from the inside is consumed there. In this model, the decreasing UV intensity is calculated by Lambert-Beer's law shown in **Fig.4.** The numerical analysis concerning the Ivory PE and Brown PE was carried out by the computation of the model function as the parameters k, D, D_A. k is the constant of AO consumption in proportion to the UV intensity, in other words, the AO consumption at the first mesh cell of PE surface. D is the diffusion coefficient in PE, and D_A is the diffusion coefficient in adhesive.

The results of the numerical analysis are shown in **Fig.7.** The theoretically calculated values corre-
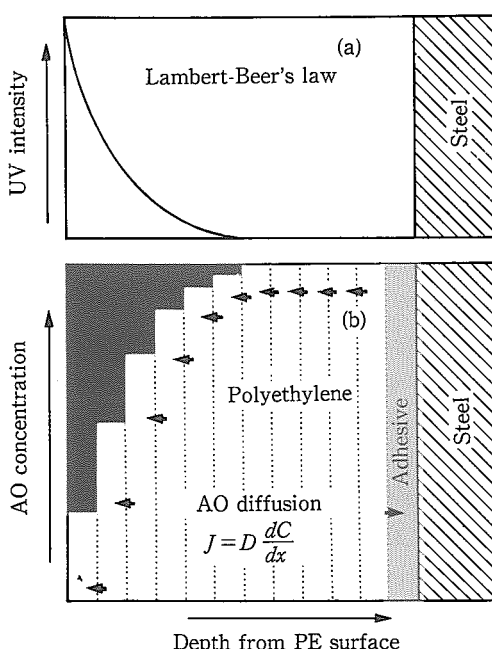

Fig. 6 AO consumption and diffusion model

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spond with the experimentally obtained values as the parameters $k = 6.5 \times 10^{-9}$ (g/cm²·s) and $D_A = 8.3 \times 10^{-11}$ (cm²/s), and $D_i = 1.7 \times 10^{-10}$ (cm²/s) in the case of Ivory PE, and $D_B = 8.3 \times 10^{-10}$ (cm²/s) in the case of Brown PE. In **Fig.7,** the position, where AO concentration is 0, of Brown PE is deeper than that of Ivory PE. Consequently, the computation of the model is capable of predicting the AO concentration at any position and in any time, but, it is impossible to predict the service life without knowing the correlation with mechanical properties and degradation depth.

In order to determine the correlation between the degradation depth and the retention of elongation, the samples which have the diverse degradation depth controlled artificially were prepared[12], and the elongation was then tested in accordance with ASTM D638. The total thickness of PE sheet was 2.5mm in thickness. The results are shown in **Fig.8.** The retention of elongation didn't decrease gradually with the increasing of the degradation depth, but it drastically decreased in the case of the 80μm degradation depth. Therefore, the mechanical property degrades when degradation due to UV extends to more than 80μm depth from the PE surface.

3.4 Service Life Prediction of Color PE Coating

The change in the retention of elongation as a function of exposure time to AAET was calculated by the combination of the computation of the depth in which AO concentration is 0 after exposure, and the correlation between the degradation depth and elongation shown in **Fig.8.** In **Fig.9,** the retention of the elongation calculated by the above method corresponds with that of the actual measurement.

The service life of PE coating in AAET is predicted quantitatively by the computation. Furthermore, the adequacy of this model has been proved in the natural environment[14]. Therefore, the long term durability of color PE coating is quantitatively predicted in a natural environment by the computation of the parameters concerning AO consumption and diffusion in a natural environment. In other words, AO content is determined for the required service life of PE coating.

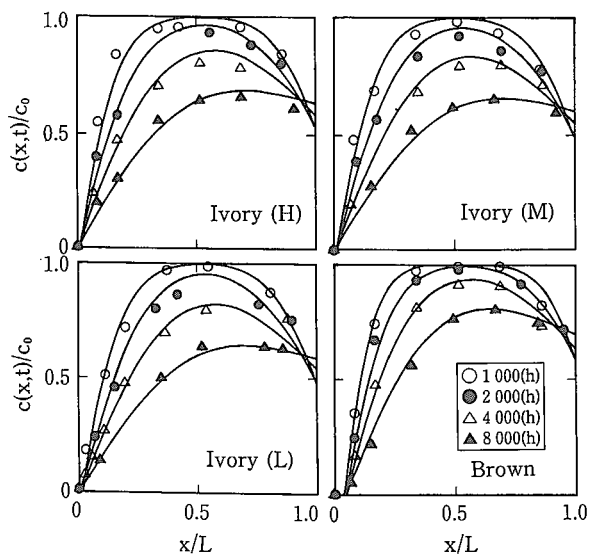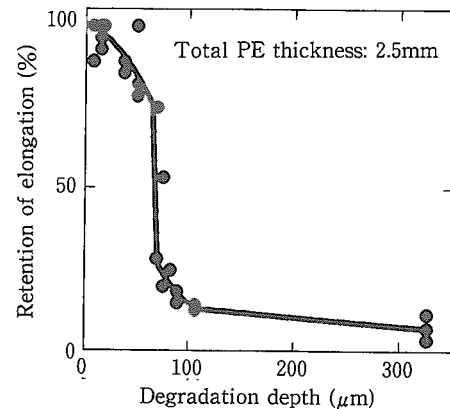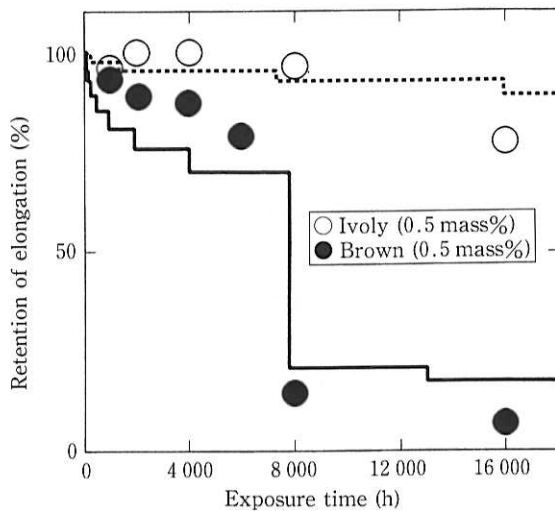Fig. 8　The effect of degradation depth on retention of elongation

Fig. 7　Comparison of theoretically calculated (solid lines) and experimentally obtained (points) AO concentration
x is the position from PE surface; L is the thickness of color PE without adhesive; c(x,t) is the concentration at position x and time t; c_0 is the initial AO concentration

Fig. 9   Prediction of the change in elongation
(Points: measured, lines: calculated)

4. Conclusion

The color polyethylene coated steel pipe shows excellent performance in corrosion resistance because of its barrier effect to water, high electrical resistance, and superior mechanical properties.

The weatherability of color polyethylene coating depends upon not only antioxidant content but also upon UV screening properties with pigments and ultraviolet absorbers. The service life of color polyethylene coating is predicted quantitatively by the computation of the newly constructed AO consumption and diffusion model function.

The newly developed color polyethylene coated steel pipe has high corrosion resistance in severe corrosion environments as well as weatherability of more than 20 years.

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