# Effect of Ultraviolet Rays on Electric Properties of High Polymer Materials

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# Effect of Ultraviolet Rays on Electric Properties of High Polymer Materials

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Hereunder is presented the report concerning the experimental studies made of the effect of ultraviolet rays on the electric properties of typical mould type high polymer materials such as epoxy resin, polyester resin and silicone resin, and the discussion is made on how such an effect has been brought about. Exposure of specimens to radiation of ultraviolet rays consists of two processes, their exposure in the fademeter and their natural aging. Natural aging is carried out outdoors by fixing its specimens on the exposure stand at the angle of 45° facing south under glass cover. The specimens have been tested with respect to their electric properties, such as insulation resistance, electric breakdown strength and arc resistance, and with respect also to their mechanical properties such as tensile strength and compressive strength from the practical point of view as electric insulation materials.

On the result, the effect of ultraviolet rays was observed with respect to insulation resistance and arc resistance remarkably and the cycloaliphatic type epoxy resin was considered to be the most efficientresistor to ultraviolet rays in epoxy resin.

## 1. Introduction

Because of the efficient electric properties and the capability of curing at normal temperature of cast resins such as epoxy resin, polyester resin and silicone rubber, their applications to the electric machine have been done variously, for example, the uses for the insulation or the mould of electronic apparatus and transformer, the capsulating of electric parts, the composite material of insulator, wall tube insulator, breaker, disconnecting switch and switch board and the covered material of electric wire have been presented. Hence, it is capable enough that these apparatus are exposed to heat, high humidity, ultraviolet ray (It exists in natural light through the window and in light of fluorescent lamp as the lighting source[1]) including the use in the room.

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Consequently, it is quite important problem in insulation design of electric machine whether each resin used there, hold electric properties such as insulation resistance, arc resistance, etc. adequatelly or not, by the deterioration due to the above physical phenomena.

From these points of view, an effect of ultraviolet ray on electric properties was mainly investigated in this paper and the discussion was made on how such an effect has been brougt about.

## 2. Experimental and test specimens

The exposure of specimens to ultraviolet light consists of two processes, their exposure in the FA-2 type fademeter {Carbon arc was used as the light source. After filtering by the pylex class glass glove, carbon arc light gives ultraviolet ray which is the almost similar wave length distribution to natural light and the wave length distribution is like sufficienlly in the behavior of one between 300 and 400 mμ.*1} and their natural aging.

Natural aging was carried out outdoors by fixing its specimens on the exposure stand at the angle 45° facing south under glass cover. In our case, the exposure term is from May 1969 to May 1971.

Three types of epoxy resin have been employed, bisphenol type (Epikote 828), novolac type (Epikote 152, 154) and cycloaliphatic type (Epikote 172, 190, Araldite CY 175). In addition, two types of curing agent have been used, amin type and acid anhydrous type. These curing agents were mixed with the various percentage of resin.

The species of curing agent and the basic amounts are shown in Table 1. On

Table 1. Various curing agents and their quantities.

| Curing agent | Quantities of mixture(phr) | Curing condition |
|---|---|---|
| Diethylene triamine (DTA) | 8 | 20°C, 2hr+115°C, 30min |
| Triethylene tetramine (TTA) | 14 | 20°C, 2hr+115°C, 30min |
| P,P'-diamino diphenyl methane (DAM) | 27 | 100°C, 1hr+150°C, 2hr |
| K61B | 10.5~13.5 | 80°C, 2hr+65°C, 4hr |
| DMP-30 | 10 | 23°C, 4day |
| Dodecenyl succinic anhydride (DDSA) | 130 | 100°C, 6hr |
| Hexahydrophthalic anhydride (HHPA) | 80 | 80°C, 2hr+150°C, 4hr |
| Methylnadic anhydride (MNA) | 89 | 80°C, 2hr+150°C, 4hr +260°C, 2hr |
| HT907 | 95 | 120°C, 6hr |

*1 Generally, wave length in natural aging which makes to deteriorate the high polymer materials is short one below 400 mμ, i. e., ultraviolet ray.(2)

Since natural light on the earth is not including short wave length below 300 mμ, the test for the behavior of wave length between 300 and 400 mμ is reasonable.

novolac type resin and cycloaliphatic type resin, acid anhydrous type curing agents MNA and HHPA were employed as the curing one in each case.

In addition, fillers and others were matched to these resins as the submaterials and the mixture was cured. The specimens were made to plate type.

Here, as polyester resin, Epolac G110AL and G155AL were employed. Methylethylketon peroxide liquid (60%) mainly used to the curing at normal temperature was employed as catalyst and cobalt type liquid was employed as promotor.

Furthermore, RTV type silascon 6521 (sulphurate silicone rubber at normal temperature), etc. were employed as silicone rubber and several types of catalyst such as A, H, K and L were used to cure them.

To investigate the variation of properties after the deterioration due to the exposure of ultraviolet light, electrical and mechanical properties such as insulation resistance, dielectric breakdown strength, arc resistance, tensile strength and compressive strength were tested. The test of arc resistance is nearly applied to ASTM D495-61 standard method.

Mechanical properties such as tensile strength and compressive strength were tested by Amsler Universal Testing Machine.

There is some difference of opinion on the need for washing the test specimens before testing. However, the deciding factor seems to be the use for which the data are intended. If a correlation with service condition is desired, or result which will be of use to design engineers, unwashed species might be employed since electrical components in the field are not washed. However, the reason why a plastic loses its electric resistance, its arc resistance, etc. can obviously be found only by testing cleaned specimens. Experiments have been conducted both ways and the trends are the same. Therefore the following data are reported only on test plaques unwashed before and after the exposure.

The properties of resins stored 1 year in the dark at room condition show no change from initial values in each resin, hence changes reported must be caused by the exposure conditions to ultraviolet rays.

## 3. Experimental results and discussions

### 3.1 Relation between the appearance of specimens and the elapsed time of exposure.

The change of appearance of specimens in deterioration test of resins by fademeter was observed for 2,000hr of exposure. On the changes of colour, two types of trend were presented in epoxy resin. One is the change of colour that resin discolours firstly after the exposure and it colours after the longer exposure time and the other is the change of colour that resin colours firstly and the degree of colouration comes to be large on the elapsed time of exposure. Generally, bisphenol type and novolac type resin show brown or black brown colour after 2,000hr of exposure.

On the other hand, cycloaliphatic type resin is yellow brown after the same exposure time and the change of colour is small in this case.

It is thought that the relation depends partly on the species of curing agent, although direct decission of relation between these changes of colour and the compositions of specimens is difficult. That is, it is known that the discolouration generally arise on the resin with acid anhydrous type curing agents. This is considered to be due to the fact that cured resin is bleached and discolourated with oxygen and water by the action of ultraviolet light. And it is thought that the colouration comes to arise again by photo-oxidation after some exposure times.

On the other hand, it is thought that these bleaching actions are not appeared on the resin with amin type curing agent and colouring phenomena arise from the begining by photo-oxidation. The change of colour is not appeared remarkably in cycloaliphatic type resin, in spite of acid anhydrous curing agent. This is due to the fact that resin is quite stable to photo-oxidation and the resistances to ultraviolet ray are efficient. Then, the loading of ultraviolet light absorbent reduces the variation of colour. It seems to be due to reduce photo-oxidation such as above bleaching action by the absorbing of ultraviolet light. In addition, the variations of colour in loading of talcum, hydrated almina and silica as the mineral fillers were black-tinted a little and the remarkable changes were not appeared. Thus, it is thought that the changes of these colours are the colouration of filleres themselves by photo oxidation, rather than the colouration of resin itself.

On the other hand, although the species of catalyst also were of small number and typical forms of change as in epoxy resin were not appeared evidently in polyester resin, white change of colour of surface or milk-white one, i. e., chalking was appeared by the exposure within about 2,000 hr. There was no difference of variation of colour between resin cured at normal temperature and one cured sufficiently by heating. However, there is a report also which deteriorations of resin cured at normal temperature are rapid.[3] Same variation of colour was appeared in fademeter aging and in natural aging. Hitherto there is an example also measured the change of lustre on these subjects.[4] Dean and Manasia investigated the relation between the species of photo stabilizer and the variation of colour in fademeter aging and found that the use of ortho-hydroxithy-benzophenon derivetive was effective.[5] The variation of colour is due to the change of light absorption for resin as the result of chemical degeradation, i. e., it is due to the change of absorption spectrum of visible light behavior and ultraviolet one. However, there is no evidence enough on the relation between the variation of colour and the mechanism of degradation yet. On siliconerubber, the variation of colour is not appeared, owing to its pale yellow colour itself, but the appearance of surface seems contaminatively.

Then, tiny trenches are formed on the surface after 2,000 hr of exposure, for example, in Epikote 828-DAM system. On the other hand, large trenches are formed in Epikote 828-MNA system. The changes on these surfaces are not appeared in natural aging of about a month. The formation of these trenches seems to be promoted thermally by the oxidation[5] due to oxygen activated by light. In addition, there was the case that the chalking and the frosting were also appeared on polyester resin. Silicone rubber with no cracking or chalking is efficientresistor to ultraviolet ray.

### 3.2 Relation between the insulation resistance and the elapsed time of exposure of ultraviolet light.

The losses in insulation resistance after the test in fademeter are shown in Fig.1.*2 From that figure, it is known that the changes of insulation resistance to the elapsed time of exposure become to be decreased gradually or abruptly on the

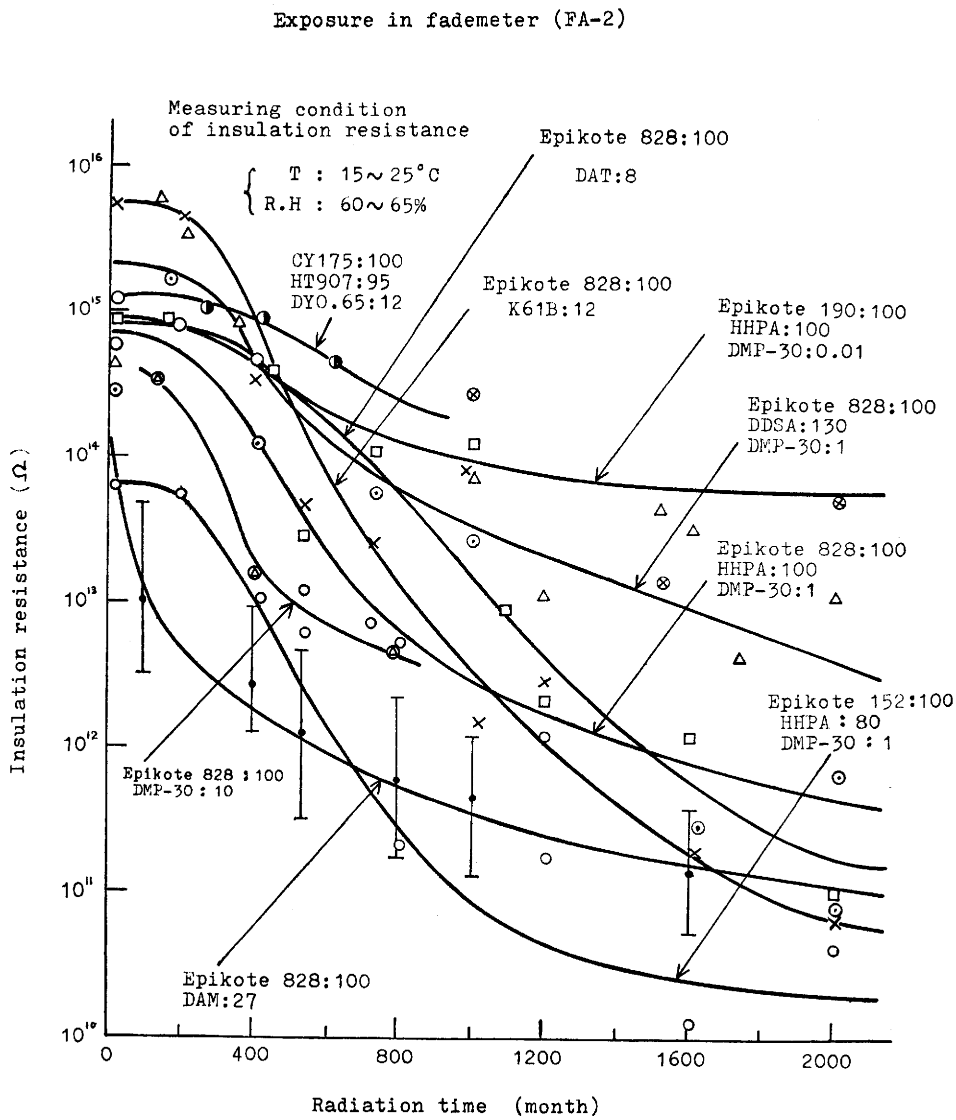


Fig. 1 Relation between the insulation resistance and the radiation time. Error bars were placed on one curve only to prevent overcrowding.

elapsed time of exposure in epoxy resin. {Generally, the loss in insulation resistance of epoxy resin must be dependent on the presence of a conductive species. The conductive species may be (1) low polymeric substance no cured, (2) impurities or various additives, (3) polar substances produced by photo-oxidation. However, it is known that the conductive material is not the low polymeric substance no cured, impurities or various additives since insulation resistance of specimens made from moulding compounds extracted with dimethylformamide, etc. increase to the same extent as one of specimens made from unextracted moulding compound. (Weight loss of solvent extracted moulding compound is below 10%. This weight loss must not be dependent on the fusion and must be dependent on extraction of impurities.) Insulation resistance of specimens rasped off the surface nearly recover to the initial one, so the conductive species may be the polar substance produced by photo-oxidation.} Then, on bisphenol type resin, insulation resistances of same order generally remain after about 4,000 hr of elapsed time of exposure in spite of species of curing agent. Although on cycloaliphatic type resin, the decrease of insulation resistance is comparatively small on the large elapsed time of exposure also, this is dependent on the efficient stability to photo-oxidation and the efficientresistor to ultraviolet ray as known from above-mentioned variations of colour.

On silicone rubber, the minimum value of insulation resistance occurs between 240 and 480hr, after that the maximum value occurs between 480 and 2,000 hr and insulation resistances reduce hereafter on the elapsed time of exposure. The reason why the maximum value occurs on the elapsed time of exposure may be due to the increase of insulation resistance by the interlinkage produced in oxidation. In short, the reason why the minimum value occurs in comparatively small exposure time is not evidently.

The change of insulation resistance in natural aging is shown in Fig. 2. There is generally no strict relation between the trend of insulation resistance in fademeter aging and one in natural aging. This may be mainly dependent on the difference between wave length distribution of ultraviolet light of carbon arc in fademeter aging and one in natural aging. The effect of condensation of moisture and vaporization will be a factor in natural aging different from the test in fademeter aging. On weathering condition of recent two years, fine weather was about 10%, rainy weather was about 23% and cloudy weather was about 53%. Average temperature was about 14°C and average relative humidity was about 80%.

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*2 The tests of insulation resistance were done at the relative humidity within between 60 and 70%. Generally, even in almost same moisture absorption, insulation resistances of exposed specimens change larger than that of unexposed one. From this point of view, it is thought that the moisture absorption is not a necessary factor.

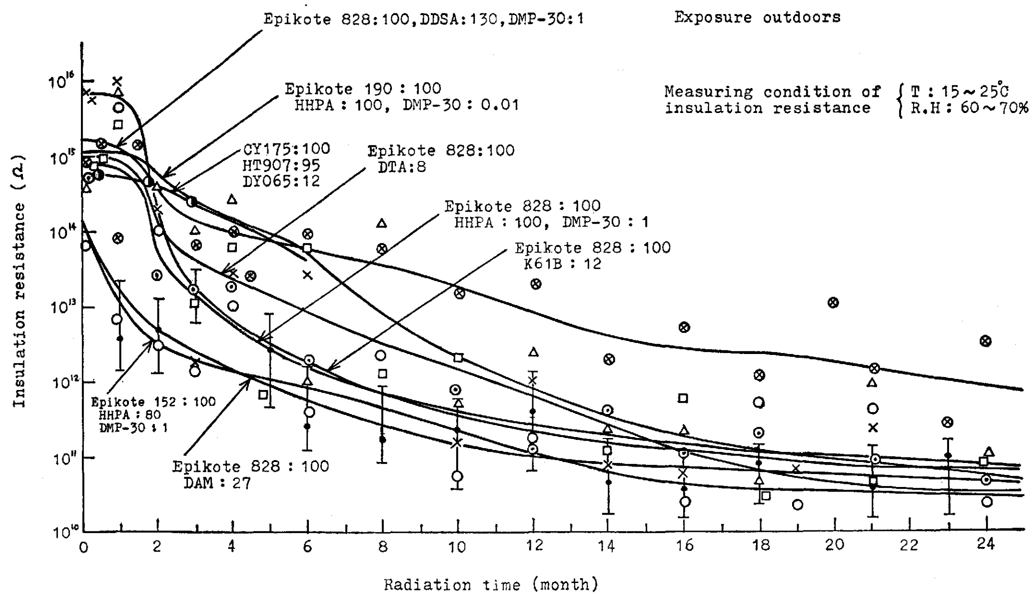



Fig. 2 Relation between the insulation resistance and the radiation time in the exposure outdoors. Error bars were placed on one curve only to prevent overcrowding.

## 3.3 Relation between the dielectric breakdown strenght and the elapsed time of exposure.

On dielectric breakdown strength of silicone rubber, the maximum value occurs on the elapsed time of exposure. Same trends are appeared both in natural aging and in fademeter aging. (Fig.3) The reason why the maximum value occurs is obsucure,

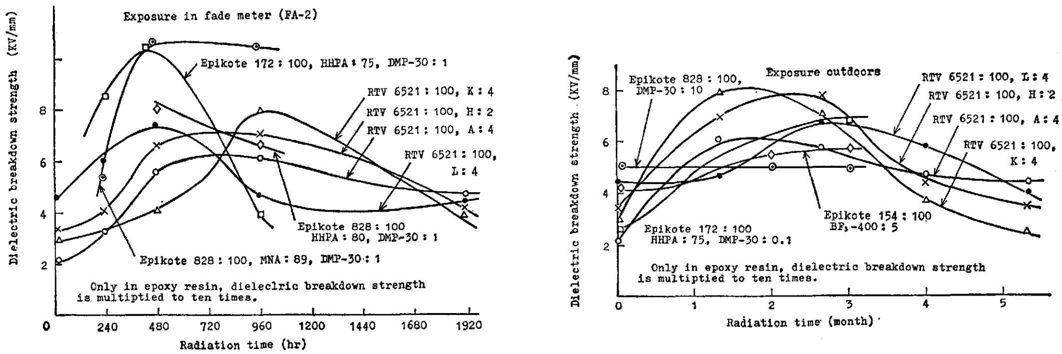



Fig. 3 Relation between the dielectric breakdown strength and the radiation time

while it may be thought that the interlinkages are made by the oxidation due to the exposure of ultraviolet light and then dielectric breakdown strength increase. On the other hand, it is thought that dielectric breakdown strength decrease by the degradation in the larger exposure time.

**3.4 Relation between the arc resistance and the elapsed time of exposure.**

The changes of arc resistance in fademeter aging were tested. (Fig. 4) There are two trends on the changes of arc resistances on bisphenol type epoxy resin, the trend that decrease abruptly within about 1,000hr and then remains nearly constant and the trend that gradually falls all through from the begining. In addition, arc resistances fall abruptly within initial 100hr and put forward to about 50% value of nonexposure one, or hereafter they fall nearly linearly with the slow inclination on the elapsed time of exposure, on novolac type resin. On the other hand, with the specimens of cycloaliphatic type epoxy resin, their arc resistances are efficient, their changes are quite small and are nearly constant on the elapsed time of exposure, i. e., nearly constant value (about 100 sec) is maintained, in comparison with those of bisphenol type resin. That is, at 1,000hr of exposure time in case with specimens of bisphenol type and novolac type, arc resistance between 10 and 80% of one in nonexposure reduce, while about 1% of one only reduce in the case with specimens of cycloaliphatic type resin. At 2,000 hr of exposure time, these differencies are remarkable. Arc resistance between 25 and 91% of one in nonexposure reduce in the former, while about 1.5% of one reduce in the latter. In addition, the variation of

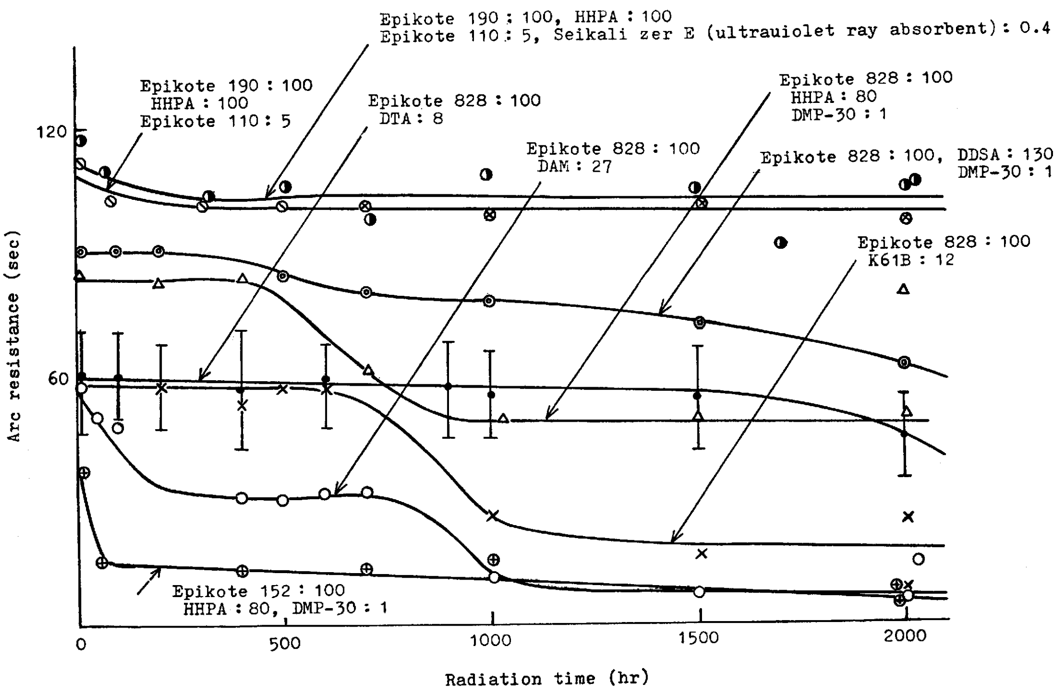



Fig. 4 Relation between the arc resistance and the radiation time. Data points are averages of 10 measurements. Error bars were placed on one curve only to prevent overcrowding.

arc resistance was not almost appeared, although ultraviolet light absorbent was loaded to cycloaliphatic type resin.

On polyester resin, the trends decrease abruptly at initial about 500hr are shown. (Fig. 5) However, there are two trends of variation on the specimens loaded filleres, the trend that decrease within the initial 500 hr and the trend that is nearly constant on the elapsed time of exposure. In addition, on silicone rubber, the minimum value occurs at the initial about 100hr (It is 300 hr in catalyst A), even in each catalyst, hereafter the maximum value occurs and after 1,500 hr nearly constant value is presented. (Fig. 6)

In addition, the results in natural aging are presented as in Fig. 7. The trend is comparatively same to one in fademeter aging. From these results, the results for 8 months in natural aging are thought to be nearly equal to that for hour between 700 and 1,000 hr in fademeter aging. However, there is no strict relation between the results of two aging test, i. e., that is the reason why the condition of degradation is different in fademeter aging and in natural one. (There is two trends on polyester resin, the trend of arc resistance decrease abruptly within about 2 months and after that remains constantly and the trend it remains constantly from the outset.)

Then the strict relation between the change of colour of specimens and the arc resistance is not presented in comparison with the result of change of colour shown in §1. Although on this subject, the change of colour is thougt to be due to the change

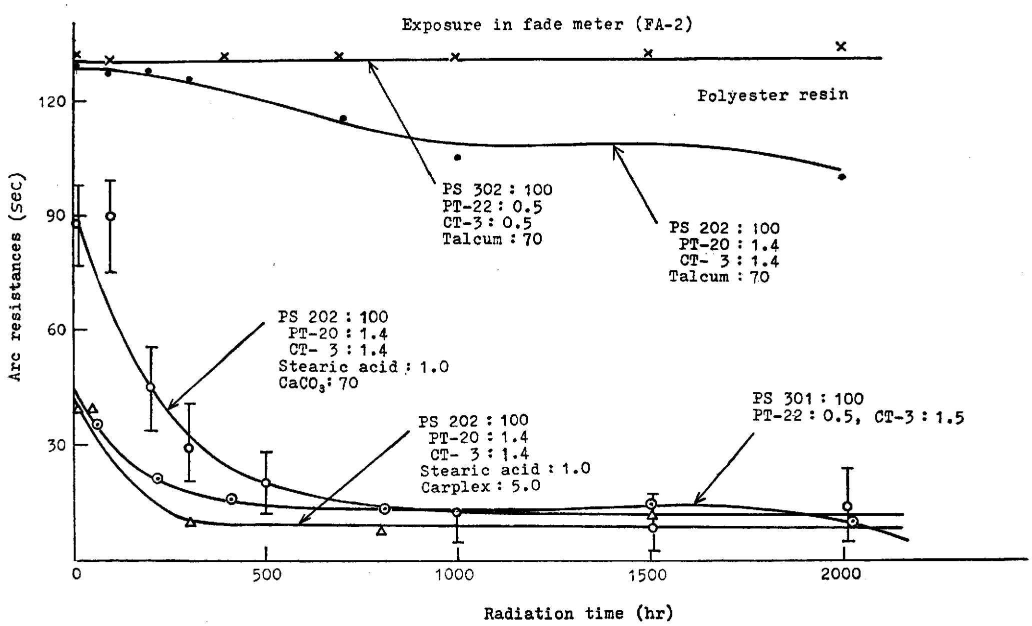



Fig. 5 Relation between the arc resistance and the radiation time. Data points are averages of 10 tests. Error bars were placed on one curve to prevent overcrowding.

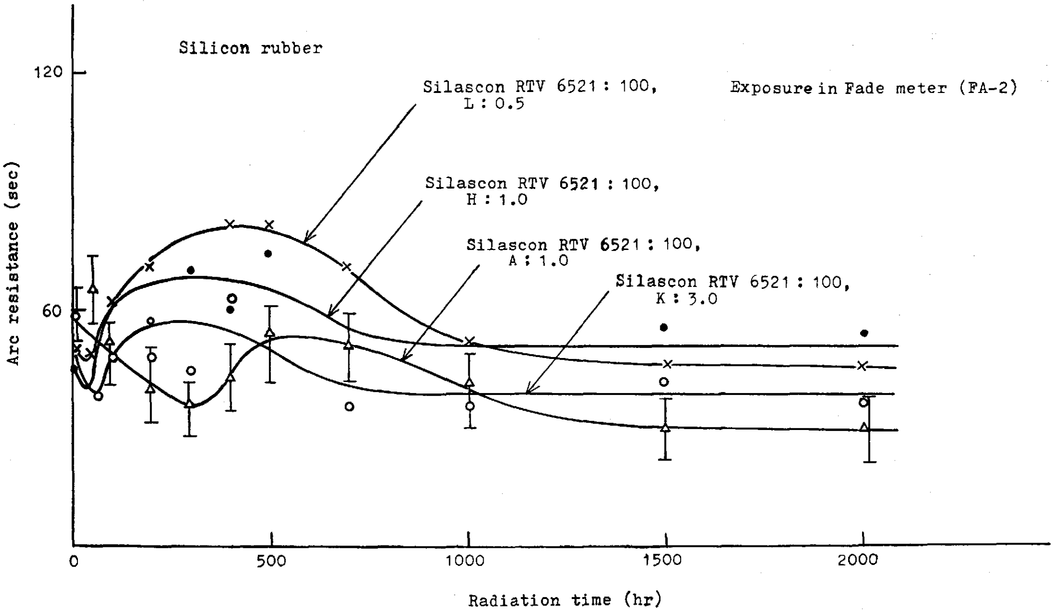
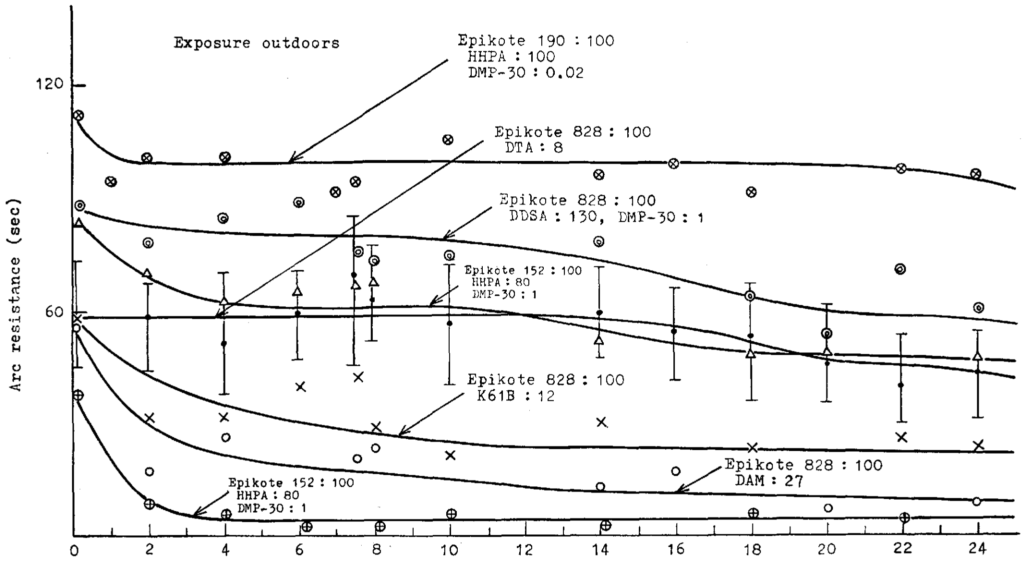
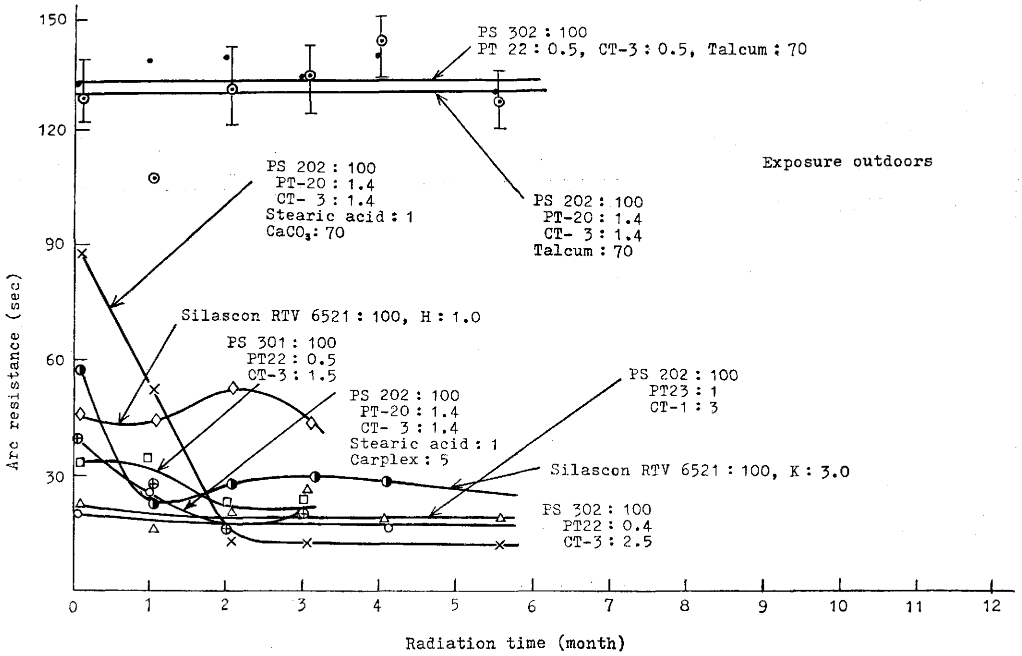



Fig. 6 Relation between the arc resistance and the radiation time. Data points are averages of 10 tests. Error bars were placed on one curve only to prevent overcrowding.




(a)




(b)

Fig. 7 Relation between the arc resistance and the radiation time in the exposure outdoors. Data points are averages of 10 measurements. Error bars were placed on one ourve only to prevent overcrowding.

of light absorption by the photo degradation of specimens,[7] therefore the absorbing spectre of visible light behavior and ultraviolet light one changes, it is supposed to be due to the fact that this chemical degradation has little to do with arc resistance of specimens directly.

### 3.5 Relation between the mechanical properties and the elapsed time of exposure.

To investigate the effect of exposure on the inner part of specimens and from the practical point of view as electric insulation materials, the effects of exposure on mechanical properties were tested. The variations of mechanical properties of epoxy resin in fademeter aging are shown as in Fig. 8. Generally, the variations of mechanical properties are not remarkable. Tensile strength seemes to fall slightly on the elapsed time of exposure and compressive strength and impact strength also illustlate the trends of fall monotonously. It seems that there is no relation between the variations of colour and one of mechanical properties in our case. On the other hand, same trends of properties as in fademeter aging have presented in natural aging also, and it falls gradually on the elapsed time of exposure even in each property. In addition, on the data of bending test, bending strength on aliphatic type amin cured resin, diaminodiphenylsulfon cured resin and dodecenylsuccinic anhydride cured resin falls, hence it may be said that the reduction on acid anhydrous cured resin is most smallest.[8]

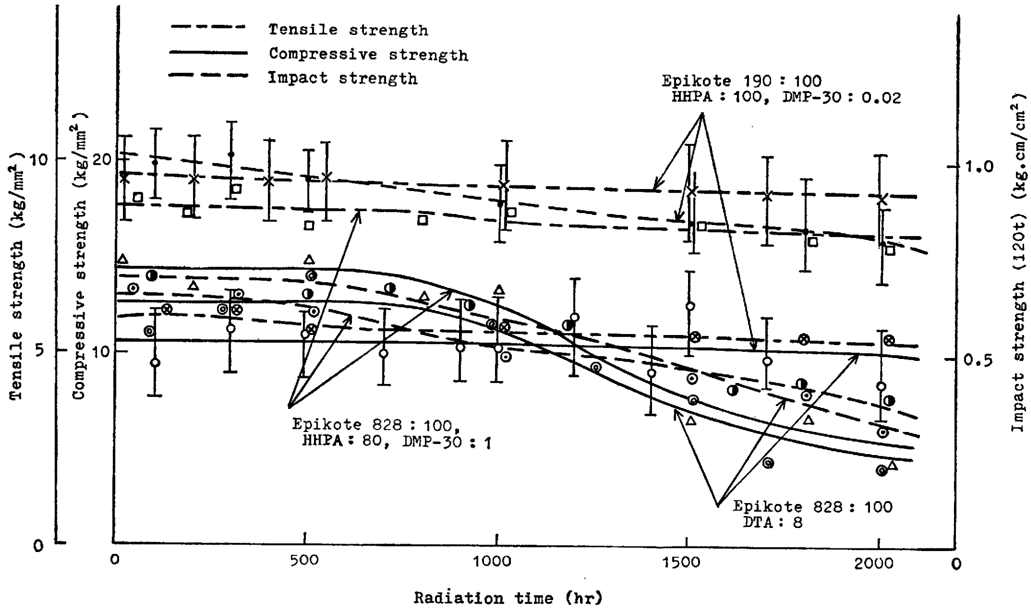



Fig. 8 Relation between the tensile strength, the compressive strength, the impact strength and the radiation time in the fade meter. Error bars were placed on the curves of one resin only to prevent overcrowding.

From the above-mentioned, considering the previous electric properties together, the properties on cycloaliphatic type epoxy resin is efficientresistor to ultraviolet ray. (As the curing agent, one which has no aromatic ring is effective.) It is known that the good property is obtained on bisphenol type epoxy resin, if curing agent is selected. Curing agent without aromatic ring is desirable, hence it appears that the efficient properties are presented with DTA and HHPA as the curing agent.

Then, in our case it seems that the properties on specimens in natural aging between 5 and 6 months are nearly equal to those in fademeter aging between 400 and 700 hr.

In addition, the variations of mechanical properties on polyester resin are small in comparison with the variations of colour as shown in epoxy resin. Tensile strength, bending strength, compressive strength, impact strength, etc. were investigated, however the test of tensile strength and elongation were difficult. Impact strength in natural aging are shown in Table 2. Its property is similar to one by Goto and et. al..[9] Data of tensile strength, bending strength, etc. are also illustlated in above Table. Next, the effects of exposure on silicone rubber are illustlated in Table 3. Konkle[10] has been investigated on the degradation of silicone rubber hitherto and Tsuji[11] has been reported the data of exposure test for a year. On the results, they say that the crack and the chalking are not appearted on silicone rubbur, therefore silicone rubber is efficientresistor to ultraviolet light.

Table 2. Effect of radiation outdoors on the mechanical properties.

(1) Non radiation

| Resin | Tensile strength ($kg/mm^2$) | Flexial strength ($kg/mm^2$) | Impact strength (sharpy) ($kg \cdot cm/cm^2$) |
|---|---|---|---|
| PS 301 | 440 | 970 | 4.6 |
| Epolac 110AL | 282 | 830 | 3.7 |

(2) One year exposure outdoors. *Exposure time : 2,000hr

| Resin | Tensile strength ($kg/mm^2$) | Flexial strength ($kg/mm^2$) | Impact strength (sharpy)($kg \cdot cm/cm^2$) |
|---|---|---|---|
| PS 301 | 461 | 929 | 4.0* |
| Epolac 110AL | 207 | 824 | 3.0* |

Table 3. Result of exposure test of silicone rubber.

| Silastic No | 12months exposure outdoors. | | 100days fade meter test | | |
|---|---|---|---|---|---|
| | RTV 6521 | RTV 6589 | RTV 6521 | RTV 6502 | RTV 6589 |
| Hardness (shore) before exposure | 52 | 63 | 72 | 66 | 78 |
| Hardness (shore) after exposure | 57 | 69 | 76 | 67 | 80 |
| Preserve ratio of elongation (%) | 82 | 82 | 70 | 94 | 68 |
| Preserve ratio of tensile strength (%) | 94 | 75 | 83 | 71 | 96 |

## 4. Conclusion

Variations of electrical and mechanical properties have presented on epoxy resins, polyester resins and silicone rubberes both in fademeter aging and in natural aging.

The results summarised are as follows.

(1) There are two properties, the property that the colour of specimens (epoxy resin) due to the exposure of ultraviolet light discolours from the outset by the exposure and colours on the large elapsed time of exposure and one that the colouration occurs from the outset by the exposure and hereafter the degrees of colouration come to be large on the elapsed time of exposure. These properties seem to relate with the species of curing agents, and then it appears that the former is

presented on specimens with amin type curing agent and the latter is presented on specimens with acid anhydrous type one. White change or milk white change of colour on the surface of polyester resin was appeared within about 2,000 hr of exposure time, although the species of calalyst was few and typical forms of variation were not presented evidently.

(2) Exposure of specimens to the radiation of ultraviolet light in the fademeter has had an effect of reducing the insulation resistances on epoxy resins, as shown in the declining curves, whether gradually or abruptly depending on the elapsed time of exposure.

Generally, the decrease in insulation resistance is comparatively smaller with specimens of cycloaliphatic type epoxy resin, so it is the efficientresistor to ultraviolet light. Here the factor of reducing of insulation is thought to be the polar-compound produced by photo-oxidation. On silicone rubber, the minimum value occurs for initial hour between 240 and 480hr, after that the rise of insulation resistance appeares again, the maximum value occurs for hour between 400 and 2,000 hr and hereafter the value falls on the elapsed time of exposure. The reason why the maximum value occurs on the elapsed time of exposure is thought to be due to the fact that the interlinkage is produced by oxidation and on the result the high resistivity is maintained.

(3) There are two cases, the case that arc resistance decrease abruptly within about 1,000 hr and then remains nearly constant and the case that arc resistance quite gradually falls all through from the outset, on the effect of exposure in fademeter aging. On the other hand, arc resistance on cycloaliphatic type epoxy resin is generally large in comparison with that on bisphenol type epoxy resin, the variation is quite small, the decrease is not almost appeared on the elapsed time of exposure and is maintained nearly constant. In addition, with the loading of ultraviolet ray absorbent, the sufficient increase of arc resistance has not been appeared. The arc resistances on polyester resin decrease abruptly for the initial about 500hr. However, with loading of fillers there are two cases, the case the arc resistances decrease for within initial 500hr and the case they remains nearly ocnstant. In addition, on silicone rubber, the minimum value of arc resistance occurs at the outset, the maximum value of one occurs hereafter and after 1,500 hr of exposure time nearly constant value of one presents, even in each calalyst.

Then it seems to be thought that arc resistance in natural aging for 8 months are correspond with those in fademeter aging between 700 and 100 hr.

(4) Generally, mechanical properties of specimens such as tensile strength, compressive strength and impact strength due to the exposure of ultraviolet light decrease gradually on the elapsed time of exposure. Even in polyester resin and silicone rubber, those variations are not remarkably.

(5) So far as practical industry is concerned, cycloaliphatic type epoxy resin is considered to be the most efficient electrical insulation material.

If bisphenol type epoxy resin is preferred for the purpose, the use of DTA or HHPA is recommended as efficientresistor to ultraviolet rays.

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