

# EFFECT OF IMPURITIES ON DIELECTRIC BREAKDOWN IN PLASTICIZED POLYVINYL CHLORIDE

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## 1. Introduction

Authors have studied on the electrical properties of solid insulating materials for a long time. In the previous paper,<sup>1)</sup> the relations between electric strength and polymerization of unit molecule, plasticizer concentration and its kind to be involved in the plasticized polyvinyl chloride which is important as covering insulator of electric wire and cable were investigated.

In general, method of polymerization, moulding condition and intermixture of various kinds of additions in manufacturing process give much influence on the dielectric breakdown of the synthetic polymer used in practice through the change of physical and chemical properties of the compound, while the molecular structure of polymer plays an important rôle.

In the present paper, effect of various additions on the dielectric breakdown of polyvinyl chloride resin is investigated in the view that they are a kind of impurity in the polymer.

## 2. Kind of Additions used and Preparation of Breakdown Specimen

It is usual that when P.V.C. (polyvinyl chloride resin) is made up to the practical form various additions, such as stabilizer, filler, pigment and lubricant etc., are intermixed with small amounts to satisfy the required conditions in practice. Kinds and quantities of addition used are shown in Table 1 which were mixed into the basic composition of plasticized P.V.C., i.e., P.V.C. 100 parts and plasticizer D.O.P. (Di-Octyl Phthalate) 50 parts, and these compound were moulded into a sheet form 1 mm thick according to the heat moulding device, of which the moulding conditions were as follows;

Mixing	145°-155° C, 5 minutes
Pressing	150°-160° C, 5 minutes.

Generally, the electric strength of the solid insulators depends not only on their properties, but also on other secondary factors which are referred with electrode arrangement, specimen form and ambient medium etc. Then, the breakdown specimen with a recessed part as shown in Fig. 1 was prepared with the small moulding device, given in Fig. 2, as well as used by Austen and Pelzer<sup>2)</sup> to eliminate these secondary effects and to get a intrinsic electric strength of the specimen. In the specimens prepared, the breakdown may occur mainly at the thinnest position in the recessed part.

TABLE 1. Additions Used\*

	Name of addition	Quantity range (Parts)
Stabilizer	<i>Tribase</i> (Tribasic lead sulphate)	0-10
	<i>D.B.T.D.L.</i> (Di-Butyl Tin Di-Laurate)	0-20
Filler	<i>Clay</i>	0-20
Pigment	<i>Whatumg Red</i>	0- 7.5
	<i>Phthalcyanin Blue</i>	0- 7.5
	<i>Benzidine Yellow</i>	0- 7.5
	<i>Carbon Black</i>	0- 5
	<i>Titan White</i>	0-15
Lubricant	<i>Barium Stearate</i>	0- 1

\* Basic composition in which these additions are mixed, will be given in each figure and table.

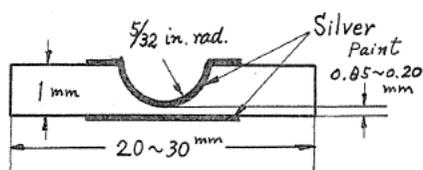


FIG. 1. Breakdown specimen.

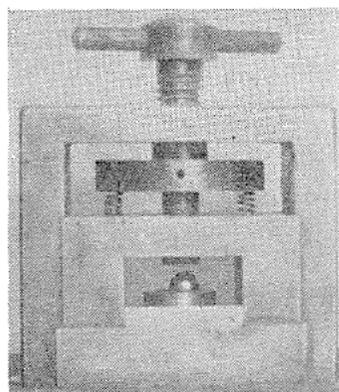


FIG. 2. Recessing device.

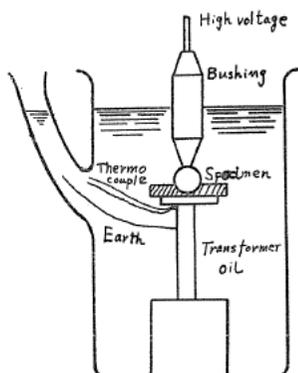


FIG. 3. Experimental device.

### 3. Experimental Device

Fig. 3 shows the experimental device, through which direct current voltage and alternating current voltage with 60 c/s were applied to the specimen using silver electrode and immersed in the transformer oil kept at 30°C constant temperature as ambient medium, with the steady rate of rise of 500 volts/sec.

### 4. Effect of Electrode Treatment

In order to apply the voltage to the specimen without giving the discharge within the ambient medium it is required to make a good contact between electrode and specimen. For this purpose, the electrode was produced by aluminum sputtering in vacuum and painting of silver powder or "Aquadag" (colloidal

solution of graphite and it was found from the experimental results that when *Aquadag* and silver paint which is consisted of silver powder, small amounts of resin as binder and its solvent (Ethylacetate) are used, some caution should be taken to eliminate undesirable effect of the solvent on the measurement of the intrinsic electric strength.

As an example, the relation between the electric strength and the time that the specimen was exposed in natural room and in the surrounding conditioned until applying of voltage after the painting with silver powder and *Aquadag* is shown in Fig. 4. It is given clearly in this figure that there is a marked decrease of electric strength in the region of small time in natural room, but in the case of exposure in the conditioned surrounding the rate of decreasing is not so large in comparison with the former case, and for each surrounding condition the electric strength approaches a saturation value, after more two hours, which is nearly the same with the electric strength in the case of sputtered electrode (see, Table 2). Then, it seems that the increase of electric strength with exposure time is due to the evaporation of solvent from the specimen.

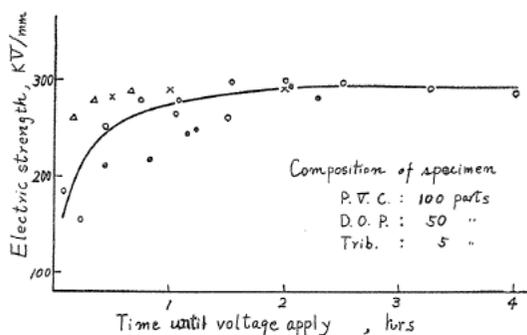


FIG. 4. Variation of D.C. electric strength at 30° C with exposure time in surroundings after painting of electrode until voltage apply.

- : Stored in room, 25-28° C, R.H. (relative humidity) 60-67%, after silver painting.
- : Stored in room, 27° C, R.H. 60%, after *Aquadag* painting.
- × : Stored in hot air, 80° C, after silver painting.
- △ : Stored in vacuum desiccator, 20-40 mm Hg, after silver painting.

Table 2 shows the effect of after treatment of specimen with three kinds of electrode system on the above saturated value of electric strength. The specimens kept in the surrounding with high humidity give a decrease of the saturated value of electric strength mentioned above, which may correspond to water absorption of the specimen. On the other hand, each saturated value of electric strength of the specimens kept in rather lower humidity is nearly of so much the same order respectively, as is able to neglect the effect of electrode materials within the experimental error.

TABLE 2. D.C. Electric Strength for Various Electrode Materials and Treatments\*

Treatment	Electrode	Electric strength (KV/mm)
Stored in concentrated sulphuric acid desiccator, for 24 hours	A**	292
	B**	287
	C**	286
Stored in dilute sulphuric desiccator, R.H. 57%, for 20 hours	A	296
	B	283
Stored in dilute sulphuric desiccator, R.H. 80%, for 24 hours	A	257
	B	239
Stored in water desiccator, for 24 hours	A	220
	B	154
	C	180
Exposed in room, 23-27° C, R.H. about 70%, for 24 hours	A	285
	B	290
	C	292

\* Specimens are of the same composition as given in Fig. 4.

\*\* "A" shows the silver painted electrode, "B", *Aquadag* and "C", aluminum sputtering in vacuum.

From the above experimental results, mainly the silver painted electrode was taken and the voltage was applied to the specimen kept in the desiccator for more twenty hours after painting.

### 5. Effect of Specimen Thickness

Electric strength was measured for the thickness range, 0.05-0.25 mm, because of occurrence of the mechanical cracks in the recessed part during the moulding process of the specimen below the lower limit 0.05 mm and no voltage available

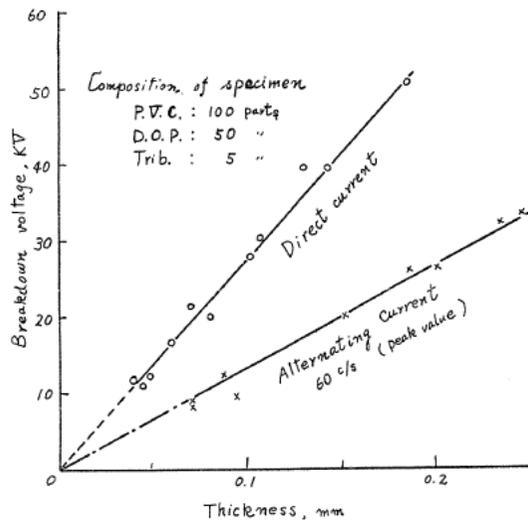


FIG. 5. Breakdown Voltage as a function of specimen thickness at 30° C.

to our device above the upper limit 0.25 mm. In this thickness range, the break-down voltage has a linear relation with thickness for D.C. and A.C. voltage, which is measured with peak value, respectively and their straightly intercepted lines pass across the origin of co-ordinate as shown in Fig. 5. This means that electric strength is constant in the thickness range, 0.05–0.25 mm.

## 6. Effect of Impurities on Electric Strength

### (6.1) Stabilizer

Generally, small amounts of stabilizers are added to prevent the thermal decomposition of polymer at the heat moulding process and the aging by ultra-violet ray for a long period. Among them, two kinds of stabilizer, i.e. "*Tribase*" (Tribasic lead sulphate,  $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ ) and *D.B.T.D.L.* (Di-Butyl Tin Di-Laurate), the former being a solid powdered stabilizer at the room temperature, the latter a liquid one, were selected. Fig. 6(A) and (B) show the electric strength at a constant temperature  $30^\circ\text{C}$  as a function of the quantity of stabilizers, where the plot is the average value of several measuring points and the histograms presenting the dispersion of each of them give a satisfactory result as shown in Fig. 7. In Fig. 6, the tendencies of variation of electric strength of D.C. and A.C. with the quantity of stabilizer are nearly equal to each other. However, their absolute values at a constant quantities are not the same, namely, D.C. value is always larger than that of A.C. with a rate of about 1.4–1.7 times for all specimens of the present study and the variation of electric strength with the quantity of *Tribase* is small as shown by nearly flat line, while electric strength in the case of *D.B.T.D.L.* increases with the increase of quantity of it and approaches a saturation value which is larger than that of *Tribase*. On the other hand, the specimens containing *Tribase* are opaque, whereas those containing *D.B.T.D.L.* are transparent and slightly yellow.

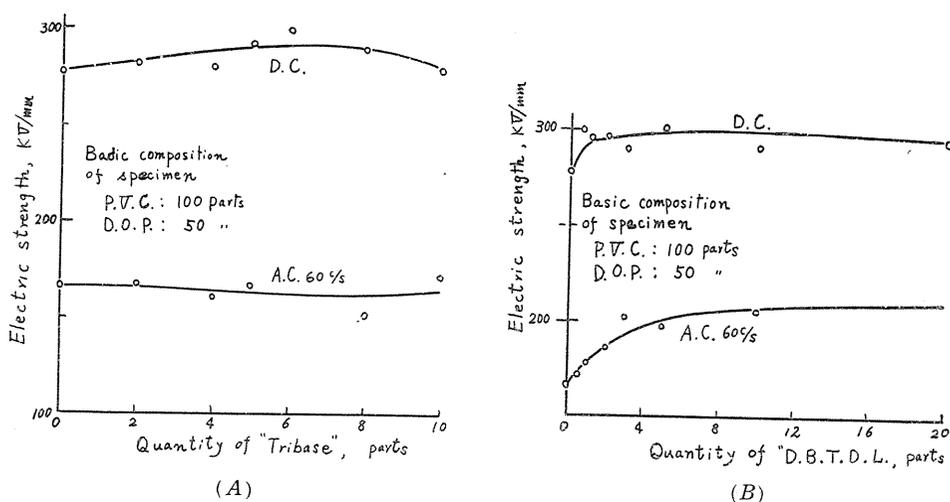


Fig. 6. Effect of stabilizers.

(A) Effect of "*Tribase*". (B) Effect of *D.B.T.D.L.*

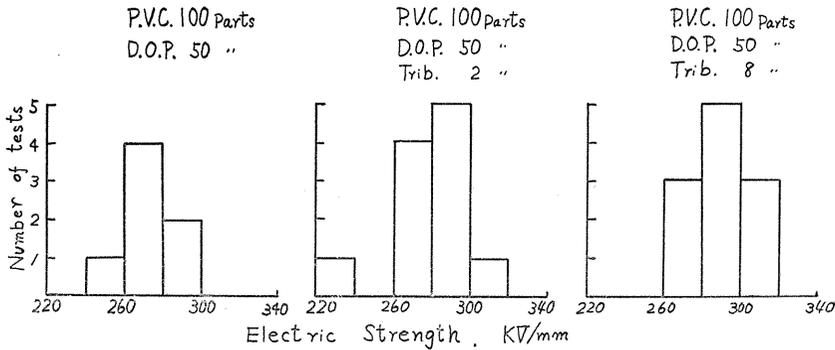


FIG. 7. Histograms of D.C. values at 30° C.

### (6.2) Filler

The specimens containing "Clay" as filler are of white opacity. Effect of Clay on electric strength given in Fig. 8 has a contrary tendency to that of Tribase. In this series of specimen, five parts of Tribase were usually added into the basic composition and if these were taken out from the basic composition, the electric strength decreases more as shown in Fig. 8 with  $\otimes$  marks. It seems that this effect is due to the stabilizing effect of the stabilizer.

### (6.3) Pigment

Among the pigments used, Red, Blue, Yellow and Green are of the organic compound, whereas Titan-White and Carbon-Black are of the in-organic one. The results are shown in Fig. 9 (A) and (B). In the series of these pigments, the electric strength decreases with the increase of pigment quantity for all of specimens tested, but it is to be noted that Carbon-Black decreases markedly the electric strength in comparison with that of other pigments.

### (6.4) Lubricant

Lubricant is a substance to be added to prevent the adhesion of compound with the heated steel roll during moulding process and has the ability as stabilizer at the same time. In this series, several specimens different in the basic composition were investigated. The adding of small amounts of lubricant Barium Stearate increases the electric strength markedly and also, the adding of Clay in this series gives a negative effect on the electric strength, as well as in the stabilizer-filler series as shown in Table 3,

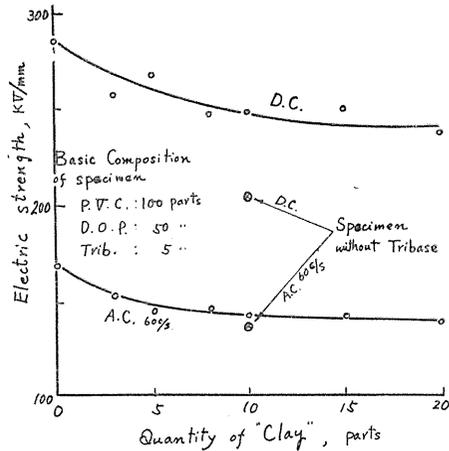


FIG. 8. Effect of "Clay".

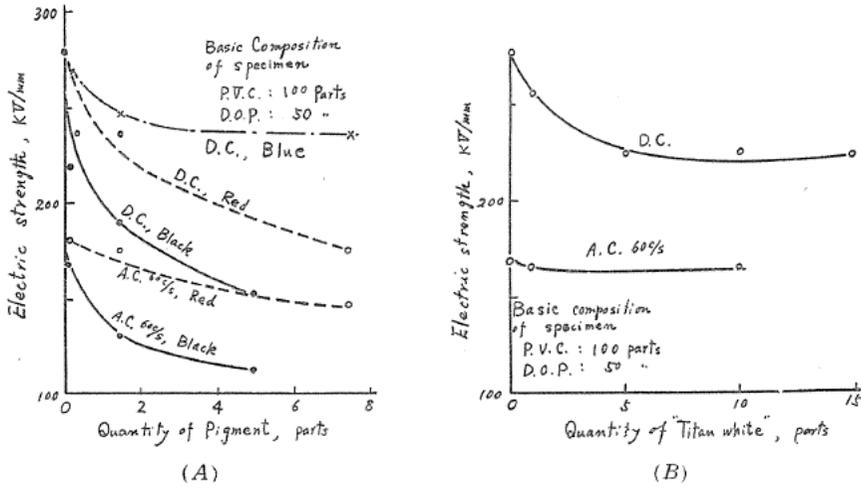


FIG. 9. Effect of pigments.

TABLE 3. Effect of Ba-St\*

Composition** (Parts)	Ba-St 0	Ba-St 0.5	Ba-St 1.0	Ba-St 0.5 Clay 10	Ba-St 0.5 Trib. 5
D.C. electric strength (KV/mm)	278	324	320	253	325
A.C. electric strength (KV/mm)	166	184	186	155	200

\* Barium Stearate. \*\* Basic composition; P.V.C. 100 parts, D.O.P. 50 parts.

### 7. Electric Resistivity in Low Electric Field and Dielectric Breakdown

In order to find what relation the characteristics mentioned above have with the internal state of specimens containing various additions, we investigated the electric resistivity of specimens in low electric field, which we got an useful knowledge about the internal state of specimens. In another report of ours,<sup>3)</sup> it was cleared that resistivity of P.V.C. compound in low electric field is mainly due to the ionic conduction which depends on the motion of impurity ion existing in specimens under the electric field, and is shown as functions of internal viscosity of moving ion and its density. At a constant temperature, where the change of internal viscosity of moving ion due to the intermixture of additions is negligible except in the case of *D.B.T.D.L.*, if the electric strength is decided by the mechanism of thermal breakdown or corresponds to the space charge formation near electrode before occurrence of the breakdown under D.C. voltage, it may be expected from the theoretical consideration that there is a close relation between resistivity and electric strength among different specimens.

Variations of resistivity as a function of the quantity of various additions are shown in Fig. 10 and Table 4. These are mainly explained with the change of ion density, for example, due to the thermal decomposition of polymer and some addition or due to ion adsorption by some addition, and it is to be noted that

intermixture of *D.B.T.D.L.* decreases markedly the resistivity while that of *Carbon Black* increases it. When compared these results with the variations of electric strength mentioned, it is difficult to find any reasonable relationship between electric strength and resistivity. Therefore, it is concluded that the factor affecting electric strength does not depend directly upon the ion density, but upon other properties of additions and it is not possible to expect the pure thermal breakdown for these specimens although the temperature dependence of electric strength shows the characteristics of high temperature region in which the electric strength decreases with increasing temperature, for all of specimens tested.<sup>4)</sup>

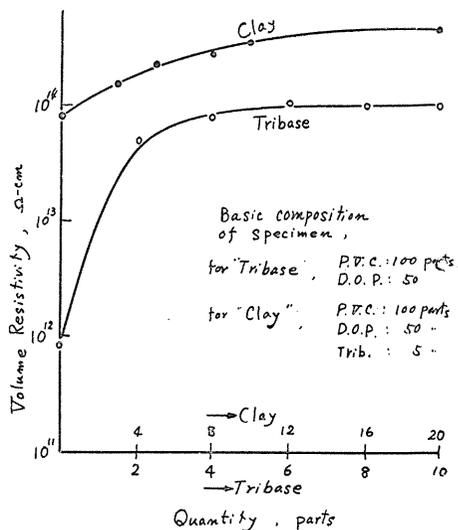


FIG. 10. Volume Resistivity as a function of the quantity of "Tribase" and "Clay" at 30° C.

TABLE 4. Volume resistivity as a function of the quantity of various additions\*  
(unit;  $\times 10^{11} \Omega\text{-cm}$ , 30° C)

Quantity (Parts)	Red	Blue	Quantity (Parts)	Black	Quantity (Parts)	<i>D.B.T.D.L.</i>	Titan white
0.15	5.5	23	0.15	80	1	28	3.8
1.5	1.9	13	1.5	140	5	5	4.3
7.5	0.4	14	5	460	10	2	9.5

\* Basic composition; P.V.C. 100 parts, D.O.P. 50 parts.

### 8. State of Addition in Specimen and Dielectric Breakdown

The quantity characteristics of electric strength of various additions are distinguished into three groups:

- Increasing characteristic: *Barium Stearate* and *D.B.T.D.L.*,
- Flat characteristic: *Tribase*,
- Decreasing characteristic: *Carbon Black*, *Titan White*, *Red*, *Blue*, *Yellow* and *Clay*.

In this classification, it is pointed out that these characteristics show a close relationship with the dispersing condition of additions in the plasticized polymer. The group having a increasing characteristic is of some stabilizers which are dispersed in the liquid form into the plasticized polymer without losing transparency of specimens under the condition of high temperature and high pressure during the heat moulding process and are existing uniformly in the state of molecular dispersion. On the other hand, the group having a decreasing characteristic is of substances in solid powdered state at room temperature which form the aggregate state gathering themselves and make the specimen opaque for the

dispersion of light.

By these considerations and the facts that first, the variation of ion density has no relation with that of electric strength, second, there are the same characteristics even for the impulse electric strength<sup>4)</sup> and third, the dielectric constant of the specimens containing *Carbon Black* and *Titan White* is larger than that of the basic composition, it is concluded that decreased electric strength is based on the increasing of the effective electric field at the local place in the specimens whose electric field is disturbed by the aggregate.

Increasing electric strength due to the intermixture of stabilizer *D.B.T.D.L.* may be explained by the decreasing of polyene structure ( $-C=C-$ , C: Carbon atom) of the polymer molecule which is produced by its decomposition. However, for these details further experimental works will be necessary to clarify the mechanism involved in this problem. Also, the flat characteristic of stabilizer "*Tribase*" will be explained qualitatively by the two factors, one being the formation of aggregate state of itself, the other the prevention of appearance of polyene structure. We are now studying on the discrepancy of D.C. and A.C. value, and their details will be reported in another paper.

#### References

- 1) Shinohara, U. and Ieda, M.: "Dielectric Breakdown of Plasticized Polyvinyl Chloride with Alternating Current Voltage 60 c/s", Jour. I.E.E. of Japan, 1955, **75**, p. 476.
- 2) Austen, A. E. W. and Pelzer, H.: "The Electric Strength of Paraffins and Some High Polymers", Jour. I.E.E., 1946, **93**, Part I, p. 525.
- 3) Ieda, M. and Shinohara, U.: "Electric Conduction of Plasticized Polyvinyl Chloride with Various Additions at Low Electric Field", Jour. I.E.E. of Japan, 1959, **79**, p. 71.
- 4) Ieda, M. and Shinohara, U.: "Impulse Electric Strength of Plasticized Polyvinyl Chloride and its Temperature Dependence", Report on the 31st Annual Meeting of I.E.E. of Japan, No. 80, 1957.