# Development of a New Generation Surface Layer for an a-Si Photoreceptor Drum

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# Abstract

We looked into the relationship between the unclear image problem and the surface free energy of an a-Si photoreceptor drum and found that the unclear image problem does not happen when low surface free energy is maintained.

We succeeded in getting a low surface free energy by fluorination (a-C:H:F) using CF4 etching and achieved anti-oxidation improvement by optimizing a-C:H film deposition. Repeated steps of a-C:H film deposition and CF4 etching were applied to fluorinate deeper into the layer.

As a result, an ideal drum was produced which did not cause any unclear images in tests.

# Introduction

The a-Si drum is widely used in copiers, printers and on-demand full color printers, which require the long life resulting from the excellent abrasion resistance of its a-SiC:H surface layer. The 1st generation drum had the problem of unclear images that appeared in highly humid environments. Heaters were necessary to prevent this. In 1997, the 2nd generation drum was introduced with a carbon enriched surface layer of a-SiC:H which enabled production of a heater-less printer. However, this drum required continuous special polishing in the printer.

Now Kyocera has developed a new generation surface layer of fluorinated a-C:H film (a-C:H:F) which shows greatly reduced surface free energy and features easy cleaning and high anti-oxidation. This new drum solves the unclear image problem.

### Causes of the unclear image effect

The unclear image occurs by lateral flow of surface charge on a photoreceptor drum when an electrically conductive water film forms in a highly humid environment. Fig.1 shows the steps in the generation of the unclear image. Currently this is eliminated by using a heater which prevents the formation of the water film (the 1st generation).

It is necessary to understand the increase in hygroscopicity of the drum surface. There are two factors that increase hygroscopicity:

1.Adhesive substances such as components of paper

and corona products on the surface.

2. Surface oxidation by ozone from the corona discharge.



Figure 1. Causes of unclear image effect

Taking measures against these two causes will prevent the unclear image from occurring. The 2nd generation drum achieved heater-less operation by improving oxidation resistance and by reducing surface hardness so that oxide film and adhesive substances on the surface can be removed easily. However, special polishing was needed for this removal, which became a burden on the printer side. Therefore, we started a new material development to have a-C:H:F surface by fluorinating a-C:H layer on top of current a-SiC:H layer to realize the following 3 points.

1.Make adhesive substances difficult to adhere or easy to remove by reducing surface free energy.

- 2.Increase oxidation resistance and maintain the initial level of surface free energy.
- 3. Maintain high durability by keeping surface hardness.

## **Experiment and Discussion**

#### Development of a new generation surface protection layer

Fig.2 shows the layer structure of an a-Si drum. It consists of 3 layers: carrier blocking layer, a-Si photosensitive layer, surface protection layer. In this experiment, we added an extra layer produced under various conditions on top of the current a-SiC:H surface protection layer and evaluated the effects. The thin film layer was deposited by plasma CVD. CF4 gas was used for fluorination.



Figure 2. Layer structure of a-Si drum

1) Surface free energy and the unclear image effect

A number of samples having different surface free energies were prepared. The measured relationship between surface free energy and unclear image is shown in Fig.3.



Figure 3. Surface free energy vs unclear image

Kyocera's Ecosys FS-3550 page printer, with its heater removed, was used for evaluation of the unclear image effect. Evaluation was made on the first print after printing 1,000 pages and then keeping the printer for 10 hours at 33C and 85% humidity. The degree of unclear image was ranked into 5 levels; rank 1 is no unclear image; rank 5 is worst.

To determine surface free energy, the contact angle was measured after cleaning adhesive substances off the drum surface after printing 1,000 pages (using Contact angle measurement equipment. CA-X type, made by Kyowa Interface Science Co., Ltd.), then analyzed based on extended Fowkes theory.

Since the samples having surface free energies less than 40mN/m did not cause unclear images, this same surface free energy level must therefore be maintained over large volume printing.

#### 2) Improvement of oxidation resistance

We determined the relationship between the surface free energy of an unfluorinated a-C:H layer and the CH4/H2 gas ratio during its deposition. Fig.4 shows the resultant surface free energy, measured on the new drums and again after exposing them to corona for 5 hours. Surface free energies of new drums were constant. Surface free energies after exposure to corona were found to be stable where the CH4/H2 ratio had been in the range of 0.8 to 1.1.



Figure 4. CH4/H2 ratio vs surface free energy

We also fluorinated the top surface and describe the result in Fig.5. The absolute value of surface free energy was reduced, both on initial measurement and after exposure to corona. However, it showed similar tendency as Fig.4 due to the influence of under layers.





We next produced samples on which 5 cycles of a-C:H layer deposition and CF4 etching were performed and show the result in Fig.6. They showed low and stable surface free energies for a wide range of ratio even after exposure to corona.



Figure 6. CH4/H2 ratio vs surface free energy (a-C:H layer + CF4 etching 5 cycles)

We confirmed through a SIMS analysis that fluorine density in the surface protection layer of the 5 cycle etching sample was one order of magnitude higher than in the 1 cycle etching sample. Usually the weak bond of C-H or C-C is cut by repeated corona discharges to produce a carbonyl group C=O. However, we assume that by CF4 etching, the weak bond is replaced by the strong C-F bond. Also, the C-F bond is known as a bond having a low surface free energy. So oxidation resistance is increased and surface free energy is decreased.

#### 3) Hardness



Fig.7 shows the relation between RF power during deposition and DUH hardness. We can see the higher the RF power, the higher the hardness.

Figure 7. RF power vs DUH hardness

#### Evaluation result of unclear image effect

Fig.8 shows the unclear image after printing 10,000 pages. For comparison, we evaluated with a-SiC:H and a-SiC:H (C-rich) drums. Test pattern is characters on a half tone image. The unclear image begins with the half tone image disappearing; then progresses to character smearing. The a-SiC:H drum had a complete wash out of characters. The C-rich drum showed some improvement but still had smeared characters. The a-C:H:F drum did not cause any unclear image and maintained the initial image level.

We further printed 100,000 pages and checked the unclear image effect. The result is shown in Fig.9. The drum did not cause any unclear image even after printing 100,000 pages.

#### **Property of the surface layer**

Table 1. summarizes the comparison of the three generations of surface layers. Initial surface free energy was reduced to about 15mN/m and was kept even after exposure to corona. Hardness was improved to the same level as the first generation a-SiC:H drum.

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Figure 8. Unclear image evaluation result 1

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Figure 9. Unclear image evaluation result 2

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Improvement item	Measurement item	Measurement standard	First generation a-SiC:H	Second generation a-SiC:H (C-rich)	Newly developed a-C:H:F
Water-repellent Cleaning Oxidation resistance	Surface free energy (mN/m)	Initial	42.5	41.0	14.5
		After 5hr Corona Expose	58.5	50.5	14.5
Abrasion resistance	Hardness(Kgf/mm²)	DUH Hardness	430	100	420
Unclear level	Judgment (5 levels)	1 Excellent-5Poor	5	3	1

## Conclusion

We succeeded in developing a surface protective layer with low surface free energy and high oxidization resistance while keeping the very high durability. Using this layer, the unclear image problem in high humidity can be prevented.

We hope that a-Si photoreceptor drums with this new layer can be supplied to the market for use in printers without heaters.

#### References

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## Biography

Takashi Nakamura graduated from University of Hiroshima, Dept. of Engineering in 1992.

Joined Kyocera Corporation, Shiga-plant, a-Si Photoreceptor drum Development Section in 1992 and Heater-less a-Si drum development team in 1998.