# A Study of "Deletion" Mechanism in High Humidity from the Point of View of Image-Forming System

Koji Otsuka, Mamoru Kido, Toru Ogawa, Nobuhide Inaba; Key Technology Laboratory Fuji Xerox Co., Ltd.; Kanagawa, Japan

# Abstract

In electrophotography, high humidity can trigger "deletion" characterized by mainly a blur or a density reduction of print images. In the recent survey we researched this phenomenon and found out the following mechanism. The main causing agent for "deletion" is ammonium compound of which deliquescence makes the surface resistance lower. Therefore we developed a novel method to measure a surface resistance and showed the correlation among surface resistivity  $\rho_s$ , amount of ammonium ions  $NH_4^+$  on a surface of a photoreceptor and CTF (Contrast Transfer Function) which was introduced to quantify image deterioration caused by "deletion". With their results found out in this study and other observations we obtained before, we have built the 5-steps of deletion occurring framework from the viewpoint of printing-systems.

#### Introduction

In electrophotography, high humidity can trigger "deletion" characterized by mainly a blur of print images due to migration of latent charge. Figure 1 is an image sample of "deletion".



#### Figure 1. Example of deletion

Occurring "deletion", density on halftone images using area coverage modulation decrease or increase (depends on the density), and areas of thin lines of characters or figures disappear. That ends up with a deletion of original document images at worst. Therefore it is requisite for printing systems to prevent this phenomenon, "deletion".

On this phenomenon occurring under high humidity, many early studies have been done. "Migration of latent charge caused by conductive foreign contaminants on a photoreceptor" [1] is a generally known mechanism of occurring deletion. And some characteristics of it have also been investigated. "BCR (Bias Charge Roll) especially generates more hydrophilic groups on a surface of a photoreceptor than corotron. Because discharge energy destroys relatively weak chemical bonding on a surface of a photoreceptor". [2] "One of causing agents is ammonium nitrate." [3] However little is known about the quantitative relation between the causing agents and "deletion"

# Correlation between relative humidity and surface resistivity $\rho_s$ of a photoreceptor

"Deletion" is caused by the migration of latent charge so as to fill in the difference in potential along the surface of the photoreceptor. So we focused attention on the surface resistivity  $\rho_s$ of a photoreceptor as an intermediate indicator.

# Measurement of surface resistivity $\rho_s$

Observing the surface of a photoreceptor which is caused "deletion" clarified the existence of conductive and mottled substance which came into contact with the surface of it in a patchy fashion and is not uniform. (describes in detail later)

So the measuring electrodes which have narrower distance between electrodes and longer pairs of ones are suitable to precisely measure the slight changes in the resistance in a certain area of a photoreceptor. These comb-like electrodes are directly formed on the cylindrically-shaped photoreceptor with a conductive paste, in addition, to reduce the contact resistance between electrodes and a photoreceptor. This measuring method for the surface resistivity  $\rho_s$  is based on the concept using a concentric ring except the difference of electrode's shape. The measuring apparatus is shown in Figure 2.



Figure 2. Apparatus of surface resistance measurement

# Correlation among surface resistivity $\rho_{s}$ , "deletion" level and relative humidity

According to the different levels of "deletion", we measured the surface resistivity  $\rho_s$  using this proposed measuring method.



Figure 3. Relation between Deletion Grade and Surface Resistivity

Figure 3 shows that  $\rho_s$  becomes lower in parallel with the down-grading of "deletion" and so  $\rho_s$  can be an intermediate indicator. Furthermore, the values of the surface resistivity  $\rho_s$  are not stable in the range less than G5, grading level of "deletion". We decide that it is possible to measure by making narrower distance electrodes.

We evaluated the surface resistivity  $\rho_s$  of a photoreceptor which is caused "deletion" for the various relative humidity at a constant temperature.

Figure 4 shows that, in addition, the relative humidity is strongly correlated with  $\rho_s$  and this correlation is reversible for decreasing or increasing it. The correlation between the changes of the relative humidity and ones of the saturated vapor pressure in an atmosphere is proportional, therefore this proportional relation means that the causing agent has deliquescence and its compound is ionized.



Figure 4. Relation between Relative humidity and Surface Resistivity

# Transition of evaluation with CTF from grading

We have been utilizing the sensory grading scale to evaluate whether the level of "deletion" is good or bad. This grading scale is suitable to easily evaluate it in a print, however it is extremely difficult to quantify the level of "deletion" which is caused by the migration of latent charge, as a result, decreasing of the surface resistivity  $\rho_s$  of a photoreceptor. Thus, clarifying the mechanism of it is the most important subject in this study.

And so, as the evaluation scale for this purpose, CTF (Contrast Transfer Function) was introduced as follows by utilizing the reflectance ratio R (%), which is converted from the density D optically measured with a scanner for a uniform ladder pattern shown in Figure 5. CTF is expressed as follows

$$CTF = (R_{max} - R_{min}) / (R_{max} + R_{min})$$
(1)

Where  $R_{min}$  is the reflected ratio for printed area,  $R_{max}$  is one for background. *R* is converted from *D* as the following equation.

 $D = -\log(R / 100)$ (2)

The migration of latent charge is caused by decreasing  $\rho_s$  and CTF also decreases. So it is important to correlate the quantity of migration of latent charge with the variation of developed mass. Choosing the appropriate spacing of a ladder pattern (spatial frequency) depending on the level of "deletion" makes to broaden the applicable range of a quantitative evaluation. The measured





*Figure 5.* CTF Pattern *Figure 6.* Deletion Quantified with CTF case for an image sample which causes a "streaky deletion" in the slow-scan direction is shown in Figure 6.

### Identification of causing agents, its behavior and relations with deletion

We surveyed on the property of causing agents, which brought about "deletion" and investigated the relations among CTF,  $\rho_s$ , the amount of causing agents.

#### Survey on property of corona products

The experimental result shown in Figure 4 suggested that the causing agents of "deletion" had deliquescent property. To examine this property, we conducted form and phase measurements on the surface of the photoreceptor with an environmental controlled Atomic Force Microscopy (AFM). We prepared an observation sample using off-line discharging machine with BCR to put the corona products on the surface.

After this process, a small piece out of the photoreceptor was set in a climate-controlled chamber, and measured by AFM. As shown in Figure 7, under high humidity, the corona products were expanded in height image, and softened and had viscosity in phase image as compare to that of low humidity condition. As a result, we assume that the corona products have deliquescent (hygroscopic) property.



Figure 7. Images of AFM Measurement

#### Measurement scheme by ion chromatography

The causing agents are suggested by having ionic property as they have conductive property by hygroscopic. Then we utilized

ion chromatography as analytical method. Followings are the analysis steps of fouling on the surface of the photoreceptor.

- Cut the photoreceptor in a fixed size after conducting the print test and/or off-line discharging test
- Stripped the layers of the photoreceptor from the base metal
- Encapsulated them to extraction bag with a certain amount of ultra pure water and extracted for a finite period of time

The chromatograms of the fouling on the surface of the photoreceptor after the off-line discharging test were shown in Figure 8.  $NH_4^+$ ,  $NO_3^-$ ,  $SO_4^{2-}$  were detected relating to "deletion" as the fouling. Among detected ions,  $NH_4^+$  had strong correspondence to it, as we will describe later.  $NH_4^+$  is the part of ammonium compounds assumed as the fouling in early works. Next we discuss the one of ammonium compounds,  $NH_4NO_3$ , which is considered a main source of them.



Figure 8. Chromatogram of Fouling

#### Generating of NH<sub>4</sub>NO<sub>3</sub>

By discharged energy,  $N_2$ ,  $O_2$  existing near the charging device are oxidized to generate  $NO_x$ ,  $O_3$ . In addition,  $NO_x$  are oxidized to generate  $N_2O_5$ . Under high humidity,  $N_2O_5$  reacts by absorbing moisture and HNO<sub>3</sub> is generated. [4]

$$NO_2 + O_3 \to NO_3 + O_2$$
 (3)

$$NO_2 + NO_3 \rightarrow N_2O_5 \tag{4}$$

 $N_2O_5 + H_2O -> 2HNO_3$  (5)

Reaction formulae of NH<sub>4</sub>NO<sub>3</sub> are presumed as follows.

$$HNO_3 + H_2O + M -> NH_3 + 2O_2 + M (M: Catalytic agent)(6)$$

$$NH_3 + HNO_3 \rightarrow NH_4NO_3 \tag{7}$$

#### Correlation with $\rho_s$ and $NH_4^+$

We investigated the correlation with  $\rho_s$  and NH<sub>4</sub><sup>+</sup>. So we made samples of which amount of fouling generated by off-line discharging test differed, and measured  $\rho_s$  and analyzed the fouling. A detected amount was converted from unit volume [ $\mu g/L$ ] to per unit area of the surface of the photoreceptor [nmol/cm<sup>2</sup>].

Figure 9 showed that  $\rho_s$  and the amount of NH<sub>4</sub><sup>+</sup> had strong negative relation. When the amount of NH<sub>4</sub><sup>+</sup> increased,  $\rho_s$  decreased. Thus in our experiment under high humidity, NH<sub>4</sub><sup>+</sup> had

strong relationship. Other detected ions, for example NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup> had weaker relationship than NH<sub>4</sub><sup>+</sup>. Therefore we presume that causing agent of "deletion" is NH<sub>4</sub><sup>+</sup>.



**Figure 9.** Relation between Surface Resistivity  $\rho_s$  and NH<sub>4</sub><sup>+</sup>

#### Correlation with CTF and NH4<sup>+</sup>

We surveyed the amount of  $NH_4^+$  of photoreceptors differing "deletion" level with three variant types which differed the surface layer. After the print test, we measured the amount of  $NH_4^+$  on the surface of the photoreceptors and CTF on printed paper.



Figure 10. Relation between CTF and NH4<sup>+</sup>

Figure 10 showed that the amount of  $NH_4^+$  decided CTF irrespective of the types of photoreceptors. So the removal of  $NH_4^+$  is important to prevent "deletion" from occurring.

#### 5-steps of deletion occurring framework

In this session we explain the 5-steps of "deletion" occurring framework from the viewpoint of printing-systems, which is built based on the experimental results we described in this paper and other observations we obtained before.

#### Step1. Occurring corona products

Corona products are generated by discharge energy with charging devices. Corona products like ammonium nitrate are generated from  $O_3$  and  $NO_x$ . We found out in our previous study that the amount of corona products is proportion to the discharge intensity.

#### Step2. Oxidation of photoreceptor

A surface of a photoreceptor is oxidized by discharge energy with charging devices. Oxidation made it difficult to remove corona products from the surface of the photoreceptor due to polar groups occurred on it. Step.1 and 2 occur at the same time.

#### Step3. Removal of corona products

Corona products on the surface of the photoreceptor are removed using cleaning devices like a cleaning blade. the same time, oxidized thin layer on the surface of the photoreceptor is shaved off. Oxidation hinders removal of corona products due to the increasing adhesion force existing with polar groups. The amount of NH4<sup>+</sup> remained on the surface, which is derived from ammonium compound, has a strong correlation with "deletion".

#### Step4. Absorption of moisture

Delinquent material, which has not been removed by cleaning devices and remains on the surface, absorbs moisture under high humidity. The surface becomes conductive with ion aqueous solution. The surface resistivity  $\rho_s$  is determined by the condition of the corona products.

#### Step5. Forming image

The photoreceptor is developed with toner after latent image forming. The velocity of the migration of latent charge depends on the electrical field caused by the potential difference between image area and background, and surface resistivity  $\rho_s$ .

That means the deterioration of "deletion" is determined by the elapsed time from exposure to development of the printing system.



Figure 11. Occurring Steps of Deletion

# $(\rho_s)^*$ as an indicator for designing tolerance of "deletion"

It would be effective to adopt an indicator based on a physical model during a technological developing phase.

Therefore we have considered introducing the surface resistivity  $\rho_s$  as an indicator for designing tolerance of "deletion". Given a criterion of "deletion" grade for the designated printing system, CTF is determined by that. In this survey, we couldn't measure  $\rho_s$  correspond to that criterion directly.  $\rho_s$  could be calculated with following two strong correlations, CTF and amount of NH<sub>4</sub><sup>+</sup>, CTF and  $\rho_s$ , obtained in this study. This  $\rho_s$ should be the lower limit. These relations are shown in Figure 12.

To increase  $\rho_s$ , conductive corona products, which are mainly  $NH_4^+$ , should be removed from the surface. And the surface layer of the photoreceptor should be worn out more than a certain rate by cleaning devices like a cleaning blade. [5]



**Figure 12.** Relation between CTF,  $\rho_s$  and NH<sub>4</sub><sup>+</sup>

There is no upper limit of  $\rho_s$  for the tolerance of "deletion". But the excessive ware rate leads to a short life of devices including a photoreceptor and a cleaning blade, so the system design should be balanced with these two factors.

### Conclusion

In conclusion of this paper, we established the quantitative measurement for "deletion" which is caused by the migration of latent charge and, as a result, decreasing of the surface resistivity  $\rho_s$  of a photoreceptor under the high-humidity environment and identified the causing agent NH4+ of it. In addition, we clarified quantitatively the correlation among  $\rho_s$ , the amount of NH<sub>4</sub><sup>+</sup> and CTF.

From a point of view for optimizing throughout a whole image-forming process for "deletion", in addition, we have to clarify the essential cause of it, in particular, (1) analyzing an adhesion of corona products and removal mechanism, (2) clarifying deliquescence in moist air, (3) quantifying a migration rate and broadening of latent charge, and so on.

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# Author Biography

Koji Otsuka received his M.Eng. degree in Administration Engineering from Keio University (1992). Since then he has worked at Fuji Xerox Co., Ltd. His main research interests include development of discharge devices and failure analysis for electrophotography unit in copier/printer.