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UNDERWATER DEGRADATION OF POLYETHYLENE FOR WIRE INSULATION

BY

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Photo 1
Specimens in Glass Bottle



Photo 2
Experimental Set

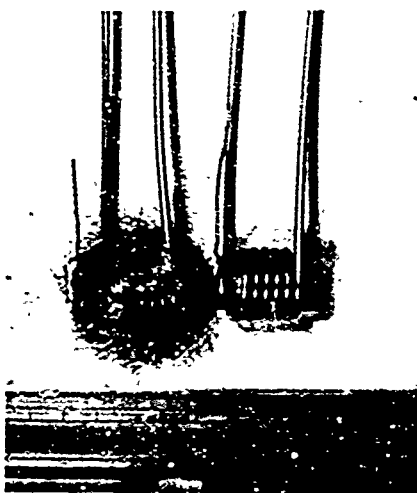
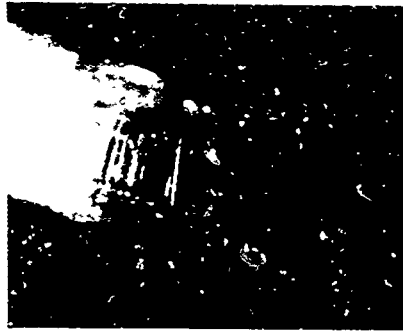


Photo 3
Outside Electrode for Aging in Air

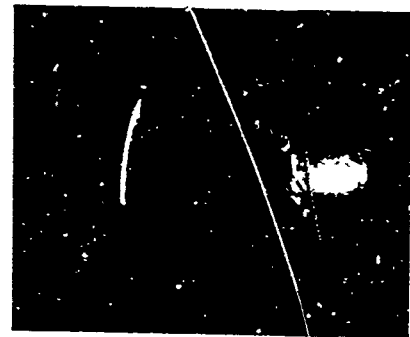


Photo 4
Specimens Sealed in Glass Bottle

Photo 5
Cracks Observed on
Polyethylene Insulation without Antioxidant
400V Applied, after 25 day's Aging at 80°C in Water and in Air
(× 6)



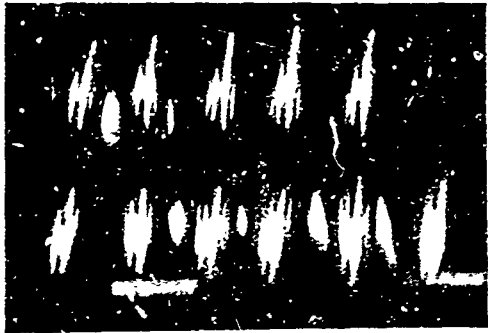
in Air



in Water

Photo 6

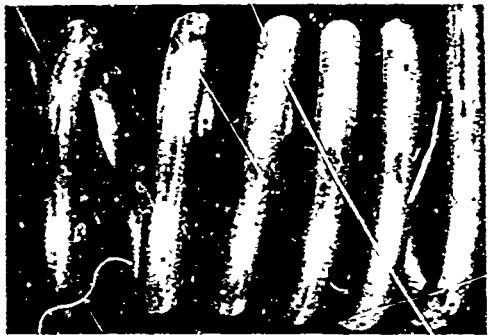
Propagation of Cracks on the Surface of Polyethylene Insulation without Antioxidant
400V Applied, Aging at 80°C in water (× 2)



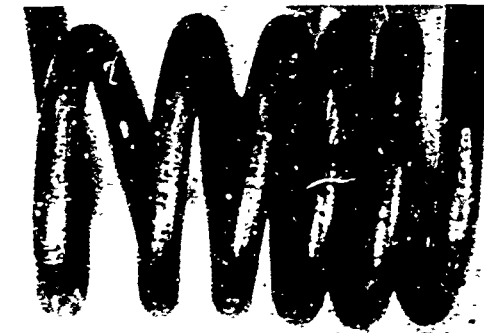
original



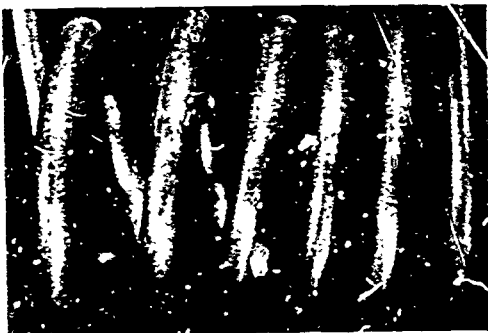
82 days



58 days



89 days



64 days



98 days



68 days



104 days



75 days



110 days

UNDERWATER DEGRADATION OF POLYETHYLENE FOR WIRE INSULATION

by

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ABSTRACT

This report concerns studies made on the degradation mechanism of polyethylene insulated wire. The purpose of this study was to make the following points clear.

- 1) To see whether polyethylene insulated wire is especially susceptible to degradation in water.
- 2) To see how applied voltage will affect polyethylene insulated wire.

In addition, a few other factors which are believed to have effects on polyethylene degradation were examined to see what their actual effects are.

In this experiment, a statistically designed experiment was employed, simulating the environmental conditions in which polyethylene insulated wire is actually used.

Quantitative evaluation were made to see what effect each of the various factors would have on degradation when they were changed.

As a result, the following points were made clear.

- 1) In case of polyethylene insulated wire, degradation begins as the polyethylene is oxidized. The applied voltage and environmental stress cracks are not directly responsible for degradation.
- 3) Degradation is promoted by temperature and applied voltage.
- 4) External stress and internal stress are the main factors that cause the degraded areas to propagate into cracks.
- 6) There was no apparent difference in the oxidation characteristic of polyethylene between in-water and in-air conditions, except that oxidation progresses faster in air than in water.

1. INTRODUCTION

As a general rule, polyethylenes have excellent water resistant properties, especially, excellent moisture permeability resistance. Thus, in communication cables, they are widely used in the Alpeh and Stalpeh sheaths or as insulating or sheathing material for PE-P cables. Furthermore, in the field of power cables, they are widely used as electric wire insulation for submerged motors, and insulation for submarine cables.

Thus, it is predicted that the demand for polyethylenes will continue to grow in the fields of communication cables and power cables.

However, there was an incident in Japan about 10 years ago where cracks developed in the core insulation of a PE-P cable. This cable was in actual service as underground cable in the Hakone district.

On account of faulty connections, underground water entered the cable, and poor insulation was observed about one year after the installation.

A number of experiments were made to investigate the cause of this trouble, but no clear-cut explanation was obtainable. Many studies have been conducted on this type problem both in Japan, and overseas, but it has yet to be determined what the contributing factors for degradation (3)–(5).

This report discusses mainly the results of the experiments conducted in order to investigate the degradation mechanism of polyethylene is used with an electrically charged conductor in water, and to consider what are the factors that affect polyethylene degradation.

A 2 mm ϕ conductor coated with 0.5 mm of polyethylene was used as specimen and subjected to various forced degradation tests.

Previously, experiments on degraded insulation had been conducted mostly from the electrical point of view. In contrast, our experiments were conducted to investigate chemically, how the degradation of polyethylene insulated wire progresses, and determine the cause of such degradation.

Moreover, taking into consideration the fact that electric wires in actual service are in complicated environmental conditions, in the experiments performed by the writer, factors that are believed responsible for the degradation were selected and used in different sets of combinations by the statistically designed experiment.

An attempt was made to evaluate quantitatively the effect that each factor had on the degradation in varied combinations.

2. EXPERIMENT

2.1 Factors Affecting Degradation

The factors affecting degradation of polyethylene insulated wire are summarized in Table 1. This is based on our preliminary experiments and other experiments.

Table 1
Factors Affecting Degradation

Source	Factor
Chemical action	Concentration of oxygen, Temperature
	Concentration of antioxidant, Plating
Electrical action	Applied voltage
Physical action	External Stress, Internal Stress
	Crosslinking, Environment, Wall thickness

It is believed that degradation of polyethylene is caused by these chemical, electrical and physical actions, which are attributable to the manufacture conditions and in which the wire is used.

2.2 Experimental Conditions

We conducted the experiments in three steps, using the following two method.

1) Observation of degradation phenomenon.

No. 1 Experiment

2) Investigation of the causes of degradation

No. 2 Experiment, No. 3 Experiment

The manufacturing condions of polyethylene insulated wire are common among the three experiments as shown in Table 2.

Table 2
Wire Manufacturing Conditions

Polyethylene	: Trade name NUC 9025 (density 0.915, MI 1.6) no additive except antioxidant for processing
Copper wire	: 2.0 mm ϕ single core tin plating (in case of plating)
Antioxidant	: 4-4'-thiobis (6-tert-butyl-3-methyl phenol)
Type of polyethylene composition	
A	: PE
B	: PE+0.3% antioxidant
C	: PE+0.3% antioxidant (Chemical crosslinking)
D	: PE+0.3% antioxidant (Crosslinked by irradiation)
The gel ratio of both crosslinked polyethylenes was measured as 80%	

The details of each step of experiments are as follows.

No. 1 Experiment.

Observation of polyethylene degradation phenomenon in water being its purpose, this experiment was conducted by using simple combinations of the various factors, with the object to obtain long range measurement.

The factors and the levels used in the experiment are shown in Table 3.

Table 3
Factors and Levels of No. 1 Experiment

Factor	Level		Fixed Condition
Temperature	50°C	80°C	Wall thickness 0.5mm
Voltage	0	400V	Tin plating, In water
Wire Type	A. B. C. D.		External stress 17%

No. 2 Experiment

In this experiment, we made orthogonal arrays studies⁽¹⁾ for the following two reasons:

- 1) To obtain information applicable to practical use
- 2) To obtain reliable data

In this experiment, we took up many factors and macroscopically evaluated factors affecting the degradation.

We carried out experiments in air to compare the results with those obtained in water. The factors and levels of No. 2 Experiment are shown in Table 4 and the design of No 2 Experiment in Table 5.

Table 4
Factors and Levels of No 2 Experiment

Factor	Level			
A Temperature	50°C	80°C		
B Voltage	400V	0		
C Environment	In water	In air		
D Wire type	A.	B.	C.	D.
E External stress	18%	50%		
F Wall thickness	0.5mm	1.0mm		
G Plating	Without	With		

Table 5
Design of No 2 Experiment

Orthogonal array L ₁₆															
Factor	D		A	E	B	e	F	G	e	C	e	e	e	C X B	
Column	1.	6.	7.	2.	3.	4.	5.	8.	9.	10.	11.	12.	13.	14.	15.

No 3 Experiment

This experiment complements No 2 Experiment.

Its object was to investigate the effects of such factors as applied voltage, environment and internal stress which had been neglected in No 2 Experiment, because the effects of antioxidant on degradation was so great. In this experiment, we fixed the temperature at 80°C, type of wire as "A" in Table 2, wall thickness at 0.5mm.

To obtain more reliable data, we used more specimens than in former experiments. And to examine the particular degradation phenomenon, we investigated the interactions between two factors to see if there were any unusual phenomena that are difficult to predict.

Furthermore, examine more closely the effects of applied voltage and environments, we carried out some comparative experiments in which 1000V.A.C. applied to the conductor and wires were immersed in mercury, surfactant, inert gas, oxygen gas and water vapor.

The factors and levels chosen in this experiment are shown in Table 6 and the design in Table 7.

Table 6
Factors and Levels of No 3 Experiment

Factor	Level	
A Voltage	400V	0V
B Environment	In water	In air
C Internal stress	40%	50%
D External stress	17%	50%
E Plating	Without	With

Table 7
Design of No 3 Experiment

Orthogonal arrays L_{16}															
Factor	E	C	C	A	A	A	B	B	B	B	A	A	C	D	D
Column	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.

2.3 Ageing Procedure

The samples were cut into 1.5m lengths and wound in coils of 3 mm and 15mm diameters. For each test, 30 specimens were set in a glass bottle (Photo 1), which was put in a water bath (Photo 2) at 50°C and 80°C.

In the underwater degradation test, we used tap water and applied 400V and 1000V, 50 cycle alternating current to the conductor. In the air-degradation test, voltage was applied between the conductor and outside electrode (Photo 3). The degradation test in inert gas was carried out in a sealed glass bottle (Photo 4). We measured the degradation degree of the samples after the following ageing periods.

No. 1 Experiment	6, 12, 25, 53, 110, 230, 460 (days)
No. 2 Experiment	160 (days)
No. 3 Experiment	25 (days)

2.4 Method Used to Measure Properties

Previously, measurement of changes in insulation resistance has been the most widely used method in examining deterioration of wire.

However, since insulation resistance suddenly drops at some point in the process of degradation and is unnoticeable till that time, in this experiments we measured A. C. breakdown voltage directly

related to the degradation degree. And at the same time, to examine the changes that occur in molecular structures of polyethylene, we measured the changes in carbonyl absorbance by infra-red spectrum. In addition, we measured the changes in tensile properties, density and melt index as supplemental data.

Table 8 shows the measured properties and the method in which they were measured.

Table 8 Measured Properties and Method

Property	Method
A. C. breakdown Voltage	25 KV per 5 minutes step up from 2.5kv
Density	ASTM D 1505-63T
Carbonyl absorbance	1720cm ⁻¹ band measured by i. R. calculated absorbance $D = \log_{10} (I_0/I)$ by base line method
Melt index	ASTM D 1238-62T
Tensile properties	measured by Instron type tensile tester at speed 200mm per minute

3. RESULT

The changes in A. C. breakdown voltage measured in No. 1 Experiment are shown in Fig 9 and carbonyl absorbance in Fig 10. The rest of the data are not cited here.

For No. 2 Experiment, details are shown in Table 9 and the results in Table 10.

For No. 3 Experiment, details are shown in Table 11 and the results in Table 12.

We made an analysis of variance with the No. 2 and No. 3 experimental data to supply criteria for determining whether a given factor influence the results.

Table 9 Test Conditions Used in No. 2 Experiment

Specimen No.	Wire Type			Condition of Degradation			
	Plating	PE Thickness [mil.]	PE Type	Temp. [°C]	Applied Voltage [V/0.5mm]	Environment	External Stress [%]
1	without	0.5	A	50	400	in water	17
2	with	1.0	A	50	400	in air	17
3	without	0.5	B	50	0	in water	17
4	with	1.0	B	50	0	in air	17
5	without	0.5	B	80	400	in air	50
6	with	1.0	B	80	400	in water	50
7	without	0.5	A	80	0	in air	50
8	with	1.0	A	80	0	in water	50
9	with	0.5	C	50	400	in air	17
10	without	1.0	C	50	400	in water	17
11	with	0.5	D	50	0	in air	17
12	without	1.0	D	50	0	in water	17
13	with	0.5	D	80	400	in water	50
14	without	1.0	D	80	400	in air	50
15	with	0.5	C	80	0	in water	50
16	without	1.0	C	80	0	in air	50

Table 10 Result of No. 2 Experiment

Specimen No.	Carbonyl Absorbance	Density Increase [%]	Retention of A. C. B. D. Voltage [%]	Retention of Tensile Strength [%]	Retention of Elongation [%]
1	0.008	0.34	100	84	84
2	0.005	0.15	100	100	97
3	0.010	0.03	100	95	60
4	0.010	0.08	100	83	87
5	1.430	5.53	0	0	0
6	0.584	1.45	0	0	0
7	0.025	0.48	100	56	98
8	0.005	0.36	80	97	96
9	0.011	0.14	90	93	86
10	0.005	0.24	100	92	93
11	0.024	0.21	100	99	57
12	0.023	0.25	100	94	91
13	0.070	0.75	90	100	95
14	0.056	0.28	100	90	98
15	0.011	0.60	100	100	100
16	0.010	0.44	100	63	65

Table 11
Test Conditions Used in No. 3 Experiment

Speciment No.	Wire Type		Condition of Degradation			Reference Specimen No.
	Plating	Internal Stress [%]	Applied Voltage [V/0.5mm]	Environment	External Stress [%]	
1	without	40	400	in water	17	orthogonal array L ₁₆
2	without	40	400	in air	50	
3	without	40	0	in water	50	
4	withont	40	0	in air	17	
5	without	50	400	in water	50	
6	without	50	400	in air	17	
7	without	50	0	in water	17	
8	without	50	0	in air	50	
9	with	40	400	in water	50	
10	with	40	400	in air	17	
11	with	40	0	in water	17	
12	with	40	0	in air	50	
13	with	50	400	in water	17	
14	with	50	400	in air	50	
15	with	50	0	in water	50	
16	with	50	0	in air	17	
17	with	50	1000	in air	17	No. 16
18	with	50	1000	in water	17	No. 13
19	with	50	1000	in mercury	17	No. 13
20	with	50	1000	in surfactant	17	No. 13
21	without	40	0	in oxygen	17	No. 4
22	without	40	0	in nitrogen	17	No. 4
23	without	40	0	in argon	17	No. 4
24	without	40	0	in water vapor	17	No. 4

Table 12
Results of No. 3 Experiment

Specimen No.	Carbonyl Absorbance	Density [g/cc]	Melt Index [g/10min]	Retention of Tensile Strength [%]	Retention of Elongation [%]	A. C. B. D. Voltage [kv/0.5mm]
1	0.186	0.9208	6.0	47	10	14.1
2	0.270	0.9224	2.8	0	0	0
3	0.068	0.9180	3.1	0	0	0
4	0.294	0.9204	28.4	44	8	20.7
5	0.112	0.9182	2.8	0	0	0
6	0.357	0.9250	66.5	49	7	19.6
7	0.233	0.9194	2.8	75	82	20.0
8	0.115	0.9259	47.6	0	0	7.0
9	0.079	0.9191	3.0	0	0	0
10	0.045	0.9162	1.8	51	36	20.1
11	0.088	0.9189	2.2	50	13	13.0
12	0.078	0.9175	2.4	0	0	0
13	0.187	0.9201	41.7	52	28	13.2
14	0.058	0.9167	2.9	0	0	13.0
15	0.035	0.9172	1.7	0	0	14.1
16	0.050	0.9162	1.8	64	59	20.9
17	0.023	0.9164	2.1	56	43	21.1
18	0.097	0.9194	2.7	54	20	10.3
19	0	0.9181	1.7	97	100	21.5
20	0	0.9153	1.5	98	100	21.7
21	0.266	0.9223	42.4	45	6	13.7
22	0	0.9149	1.6	94	97	20.8
23	0	0.9144	1.8	97	98	23.0
24	0.366	0.9264	33.4	44	3	18.1

degradation after 25 days

4. DISCUSSION

A series of experiments was performed in order to discover the causes of degradation for polyethylene insulated wire.

An analysis of variance was conducted on the data thus obtained. On the basis of these results and literatures which have been published to date, we will consider how each factor affects the degradation of polyethylene insulated wire.

4.1 Effect of Antioxidants

Fig. 1 shows the relations between the aging time and the percentage retention of the A.C. breakdown voltage of polyethylene insulation both containing and not containing antioxidants. As it is clear from this figure, polyethylene insulation which does not contain antioxidants shows a remarkable drop in A.C. breakdown voltage whether the temperature is 50°C or 80°C. Furthermore, as it is clear from the No. 2 experiment results shown in Fig. 3, regardless of whether crosslinked or not or how they are crosslinked, it is only this polyethylene insulation which does not contain antioxidants that shows an abrupt drop in A. C. breakdown voltage.

These results were obtained while the factors shown in Table 4 varied in their specific levels. Thus, it may be said that the average values are shown.

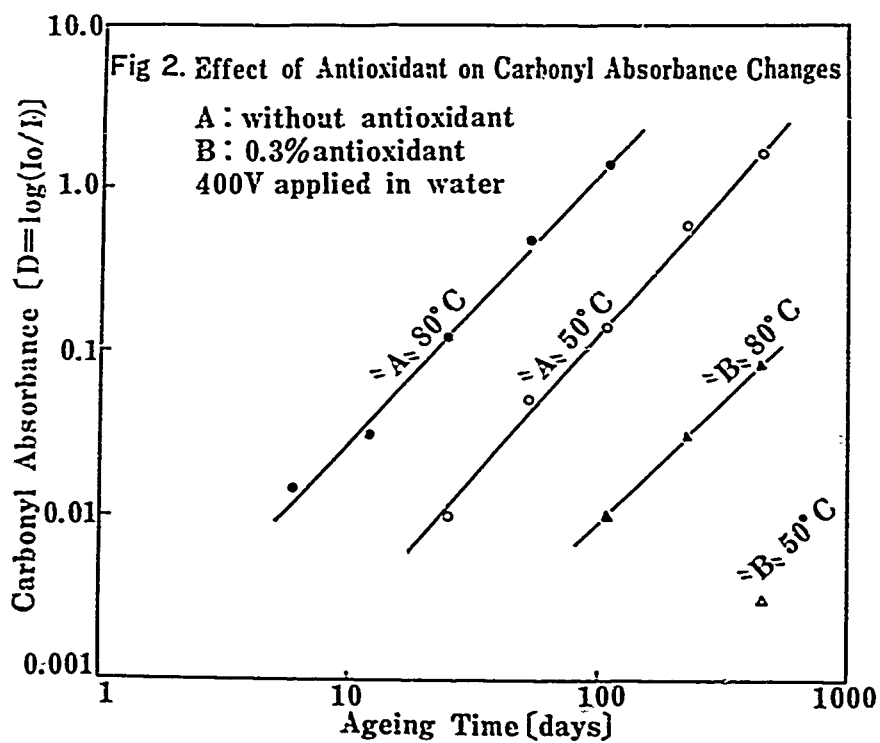
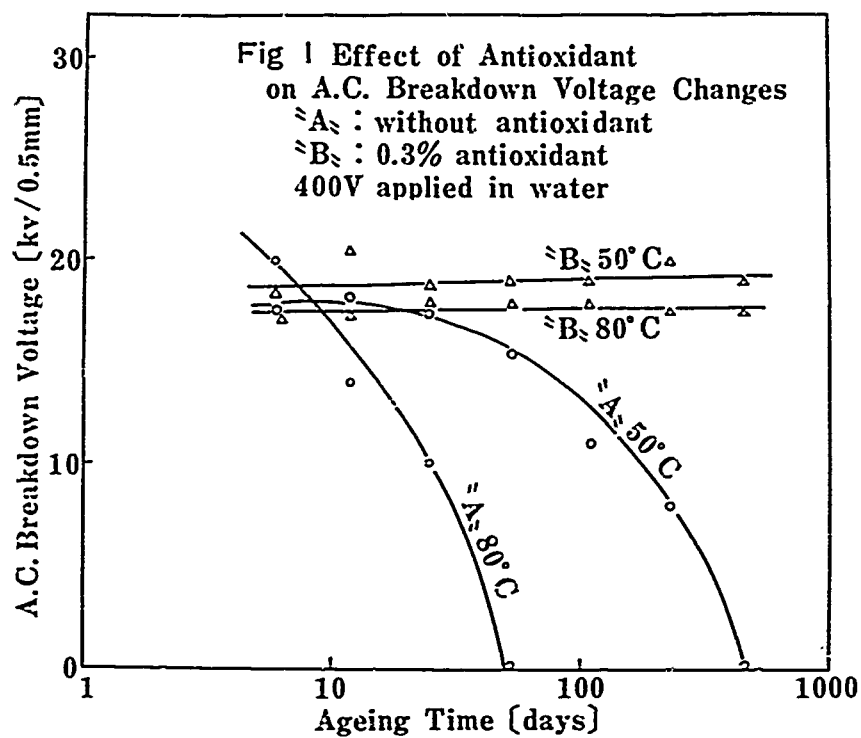
In other words, polyethylene insulation which contains antioxidants does not show a drop in A.C. breakdown voltage even when it is placed under severe conditions such as 160-days forced degradation, temperature as high as 80°C, large external stress such as encountered when it is wound in its own diameter, internal stress as large as 50%, and applied voltage as high as 400 V A. C..

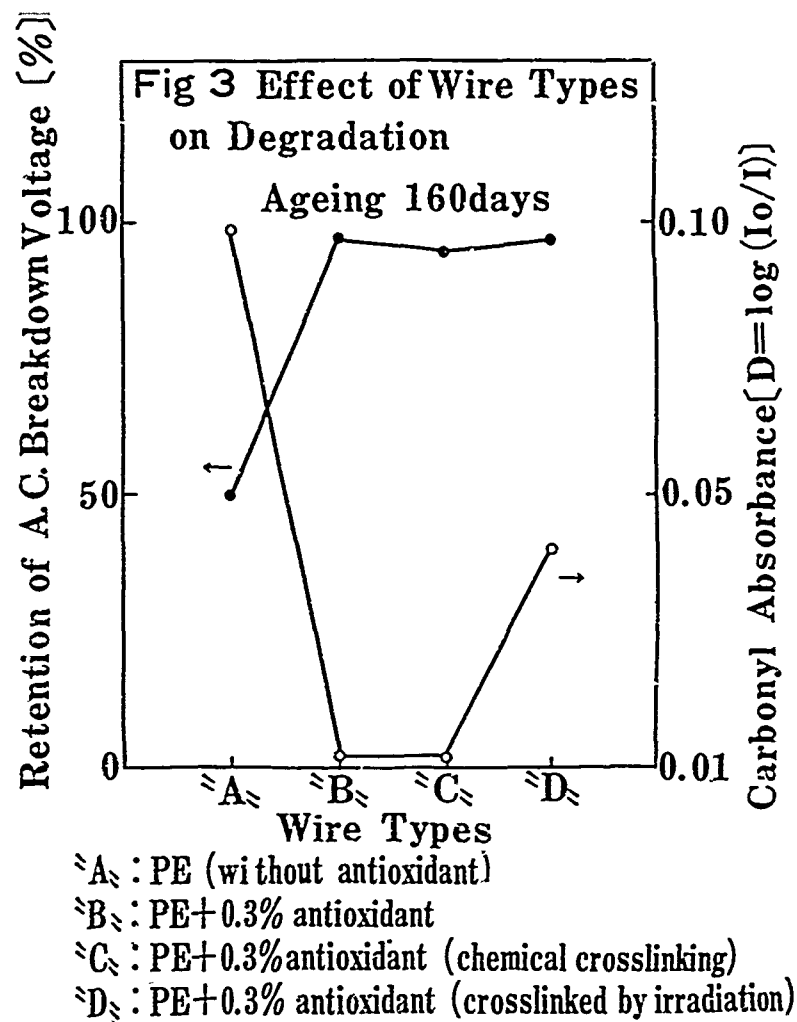
Then, what kind of changes occur in the internal structures of polyethylene insulations, containing or not containing antioxidants?

In Fig. 2, the carbonyl concentration by infra-red absorption spectra of polyethylene insulation and time-dependent changes are shown. As it is clear from this figure, the samples which do not contain antioxidants are oxidized considerably.

The effect of antioxidants on oxidation of polyethylene varies greatly as quoted below from literature. (2)

"Using 0.02% 2,6-di-*t*-butyl-4-methyl phenol, the oxidation induction period of peroxide formation was greater than 10 hours compared with 4½ hours for unstabilized polyethylene." This means that degradation of polyethylene insulation is due chiefly to the oxidation effect, and effects of electrical and physical actions such as electric field and promotion of crystallization are not so significant.





4. 2 Effect of Crosslinking

As for the effect of crosslinking, there is the experiment (3) by W.D. Paist.

In his report, the author states, "In case 60 cycles 600V was applied to the polyethylene insulated wire (12±1 mils of insulation on #19 wire) immersed in 75°C water, and the changes in the insulation was measured, it was found that if crosslinking was done by irradiation, the higher levels of irradiation (50 MR) showed a lower initial value than the one done at lower levels.

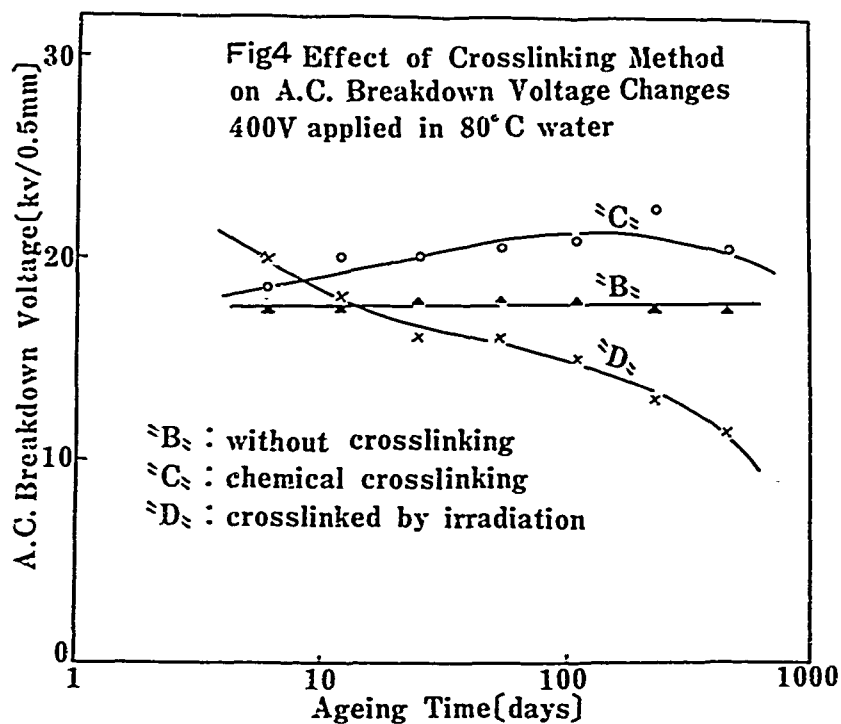
However, the drop in insulation resistance is small. Furthermore, the crosslinked ones are more or less stronger."

As shown in Fig. 3, in our experiment, the samples which contain antioxidants, whether they crosslinked or not, showed hardly any degradation after 160 days of forced degradation. In addition to this, the long term data obtained from other experiments indicate no definite effect of crosslinking. However, it is presumable that crosslinked samples degrade or oxidize slightly easier.

The reason for this is as follows: In case of the samples crosslinked by irradiation, large electron bombardment amounting to 7 MeV is utilized, and this causes the polyethylene to degrade and the antioxidant to decompose. With the chemically crosslinked samples, the curing agent has the same effect as the electron bombardment.

However, when we take into consideration the growth of cracks, it seems that crosslinked polyethylenes have better crack resistance than those which are not crosslinked.

Although crosslinking will deter the propagation of cracks in a polyethylene wire, the oxidation and degradation during the crosslinking process will perhaps have some adverse effect on the life of the polyethylene insulated wire.



4. 3 Effect of Applied Voltage

What effect will there be on the degradation if low voltage below 1000V is applied on a small size polyethylene insulated wire? Although many points were made clear by the undermentioned experiments conducted hitherto, it seems that the effect of the applied voltage is not yet clear.

Results of experiments performed by C. A. Liddicoat and B. F. Brown (4).

"Polyethylene electric wire (Samples of 19 AWG copper wire which is coated with polyethylene insulation having a wall thickness of 0.012 ± 0.001 inches) was immersed in 75°C water, and the changes in insulation resistance were measured.

As a result, the dropping of insulation resistance was found to be remarkable with the ones to which voltage has been applied compared with those which had not been so exposed. However, differences in levels of applied voltage, and frequencies of current have no effect on degradation."

Results of Experiment by T. Yasui (5)

"A polyethylene insulated wire (core 2.0mm ϕ , thickness 0.7mm) was immersed in hot water of 70°C for 250 days, applied with voltages of 220V and 440V, and compared with a wire which was not applied with voltage. Although the insulation resistance and A.C. short time break-down voltage decreased in case of wires applied with 220V and 440V, no such decrease could be observed for the ones which were not applied. Furthermore, there were no difference between the wire charged with 220V and the one charged with 440V."

Evidently, the applied voltage has some effect on the extent of degradation.

In the following paragraphs, a study will be the effect that the applied voltage has on the degradation.

The effect of applied voltage on the various properties of the polyethylene wire obtained from No. 3 experiment is shown in Table 13.

From these results, it can be seen that the A.C. breakdown voltage of the polyethylene insulated wire applied with 400V actually drops. Furthermore, the carbonyl absorbance is greater with the one which is applied with voltage. Besides, there is no difference in level of significance between applied and non-applied wires with respect to density, Melt Index, tensile strength and elongation.

In addition to the above, in samples No. 16 and No. 17 in air, and in samples No. 13 and No. 18 in water of Table 11, 12, the differences between the applied voltages of 400V and 1000V are shown.

There are no differences in degradation due to the differences in the applied voltage in air.

In water, the A.C. breakdown voltage drops slightly with the wire applied with 1000V, A.C. breakdown voltage compared with that applied with 400V.

However, the carbonyl absorbance and property values such as M.I. which will serve as a measure of oxidation dropped in case of wire with 400V.

Even when 1000V are applied, if they are immersed in mercury as shown in sample No. 19 or in polyoxyethylenealkylphenolether type non-ionic surfactant as shown in sample No. 20, the property values of the polyethylene insulation hardly drop. The above points were made clear with respect to the effect of applied voltage as a result of our experiments.

As an effect on the degradation caused by applied voltage, corona discharge and bombardment of electrons accelerated by electric field against the polyethylene molecules can be considered. However, corona discharge will not actually occur at a voltage of about 1000V or so.

On the other hand, if we roughly calculate the bombardment energy of electron accelerated in the electric field against the molecules, in case of polyethylene applied 400V/0.5mm, G_{max} will become about 1000V/mm. If we assume the mean free path of the electron within the polyethylene to be 10\AA , the bombardment energy of the electron will be about 0.02eV. As for the bonding strength of C-C and C-H, as a result of the investigation made by Field (6) et. al. on various lower hydrocarbons, it was assumed that C-H would be about 4eV, and C-C about 3.5eV.

Judging from this, even in case of the maximum potential gradient or longest mean free path, the bombardment energy of the electron accelerated by the electrical field 0.02 eV is rather small for chain scission of polyethylene. On the other hand, the above-mentioned polyethylene insulated wires immersed in mercury and an aqueous solution of surfactant does not degrade at all even when 400V is applied.

The reason that polyethylene insulation is hardly oxidized in a water solution of the surface active agent is believed to be: As the surfactant is associated with water in aqueous solution, the mobility of water molecule will be slow. As a result, the permeability of water into polyethylene will decrease. On the other hand, the surfactant has a poor compatibility to polyethylene, so it makes barriers on the surface of polyethylene, and may prevent the oxygen dissolved in the water from diffusing into the polyethylene. As a result, it may prevent the oxygen gas dissolved in the water from diffusing into the polyethylene. In case of mercury immersion, since little oxygen is

present in mercury, polyethylene does not degrade. Therefore, application of voltage alone, without the presence of oxygen, does not cause oxidation, chain scission, electrical or mechanical degradation. From the data obtained in the literature above, and the result of this experiment, it may be stated that there are differences between wires applied voltage and wires not applied voltage. However, the fact that differences in voltages applied do not affect degradation may be explained as follows:

A wire charged under the presence of oxygen is oxidized; It is then assumed that the electrical charging accelerates oxidation, this assumption based on the following two points. It was assumed, firstly, that the action of applied voltage on degradation is to make a penetration route in the polyethylene insulation for the oxygen and water by its alternative motive force on dipole orientation to the polar part in polyethylene, and secondly that such action promotes the mobility of oxygen and water molecules partially ionized in water by its electrical driving force; consequently the permeability of oxygen and water molecules into polyethylene increased and the oxidation of polyethylene promoted.

If these assumptions were correct, the effect of applied voltage on polar orientation in polyethylene molecules or on the increment of mobility of partially ionized oxygen and water molecules would not vary even when the energy level exceeds the expected level. This would explain why the level of applied voltage does not affect degradation.

Table 13
Effect Applied Voltage on Various Properties

Applied Voltage [V/0.5mm]	Carbonyl Absorbance	Density [g/cc]	M - I [g/10min]	Retention of Tensile Strength [%]	Retention of Elongation [%]	A. C. B. D. Voltage [kv/0.5mm]
400	0.162	0.9193	15.9	25	10	10.0
0	0.120	0.9191	11.2	27	13	11.9
F ratio	**					**
** Ninety-nine per cent confidence						

Table 14
Effect of Temperature on Various Properties

Temperature [°C]	Carbonyl Absorbance	Retention of Elongation [%]	Retention of Tensile Strength [%]	Retention of A. C. B. D. Voltage [%]
80	0.032	63	59	70
50	0.013	85	89	93
F ratio	**	**	**	**
** Ninety-nine per cent confidence				

4. 4 Effect of Temperature

According to the above-mentioned report of C. A. Liddicoat, the insulation resistance of polyethylene insulated wire declines more when the temperature is higher. Why a higher temperature causes the characteristic of polyethylene insulated wire to decline?

In our No. 1 experiment, the effect of temperature on changes of A. C. breakdown voltage was as shown in Fig. 1. This shows that, when polyethylene insulation does not contain antioxidant,

breakdown voltage begins to drop after 25 days, forced degradation at 80°C and after 110 days at 50°C. It is quite evident from this finding that degradation develops faster at 80°C than at 50°C.

On polyethylene insulation which contains antioxidant, the effect of temperature difference on degradation has not become apparent.

Further, in experiment No. 2 the following results were obtained.

These results indicate that the carbonyl absorbance increased and mechanical strength, electrical characteristics, etc., dropped, at much greater rates at 80°C. Investigating the areas where cracks occurred on the wire insulation, it was found that the density and the carbonyl absorbance increased considerably and that oxidation progressed significantly.

Thus the higher the temperature rises, the more the degradation of polyethylene insulation is accelerated. The factors that contribute to greater degradation at higher temperatures are believed to be environmental stress cracking, oxidation of polyethylene, and permeability of water into polyethylene. On the first factor, L. L. Lander (7) who studied the effect of temperature on environmental stress cracking, demonstrated that the higher the temperature rises, the faster cracks grow. However in our experiments, cracks occurred only in polyethylene insulations without antioxidants; no cracks developed in insulations with such an additive. Judging from this, it is presumed that higher temperatures affect oxidation of polyethylene rather than promote environmental stress cracking.

The effect of temperature on oxidation of polyethylene has been investigated extensively by W. I. Hawkins (8) et. al. They state in their report, "With the 30 degrees difference between 60°C and 90°C, the induction period for oxygen absorption becomes about ten times longer, from 300 hours to 3000 hours". All these suggest that higher environmental temperatures promote the oxidation of polyethylene considerably.

Generally, it is said that the reaction rate increases two times for every 10°C rise, but in our experiments, polyethylene insulation degraded 3 to 4 times faster at 80°C than at 50°C. In addition to this, it is considered that when a wire is immersed in water, the permeability of water into polyethylene causes the polyethylene to decline in insulation resistance. In Table 15, the permeabilities of water and oxygen gas into polyethylene are shown. (9)(10) It is apparent from this table that the permeabilities of water and oxygen at 80°C are respectively 15 times and 30 times greater than at 50°C. These results indicate that, though temperature rises take part in a degradation of polyethylene by promoting its oxidation, they do so in a greater degree by increasing the rate of permeation of oxygen into polyethylene.

Table 15
Dependence of Permeabilities of Oxygen Gas and
Water into Polyethylene on Temperature

Temp.	Oxygen	Water
	Permeability Coefficient *	Permeability Constant **
50°C	1	1.3
80°C	3.1	18
	* cc-cm/sec cm ² cmHg	
	** gmm/24hm ² mmHg	

4. 5 Effects of Environments

It seems that few experiments have been conducted to date to compare degradation phenomena in water and in air, and especially the mechanism of underwater degradation has not been made clear. Our experiments has been conducted to clear this point, and the results obtained from the experiment are summerized as follows; polyethylene insulation is oxidized more easily in air than in water, but the electrical properties of wire, especially A. C. breakdown voltage, deteriorate to a much greater extent in water than in air.

The results of experiment No. 2 are shown in Table 16. Further, as the interaction between two factors, namely, environment (water and air) and plating, was extermely great in this experiment, an analysis was made of the effect of these factors. The results are shown in Fig. 5. As is clear from Table 16, the carbonyl absorbance and M.I. which are characteristic values that serve as a measure for electrical deterioration, also shows a greater decrease in water than in air. Furthermore, as shown in Fig. 5, plating results in smaller increses in carbonyl absortbance and M.I. and a polyethylene insulated wire without plating is oxidized much more in air than in water, in contrast, a wire with plating is oxidized more in water than in air. Now, we will consider the reason why oxidation occurs more easily in air than in water. Comparing oxygen concentration in air and water at 30°C, 1 atm, 1 litre of air contains 200cc of oxygen whereas 1 litre of water has 5cc of oxygen dissolved in it. This shows that oxygen content is 40 times higher in air than in water. On the other hand, permeability of air into polyethylene is much greater than that of water; therefore polyethylene insulation is oxidized more easily in air than in water. Then, why do the electrical properties, especially A.C. breakdown voltage, decrease more rapidly in water than in air? The reason is explained as follows. Although polyethylene insulation is less oxidized in water than in air, once oxidation begins and chain scission occurs in the polyethylene molecules, water penetrating into the polyethylene causes cracks to grow with its evnironmental stress cracking action. Then the growing cracks lead to a short circuit in the polyethylene insulation, which in turn causes the A.C. breakdown voltage property of the insulation to decrease.

On the other hand, although oxidation of polyethylene and chain scission of polyethylene molecules occur more rapidly in air than in water, air does not act as an activator for environmental stress cracking as water does, so the chain scission in polyethylene molecules does not result in growth of cracks, and therefore, the A. C. breakdown voltage does not drop so fast. In our experiment, the wire without plating aged in air showed, a number of microcracks which looked as if the insulation had been cut with a sharp razor, but these hardly grew. In the case of ageing in water, however, permeation of the water tend to widen such micro-cracks into larger cracks. (Photo 2)

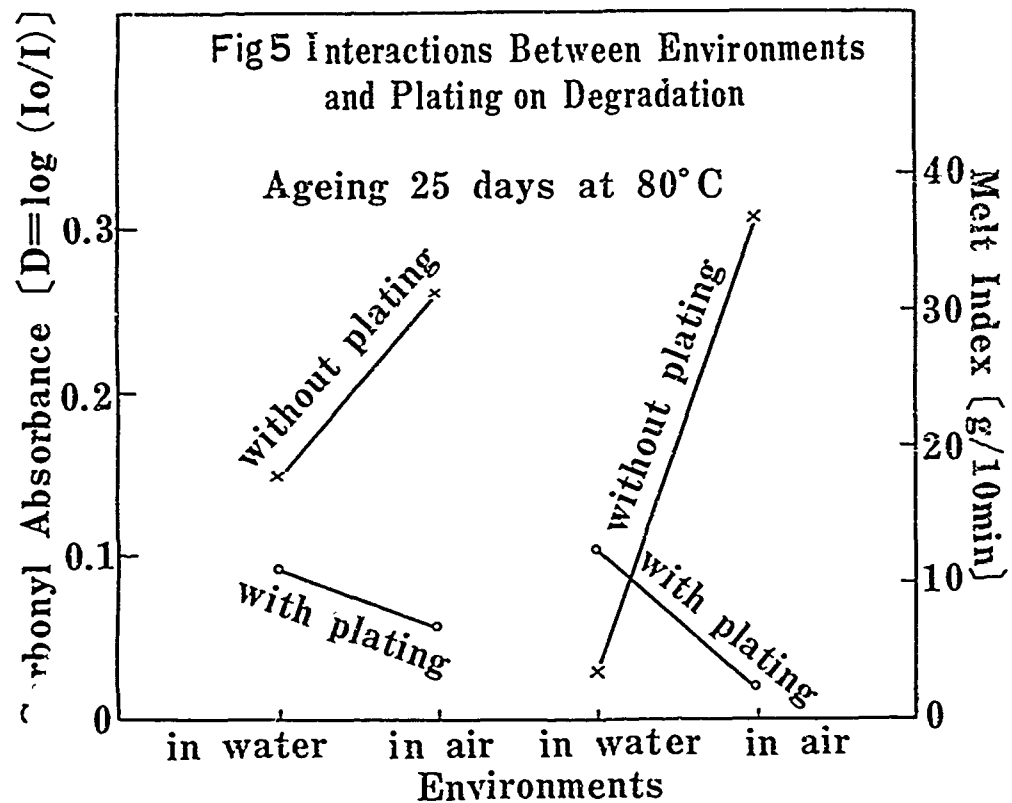
This is supported by the report of J. B. Howard (11) concerning the environmental stress cracking of polyethylene. He stated in his report "It has been found that water, which is normally not considered a strong cracking agent, promotes failure considerably." Photo 3 shows a propagation of cracks in water.

From these photographs it can be seen that micro-cracks grow to be macro-cracks quite rapidly in water. In this way, water contributes directly to declines in the insulating properties of polyethylene insulated wires. An actual example of this is the PE-P cable failure which occurred in Hakone as mentioned in Introduction.

Table 16
Effect of Environment on Various Properties

Environment	Carbonyl Absorbance	M. I. [g/10min.]	Density [g/cc]	Retention of Tensile Strength [%]	Retention of Elongation [%]	A. C. B. D. Voltage [kv/0.5mm]
in water	0.124	7.9	0.9189	28	17	9.3
in air	0.158	19.2	0.9200	24	7	13.0
F ratio	**	**	**			**

** Ninety-nine percent confidence



4. 6 Effect of Plating

The core wires of communication cables are normally used without plating, and the copper is in direct contact with the polyethylene. Therefore it can be considered that the copper causes various problems to the polyethylene. In this section, we will discuss mainly the catalytic action of copper, but will also consider other effects of copper on degradation as shown below.

O. Kamada (12) cites the following point as being one of the causes for degradation of polyethylene insulated wire. "Degradation of polyethylene insulation can be attributed to the forming of ion flow path based on the diffusion of the copper ion contained in the insulation, and the permeation of water into that portion."

Now, let us consider the effects of conductors on degradation. We used two types of conductors, one of which is bare copper and the other tin-plated copper. The results obtained in our No. 3 experiment are shown in Table 17. The carbonyl absorbance, density, M.I., etc. drop more remark-

ably in case of the bare copper than with the tin-plated. This indicates that oxidation of the polyethylene has progressed considerably in case of the bare copper conductor. And the A.C. breakdown voltage drops slightly more with the bare copper conductor than with the tinned copper conductor.

Why does bare copper accelerate the oxidation of polyethylene more greatly than tinned copper? Tin has a higher ionization tendency than copper, and the ionization potential ($M \rightarrow M^+$) of tin (7.3 eV) is smaller than that of copper (7.7 eV). When it is assumed that metallic ion has some effect on degradation, tin should degrade faster than copper. In our experiment, however, the degradation was clearly greater with copper than with tin. R.H. Hanser states as follows in his report (13) on the oxidation of polyethylene. "Acceleration of oxidation by the addition of 1.4% by weight of copper dust is about half that obtained by increasing test temperature by 20°C." Furthermore, it is well known that small amounts of metals such as cobalt, manganese, or iron accelerate the oxidation of polyethylene. The accelerating action of these metals on oxidation is attributed to a catalytic action on oxidation. In case of polyethylene contacting with bare surface of copper conductor, oxygen that permeated through polyethylene to the conductor would oxidize the polyethylene at an accelerated rate with the catalytic action of the copper.

Furthermore, the copper ion that diffused into polyethylene would affect the oxidation of polyethylene in the same way. However, even if copper diffused into polyethylene, we would consider that diffused copper does not act directly on degradation by forming an ion flow path, but rather acts, it indirectly on degradation by accelerating the oxidation of polyethylene with its catalytic action.

Table 17
Effect of Plating on Various Properties

Surface Metal of Conductor	Carbonyl Absorbance	M. I. [g/10min]	Density [g/cc]	Retention of Tensile Strength [%]	Retention of Elongation [%]	A. C. B. D. Voltage [kv/0.5mm]
Copper	0.205	20.0	0.9213	27	14	10.2
Tin	0.078	7.2	0.9177	25	10	11.8
F ratio	**	**	**			**
** Ninety-nine per cent confidence						

4.7 Effect of External and Internal Stress

In the practical application of polyethylene insulated wire, the wires are liable to be bent and subjected to external stress. On the other hand, in the manufacture of wire and cables, frozen stress remains in the insulation. It seems that this residual stress remains unrelaxed at normal service temperature. We believe that these two types of stresses (external and internal) are extremely important factors in the life of polyethylene insulated wires. In our experiment, external stresses were applied to the wire samples by making 3mm and 15mm diameter coils.

The amounts of the stresses so applied are calculated to be equivalent to 50% and 17%, respectively.

The results obtained in this experiment are shown in Table 18.

When the external stress is large, oxidation is promoted and the mechanical and electrical properties are lowered considerably. On the other hand, the internal stresses were 40% and 50%, respectively, and the results obtained were as shown in Table 19. It can be seen in this table that the polyethylene insulated wires having larger internal stresses shows a greater oxidation. For example, M.I. which provides a measure for the chain scission of polyethylene molecules, changes considerably when the internal stress is great. In our study of external stress and internal stress, both proved substantially the same in their effects on polyethylene molecules, in that they are related to the orientation and extension of polyethylene molecules. When a stress is added to polyethylene, the intermolecular distances in polyethylene grow larger, and the intermolecular cohesive energy becomes smaller. Consequently, the mechanical properties are greatly influenced by the stresses.

At the initiation of oxidation, as an increment of stresses acts to weaken the intermolecular cohesive energy of polyethylene the permeabilities of oxygen and water molecules are much increased, and this leads to an increase in degradation. Besides, stress has large effects for promoting the growth of cracks. That is to say that when stress is added, dislocation of molecules becomes easier, and the growth of micro-cracks caused by oxidation into macro-cracks is accelerated.

For example, samples, No. 5 and No. 6, shown in Tables 9 and 10 which had larger external and internal stresses than other samples, degraded much faster than expected. This clearly indicates the effect of stresses. Such effect in promoting degradation is especially evident when both external and internal stresses are large.

Thus the foregoing shows that stresses are not directly related to initiation of degradation, however, they are related to propagation of degradation in that they promote the growth of cracks.

Table 18
Effect of External Stress on Various Properties

External stress [%]	Carbonyl Absorbance	Retention of Elongation [%]	Retention of Tensile Strength [%]	Retention of A. C. B. D. Voltage [%]
50	0.032	57	60	69
17	0.012	91	88	94
F ratio	**	**	**	**
** Ninety-nine per cent confidence				

Table 19
Effect of Internal Stress on Various Properties

Internal stress [%]	Carbonyl Absorbance	M. I. [g/10min]	Density [g/cc]	Retention of Tensile Strength [%]	Retention of Elongation [%]	A. C. B. D. Voltage [kv/0.5mm]
40	0.139	6.2	0.9192	24	16	8.5
17	0.143	20.9	0.9198	28	15	13.5
F ratio	**	**				**
** Ninety-nine percent confidence						

5. CONCLUSION

Our conclusions on this study are as follows:

- 1) The main factor contributing to degrading of the insulating properties of polyethylene insulation is oxidation degradation. This is the initiation of overall degradation.
- 2) Crosslinking has little effect on oxidation degradation, but it has a large preventive effect on propagation of cracks caused by the action of environmental water; therefore, crosslinked polyethylene insulated wire has an excellent resistance to underwater degradation.
- 3) Applied voltage does not directly affect degradation, but it has an indirect effect in that it promotes oxidation of polyethylene by assisting in the permeation of oxygen dissolved in the water into the polyethylene.
- 4) The higher the temperature, the more the oxidation is promoted. However, our results seem to indicate that a rise in temperature acts rather to increase the permeability of oxygen into polyethylene and to contribute indirectly to oxidation than to promote the oxidation reaction itself.
- 5) Oxidation occurs more rapidly in air than in water. This is due to higher oxygen concentration in air than in water. However oxidation itself does not cause deterioration of the insulating properties of polyethylene insulation, but the growth of cracks accelerated by water following the oxidation actualizes the deterioration.
- 6) Plated metal layer on conductor delays the oxidation of polyethylene insulation. This effect is due to the barrier action of plated metal layer to isolate the polyethylene from the copper and to prevent the catalytic action of copper in the oxidation of polyethylene.
- 7) External stresses and internal stresses accelerate the growth of cracks and promote deterioration of the insulating properties of polyethylene insulation.

These are summarized as follows:

- Underwater degradation of polyethylene insulation is initiated with oxidation caused by oxygen dissolved in the water and then is propagated with the growth of cracks caused by water permeation. And to prevent degradation of polyethylene insulated wire, especially for underwater use, it is believed desirable to use a wire which consists of a tin-plated conductor and a coating of polyethylene, crosslinked if possible, containing optimum antioxidant and minimum internal stresses.

6. REFERENCES

1. Gen'ichi Taguchi, "Design of Experiment," Maruzen L.T.D (1962)
2. B. Baum, "The mechanism of Polyethylene Oxidation," Journal of Applied Polymer Science Vol II No. 6 p. 281 (1959)
3. W. D. Paist, "Insulation Resistance Changes in Polyethylene when Exposed to High Temperature and Humidity," Wire and Wire Products p. 1587 October (1974)
4. C. A. Liddicoat & B. F. Brown, "Insulation Resistance of Polyethylene on Wire Effect of Heat, Water and Electrical Stress," Wire and Wire Products p. 1874 December (1963)
5. T. Yasui & M. Watanabe, "Degradation of Polyethylene Wire when Exposed Water and Electrical Stress." Symposium Paper No. 506, IEE of Japan (1964) and Symposium Paper No. 5-13. General Meeting at Kansai District, IEE of Japan (1964)
6. F. H. Field & J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," (1957).
7. L. L. Lander, "Environmental Stress Rupture of Polyethylene." SPE Journal p. 1329 December (1960).
8. W. L. Hawkins, W. Matreyek & F. H. Winslow, "The Morphology of Semicrystalline Polymers." Journal of Polymer Science Vol XLI p. 1~11 (1959).
9. A. Renfrew & P. Morgan, "Polythene", p. 249 second Edition (1960).
10. Raff. Allison, "Polyethylene," High Polymers Vol XI (1956).
11. J. B. Howard, "A Review of Stress-Cracking in Polyethylene." SPE Journal p. 397 May (1959).
12. O. Kamada, "Insulation Characteristics of the Magnet Wire for Submerged Motors." The Hitachi Hyoron Vol 48 No. 4 p. 53 (1966).
13. S. H. Hansen, W.M. Martin and T. De Benedictis, "Determining Effectiveness of Antioxidants in Polyolefins." Modern Plastics, June p. 137 (1965).
14. N. D. MacLeod, "The Ageing of Polythene Compositions." 3rd Annual Symposium Wire and Cable, Signal Corps Engineering Laboratories, N. Jersey (December 1954).

Errata

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Page	Line (From the Top)	Error	Correction
2	17	reprot	report
3	13	condions	conditions
Table 2	1	Polyethlene	Polyethylene
4	1	experimet	experiment
Table 3	4	External	External
4	9	Experimant	Experiment
Table 4	Title	Expersment	Experiment
5	4	examine	to examine
5	15	(Pheto 3)	(Photo 3)
6	7	Fig 9	Fig 1
6	8	Fig 10	Fig 2
Table 9	1	A	C
"	2	A	C
"	3	B	A
"	4	B	A
"	5	B	A
"	6	B	A
"	7	A	C
"	8	A	C
"	9	C	B
"	10	C	B
"	15	C	B
"	16	C	B
10	8	persentage	percentage
12	4	weter	water
12	5	mesured	measured
13	16	effect	effect
13	16	degradrtion	degradation
13	22	Furthemore	Furthermore
14	30	Judgidg	Judging
14	31	electaical	electrical
15	6	in	is
15	6	;	.
15	11	premeability	permeability
15	21	tempeecature	temperature
17	13	absorbance	absorbance
20	14	becemes	becomes
22	6	(1974)	(1964)

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