

THE KINETICS OF CHARGE-ACCUMULATING PROCESS ON THE SURFACE OF PHOTOCONDUCTIVE COATING FILM*

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ABSTRACT

The charge-accumulating process of polymeric photoconductive coating film used in electrophotography as well as factors controlling the charging rate have been studied, and the characterization of charging process and kinetic equation have been established.

INTRODUCTION

It was known that the photoreceptor used in electrophotography especially for fast copying process, must possess both high acceptability of charge and fast rising rate as much as possible in order to reach necessary surface potential instantaneously, otherwise it is not permissible to be used in the fast copying machine. Hence it is one of the essential quality factors of photoconductive material for electrophotography. It is therefore apparently that for the purpose of choosing the coating material and technological treatment, a study of the basic characteristics of charging process on the surface of coating and their controlling factors are very important. But up to now, the investigation on this charging process and its characterized method has not yet been reported in literature. In this paper, the electric property in coating surface of the charge-transfer complex system—polymeric photoconductor poly-N-vinylcarbazole (PVK) and 2, 4, 7-trinitrofluorenone (TNF), and the macroscopic kinetics in rising process of surface potential have been studied. The system of PVK/TNF, due to its some advantages, such as high photosensitivity^[1] and fair film-forming ability, has been used in practical copying and photoconductive holography^[2,6].

PREPARATION OF COATING FILM AND THE MEASURING CONDITION

(A) Preparation of sample: PVK and TNF was separately dissolved in a mixed solvent consisting of tetrahydrofuran and cyclohexanone, after this, they were mixed to form a charge-transfer complex, the mixed solution was stirred for several hours, and then filtered. A polyester support with an aluminated layer was coated by above resulting solution to give a dry organic coating layer. After 2—3 days, the coated film was under heat-treatment at 70°C for 6—8 hours.

(B) Charging and measurement of surface potential: All the coating films were nega-

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tively charged up with corona. Main instrument is Model SP-428 Static Paper Analyzer. Instrument temperature was 17°C (isothermal measurement), relative humidity 45—47%, corona current 50 μ A. The measuring condition here is the same from beginning to end, unless otherwise mentioned.

RESULTS AND DISCUSSION

1. Characteristics of charging process on the surface of coating film and the general equation of rising rate

In Fig. 1, charging condition was 50 μ A and 6250 V, at 16—18°C. As shown in Fig. 1,

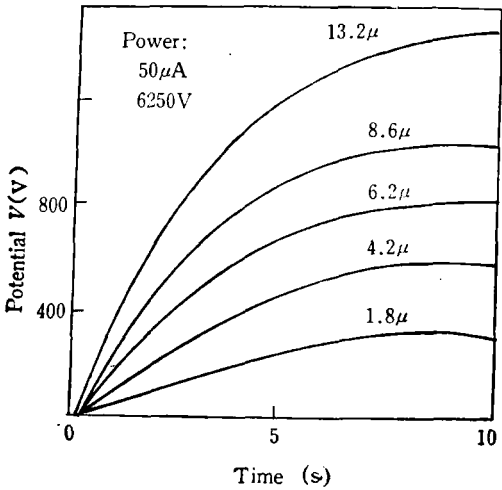


Fig. 1 Rising curves of surface potential with time for different thickness

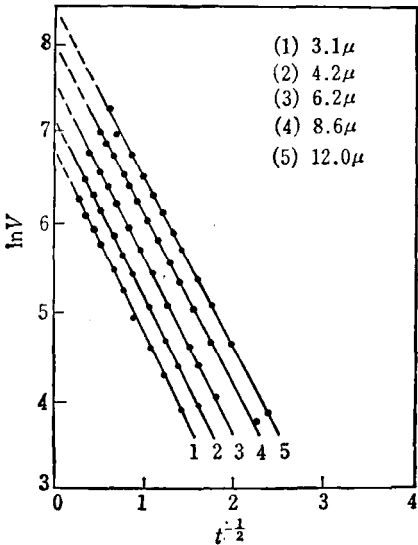


Fig. 2 Logarithm of surface potential vs. reciprocal of the square root of time t for different thickness

the surface potential V rises with time t , the rising rate in initial stage is very slow and then gradually becomes fast, and the rising process is an exponential mode, finally tends to slow again and to be saturation in the last stage. Perhaps it is because there is a number of defect state in organic or polymeric photoconductors, when charging is carried out on the surface of photoconductive coating, these defects will consume a part of charge at first. After this, the static charge begins to accumulate on the coating surface, therefore, the rising rate of surface potential gradually change from slow to fast. However, the strength of electric field increase rapidly with surface potential, at the same time the dark conductivity of coating film increase too, so the rate of charge-accumulating slow down again and gradually trends to saturation.

From fig. 2, it can be seen that there is a good linear relation when the diagram is plotted by the logarithm of surface potential $\ln V$ against the reciprocal of square root of time, $t^{-1/2}$, so we can write from Fig. 2,

$$\ln V = A - k/t^{1/2}$$

where k is the slope of straight line, A is intercept and $A = \ln V_{\infty}$. As a consequence, the kinetic equation may be expressed as follows,

$$V = V_{\infty} e^{-kt^{-1/2}} \quad (1)$$

or

$$V = V_{\infty} e^{\frac{-t^{-1/2}}{\tau}} \quad (2)$$

The differential forms of the above equations are

$$\frac{dV}{dt} = \frac{k}{2} V t^{-3/2} \quad (3)$$

or

$$\frac{dV}{dt} = \frac{V}{2\tau} t^{-3/2} \quad (4)$$

where k is the impeding constant in $(\text{sec})^{1/2}$, $\tau = 1/k$ is the rising rate constant in $(\text{sec})^{-1/2}$. While temperature is 17°C , k is $-1.98 \pm 0.08 \text{ sec}^{1/2}$ under the above condition.

It can be seen from above equations that the rising rate of potential is proportional to surface potential V at time t , and inversely proportional to three seconds power of time, $t^{3/2}$, for any thickness.

Preexponential factor V_{∞} is the saturation potential, under a given condition, when time approaches to infinite. Obviously, formula (1) or (2) is an asymptotic and exponential equation which may describe the behaviour and characteristics of the charging process on the organic coating surface in dark.

2. Relation between charge-accumulating rate and film thickness

We define here the mean charging rate $\bar{v}$ as $\bar{v} = \frac{V}{t}$, where t is the time during which the surface potential reaches to V (taken from 250 to 600V). Fig. 3 shows that both V_{∞} and $\bar{v}$ are proportional to the thickness L , namely, $\bar{V} \propto L$ and $V_{\infty} \propto L$, so that

$$\bar{v} = \rho L \quad (5)$$

and

$$V_{\infty} = PL \quad (6)$$

where both ρ and P are the slope of plot in Fig. 3 separately.

From Fig. 2, it is sure that variation of film thickness has no influence on the slope (i.e. k),

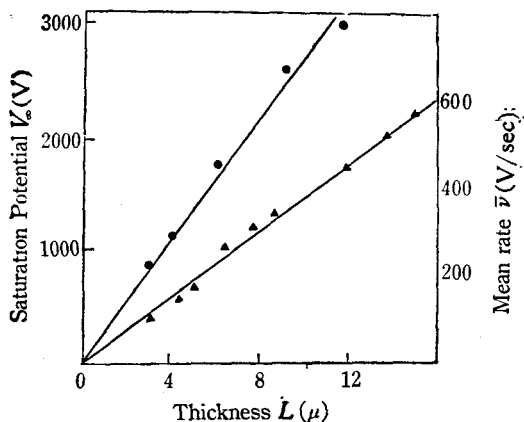


Fig. 3 Relation of V_∞ and $\bar{v}$ to thickness L

● V_∞ ▲ $\bar{v}$

but by contrast the saturation potential V_∞ (antilogarithm of intercept) increase with film thickness.

From Fig. 2, Fig. 3 and equations (1) and (3), we have following equations for the dependence of thickness L on the charging rate:

$$\frac{dV}{dt} = \frac{k}{2} \bar{v} t^{-\frac{1}{2}} \quad (\because V/t = \bar{v}) \quad (7)$$

or

$$\frac{dV}{dt} = \frac{k}{2} \rho L t^{-\frac{1}{2}} \quad (8)$$

As also

$$V = PL e^{-k/t^{\frac{1}{2}}} \quad (9)$$

and

$$\frac{dV}{dt} = \frac{k}{2} PL t e^{-k/t^{\frac{1}{2}}} \quad (10)$$

From above equations, it is clear that charging rate dV/dt is proportional to mean rising rate $\bar{v}$, as well as to coating thickness L .

Where ρ and P are constants which are dependent on the power, temperature and instrument condition etc.

ρ (in V/sec·cm or E/sec) is the maximum rising rate, being able to come up, per unit thickness, it may be called as "field rate coefficient". In general, value of ρ is about 40 V/sec· μ for PVK/TNF (1:1) system, it means that the mean charging rate can increase about 40 V/sec as the increment of film thickness is 1 μ .

P is the limit field strength (in V/cm) that is the limit potential which is able to be accepted for unit thickness under a given power condition. Obviously, the greater the P , the better the charging ability of photoconductor. For PVK/TNF (1:1) system, P is about 300 V/ μ , that is 3×10^6 V/cm, of course, it is only an extrapolated value.

3. The effect of corona power w on the rising rate of surface potential

Fig. 4 shows clearly the effect of power on charging rate. It may be seen that the impeding constant k become smaller when the corona power increase, it implies the accumulating rate of surface charge increase with power, as well as shown in Fig. 5 for different power. In

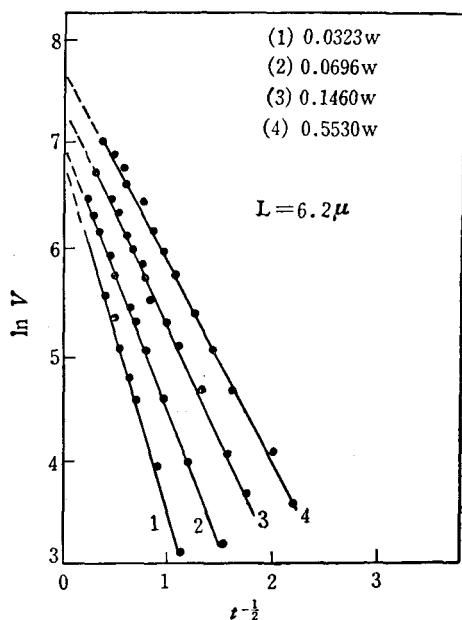


Fig. 4 Plot of $\ln V$ vs. $t^{-1/2}$ for different powers

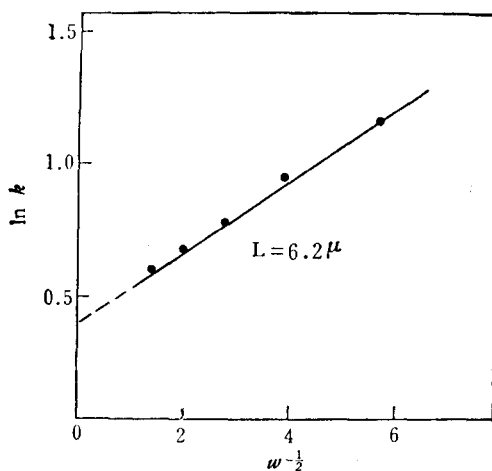


Fig. 5 Dependence of $\ln k$ with $w^{-1/2}$

Fig. 5, slope S is the power constant which is $0.132 \pm 0.002 w^{1/2}$. From Fig. 5, we have an asymptotic equation for different power:

$$k = k_{\infty} e^{S w^{-1/2}} \quad (11)$$

where k_{∞} is the limit impeding constant which is a minimum value as the power w approaches "infinite" under a given condition. Here, for the PVK/TNF (1:1) system, k_{∞} was determined to be $1.52 \text{ sec}^{1/2}$.

As a matter of fact, when corona power is infinitely increased to a certain extent, charging

rate will no longer increase with power. It may be attributed to that there is a limitation for charge-acceptability of coating layer, and that the higher the power, the larger the energy consumed, as well as the lower the efficiency of air ionization, and in addition, because the dark conductivity of coating also increase with field strength, as a result, charging rate finally trends to a saturation value.

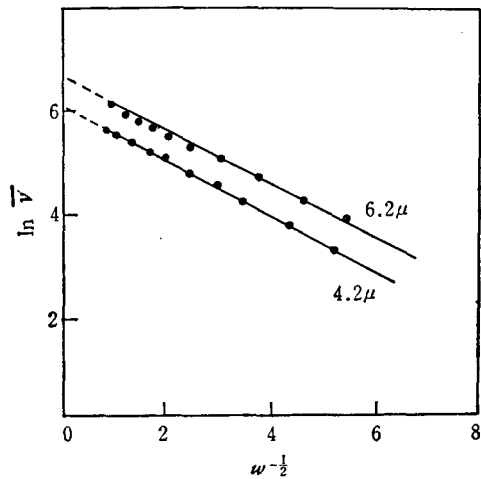


Fig. 6 The dependence of $\ln \bar{v}$ on $w^{-1/2}$

To be the same as above, from Fig. 6, it can be seen that the same effect of power on the mean rate, thus we may obtain following equations for charging kinetics:

$$\bar{v} = \bar{v}_{\infty} e^{k_w w^{-1/2}} \tag{12}$$

$$\frac{dV}{dt} = \frac{1}{2} k_w \bar{v} w^{-3/2} \tag{13}$$

It is evident that equations (12) and (13) are formally similar to equations (1) and (3), where k_w is the power impeding constant (in $w^{1/2}$), to be about $-0.50 w^{1/2}$, which is only dependent on

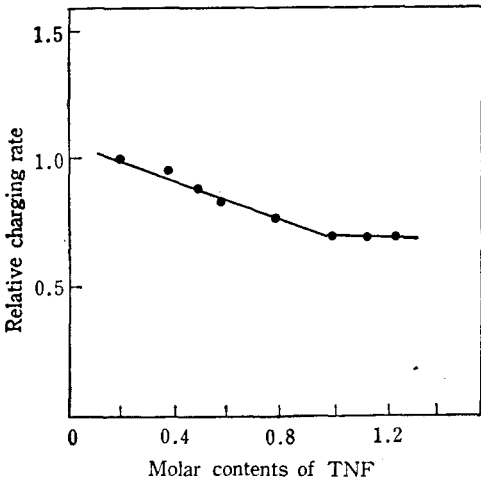


Fig. 7 Relationship between relative charging rate vs. molar rate of TNF/PVK,
 $L = 6.2 \pm 0.2 \mu$

the material nature but independent of the thickness of coating. $\bar{v}_\infty$ is the limiting mean rate that is a maximum mean rate which can be obtained as corona power trends to "infinite".

4. The influence of molar ratio of TNF/PVK complex on the charging rate

It may be seen from fig. 7 that charging rate decrease linearly with the content of TNF, but as long as the molar ratio of TNF/PVK reaches to 1:1, the relative rate no longer decreases with increase of TNF contents. It is possible that the amount of the charge-transfer complex increase, so that dark resistance of coating layer reduces. It was known that the lower the resistance, the worse the charge-accepting ability, as a consequence the rising rate of surface potential slows down; but when the molar ratio of TNF/PVK is larger than 1/1, the concentration of charge-transfer complex shall no longer increase, so that the conductivity of system shall no longer increase too, thus the charging rate trends to steady.

CONCLUSION

Charging process on the coating surface proceeds in exponential form, and it is also a convergent process whose limit is V_∞ . In equations, which characterize well the kinetics of charging process, the preexponential factors ρ , P and exponential factors k , S are important characteristic constants for a photoconductive material, the saturation potential V_∞ is dependent on the coating thickness, but k is independent of thickness. In fact, V_∞ depends on the resistance R of coating layer, but k only depends on the resistivity of coating layer and not on the resistance.

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