New Measurement Method for Antistatic Film

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Abstract

Up to this time, the direct current was used for measurement methods for electrostatic propensity on an antistatic film. For example, the specific surface resistance of a film was used conveniently. But conventional methods to use the direct current and the test method to use the ash didn't correlate to each other. With this research, the measurement method to use an alternating current was examined. In the result, absolute value of impedance correlated with the value of this ash test. About the impedance inflection of many samples, it was investigated in detail. The results of antistatic films coated using the conductor showed large frequency reliance, and were researched about this behavior. Then, it was found that the percolation transition of the conductive materials was related to greatly. For the consideration regarding the measurement value of samples, the simulation with the circuit model to use the resistance and the condenser was calculated. In the result, the behavior in frequency reliance of absolute values of the impedance was able to be explained by this circuit model.

Introduction

Generally, plastic films have a strong electrification property. Therefore, lots of attempts and proposals for improving electroconductivity of photographic supports or the surfaces of various coating layers have so far been proposed and application of various kinds of surface active agents, polymers, etc. have been attempted. For the purpose of improving degradation of the photographic properties under low humidity condition, Japanese Patent Publication No.35-6616 (1960) disclose a technology of using metal oxide as an antistatic agent[1]. Layers containing such conductive fine particles have been studied for 30 years or more since 1960.

When two-phase system with a binder and conductive particles was studied, a problem on the amount of addition was found, and the influence of fine particles on the percolation transition of electrical conductivity was studied[2)3)]. The addition of excess conductive particles will lower the surface resistivity of the film using the two-phase system. But the transparency of the film will be lowered by this method. It is difficult to control the specific surface resistance without degradation of the photographic properties because of the percolation transition .

Up to this time, the direct current was used for measurement methods for electrostatic propensity on an antistatic film. With this research, the measurement method to use an alternating current was studied , and the relation between the absolute value of impedance and the value of the conventional methods was examined.

Experimental

1. Preparation

60 g of stannic chloride hydrate was dissolved in 2000 cc of an aqueous water. Next, the resulting solution was boiled so as to obtain a co-precipitant. The resulting precipitant was taken up from decantation, and then the precipitation was washed for numerous times with distilled water. In the distilled water wherein the precipitation was washed, silver nitrate was dropped for confirming that there is no reaction of chlorine ions. The precipitant was added to 1000 cc of distilled water and dispersed. Following this, the total amount was arranged to 2000 cc of solution. In addition, 40 cc of 30% aqueous ammonia was added to the solution. When the resulting solution was heated in a water bath, SnO_2 sol solution is generated. When this solution is used for a coating solution, the density is condensed while spraying ammonia to the sol solution to be used.

2. Subbing coating

The following subbing coating solution A was coated on the polyethylene terephthalate film (PET film) which

was subjected to corona discharge. Copolymer latex solution comprised of 30% by weight of butyl acrylate, 20% by weight of t-butyl acrylate, 25% by weight of styrene and 25% by weight of 2-hydroxyethyl acrylate.

Subbing coating Solution A:

(1) Copolymer latex solution (the solid portion was 30%)	10g
(2) SnO_2 sol (the solid portion was 6%)	x g
(3)Water	

3. Measurement method

Under 23℃ and 20%RH, the surface of the PET film was rubbed with a rubber roller. Next, the ash of cigarette was held near so that whether or nor it was attracted to the film in accordance with the following criteria:

A: The ash is not attracted even when the cigarette was held as close as 1 cm.

B: The ash is attracted when the cigarette was held as close as 1-4 cm

C: The ash is attracted even when the cigarette was separated at 4 or more cm.

Specific surface resistance was measured under the conditions of the imprinted voltage of 100v, 23℃ and 20%RH by the use of a Teraohmmeter VE-30 produced by Kawaguchi Denki.,Co.,Ltd.

Measurement method of the absolute value of the impedance was as follows. When impedance was measured, Precision LCR meter HP4284A and HP16451B produced by Yokogawa Hewletter Packard (YHP) were combined to be used. Under atmosphere of 23℃ and 20%RH, the absolute value of the impedance of the film material was measured by means of a Non-Contacting Electrode Method. Using an electrode wherein the diameter of the main electrode was 3.8 cm, the sample was cut to a square of 5.5 x 5.5 cm.

Parameters Needed:

Cs1 Series capacitance when the test material is not inserted (F)

D1 Dissipation factor when the test material is not Inserted

tg Gap between Guarded/Guard electrode and Unguarded electrode (m)

Cs2 Series capacitance when the test material is inserted (F)

D2 Dissipation factor when the test material is inserted

ta Average thickness of test material (m)

Equations:

$$\varepsilon = \frac{1}{1-(1-Cs1/Cs2)\times tg/ta}$$

$$Dt = D2 + \varepsilon \times (D2 - D1) \times (tg/ta - 1)$$

Where ε is dielectric constant of test material and Dt is dissipation factor of test material. The absolute value of the impedance was calculated with these parameters.

The circuit of this method was shown in Figure 1, the gap between guard electrode and unguard electrode was measured by the accurate micrometer equipped with HP 16451B.

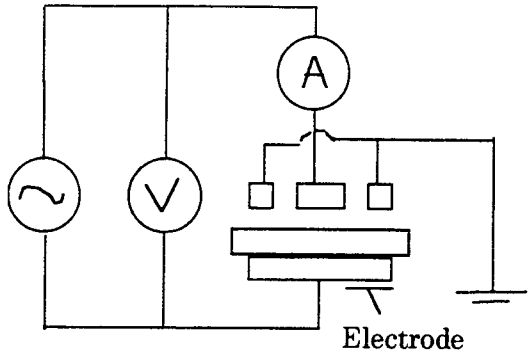

Figure 1:The circuit of measurement method of the impedance

Results and Discussions

With regard to the specific volume resistance of the particles contained in SnO_2 sol solution, a thin layer was formed on a silica glass by the use of a sol solution, and a value measured by the use of a four probe method of resistivity measurement that was defined to be the specific volume resistance value was 3.4×10^5 Ω cm.

A finely dispersed SnO_2 sol in subbing coating solution was observed. The film was coated on one side with subbing layer having a dried coating thickness of 0.8 μm, followed by drying at 120 ℃ for 1 minute. The volume fraction v% of SnO_2 particles was determined by measuring the specific gravity of SnO_2 powder. Depending on the volume fraction of SnO_2, the specific surface resistance of the film with subbing layer decreased to 10^8-10^9 Ω. The volume resistance of subbing layer having the thickness t was determined as follows.

$$t \times \rho_s = \rho_v$$

where ρ_v is specific volume resistance, and ρ_s is specific surface resistance. The specific volume resistance of the subbing layer at the volume fraction 50% was estimated to be 7×10^4 from the specific surface resistance of the film. This value was consistent with the specific volume resistance of the particles contained in SnO_2 sol.

The Non-Contacting method was applied in the electrical property of films by the measurement method to use an alternating current. This method accurately derives the dielectric constant from the capacitance difference

between two measurements, without the test material, the other with the test material. These two measurements are made with the distance between the electrodes held constant. This method is especially applicable for film materials. The merits and demerits of this method are as follows:

1. Merits

+Air film (error caused by air gap between the electrode and the surface of test material) does not cause error.

+It is not necessary to apply thin film electrodes.

2. Demerits

-It is necessary to measure capacitance twice.

-Equation to derive the dielectric constant is complex.

Figure 2 shows the absolute value of the impedance as a function of frequency at the volume fraction 0vol%, 5vol% and 40vol% of SnO_2, respectively. The absolute values of the impedance at low frequency increase with an increase in the volume fraction of SnO_2, and the values of films containing SnO_2 at high frequency corresponded with the values of film coated with copolymer latex.

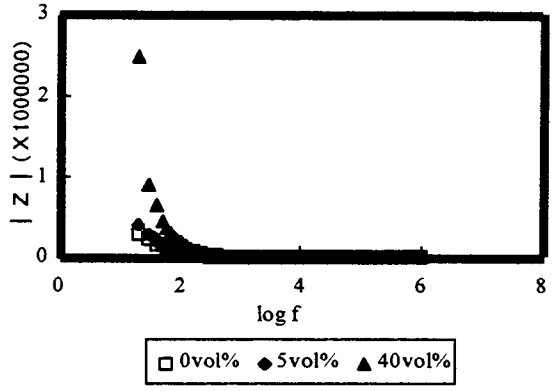

Figure 2: The absolute value of the impedance as a function of frequency

The relations between the absolute values of the impedance at 20Hz and the specific surface resistance were shown in Figure 3. The relation between the specific surface resistance and the content of SnO_2 was depicted by a curve, and showed that the percolation transition was observed and occur within a range from 5 vol% to 40 vol%. But the variation of the absolute values of the impedance with the content of SnO_2 was drastically, and the experimental data gave linear plots within a range from 5vol% to 20vol%. An estimation of the percolation threshold Pc was given by the absolute values of the impedance at 20Hz. Pc may be about 20 vol%. Pc =18vol% which was calculated using the value of the aspect ratio of SnO_2, correspond to the value of this system.

We consider how the absolute values of the impedance varies with frequency. If the subbing layer consists of n+1 kinds of circuit, and each circuit consists of n resistance and N-n condencer. The impedance Z_n of a circuit No.n is as follows:

$$Z_n = nR + (N-n)/2\pi fCj \quad (1)$$

where R and C are the value of resistance and condencer, f is frequency, and j is imaginary number.

$$1/Z_{total} = 1/Z_0 + 1/Z_1 + \text{-----} + 1/Z_N \quad (2)$$

The number N is set to ∞,

$$1/Z_{total} = \int dx/(xR+(1-x)/2\pi fCj) \quad (3)$$

Figure 4 shows the various value of the impedance calculated by Equation (3), when a component of the direct resistance is 10^7 Ω. The variation of the absolute values of the impedance is depicted by a curve similar to that in Figure 2. And that results from the variation of capacitance of condencer.

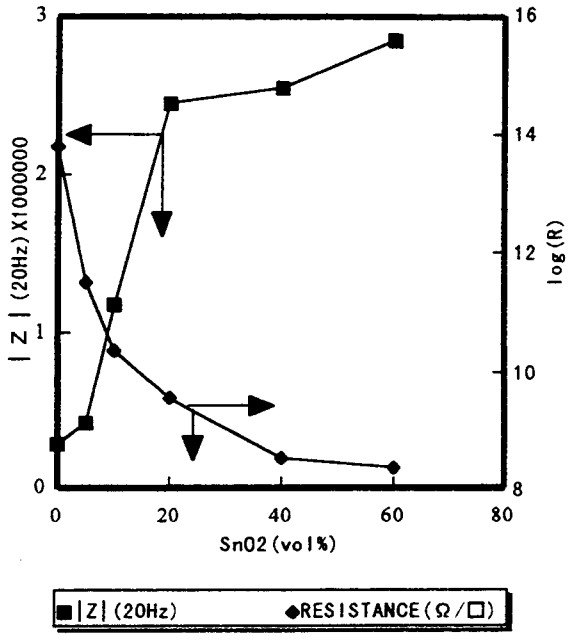

Figure 3: The relations between the absolute values of the impedance at 20Hz and the specific surface resistance

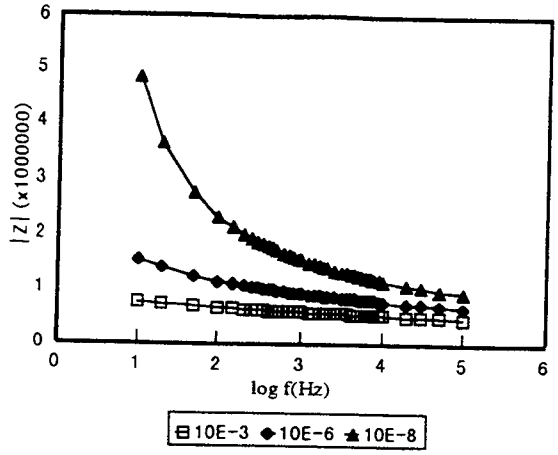

Figure 4: The simulation with the circuit model

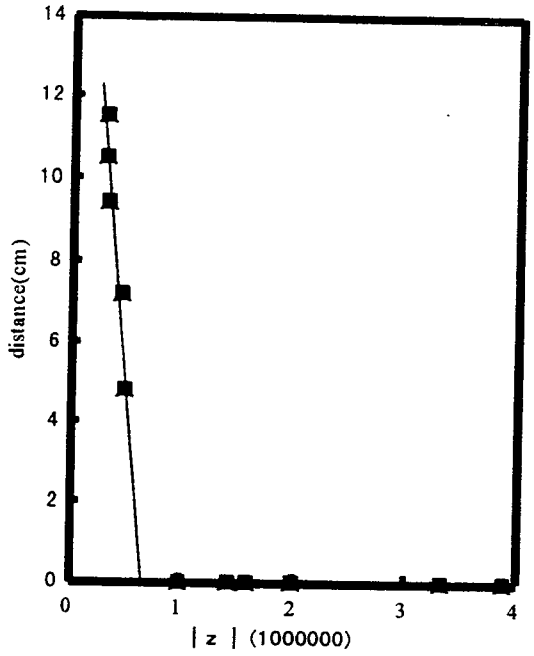

Figure 5. The relations between the distance of ash test and the absolute values of the impedance

The results of ash test were summarized in TABLE 1. The ash of cigarette was not attracted to the films coated with the layer comprising SnO_2 in an amount of 20 %. The specific surface resistance of the film was $3.5x10^9\Omega$, though some kinds of film having the specific surface resistance of $10^9\Omega$ attracted the ash of cigarette under atmosphere of 23℃ and 20%RH.

The absolute value of the impedance of various kinds of the light-sensitive photographic materials which were tested by ash test were measured, and was depicted in Figure 5. The value of some specimen which have C or B grade in ash test varies with the distance between the film and the cigarette.

TABLE 1. Experimental results

No.	SnO_2(Vol%)	Ash Test
1	0	C
2	5	B
3	20	A
4	40	A

Conclusions

New measurement method for the antistatic film coated with the two-phase system with a binder and a conductive particles was studied.

1. SnO_2 sol was used as the conductive particle. The specific volume resistance of the particle in sol was 3.4 x 10^5 Ω cm.

2. The measurement method to use an alternating current was examined . The Non-Contacting method was applied in the electrical property of films after studying the merits and demerits of this method.

3. The absolute value of impedance correlated with the grade of ash test. And the value of the specimen which has C or B grade in ash test increases linearly with decreasing distance between the film and the cigarette.

4. The percolation threshold was given by the absolute values of the impedance at 20Hz. And the percolation transition of the conductive materials may be related to the absolute values of the impedance greatly.

5. The simulation of the two-phase system with the circuit model to use the resistance and the condenser was calculated. In the result, the behavior in frequency reliance of the absolute values of the impedance was able to be explained by this circuit model.

References

1. Y.Kurachi and K.Yamanaka, Konica Technical Report, **9**,93(1996).
2. M.Sumita , Kobunshi Ronbunshu ,**40**, 203(1983)
3. K.C.Chang and T.Odagaki, Physical Review B,**35**,6,2598 (1987)